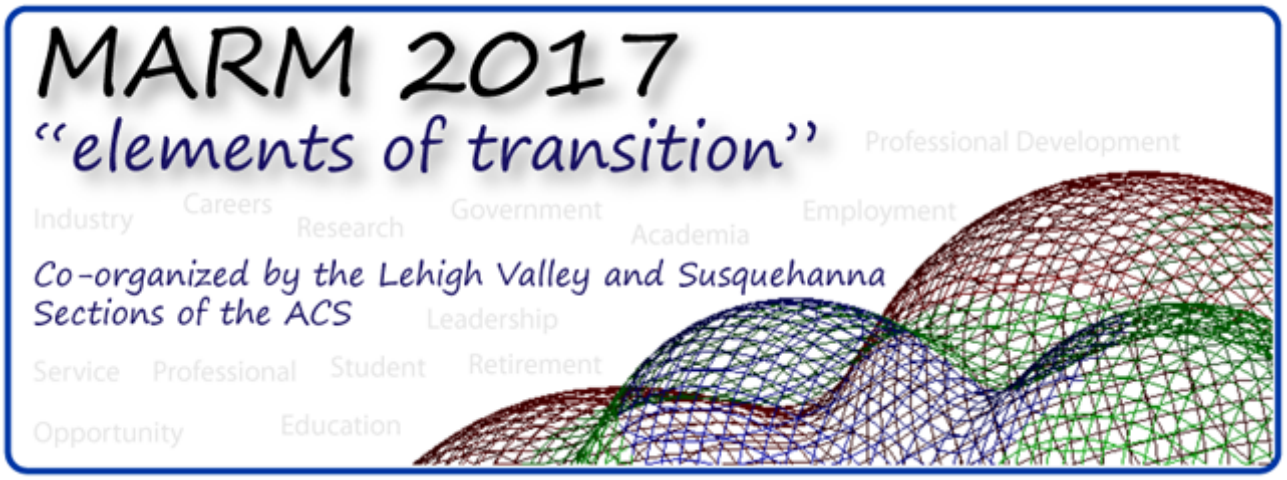
45th Middle Atlantic Regional Meeting of the American Chemical Society June 4-6, 2017



ACS Chemistry for Life®

HERSHEY Lodge

Hershey Lodge, Hershey PA

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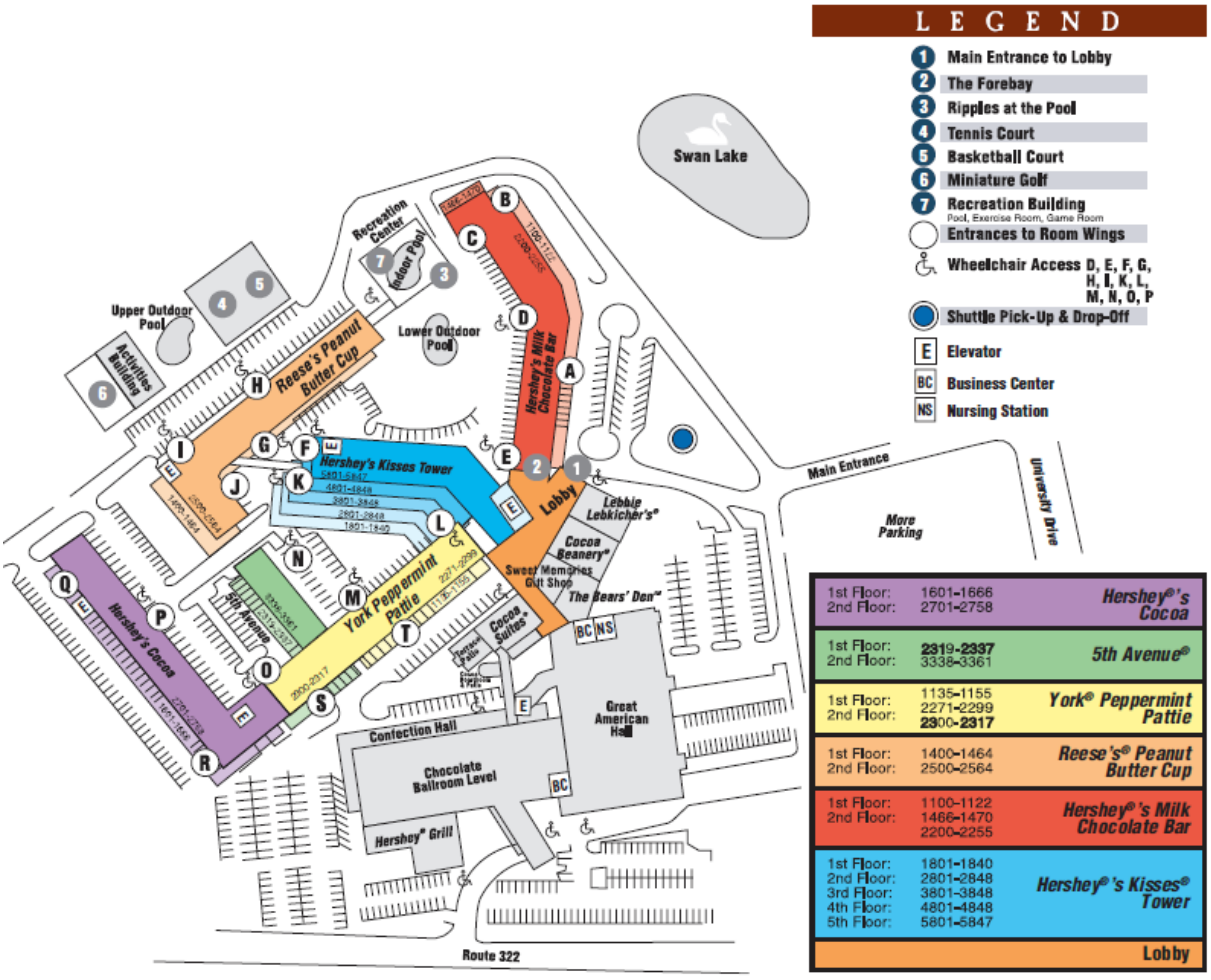
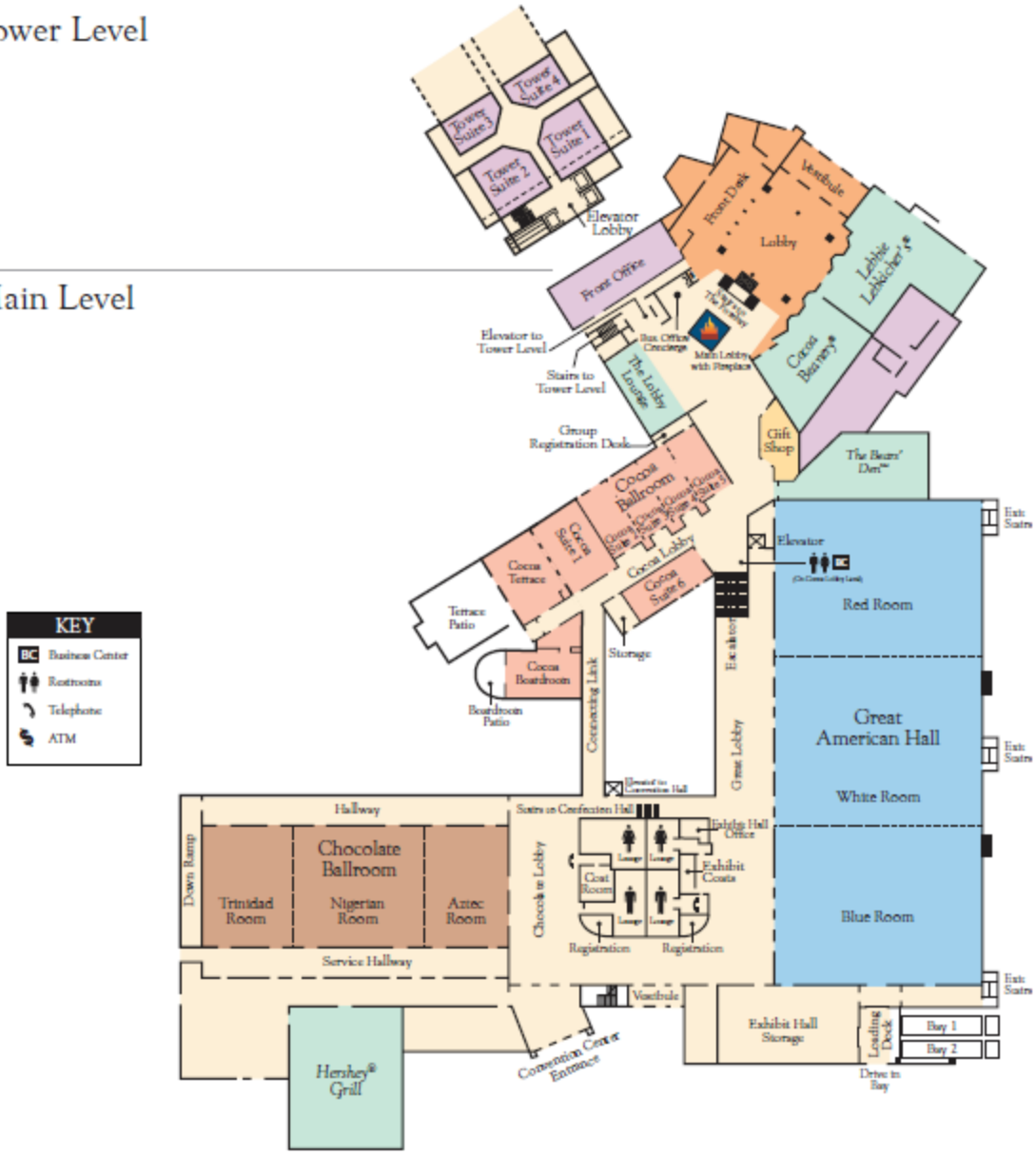
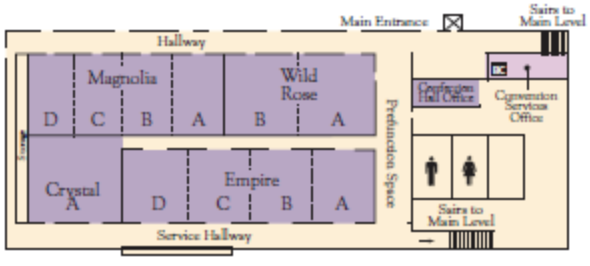

LEGEND
1 Main Entrance to Lobby
2 The Forebay
3 Ripples at the Pool
4 Tennis Court
5 Basketball Court
6 Miniature Golf
7 Recreation Building
Pool, Exercise Room, Game Room
Entrances to Room Wings
Wheelchair Access D, E, F, G, H, I, K, L, M, N, O, P
Shuttle Pick-Up & Drop-Off
E Elevator
BC Business Center
NS Nursing Station
Swan Lake
Recreation Center
Indoor Pool
Upper Outdoor Pool
Lower Outdoor Pool
Activities Building
Reese's Peanut Butter Cup
Hershey's Milk Chocolate Bar
Hershey's Kisses Tower
5801-5847
4801-4848
3801-3848
2801-2848
1801-1840
Lobby
Lebkicher's®
Cocoa Beanery®
Sweet Memories Gift Shop
The Bears' Den®
Cocoa Suites®
York Peppermint Pattie
5th Avenue
Hershey's Cocoa
Confection Hall
Great American Hall
Chocolate Ballroom Level
Hershey® Grill
Main Entrance
University Drive
More Parking
Route 322
1st Floor: 1601-1666
2nd Floor: 2701-2758
Hershey®'s Cocoa
1st Floor: 2319-2337
2nd Floor: 3338-3361
5th Avenue®
1st Floor: 1135-1155
2nd Floor: 2271-2299
2300-2317
York® Peppermint Pattie
1st Floor: 1400-1464
2nd Floor: 2500-2564
Reese's® Peanut Butter Cup
1st Floor: 1100-1122
2nd Floor: 1466-1470
2200-2255
Hershey®'s Milk Chocolate Bar
1st Floor: 1801-1840
2nd Floor: 2801-2848
3rd Floor: 3801-3848
4th Floor: 4801-4848
5th Floor: 5801-5847
Hershey®'s Kisses® Tower
Lobby

Tower Level

Main Level



Confection Hall Level



Meeting Schedule at a Glance

EVENT	SUN AM JUN 4	SUN PM JUN 4	MON AM JUN 5	MON PM JUN 5	TUE AM JUN 6	TUE PM JUN 6	LOCATION
TECHNICAL SESSIONS							
Med-Chem Strategies for Chronic Hepatitis B Virus Infection		1:30-3:30					Magnolia B
Implementation of Innovative Projects in Upper-Level Chemistry Courses		1:30-4:00					Cocoa Suite 5
Membrane Structure & Assembly		1:30-4:00					Magnolia D
Molecular Modeling in the High School Curriculum		1:30-3:30					Tower Suite 1
Active Learning: Strategies for Making It Work in Your Class		1:30-4:30					Empire C
Solid State & Materials Chemistry		1:30-4:50					Magnolia A
Cope Scholar Symposium: Progress in the Synthesis of Complex Molecules		1:30-5:00					Crystal A
Nanoscience: Fundamentals & Applications		1:30-5:00					Empire B
Coordination Chemistry		1:30-5:20					Empire A
Ionic Liquid Bulk & Interfacial Chemistry		1:30-5:20					Cocoa Suite 4
Forensic Chemistry		1:30-5:30					Empire D
History of Chemistry			8:00-11:30				Cocoa Suite 5
Theory & Computation Toward Electronic Properties of Molecular Materials			8:30-11:00				Empire A
Ionic Liquid Bulk & Interfacial Chemistry			8:30-11:40				Cocoa Suite 4
Nanoscience: Fundamentals & Applications			8:30-11:40				Empire B
Fluorescence & Luminescence Spectroscopy			8:30-11:50				Magnolia C
Women in Organic Chemistry			8:30-12:00				Crystal A
Med-Chem Strategies for Chronic Hepatitis B Virus Infection			9:00-11:00				Magnolia B
Teaching Inorganic Chemistry			9:00-11:40				Magnolia A
Active Learning: Strategies for Making It Work in Your Class			9:00-11:40				Empire C
Lanthanide Chemistry			9:00-11:50				Magnolia D
Methods & Applications of Metabolomics			9:00-12:00				Empire D
Food Safety			9:00-12:00				Wild Rose B
Physical Chemistry of Materials			9:00-12:00				Wild Rose A
Physical Chemistry of Materials				1:00-3:30			Wild Rose A

Meeting Schedule at a Glance

EVENT	SUN AM JUN 4	SUN PM JUN 4	MON AM JUN 5	MON PM JUN 5	TUE AM JUN 6	TUE PM JUN 6	LOCATION
TECHNICAL SESSIONS							
Current Topics in Bioactive Molecules, both Large & Small				1:00-3:40			Magnolia C
Evolving Landscape of Drug Discovery & Development				1:00-4:00			Magnolia B
Food Safety				1:00-4:00			Wild Rose B
Ionic Liquid Bulk & Interfacial Chemistry				1:00-4:20			Cocoa Suite 4
Insights into the Chemistry of Protein Function				1:00-4:20			Magnolia D
History of Chemistry				1:00-4:30			Cocoa Suite 5
Bio-Inorganic Chemistry				1:00-4:40			Magnolia A
Advances in Organic Chemistry				1:00-4:40			Empire D
Women in Organic Chemistry				1:00-4:50			Crystal A
Revitalizing General & Organic Chemistry Laboratory Experiments				1:00-4:50			Empire C
Cosmetic Chemistry				1:00-5:00			Empire B
Theory & Computation Toward Electronic Properties of Molecular Materials				1:00-5:00			Empire A
Catalysis					8:30-11:40		Magnolia A
Organometallic Chemistry					8:30-12:00		Wild Rose B
Evolving Landscape of Drug Discovery & Development					9:00-11:10		Magnolia B
Small Chemical Business					9:00-11:20		Magnolia D
Advances in Nanotechnology, Polymers, Terahertz & Analytical Research					9:00-11:30		Wild Rose A
Chemistry at Interfaces: Living on the Edge					9:00-11:30		Empire A
Innovations in Analytical Chemistry Education					9:00-11:30		Empire C
Fate & Transport of Environmental Contaminants					9:00-11:30		Empire B
Life & Times of Joseph Priestley					9:00-11:40		Empire D
Biomarker Synthesis & Clinical Chemistry					9:00-11:50		Crystal A
Structure, Function & Stability: Proteins with Unnatural Amino Acids					9:00-11:50		Magnolia C
Computational Chemistry in the Undergraduate Curriculum: Present & Future					9:00-12:00		Tower Suite 1

Meeting Schedule at a Glance

EVENT	SUN AM JUN 4	SUN PM JUN 4	MON AM JUN 5	MON PM JUN 5	TUE AM JUN 6	TUE PM JUN 6	LOCATION
TECHNICAL SESSIONS							
Opportunities for Academic-Pharma Collaborations						1:00-3:10	Magnolia B
Innovations in Analytical Chemistry Education						1:00-3:30	Empire C
Fate & Transport of Environmental Contaminants						1:00-3:30	Empire A
Synthetic & Biological Catalysis						1:00-3:40	Magnolia D
Chemistry of Molecular Imaging						1:00-3:50	Crystal A
Medicinal Chemistry & Heterocyclic Synthesis						1:00-4:00	Cocoa Suite 5
Chemistry of Materials: Designing Structure						1:00-4:00	Wild Rose B
Catalysis						1:00-4:10	Magnolia A
Organometallic Chemistry						1:00-4:30	Wild Rose A
Bio-Inorganic Chemistry						1:00-4:40	Empire D
Advances in Chromatography, Mass Spectrometry & Biosensors						1:00-5:00	Magnolia C
Protein Misfolding & Quality Control						1:00-5:00	Cocoa Suite 4
Chemistry at Interfaces: Living on the Edge						1:00-5:00	Empire B
POSTER SESSIONS							
Undergraduate Posters		4:00-6:00					Red & White Room
Biochemistry				4:00-6:00			Red & White Room
Environmental, Green & Sustainability				4:00-6:00			Red & White Room
Industry & Pharma				4:00-6:00			Red & White Room
Organic Chemistry				4:00-6:00			Red & White Room
Chemical Education						4:00-6:00	Red & White Room
Computation & MoleCVUE						4:00-6:00	Red & White Room
Inorganic Chemistry						4:00-6:00	Red & White Room
Physical Chemistry						4:00-6:00	Red & White Room
Polymer, Colloids, Nano & Materials						4:00-6:00	Red & White Room
Analytical, Bioanalytical & Forensic						4:00-6:00	Red & White Room

Meeting Schedule at a Glance

EVENT	SUN AM JUN 4	SUN PM JUN 4	MON AM JUN 5	MON PM JUN 5	TUE AM JUN 6	TUE PM JUN 6	LOCATION
WORKSHOPS							
"Using technology to move your chemistry course towards STEM"	9:30-10:30						Empire B
Undergraduate/graduate career workshop: "What's it like to be a scientist in industry?"	10:00-11:00						Empire C
Vernier technology teacher's workshop	10:30-12:00						Magnolia A
Undergraduate resume workshop	11:00-12:00						Empire C
"Molecular Modeling in the high school curriculum"		1:30-3:30					Tower 1
You be the chemist essential elements workshop		1:30-3:30					Cocoa 2
Chemagination competition		1:30-5:00					Wild Rose A/B
Chemagination awards		5:30-6:30					Wild Rose A/B
ACS career pathways workshop: "Finding yourself: Identifying a career that matches your strengths and values"			8:00-11:30				Cocoa 6
Law and intellectual property workshop: "Strong patents begin in the lab: A patent law primer for research chemists			9:00-11:00				Aztec
MoleCVUE Workshop on Computational Chemistry in the Undergraduate Curriculum			9:00-12:00	12:00-5:00			Tower 1
CrIME: Criminal Investigation through Molecular Examination				1:00-4:00			Cocoa 6
ACS Resume Reviews				1:00-4:00			Tower 3
MolecVUE round table event followed by invited luncheon (from 12-1:30)					8:00-12:00	12:00-1:30	Tower 1
Finding *Your* Path as a Chemical Professional: A Conversation						12:00-1:30	Forebay restaurant

Meeting Schedule at a Glance

SOCIAL EVENTS

EVENT	SUN AM JUN 4	SUN PM JUN 4	MON AM JUN 5	MON PM JUN 5	TUE AM JUN 6	TUE PM JUN 6	LOCATION
Brainstorm 2017/Student Chapter Breakfast	9:00-10:00						Empire A
Opening Luncheon Featuring Mr. and Mrs. Chocolate		12:00-1:30					Aztec & Nigerian Room
Chemagination Luncheon		12:30-1:30					Wild Rose A/B
Opening Reception		5:30-7:30					Great Lobby
Ice cream social for student chapters		7:00-8:30					Empire A
Chemistry trivia night		8:30-10:00					Empire B
Opening Cocktail Hour		8:30-10:00					Cocoa Terrace
Senior Chemists Breakfast			7:30-9:00				Tower 2
Coffee break			7:30-9:00				Confection Lobby
Younger Chemists Committee 5K			7:30-8:30				Hershey Medical Center Grounds
ACS Governance Luncheon				12:00-1:30			Aztec Room
Coffee break				2:00-3:30			Red/White Room
Awards Dinner and Ceremony				6:00-8:00			Aztec Room
Diversity and Inclusion Breakfast				7:30-9:00			Tower 2
Coffee break					7:30-9:00		Confection Lobby
Local Section Officers Lunch						12:00-1:30	Tower 2
Coffee break						2:00-3:30	Red/White Room
Brewery Tour (Must be 21 and older)						5:00-6:30	Troegs Brewery
Wine-Chocolate Tasting (Must be 21 and older)						5:00-6:30	Tower 1

Participating ACS Local Sections

Middle Atlantic Regional Meeting
MARM

Representing Over 30,000 Members

Chemical Society of Washington DC
Delaware
Lehigh Valley
Maryland
Monmouth County
New York
North Jersey
Ocean County
Philadelphia
Princeton
South Jersey
Southeastern Pennsylvania
Susquehanna Valley
Trenton
Western Maryland

Your Host Sections:
Lehigh Valley and Susquehanna Valley

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Posters	Lee Silverberg	The Pennsylvania State University, Schuylkill Campus
Chemagination	Carol Stein	Intertek
	Louise Lawter	Retired
Workshop Coordinator	Shannon Nowotarski	The Pennsylvania State University, Berks Campus,
Chemical Safety Workshop	Danielle Ringhoff	Northampton Community College
Career Pathways Workshop	Bill Suits	CIT Chemjobs
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American Chemical Society

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WASHINGTON, D.C. 20036
Phone: 202-872-4534
executivedirector@acs.org

June 4, 2017

Dear Middle Atlantic Regional Meeting participants,

It is our pleasure to welcome you to the 45th Middle Atlantic Regional Meeting (MARM) in Hershey, Pennsylvania, also known as Chocolatetown, USA.

Regional meetings, like MARM, provide an excellent opportunity for ACS members to share science, collaborate and network. At this meeting, we encourage you to take advantage of the 50+ outstanding technical sessions, of which we have received more than 600 abstract submissions. We are expecting approximately 800 of your fellow members and colleagues from academia, industry, government, and NGOs to attend this regional meeting.

To add to Dr. Campbell's meeting highlights in her welcome letter, we are pleased that Dr. Esther Takeuchi will deliver the plenary keynote during the Awards Banquet on Monday, June 5, 2017 at 8:00 p.m. Dr. Takeuchi was awarded the National Medal of Technology and Innovation by President Obama in 2009, and in May, 2011, she was inducted into the National Inventors Hall of Fame. We're confident she will deliver a captivating speech.

Also in the meeting program you will note that there is an ACS Chemical Health & Safety workshop on Sunday, June 4, 2017 from 8:30 a.m. – 4:00 p.m. You may recall that Safety and Ethics have been added to the Professionalism ACS core value to emphasize the importance of these two areas in the chemical enterprise.

In closing, great meetings start with great planning. We want to express our sincere thanks to MARM co-chairs Lorena Tribe and Dee Casteel who have worked diligently with the team of division and committee chairs, as well as with all the volunteers, to help make this meeting a success. We also extend our utmost appreciation to the members of the Lehigh Valley and Susquehanna Local Sections who are hosting this meeting. Collectively, you are helping achieve the ACS vision "Improving people's lives through the transforming power of chemistry".

Sincerely yours,

Pat N. Confalone, PhD.
Chair, ACS Board of Directors

Thomas M. Connelly, PhD.
ACS Executive Director & CEO

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HERSHEY Lodge

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Dear Meeting Participants:

Welcome to the 45th Middle Atlantic Regional Meeting. Our theme this year is "Elements of Transition," inspired by the many changes encountered by the chemical enterprise and during our professional lives. We are delighted that you have chosen to join us and are very proud of the program that has been organized for you.

We are also pleased to be returning to Hershey Lodge, a wonderful venue for sharing science, meeting friends old and new, and enjoying the local attractions.

This year's meeting has 45 symposia, 62 half-day session, and 3 poster sessions highlighting advances in the traditional areas of chemistry, as well as in cosmetics, materials, nanotechnology, drug discovery, metabolomics, biosensors, ionic liquids, imaging, and green chemistry.

Our special events include an awards banquet on Monday evening where regional award winners will be celebrated. Our guest speaker for that evening is Esther S. Takeuchi of Stony Brook University, whose work on efficient energy storage systems was instrumental in the development of implantable cardiac defibrillators, lithium batteries, and over 150 patents.

There are numerous workshops, special programming for undergraduates, Chemagination, and so much more. Please be sure to visit the Expo, which features over 30 exhibitors showcasing opportunities and cutting edge technologies. A wide variety of programs available have been supported by our wonderful sponsors, and were made possible by a dedicated team of volunteers.

In name of the MARM 2017 team, we hope you have a wonderful time during the meeting at Hershey.

Best wishes,

Lorena Tribe
General Co-Chair

Dee Ann Casteel
General Co-Chair

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Established in 1846 as the University at Lewisburg; renamed Bucknell University in 1886 in honor of William Bucknell, a major benefactor. The University is highly selective, private, nonsectarian, coeducational (since 1883), residential and undergraduate, with a small graduate program. Bucknellians of all generations share curiosity, creativity, ambition and drive. Working with them, you'll achieve the education you deserve and you'll grow in ways you never thought possible. You'll think critically, express yourself fully, thrive on challenge, and succeed in your career.

https://www.bucknell.edu/academics/arts-and-sciences-college-of/academic-departments-and-programs/chemistry.html

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From its beginnings as Wyomissing Polytechnic Institute (WPI) to becoming part of the Penn State system in 1958, the Berks campus has experienced many changes. WPI occupied the original Sacred Heart Church building on Hill Road, where the McDonald's Restaurant now stands, from 1930 to 1958 when its facilities were offered to Penn State to establish Penn State Wyomissing Center, now Penn State Berks campus. It moved to its present Spring Township location in 1972. With the addition of the residence halls in 1990, Berks became a residential and commuter campus. In 1997 Penn State Berks was granted "college" status and began offering a variety of four-year baccalaureate degree programs. Today Penn State Berks includes 30 buildings on 258 acres of land, and there are 231 full-time and adjunct faculty members. Residence halls provide housing for 805 students.

http://berks.psu.edu/

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Medicinal Chemistry is a discipline resting at the intersection of synthetic organic chemistry, biochemistry, pharmacology and focuses on the design, chemical synthesis and development of bio-active molecules and pharmaceutical agents. The Division of Medicinal Chemistry (MEDI) is one of the Technical Divisions of the American Chemical Society, which is the largest scientific society in the world having over 161,000 members. The MEDI Division is one of the largest divisions having ~9,600 members from 79 countries.

https://www.acsmedchem.org/?nd=home

Over the last 135 years ExxonMobil has evolved from a regional marketer of kerosene in the U.S. to the largest publicly traded petroleum and petrochemical enterprise in the world.

http://corporate.exxonmobil.com/

The institution we know today as Wilkes University began in 1933 when Bucknell University established its Junior College in Wilkes-Barre, Pennsylvania. Bucknell University Junior College (BUJC) attracted eager, highly motivated, and able young persons, virtually all of whom were the first members of their families to benefit from higher education.

http://www.wilkes.edu/academics/colleges/science-and-engineering/index.aspx

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The 15-member Joint Board-Council Committee on International Activities (IAC) was established by action of the ACS Board of Directors on June 27, 1962 and was upgraded in 1974 to a joint Board-Council Committee. The IAC is responsible for studying and recommending appropriate SOCIETY participation and cooperation in international undertakings pertaining to chemical education, professional activities, and scientific matters of interest to chemists and chemical engineers, and coordinating its efforts with those of other organizations.

https://www.acs.org/content/acs/en/about/governance/committees/international.html

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The Hepatitis B Foundation is a national nonprofit organization dedicated to finding a cure and improving the quality of life for those affected by hepatitis B worldwide. Our commitment includes funding focused research, promoting disease awareness, supporting immunization and treatment initiatives, and serving as the primary source of information for patients and their families, the medical and scientific community, and the general public.

http://www.hepb.org/

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The Pennsylvania Turfgrass Council is an organization dedicated to the improvement of the Turfgrass Industry through education and research. The Council was founded in 1955 by a group of individuals who perceived the need for independent funding for turfgrass research in Pennsylvania. Since its beginning, P.T.C.?s role has expanded considerably, and the organization's goals can now be divided into three major areas: fundraising for education, and research, conducting educational conferences, and representing the Turfgrass Industry.

https://paturf.org/

The goal of the Division of Colloid and Surface Chemistry is to promote discovery, scholarship, and innovation in colloid, surface, interface, and nanomaterials chemistry as pursued by a global and multidisciplinary scientific community. The goal is achieved through scientific meetings, publications and awards

http://colloidssurfaces.sites.acs.org//

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AMERICAN CHEMICAL SOCIETY

SCHB
Division of Small Chemical Businesses

The ACS Division of Small Chemical Businesses (SCHB) has objectives "To aid in the formation, development, and growth of small chemical businesses." SCHB helps chemists working in small enterprises, including self-employed, with the legal, social, educational, legislative, regulatory, and economic aspects of their unique professional status. SCHB serves as a clearinghouse of information, a forum for discussion, and a liaison between small businesses and students.

http://acs-schb.org/

Elizabethtown College is a selective, independent, residential coeducational college located on an attractive 203-acre campus in south central Pennsylvania. Its approximately 1,800 students hail from nearly 30 states and 40 foreign countries. Our commitment is to Educate for Service. We believe that learning is most noble when used to benefit others, regardless of chosen career path. We prepare our students to lead rich lives of purpose and meaning, while advancing independent thought, personal integrity and social responsibility. These are the foundations for a life of learning. We foster the values of peace, non-violence, human dignity and social justice.

https://www.etown.edu/

Bronze Sponsors

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https://www.bruker.com/

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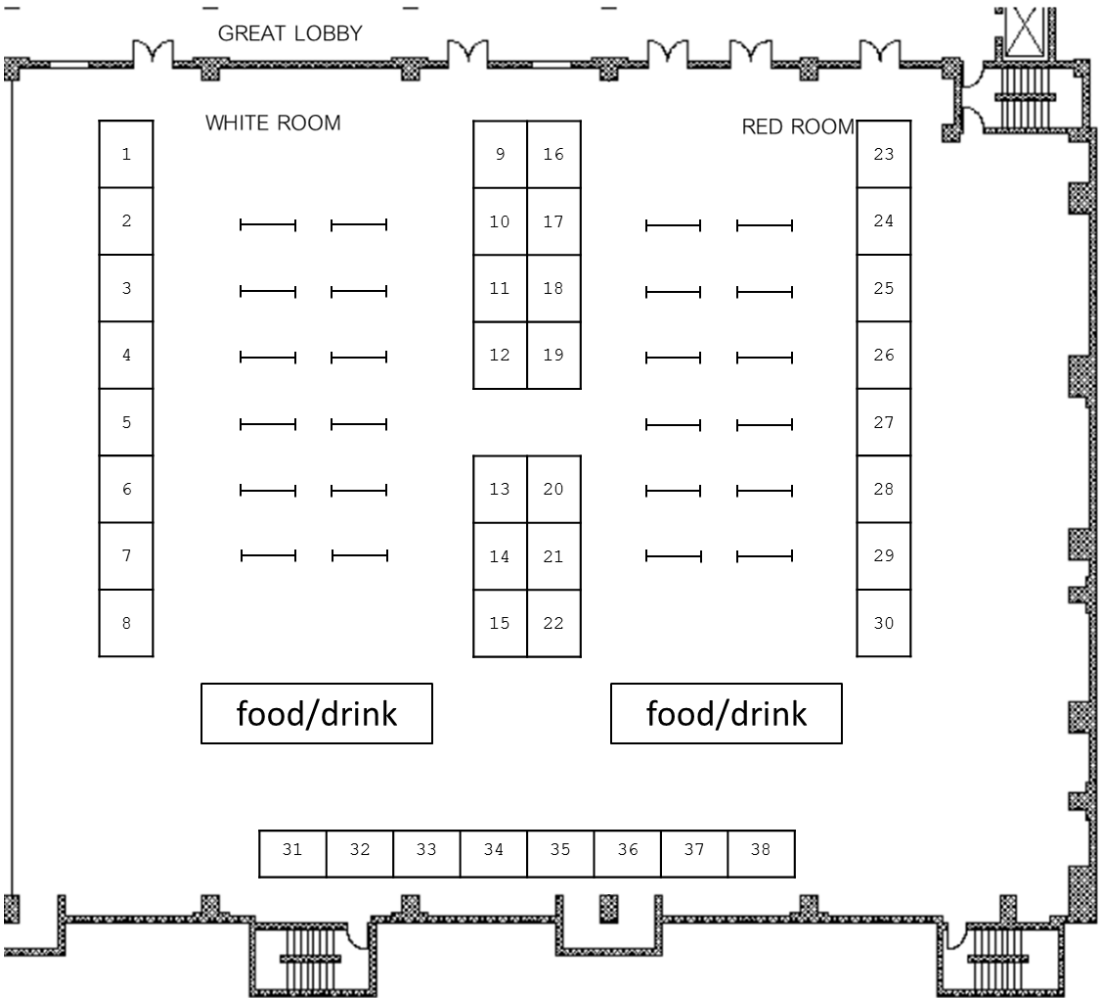
http://www.brenntag.com/north-america/en/

45th Middle Atlantic Regional Meeting Exhibitors and Booth Assignments



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Exhibitors

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The early history of Penn Arts & Sciences is intertwined with that of the first years of the University of Pennsylvania, which was established in 1740. Building on founder Benjamin Franklin's vision of combining a traditional and practical education, the College was the first colonial institution to teach the sciences, government and commerce, as well as classical subjects such as Latin, literature and philosophy. The College also had the colonies' only non-sectarian faculty. Graduates and trustees were instrumental in the development of the new nation, serving as members of the Continental Congress and signers of the Declaration of Independence and Constitution. By 1779, however, the state legislature considered the College a hotbed of loyalism and transferred its assets to the new University of the State of Pennsylvania. After a long legal battle, the two institutions were merged, creating the University of Pennsylvania in 1791.

https://www.sas.upenn.edu/

2

Founded in 1981, Vernier pioneers award-winning interfaces, sensors, software, and curriculum to transform how educators teach science and how students collect, analyze, and interpret scientific data. When it comes to scientific data collection, Vernier has perfected the development and production of affordable, easy-to-use data-acquisition products (probeware) for science classrooms and labs around the world.

https://www.vernier.com/

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3

Biolin Scientific is a leading Nordic instrumentation company with roots in Sweden and Finland. Our customers include companies working with pharmaceuticals, energy, chemicals, and advanced materials, as well as academic and governmental research institutes. Our precision instruments help discover better drugs faster, develop better solutions for energy and materials, and perform research at the frontiers of science and technology.

http://www.biolinscientific.com/

4

Since 1949, the JEOL legacy has been one of outstanding innovation in developing instruments used to advance scientific research and technology. JEOL has 60 years of expertise in the field of electron microscopy, more than 50 years in mass spectrometry and NMR spectrometry, and more than 40 years of e-beam lithography leadership.

http://www.jeolusa.com/

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A leading public institution, Rowan University combines liberal education with professional preparation from the baccalaureate through the doctorate. Rowan provides a collaborative, learning-centered environment in which highly qualified and diverse faculty, staff, and students integrate teaching, research, scholarship, creative activity and community service. Through intellectual, social and cultural contributions, the university enriches the lives of those in the campus community and surrounding region.

http://www.rowan.edu/

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Already in 1919 Philips brought the first X-ray tube to the market and in 1945 the first X-ray diffractometer was developed, forming the basis for the founding of the X-ray analysis group within Philips. Under the name of 'Philips Analytical' we grew continuously and the successes of our X-ray diffractometers (XRD) and X-ray fluorescence spectrometers (XRF) have made us the world-leader in X-ray analysis equipment. In 2002, PANalytical was incorporated into Spectris as an autonomous operating business. Since 1 January 2017 PANalytical has merged its activities with Malvern Instruments, a UK-based provider of materials and biophysical characterization technology and also an operating company within the Materials Analysis segment of Spectris. We continue to be committed to leadership and innovation, customer satisfaction, safety, environmental health, ethical standards, integrity, fairness, trust and mutual respect.

http://www.panalytical.com/Home.htm

7

Rutgers University – Newark is an urban, public research university that is not merely in, but of its environment. It is a university of the system of Rutgers, The State University of New Jersey, located in the great city of Newark, the state's largest city and cultural capital, where the great challenges facing our increasingly metropolitan nation and world increasingly can be found, as can the assets needed to take on those challenges. The RU-N community takes very seriously the urgent call to higher education today to prepare students for the world as it will be; produce scholarship that makes a difference in our city, state, nation, and world; increase access and affordability for increasingly diverse generations of students; fully recognize and reward faculty and staff for the full range of their roles; and get higher education out of its silo through collaborations locally and globally, while breaking down silos within.

https://www.newark.rutgers.edu/

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From our start we have created instruments with uncommon value and performance. Our ground-breaking design made computer-controlled potentiostats more available than ever. Our software was the first to be available on Microsoft™ Windows, and allowed unprecedented customization of the experiments using EXPLAIN™, our experimental control language. Utilizing state of the art digital signal processing, we were the first instrument company to use sub-harmonic sampling on our full line of instruments. This technology allows Gamry instruments to make Electrochemical Impedance measurements without the need for additional hardware. In addition to exceptional performance, we also pay attention to physical instrument design. We maximize the use of surface mount components with state of the art circuit board layout to minimize instrument size and increase long term reliability. All of Gamry's instruments are also ecologically friendly. We make extensive use of highly recyclable aluminum and use completely lead free circuit board assemblies.

http://www.gamry.com/

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The mission of Bryn Mawr College is to provide a rigorous education and to encourage the pursuit of knowledge as preparation for life and work. Bryn Mawr teaches and values critical, creative and independent habits of thought and expression in an undergraduate liberal arts curriculum for women and in coeducational graduate programs in arts and sciences and social work and social research. Bryn Mawr seeks to sustain a community diverse in nature and democratic in practice, for we believe that only through considering many perspectives do we gain a deeper understanding of each other and the world.

https://www.brynmawr.edu/gsas/

10

The HORIBA Group of worldwide companies provides an extensive array of instruments and systems for applications ranging from automotive R&D, process and environmental monitoring, in-vitro medical diagnostics, semiconductor manufacturing and metrology, to a broad range of scientific R&D and QC measurements. Proven quality and trustworthy performance have established widespread confidence in the HORIBA Brand. Inspired by our unique motto, “JOY and FUN,” we focus on social responsibilities by building state-of-the-art products for scientific advancement; especially for protecting health, safety, and the environment. “HORIBARIANs,” the HORIBA employees all over the world, are looking forward to working with you and providing the best analytical solution for your needs.

http://www.horiba.com/us/en/scientific/

11

The C. Eugene Bennett Department of Chemistry provides the opportunity for students to become leaders in all fields of chemistry. There are lecture courses in the general areas of inorganic, organic and physical chemistry, in addition to more specialized courses. Undergraduates are encouraged to participate in research with faculty mentors, developing the ability to understand complex concepts. Graduate researchers work independently in their chosen fields in addition to teaching undergraduate courses.

http://www.chemistry.wvu.edu/

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Agilent Technologies

Agilent is a leader in life sciences, diagnostics and applied chemical markets. The company provides laboratories worldwide with instruments, services, consumables, applications and expertise, enabling customers to gain the insights they seek. Agilent's expertise and trusted collaboration give them the highest confidence in our solutions.

http://www.agilent.com/

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Surface Measurement Systems
World Leader in Sorption Science

To expand the frontiers of particle, materials and surface science by developing unique characterization solutions. We aim to foster a spirit of integrity and commitment, where professionalism can flourish in an environment that provides a high degree of employee satisfaction. To be attentive and responsive to our customers needs by developing positive long-term relationships. To continuously forge the company into a world class organization and remain synonymous with innovative engineering and scientific excellence.

https://www.surfacemeasurementsystems.com/

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Advion

Advion, Inc. was founded in 1993 based on the novel techniques developed within the Cornell University laboratory of Dr. Jack Henion, a leading researcher in the field of Liquid Chromatography/Mass Spectrometry (LC/MS). The company's vision was to become a leading provider of bioanalytical contract services to the pharmaceutical industry, a position it attained prior to the sale of its contract drug development laboratory business to Quintiles. Pioneers within the industry, Advion offers a variety of mission critical systems and consumables for life science research. With sales and support offices in North America, Europe, and Japan, Advion is a global company with customers in all of the top pharmaceutical companies, government life science research agencies and universities. Advion continues to expand its diverse portfolio of innovative microfluidic and mass spec – based products for the life science industry.

http://www.advion.com/products/

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MACHEREY-NAGEL Inc. is the U.S. distributor for MACHEREY-NAGEL GmbH & Co KG. MACHEREY-NAGEL is a manufacturer of chromatography consumables such as NUCLEOSIL HPLC columns, GC columns, TLC plates and sheets, syringe filters and SPE products.

http://www.mn-net.com/

16

Since 1964, Extrel's instruments have been recognized for their exceptional performance, reliability and flexibility, and are complemented by the most comprehensive application, We serve a wide range of industries such as pharmaceuticals, chemicals, food & beverage, feed, environmental analysis and academia.technical and on-site support in the industry. Providing solutions for the needs of today's leading researchers from individual components to full all-in-one systems, Extrel works with their customers to deliver the best product for their needs.

http://www.extrel.com/

17 and 18

Thermo Fisher Scientific Inc. is the world leader in serving science, with revenues of $18 billion and more than 55,000 employees globally. Our mission is to enable our customers to make the world healthier, cleaner and safer. We help our customers accelerate life sciences research, solve complex analytical challenges, improve patient diagnostics and increase laboratory productivity. Through our premier brands – Thermo Scientific, Applied Biosystems, Invitrogen, Fisher Scientific and Unity Lab Services – we offer an unmatched combination of innovative technologies, purchasing convenience and comprehensive support.

http://www.thermofisher.com/us/en/home.html/

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Nanalysis Corp was established in 2009. The company develops and manufactures portable Nuclear Magnetic Resonance (NMR) spectrometers for the laboratory instrumentation market. The NMReady™-60 is the first fully featured portable NMR spectrometer in a single compact enclosure requiring no liquid helium or any other cryogens. The NMReady-60 family of NMR spectrometers are used by chemical professionals in all types of industries (oil & gas, chemical, pharma, biotech, food processing) as well as government and university labs.

http://www.nanalysis.com/

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Sirius Analytical are specialists in the provision of physicochemical data and consultancy services to the pharmaceutical industry and other business sectors. These services, which were initiated in 1991, comprise a range of physicochemical and solid state analyses which can be applied at many points in the drug development timeline. Sirius Analytical undertakes work comprising a number of predefined analyses or flexible study based project work developed in consultation with the customer. Our pre-defined assays include screening analyses, “Gold Standard” definitive physicochemical assays and Formulation and Development studies.

http://sirius-analytical.com/

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Since its inception in 1951, Rigaku has been at the forefront of analytical and industrial instrumentation technology. Today, with hundreds of major innovations to their credit, the Rigaku Group of Companies are world leaders in the fields of general X-ray diffraction (XRD), thin film analysis (XRF, XRD and XRR), X-ray fluorescence spectrometry (TXRF, EDXRF and WDXRF), small angle X-ray scattering (SAXS), protein and small molecule X-ray crystallography, Raman spectroscopy, X-ray optics, semiconductor metrology (TXRF, XRF, XRD and XRR), X-ray sources, computed tomography, nondestructive testing and thermal analysis.

https://www.rigaku.com/

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The University of Delaware exists to cultivate learning, develop knowledge and foster the free exchange of ideas. State-assisted yet privately governed, the University has a strong tradition of distinguished scholarship, research, teaching and service that is grounded in a commitment to increasing and disseminating scientific, humanistic and social knowledge for the benefit of the larger society.

http://www.udel.edu/

23

Tokyo Chemical Industry Co., Ltd. (TCI) is a leading worldwide manufacturer of specialty organic chemicals founded in 1946. TCI provides organic laboratory chemicals as well as pharmaceutical, cosmetic and functional materials. More than 60 years of synthesis experience and multi-purpose plants enable TCI to offer more than 27,000 products as well as custom synthesis. TCI established overseas facilities in North America, Europe, China and India to serve customers worldwide.

http://www.tcichemicals.com/en/us/

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Determination and prediction of solubility, dissolution, permeability and human absorption is Pion's core business. We screen and analyze pharmaceutical compounds using instrumentation, software and laboratory services.

https://www.pion-inc.com/

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Through applying our full spectrum of innovative technologies and using our critical knowledge and expertise, we continue to provide solutions that enable greater insights and better outcomes. In collaboration with our customers and business partners, we are eager to continue to improve lives and the world around us for years to come.

http://www.perkinelmer.com/

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The institution we know today as Wilkes University began in 1933 when Bucknell University established its Junior College in Wilkes-Barre, Pennsylvania. Bucknell University Junior College (BUJC) attracted eager, highly motivated, and able young persons, virtually all of whom were the first members of their families to benefit from higher education.

http://www.wilkes.edu/

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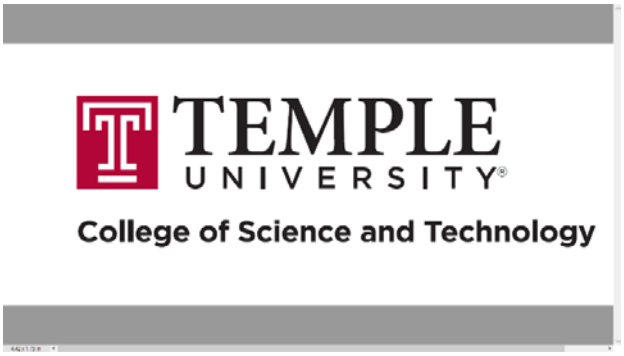

The College of Science and Technology (CST), with more than 4,000 students, is one of Temple University's fastest growing schools. At CST, students work side-by-side with experienced faculty researchers in the lab, in the field and in the classroom. Since 2007, external funding for advanced research has more than doubled, creating new opportunities for CST faculty to take on today's toughest scientific challenges

http://cst.temple.edu/forensicchemistry/

29

Magritek creates cryogen-free, compact Nuclear Magnetic Resonance (NMR) and Magnetic Resonance Imaging (MRI) systems that work on the benchtop. Magritek solutions are affordable, versatile, high performance and easy to use. Magritek's innovative and accessible products are grouped into research spectrometers, portable instruments and education systems.

http://www.magritek.com/

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Oakwood Products, Inc. is a fine organics manufacturing facility located in Estill, South Carolina, USA. We produce a wide range of organics with particular emphasis on fluorine and sulfur compounds. In addition to our extensive catalog, Oakwood also offers custom synthesis services. Feel free to contact us via phone, fax, or email regarding custom synthesis and bulk quantities.

https://www.oakwoodchemical.com/

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LEHIGH UNIVERSITY

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Oakwood Chemical
Enabling Discovery

Oakwood Products, Inc. is a fine organics manufacturing facility located in Estill, South Carolina, USA. We produce a wide range of organics with particular emphasis on fluorine and sulfur compounds. In addition to our extensive catalog, Oakwood also offers custom synthesis services. Feel free to contact us via phone, fax, or email regarding custom synthesis and bulk quantities.

https://www.oakwoodchemical.com/

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THE GRADUATE CENTER
CITY UNIVERSITY OF NEW YORK

The University's unwavering commitment to that principle is a source of enormous pride. CUNY colleges offer a seemingly infinite array of academic programs taught by award-winning faculty, as well as sports, internships, scholarships and community service opportunities found on campuses throughout New York City's five boroughs. CUNY's combination of quality academics, remarkable affordability, financial support and the convenience of 25 modern campuses offers a remarkable educational experience.

http://www.gc.cuny.edu/

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36 Shimadzu Scientific Instruments (SSI) is the American subsidiary of Shimadzu Corporation, headquartered in Kyoto, Japan. Founded in 1875, Shimadzu is a $2 billion multinational corporation with three major divisions: Medical Diagnostics, Aerospace/Industrial, and Analytical Instruments. The Analytical Division is one of the world´s largest manufacturers of analytical instrumentation and environmental monitoring equipment.

http://www.ssi.shimadzu.com/

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Many years ago, PASCO was born from a science fair project. So hands-on, inquiry-based science is built into our company DNA. Very simply, our mission is to provide educators worldwide with innovative ways to teach and learn science.

https://www.pasco.com/

Research Experiences For Undergraduates

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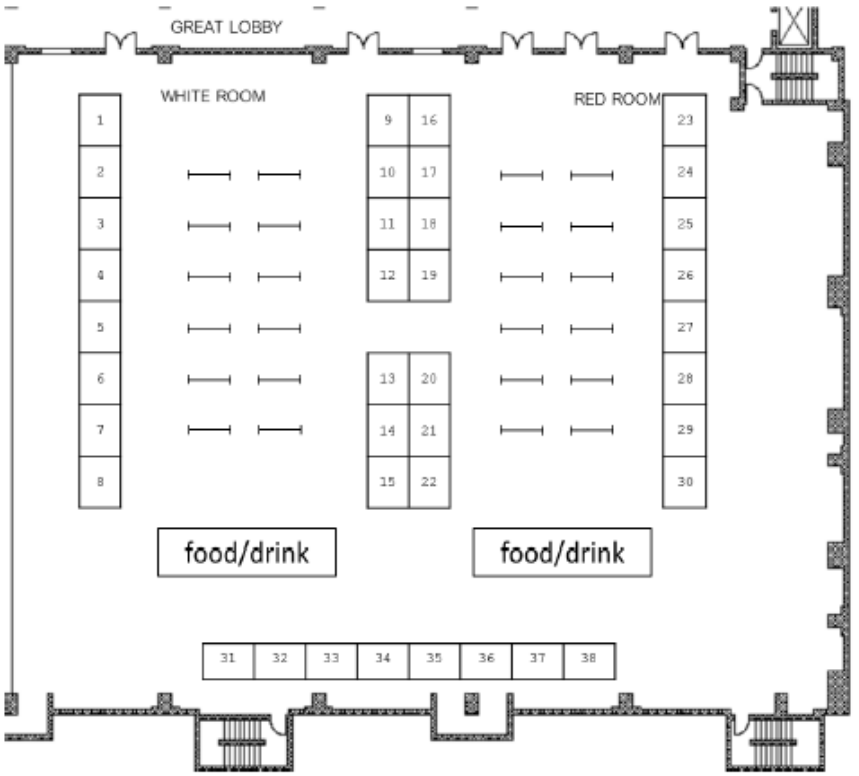
Involvement of undergraduate students in research has a positive impact on student career paths, professional development and their ability to make informed choices about their future. It provides a unique opportunity for the student to receive individual mentoring from science leaders. The Chemistry REU Leadership Group is composed of a subset of REU Site Directors and is supported by a special grant from the NSF. Its mission is to improve the REU program through workshops, travel grants, symposia, and other innovative activities and provide guidance to current and prospective REU Site PIs. The Research experience for undergraduate (REU) opportunities are available in every discipline that is supported by the National Science Foundation (NSF), as well as through interdisciplinary, international, national laboratory and museum hosts.

https://www.nsf.gov/crssprgm/reu/reu_search.jsp

45th Middle Atlantic Regional Meeting Exhibitors and Booth Assignments



Keynote Speaker

Professor Esther S. Takeuchi
Stony Brook University and Brookhaven National Laboratory
Awards Banquet, 6 – 8 pm, Monday June 5
Aztec Room, Hershey Lodge

Dr. Esther S. Takeuchi is a SUNY Distinguished Professor and holds the William and Jane Knapp Chair in Energy and the Environment in the Departments of Materials Science and Chemical Engineering and Chemistry at Stony Brook University. She also has a joint appointment at Brookhaven National Laboratory as Chief Scientist in the Energy Sciences Directorate.

Prior to her academic appointment, she was employed at Greatbatch, Inc., where her achievements in lithium battery research, particularly on cells for implantable applications, led to a number of key technological developments. Her work was instrumental in the successful development of the lithium/silver vanadium oxide (Li/SVO) battery that is the power source of life-saving implantable cardiac defibrillators (ICDs). The battery technology enabled the widespread adoption of ICDs and remains critical as >300,000 are implanted per year. Dr. Takeuchi is a prolific inventor with > 150 patents.

Dr. Takeuchi has been widely recognized. She is a member of National Academy of Engineering. In 2009, Dr. Takeuchi was awarded the National Medal of Technology and Innovation by President Obama. In May, 2011 she was inducted into the National Inventors Hall of Fame. She was elected as a Charter Member of the National Academy of Innovation in 2013. She received the E. V Murphree Award and Astellas Award from the American Chemical Society and the Electrochemical Society Battery Division Technology award. She is a Fellow of the Electrochemical Society (ECS) and the American Institute of Medical and Biological Engineering.

Dr. Takeuchi received a bachelor's degree from the University of Pennsylvania with a double major in chemistry and history and completed a Ph.D. in chemistry at the Ohio State University. She completed post-doctoral research at the University of North Carolina and University at Buffalo.

MARM 2017 Awards

Stanley C. Israel Region Award
for Advancing Diversity in the Chemical Sciences

To recognize individuals and/or institutions that have advanced diversity in the chemical sciences and significantly stimulated or fostered activities that promote inclusiveness within the region.

Sponsored by the Committee on Minority Affairs of the American Chemical Society

Stanley C. Israel

2017 Recipient: the Ph.D. program in Chemistry at the City University of New York

Diversity and inclusion are ingrained into the DNA of the PhD Program in Chemistry at the City University of New York that serves the largest urban university in the United States. A long-term and sustained commitment to diversity in faculty hiring, promotion and retention at the CUNY campuses has resulted in a richly diverse doctoral chemistry faculty by all measures. The present Chemistry Doctoral Faculty of ninety chemists boasts 34% female faculty and 7% faculty from minority groups underrepresented in science compared to national averages of 19% and 4%, respectively. This attention to diversity is also evident in the degrees awarded, 29% of all their PhD graduates are women, and in the undergraduate population that they serve at the various CUNY campuses.

The PhD Program in Chemistry will be represented by:
Brian R. Gibney, PhD
Executive Officer, PhD Program in Chemistry of the City University of New York

The ACS Division of Chemical Education (CHED) Middle Atlantic Region Award for Excellence in High School Teaching

To recognize, encourage, and stimulate outstanding teachers of high school chemistry in the Middle Atlantic Region.

2017 Recipient: Catherine Zavacki, Hillsborough High School, Hillsborough, NJ

Cathy Zavacki has been a Chemistry teacher at Hillsborough High School in Hillsborough, NJ since 2000. She has her undergraduate degree from Bloomsburg University, a Master's degree in education through the Regional Training Center, Gratz College and over 60 post-masters graduate credits. Cathy is also a graduate instructor for the Regional Training Center instructing courses on both Motivation and Kinesthetic learning. In 2016, Cathy was recognized as the Chemistry Teacher of the Year for the Princeton and Trenton sections of the ACS.

Cathy's focus as a teacher is on reaching students at all levels of learning and using novel teaching techniques to do so. She is an innovative teacher that is passionate about working with struggling learners. She works collaboratively with her special education co-teacher to ensure success for all of their students in the classroom. Cathy is an advocate of Kinesthetic learning and shares her expertise in Kinesthetic learning by co-presenting at the New Jersey Science Teacher's Conference (2015) and most recently presented at the Kentucky Science Teacher's Association Conference (2016). This summer she will be co-presenting two workshops on Kinesthetic Chemistry and Chemistry for the Struggling Learner at ChemEd17 at the University of South Dakota.

Cathy's principal stated, "It can be easy to be an Advanced Placement or honors teacher, but it is a true gift to be able to teach all levels, including special education students, with the same adeptness and enthusiasm. Mrs. Zavacki has always managed to find a way to appeal to her students bring them to be excited and willing participants in the scientific inquiry that occurs in her classroom."

E. Emmet Reid Award
in Chemistry Teaching at Small Colleges in the ACS Mid-Atlantic Region

To recognize, encourage, and stimulate high quality teaching and research at small colleges. Administered by the Organizing Committee of MARM.

E. Emmet Reid

2017 Recipient: Professor Chip Nataro, Lafayette College

Chip Nataro obtained his B.S. degree from Messiah College in 1991. He earned his PhD with Bob Angelici at Iowa State University where he studied the protonation of metal-metal bonds. Nataro went to the University of Vermont for his post doc where he split time learning about inorganic polymers with Chris Allen and organometallic electrochemistry with Bill Geiger. He has been at Lafayette since 1999 and has worked with 65 undergraduate research students and three high school students. He and his students perform research in organometallic chemistry with a particular fondness for bis(phosphino)ferrocene ligands. The group studies the electrochemistry, catalytic activity and coordination modes of these ligands. He and his students have published 36 papers detailing this work. Nataro teaches inorganic and general chemistry at Lafayette. He is a member of the leadership council of the Interactive Online Network of Inorganic Chemists (IONiC) most known for the Virtual Inorganic Pedagogical Electronic Resource (VIPEr) website, has participated in writing inorganic exams for the ACS exams institute and was the preceptor recipient of the ACS Division of Inorganic Chemistry Award for Undergraduate Research in 2013. He has also taught a first year seminar course on baseball and coaches the club baseball team at Lafayette. His amazing and understanding wife (June 6th marks a big anniversary), S. Leigh Nataro, is chair of the math department at Moravian Academy in Bethlehem, PA where his daughter, Cassie, is a rising senior.

E. Ann Nalley Middle Atlantic Region Award for Volunteer Service to the American Chemical Society

To recognize the volunteer efforts of individuals who have served the American Chemical Society, contributing significantly to the goals and objectives of the Society through their Regional Activities.

2017 Recipient: Professor JaimeLee Iolani Rizzo

Dr. JaimeLee Iolani Rizzo is Professor and Assistant Chair of Chemistry and Physical Sciences at Pace University, NYC. She was born and raised in Hawai'i and a graduate of the prestigious Kamehameha Schools. She relocated to New York and is referred to as a "fiver" – a five time graduate of CUNY. She earned an A.S., B.A, M.A. M. Phil, and Ph.D. all through the City University of New York's educational system.

Dr. Rizzo's work involves the synthesis and characterization of materials bearing antimicrobial activity where she has 15 patents and numerous publications and presentations relating to her work. She is also a co-author of two textbooks, "Phosphorus Chemistry" and "Organic Chemistry".

Dr. Rizzo serves as the Coordinator of the Professions in Health Advisory Team (PHAT) and as Faculty Advisor for Pace's Chemistry Club for the past 7 years where her Student Chapter has been awarded Honorary Mention for 3 consecutive years. She was the 2012 Chair of the New York Section of the ACS and currently serves as a Councilor for the Section. Her service to the Section also includes the following: Co-Chair of the Student Activities Committee (6 years), Project Leader of the National Chemistry Week Committee (6 years), and Session Organizer for MARM in 2008 and 2016. She was awarded two Community Interaction Grants in 2015 and 2016 for the development of an event where high school students spend the day shadowing Pace's majors and where Pace's majors spend the day at a local high school to help foster the importance of a higher education in the chemical sciences. Her most significant contribution to the Section was the development of a Chemists Celebrate Earth Day event where over 150 participants gather from local schools and institutions with their friends and families. Following a keynote address, participants parade over the iconic Brooklyn Bridge to help bring awareness of the importance of chemistry and the various ways it can help to conserve our planet. She was awarded an Innovation Project Grant for this new CCED event and has been organizing it for the past 6 years.

Partners for Progress and Prosperity (P3) Region Award

To encourage and recognize successful and exemplary partnerships. These partnerships can be between industry, academia, government, small business and/or other organizations, including ACS local sections, ACS divisions, ACS international chapter, other societies or various entities domestic or overseas resulting in impactful outcomes in one or more of the following categories: improving the public perception and appreciation for chemistry; promoting career advancement opportunities and/or supporting entrepreneurship in the chemistry enterprise; advancing advocacy efforts with government and other thought leaders; supporting STEM education and/or research.

Award created by Marinda Li Wu during her ACS Presidency; now supported by the MARM board.

2017 Recipient: NCW – New York Hall of Science (NYSCI) Program

The award-winning partners were the New York Hall of Science, the ACS New York Section, St. John's University and their student ACS chapter, the United States Merchant Marine Academy, and PepsiCo.

The New York Local Section (NYACS) is proud decade-long partner of the New York Hall of Science (NYSCI) in present a fun-filled day of experimentation and exploration of chemistry during National Chemistry Week. The partnership has positive impacts on there of the
Partners for Prosperity and Progress Award:

• Improving the public perception and appreciate for chemistry

The celebration of National Chemistry Week at the New York Hall of Science is the foremost outreach activity of the New York Local Section. The event attracted 1,180 visitors to the NYSCI last year.. The majority of the visitors to the hands-on demonstrations at NCW are grade school children and their parents who come from the diversity that is New York City. The success of the event is the combination of volunteers in the
NYACS collaborating with the staff of NYSCI and volunteers from industry putting together thought provoking scientific demonstrations suitable for grade school children in a safe and supportive environment. The energy in the room is fantastic as the visitors are shown the positive impact of chemistry on their lives. The NYSCI is a great venue in which to improve the public's perception of chemistry, chemists and the chemical enterprise.

• Advancing advocacy efforts with government and other thought leaders

Each year, the NYACS Coordinator of NCW reaches out to local dignitaries and politicians to participate in the festivities. Recently, New York State Senator Jose Peralta (2016) and New York Schools Chancellor Dennis Walcott (2013) have visited the celebration of National Chemistry Week at the NYSCI. This provides the NYACS and NYSCI the opportunity to open a dialogue with which to advocate for chemistry with local and state leaders.

• Supporting STEM education and/or research

The celebration of National Chemistry Week at the NYSCI brings together chemistry faculty and undergraduate students from the around the region. The faculty and undergraduates collaborate on deciding which chemistry demo to present, and how best to present the underlying chemical principles. This helps the undergraduates learn how to articulate complex chemical principles using everyday language that grade school children can understand. In addition, the undergraduates are tasked with maintaining a safe working environment. Approximately 35 NYSCI Staff members actively participated in Chemistry Day.

NERM 2017 Awards

Maggie H. Estlinbaum, NERM 2017 Awardee of the ACS Division of Chemical Education (CHED) Northeast Region Award for Excellence in High School Teaching

Maggie Estlinbaum earned her Bachelor of Arts degree in Biochemistry from Colorado College in 2000. After working for an environmental organization for a couple of years, Maggie's interest turned to teaching. Thus in 2006 she earned a Masters of Arts in Teaching degree from the State University of New York at Cortland.

It was in 2006 that Maggie started her teaching career at Jordan-Elbridge High School in Jordan, NY. From 2006 until 2015 she taught in the Syracuse University Project Advance Chemistry program, as well as teaching AP Chemistry, Regents Chemistry, and General Chemistry. Having been recognized for her leadership skills, she served a number of years as the Science Department Chair and Team Leader.

In 2015 Maggie moved to Liverpool High School in Liverpool, NY. There she continues as a Master Teacher for STEM, a recognition accorded by the State of New York to Ms. Estlinbaum since 2013. Maggie has rounded out her excellent contributions in the teaching and administration of chemistry by extramural involvement in the teaching profession. Of the many professional involvements, in 2017 alone she has contributed to scholarly presentations with the titles of "Differentiating Instruction in the High School Chemistry Classroom", "Getting Started in the High School Chemistry Lab: A Hands-On Workshop for New and Pre-Service Chemistry Teachers", and "Developing Collaborations between Math and Science through a Sustainability Curriculum".

Ms. Estlinbaum has been active in many volunteer activities; it is fitting that many of these are under the mantle of the American Chemical Society (ACS), with the award being sponsored by the chemists' professional organization. Maggie serves as Liverpool High School's ACS ChemClub Advisor, as she had been at Jordan-Elbridge since 2013. Two other contributions of note are her 10-year tenure as Science Olympiad Advisor, and her volunteer work as an ACS Science Coach.

In summarizing her qualities, the words of her nominator, Sally Mitchell say it best: "Maggie Estlinbaum has stimulated the curiosity within many students, and then inspired them to develop a sound basis for comprehension of chemistry and skilled laboratory practice." Accordingly, Maggie Estlinbaum is clearly deserving of the 2017 ACS-CHED Northeast Region Award for Excellence in High School Teaching.

Julianne M. Smist, NERM 2017 Awardee of the E. Ann Nalley Northeast Region Award for Volunteer Service to the American Chemical Society

Julianne Smist embarked on her professional career by earning the Bachelor's degree in Chemistry at Elms College in 1972, her M.S. in Physical Chemistry from Boston College in 1974, and the Ph.D. degree at the University of Connecticut in 1996. Dr. Smist started her college-teaching career at American International College in Springfield, MA, followed by an appointment at Westfield State College in Westfield, MA. In 1982 Julie moved to Springfield College, where she has been ever since, moving through the ranks to Professor of Chemistry. Since 2013, she has been serving as the Chair of the Biology/Chemistry Department.

Julie started her volunteer service to the American Chemical Society (ACS) in 1986, as Secretary of the Connecticut Valley Local Section, a post she still holds! It was not long before Julie moved to service at the national level – in 2000 she was elected to represent her local section as Councilor, a position she currently serves in as well. As Councilor, Julie has been very active in the Division of Chemical Education (CHED). She has served on the Membership Committee, and on the Program Committee where she continues to be active with CHED. Julie has also been on additional national committees concurrently. From 2001 to 2007 she was a member of the Committee on Meetings and Expositions (M&E), where she chaired the M&E Subcommittee on Site Selection. In 2008, Julie moved to the Committee on Divisional Activities, serving as its secretary, as well as chairing its Subcommittee on Communication and Technology.

Also at the regional level, Dr. Smist has contributed her valuable skills and time. She was one of the founding officers of the Northeast Region of the American Chemical Society (NERACS), which was incorporated in 2005. Julie served the initial term of Chair from 2005 to 20012. Overseeing regional meetings is the most prominent activity carried out by NERACS. Dr. Smist has been active at Northeast Regional Meetings (NERMs) sponsored by her local section. She was Arrangements Chair for NERM1991, Exposition Chair for NERM2000, and General Chair for NERM2009.

Considering the breadth and depth of her service to the ACS, without any doubt Julianne Smist's various contributions to the greater ACS emphatically point to a well-deserved selection as the Northeast Region's 2017 E. Ann Nalley Volunteer Service Award.

MARM 2017 -- Workshops

Monday, June 5		
8:00 am - 11:30 am	**ACS Workshop – Career Pathways: Finding Yourself: Identifying a Career that Matches your Strengths and Values** Presented by Joe Martino Coordinator, Bill Suits	Aztec
Finding Yourself: Identifying a Career that Matches Your Strengths and Values allows you to self-assess your career values and strengths. Participants will also learn how the four sectors of chemistry employment compare and contrast. This course will also help you determine which sector best aligns to your values and strengths and plan your next steps to obtaining an ideal position.		
9:00 am - 11:00 am	**Law and Intellectual Property: Strong Patents Begin in the Lab: A Patent Law Primer for Research Chemists** Presented by Erin M. Sommers, Ph.D. and Kassandra Officer, J.D.; Finnegan, Henderson, Farabow, Garrett & Dunner, LLP Coordinators, Erin Sommers and Sherri Young	Aztec
Participants in this MARM workshop will study a hypothetical research fact pattern to learn how research in the lab impacts obtaining and keeping patent protection for those research efforts. Attendees will learn the basics of patent law, including concepts of novelty and obviousness, inventorship, disclosure requirements, and patent enforceability. This workshop is a perfect opportunity for research chemists to learn basic patent law concepts and understand how their day-to-day efforts fit into developing a strong patent portfolio.		

Monday, June 5

9:00 am - 5:00 pm	**MoleCVUE Workshop on Computational Chemistry in the Undergraduate Curriculum: Introducing Molecular Models** Presented by Carl Salter, Jim Foresman, Will Polik, and Kevin Range	Tower 1

WebMO is a web-based interface to modern computational chemistry programs (Gamess, Gaussian, Molpro, Mopac, NWChem, PQS, PSI, Quantum Espresso, VASP, Q-Chem, Tinker). Using just a web-browser, users can draw 3-D structures, run calculations, and view results. WebMO is simple enough for novice users (reasonable defaults are provided, and result are presented graphically) but flexible enough for experts (full access to input and output files is provided, and job types can be customized).

Workshop topics will include:

* Overview of WebMO features and capabilities
* Drawing molecules using the WebMO Editor
* Running various job types
* Visualization of results using the WebMO Viewer
* Importing and exporting structures and jobs
* Customization WebMO job types
* Using WebMO on Apple and Android portable devices
* Installation and administration of a WebMO server (continued)

This is a hands-on workshop suitable for high-school and college faculty. Participants are encouraged to bring their own Windows, Mac, or Linux laptop or Apple iPad. In addition to workshop activities, a WebMO developer will be available for questions and individual consultation.

Notes: There are other MoleCVUE talks and activities that are part of the technical session on Sunday afternoon and Tuesday morning.

1:00 pm - 4:00 pm	**CrIME: Criminal Investigation through Molecular Examination** Presented by Gail Marsella and Eugene Fiorini	Tower 2

The CrIME (Criminal Investigation through Molecular Examination) workshop presents activities and strategies for teaching a cross-disciplinary course in chemistry and statistics to undergraduate non-scientists, using environmental forensics as the overall theme, and a publicly staged crime scene as a final exam. Forensics is ideal for this type of project because a) it combines so many STEM fields, b) various crime shows have given students keen interest in the subject, and c) the importance of statistics to the other sciences in forensics is not well understood even to some professionals in the field. The half-day workshop will include exercises, resources, and discussion in small groups on exercises such as blood spatter analysis, hydrocarbon fingerprinting, and observation-inference. Access to an in-development teaching manual will also be provided.

Monday, June 5		
1:00 pm - 5:00 pm	**ACS Workshop – Career Pathways: Resume Reviews** Presented by Joe Martino Coordinator, Bill Suits	Tower 3
Bring your resume in for a review by career counseling professionals.		

Tuesday, June 6		
12:00 pm - 1:30 pm	**Finding *Your* Path as a Chemical Professional:** A Conversation with current and prior ACS Presidents and Directors Coordinator, Kathleen Schulz	Forebay Restaurant

Presenters:
Dr. Pat Confalone (Wilmington, DE), Chair-ACS Board of Directors
Dr. Peter Dorhout (Manhattan, KS), ACS President-Elect
Dr. Ingrid Montes (San Juan, Puerto Rico), ACS Director-at-Large
Dr. Donna Nelson (Norman, Oklahoma), ACS Immediate Past-President
Dr. Laura Pence (West Hartford, CT), ACS Director, District II
Dr. Dorothy Phillips (Natick, MA), ACS Director-at-Large
Dr. Kathleen Schulz, (Albuquerque, NM), ACS Director-at-Large

How will you decide *your* path as a chemical professional? No single path guarantees success and satisfaction for everyone. Which path, from the many options available, will give *you* the most satisfaction? Choose the one that's best for *you!*
This informal conversation is your opportunity to explore career options with experienced chemical professionals who currently serve on the ACS Board of Directors. These seven ACS leaders represent a wide variety of ACS volunteer, career and life paths in academe, industry, national laboratories, government contracting and contract research (CROs). Some of these leaders spent their entire career in one organization, others moved around extensively. Some stayed technically focused, others branched out into academic administration, management, marketing and business development. They are eager to share their experiences, and willing to discuss any questions important to you, as you explore *your* options.
Format for this session:

- Brief (5 min.) career overview from each ACS leader
- 3 Small group table discussion periods (15-20 min. each)
  -Your questions/topics
  - With leader(s) of your choice

Chemagination MARM 2017!

The 2017 Mid-Atlantic Regional Chemagination Competition
Sunday, June 4 from 12:00 pm to 5:00 pm
Hershey Lodge in Hershey, PA

Chemagination 2017 Co-Chairs
Carol Stein, cmstein03@yahoo.com
Louise Lawter, louise.lawter@gmail.com

THEME

"Describe a recent breakthrough or innovation in chemistry (and/or its applications) that has improved the quality of people's lives today."

For this event, high school students are asked to imagine that they are living 25 years in the future and have been invited to write an article for ChemMatters, a magazine for high school students that focuses on the role of chemistry in everyday life. Students are also asked to design the magazine cover. The subject of the article is: Describe a recent breakthrough or innovation in chemistry (and/or its applications) that has improved the quality of peoples' lives today. The article must be written to fit in one of four categories: Alternative Energy, Environment, Medicine/Health, or New Materials.

AGENDA

The program will consist of the poster session, judging and visit to the Technical Poster Session and Vendor Expo, followed by the Award Ceremony. The contest will be held in the Wild Rose A and B Rooms of Hershey Lodge.

Schedule:

12:00 – 1:00 pm	Lunch and poster set- up
1:00 – 3:00 pm	Judging
3:00 – 4:00 pm	Visit to Technical Poster Sessions & Expo
4:00 – 5:00 pm	Award Ceremony

Students should plan to arrive between 11:45 am-12:00 noon.
Students are invited to bring friends and relatives to the competition.

SOCIAL EVENTS FOR Sunday, June 4th:

Event	Description
Science Coaches Breakfast	Opportunity for ACS Science Coaches and Partner Teachers to meet and discuss the program, what lessons and activities they have done, how they have set-up and managed goals/projects, and any suggestions for the program. This is also an opportunity for ACS Members and Teachers interested in the program to get first-hand information from program participants.
Student Chapter Workshop Breakfast	The Brainstorm 2017! Student Chapter Workshop & Breakfast is specifically for student chapters and their advisors. The purpose of this workshop is to provide an avenue for student chapters to discuss successful and unsuccessful programming. Guest Speaker: Benjamin Hall.
Opening Luncheon	Enjoy a buffet lunch and a fun presentation by Howard and Sally Peters, aka Mr. & Mrs. Chocolate. "Chocolate: Food of the Gods" will include a brief history of chocolate, how it is grown and processed, and some chemistry, biochemistry and biology of chocolate and its active ingredients.
Chemagination Luncheon	Luncheon for participants in Chemagination. Chemagination is a high school level competition for which students were asked to imagine that they are living 25 years in the future and have been invited to write an article for ChemMatters, a magazine for high school students that focuses on the role of chemistry in everyday life. The subject of the article is: "*Describe a recent breakthrough or innovation in chemistry (and/or its applications) that has improved the quality of people's lives today*."
Opening Reception	Join the ACS MARM planning committee for free food and pictures with the ACS Mole! This is your chance to mingle with other MARM attendees and to learn more about conferences and interest groups in our area.
Ice Cream Social for Student Chapters	An ice cream social for everyone to meet, mingle, network and relax.
Chemistry Trivia Night	Looking for some friendly competition with other ACS student chapters? Come show off your chemistry trivia knowledge and for a chance to win prizes!
Opening Cocktail Hour	A perfect event to wind down a busy day. Relax with colleagues over drinks and snacks.

SOCIAL EVENTS FOR Monday, June 5th:

Event	Description
Senior Chemists Breakfast	Enjoy some breakfast and celebrate the achievements of our colleagues that have been ACS members for 50+ years!
YCC 5K Fun Run	Meet up with some friends and start the day off right with a bit exercise.
ACS Governance Luncheon	Join ACS board members for a Strategy Café to discuss the ACS 2017 Strategic Plan.
Awards Dinner and Ceremony	Come celebrate the outstanding achievements of our colleagues in the Middle Atlantic and Northeast Regions of the ACS at our banquet and awards ceremony. A presentation by the plenary speaker, Esther Takeuchi, will immediately follow the awards ceremony and is open to all attendees.

SOCIAL EVENTS FOR Tuesday, June 6th:

Event	Description
Diversity and inclusion breakfast	Ingrid Montes from the University of Puerto Rico will present "Diversity and inclusion: The art of embracing everyone uniqueness"
Career Panel	"Finding *Your* Path as a Chemical Professional: A Conversation". This informal conversation is your opportunity to explore career options with experienced chemical professionals who currently serve on the ACS Board of Directors.
Local section officers lunch	Network with Local ACS Section leaders in your region. Discuss successful and unsuccessful programming, ways to engage members, and brainstorm ideas for new events over lunch.
Brewery tour	Take a self-guided tour through fermentation, filtration, quality and packaging at Troegs Brewery, then relax over drinks in the tasting room. Note: must be 21 and older.
Wine-chocolate tasting	Hershey Lodge experts lead this unique class that pairs five different wines with Hershey's candies.

MARM

The technical portion of MARM is described on the following pages.

Special thanks are due to the following division chairs who supervised and planned the programming in their respective areas:

Physical/Biophysical/Computation:	Prof. Karen Castle , Bucknell University
Inorganic/Catalysis/Energy:	Prof. Chip Nataro, Lafeyette College
Organic/Natural Products/Med Chem:	Prof. Nicholas Sizemore, University of Scranton
Chemical Education:	Prof. Chris Hamann, Albright College
Analytical/BioAnalyt:	Prof. Kate Stumpo, University of Scranton
Pharma/Industry:	Prof. Ben Blass, Temple University
Biochemistry/StructBio/ChemBio:	Prof. Wade Johnson, Susquehanna University
Polymer/Materials/Nano:	Prof. David Rovnyak, Bucknell University
Environmental/Green/GeoChem:	Prof. Lindsey Welch, Cedar Crest College
MoleCVUE:	Prof. James Foresman, York College of Pennsylvania
Poster Chair :	Prof. Lee Silverberg, Pennsylvania State University

Please also take a moment to note the session chairs on the pages that follow. They have done a tremendous job to feature the latest science here at MARM.

Deepest thanks are due to Aviva Westheim from the American Chemical Society for her expertise and tireless work, and to Margaret Kastner, Bucknell University, for her great work on program logistics.

Please enjoy the unique scientific offerings of MARM 2017!

D. Rovnyak, *MARM 2017 Program Chair*

MARM - Summary of Technical Sessions:

Sunday, June 4 : Afternoon

Active Learning: Strategies for Making It Work in Your Class (Empire C)
Coordination Chemistry (Empire A)
Cope Scholar Symposium: Progress in the Synthesis of Complex Molecules (Crystal A)
Forensic Chemistry (Empire D)
Implementation of Innovative Projects, Activities or Laboratories in Upper-Level Chemistry Courses (Cocoa Suite 5)
Ionic Liquid Bulk & Interfacial Chemistry Structure, Dynamics & Solvation (Cocoa Suite 4)
Med-Chem Strategies for Chronic Hepatitis B Virus Infection (Magnolia B)
Membrane Structure & Assembly (Magnolia D)
Molecular Modeling in the High School Curriculum (Tower Suite 1)
Nanoscience: Fundamentals & Applications (Empire B)
Solid State & Materials Chemistry (Magnolia A)

Monday, June 5 : Morning

History of Chemistry (Cocoa Suite 5)
Fluorescence & Luminescence Spectroscopy (Magnolia C)
Ionic Liquid Bulk & Interfacial Chemistry Solvation, Polymers & Biological Systems (Cocoa Suite 4)
Nanoscience: Fundamentals & Applications (Empire B)
Theory & Computation Toward Electronic Properties of Molecular Materials (Empire A)
Women in Organic Chemistry (Crystal A)
Active Learning: Strategies for Making It Work in Your Class (Empire C)
Food Safety (Wild Rose B)
Lanthanide Chemistry (Magnolia D)
Med-Chem Strategies for Chronic Hepatitis B Virus Infection (Magnolia B)
Methods & Applications of Metabolomics (Empire D)
Physical Chemistry of Materials (Wild Rose A)
Teaching Inorganic Chemistry (Magnolia A)

Monday, June 5 : Afternoon

Advances in Organic Chemistry (Empire D)
Bio-Inorganic Chemistry (Magnolia A)
Cosmetic Chemistry Interdisciplinary Science that Inspires, Imagines & Innovates (Empire B)
Current Topics in Bioactive Molecules, both Large & Small (Magnolia C)
Evolving Landscape of Drug Discovery & Development (Magnolia B)
Food Safety (Wild Rose B)
History of Chemistry (Cocoa Suite 5)
Insights into the Chemistry of Protein Function (Magnolia D)
Ionic Liquid Bulk & Interfacial Chemistry Surface Structure & Interactions (Cocoa Suite 4)
Physical Chemistry of Materials (Wild Rose A)
Revitalizing General & Organic Chemistry Laboratory Experiments (Empire C)
Theory & Computation Toward Electronic Properties of Molecular Materials (Empire A)
Women in Organic Chemistry (Crystal A)

Tuesday, June 6 : Morning

Catalysis Electrocatalysis & Small Molecule Activation (Magnolia A)
Organometallic Chemistry (Wild Rose B)
Advances in Nanotechnology, Polymers, Terahertz & Analytical Research: Current Applications & Future Direction for the 21st Century (Wild Rose A)
Biomarker Synthesis & Clinical Chemistry (Crystal A)
Chemistry at Interfaces: Living on the Edge (Empire A)
Computational Chemistry in the Undergraduate Curriculum: Present & Future (Tower Suite 1)
Evolving Landscape of Drug Discovery & Development (Magnolia B)
Fate & Transport of Environmental Contaminants (Empire B)
Innovations in Analytical Chemistry Education (Empire C)
Life & Times of Joseph Priestley (Empire D)
Small Chemical Business (Magnolia D)
Structure, Function & Stability: Proteins with Unnatural Amino Acids (Magnolia C)

Tuesday, June 6 : Afternoon

Advances in Chromatography, Mass Spectrometry & Biosensors (Magnolia C)
Bio-Inorganic Chemistry (Empire D)
Catalysis Mechanistic Elucidation & Method Development (Magnolia A)
Chemistry at Interfaces: Living on the Edge (Empire B)
Chemistry of Materials: Designing Structure (Wild Rose B)
Chemistry of Molecular Imaging (Crystal A)
Fate & Transport of Environmental Contaminants (Empire A)
Innovations in Analytical Chemistry Education (Empire C)
Medicinal Chemistry & Heterocyclic Synthesis (Cocoa Suite 5)
Opportunities for Academic-Pharma Collaborations (Magnolia B)
Organometallic Chemistry (Wild Rose A)
Protein Misfolding & Quality Control (Cocoa Suite 4)
Synthetic & Biological Catalysis (Magnolia D)

MARM – Technical Program

SUNDAY AFTERNOON, JUNE 4

Active Learning: Strategies for Making It Work in Your Class

Empire C (Confection Hall Level)
F. J. Creegan, D. B. King, *Organizers, Presiding*

1:30 Introductory Remarks.

1:35 1. Authentic/alternative assessment V: Classification of organic compounds, reactions/mechanisms by science majors. **M. Camacho**

2:00 2. Use of a PLTL variant to increase student engagement in large enrollment Organic Chemistry recitation sections. **S.M. Stanley Fernandez**

2:25 3. Finding time for active learning in the organic chemistry classroom with Just-in-Time-Teaching (JiTT). **T.P. Umile**

2:50 Intermission.

3:10 4. Enhancing learning by using muddiest point cards with international students. **J. Xian**, D.B. King

3:35 5. Seeding your future initiative: STEM outreach for grades 5-12. **J. Mader**, S. Murphy

4:00 6. In-class experiments in a liberal arts chemistry course. **D.B. King**

4:25 Concluding Remarks.

Coordination Chemistry

Empire A (Confection Hall Level)
W. G. Dougherty, J. J. Paul, *Organizers, Presiding*

1:30 Introductory Remarks.

1:35 7. Synthesis and characterization of a series of tris(3-phenylpyrazolyl)borato zinc(II) oxocyclohexadienolate complexes derived from in situ oxidation of parent catecholate complexes. D. Isaacs, M. Bezpalko, N.A. Piro, W.S. Kassel, **W.G. Dougherty**

2:00 8. Synthesis and reactivity studies of nickel aryl chalcogenolate complexes. **L. Cordeiro**, G.P. Yap, C.G. Riordan

2:25 9. Phosphorus-31 NMR spectroscopy of molybdenum carbonyl phosphine complexes: Correlations with bond enthalpies, bond lengths, and infrared spectra. **C.H. Mahler**

2:50 10. Synthesis and characterization of aluminum complexes of nitroxide-based ligands: A new family of redox-active aluminum complexes. **C.R. Graves**

3:15 Intermission.

3:35 11. Spectroelectrochemical studies of ruthenium complexes with the 4,4'-dihydroxy-2,2'-bipyridine ligand. E. Peterson, A.E. Kuhn, N.A. Piro, W.S. Kassel, T. Dudley, **J.J. Paul**

4:00 12. Reactions of palladium compounds containing 1,1'-bis(diphenylphosphino)ferrocene. **N. Wamser**, C. Nataro

4:25 13. Towards neutral mixed-valence copper cyanide polymers. **P.W. Corfield**, J. Dayrit, C. Sheedy, T. Stavola

4:50 14. Coordination chemistry of rare earth elements to address problems in their separations and sustainability. **E.J. Schelter**, J. Bogart, B.E. Cole, M. Boreen, C. Lippincott, B.C. Manor, P.J. Carroll

5:15 Concluding Remarks.

Cope Scholar Symposium: Progress in the Synthesis of Complex Molecules

Crystal A (Confection Hall Level)
M. R. Krout, *Organizer, Presiding*

1:30 Introductory Remarks.

1:35 15. Total syntheses of nannocystins and homodimericins. J. Huang, D. Ma, Y. Liu, **Z. Wang**

2:00 16. Synthesis of icetexane anti-cancer natural products. D.J. Moon, M. Al-Amin, R. Lewis, G.P. Yap, K. Arnold, J. Sims-Mourtada, **W.J. Chain**

2:25 17. Total synthesis of natural products enabled by N-sulfinyl metallodienamines. **R.B. Andrade**

2:50 Intermission.

3:10 18. How natural product structures drive synthetic innovation. **A.J. Frontier**

3:35 19. Total synthesis of neurologically active natural products. **T.R. Newhouse**

4:00 Intermission.

4:10 20. Some efforts in natural product synthesis design. **C.D. Vanderwal**

4:55 Concluding Remarks.

Forensic Chemistry

Empire D (Confection Hall Level)
L. Quarino, *Organizer, Presiding*

1:30 21. Investigation into the analysis of narcotic analgesics from postmortem blood using Biocompatible Solid-Phase Microextraction (BioSPME). **C. Grant**, T. Brettell, S. Land, M.E. Staretz Greenfield

1:45 22. Elemental analysis of oil paints using Laser Induced Breakdown Spectroscopy (LIBS). A. Aloia, P. Rampson, **R. Chinni**

2:05 23. Assessment and optimization of chemical-based contrast enhancement techniques on mammalian pelts for shooting distance estimation. **R.K. Sandquist**, C.A. Weiss, R. Ristenbatt, J. Brooks

2:25 24. Application of FTIR microscopy to microcrystalline tests for drugs. **M. Joshi**

2:45 25. Analysis of stimulants extracted from dried blood spots via LC-MS/MS. **E.A. Williamson**, T. Brettell, M. Dawes, M.E. Staretz Greenfield

3:00 26. Method development and quantification of lisdexamphetamine and amphetamine in hair. **E. Phillips**, K. Scott

3:20 Intermission.

3:35 27. Withdrawn

3:55 28. When just knowing isn't enough: Turning unknowns into quantitative knowns in Non-Targeted Analyisis (NTA). **J.N. Grossman**, J.R. Sobus

4:15 29. Using HILIC-MS/MS for the simultaneous determination of GHB and its glucuronide. **J. Gibbs**, M.E. Staretz Greenfield, T. Brettell

4:30 30. Utilizing deconvolution reporting software with retention time locking to improve GC/MS analysis of fire debris evidence. **S. Reichardt**, H.L. Harris, K. Scott, L.N. Polite, F.X. Diamond

4:50 31. Invisible ink: The history and chemistry associated with it. **P.D. Svoronos**

5:10 32. Tracking the sexual assault kit backlog. **K.E. Crawford**, L. Ferrara

Implementation of Innovative Projects, Activities or Laboratories in Upper-Level Chemistry Courses

Cocoa Suite 5 (Main Level)
A. M. Fedor, *Organizer, Presiding*

1:30 Introductory Remarks.

1:35 33. Multistep synthesis of 2-arachidonoylglycerol (2-AG) in undergraduate organic laboratories. **M.R. Johnston**

2:00 34. Combining computational chemistry with vibrational spectroscopy to increase insight into selection rules. **M.D. Sonntag**

2:25 35. Grant writing practice in an undergraduate laboratory. **B.L. Haas**

2:50 Intermission.

3:05 36. Integrating far-infrared spectroscopy into the physical chemistry laboratory. **A.M. Fedor**

3:30 37. Development and evaluation of a team-taught online course in medicinal chemistry. **S.C. Young**, M.E. Staretz Greenfield, F.C. Mayville, H.D. Husic, N.D. Heindel, M.A. Bertucci

3:55 Concluding Remarks.

Ionic Liquid Bulk & Interfacial Chemistry : Structure, Dynamics & Solvation

Cocoa Suite 4 (Main Level)
J. T. Newberg, *Organizer*
M. Maroncelli, *Organizer, Presiding*

1:30 Introductory Remarks.

1:35 38. Pressure effects on ion dynamics in Imidazolium based ionic liquids. **S. Suarez**, K. Pilar, S. Greenbaum, J.F. Wishart, S. Paserini

2:05 39. Structure & nanostructure in ionic liquids. **R. Hayes**

2:35 40. Structural comparisons of homologous zwitterionic and ionic liquids. **B. Wu**, E. Castner

2:55 41. Role of geometrical shape and basicity of aprotic heterocyclic anions (AHAs) in 1-ethyl-3-methylimidazolium-based ionic liquids on molecular structure and interactions. S. Oh, O. Morales, **J.F. Brennecke**

3:25 Intermission.

3:40 42. Domain disturbing effects of asymmetric fluorinated anions. **M. Zhao**, E. Castner

4:00 43. CO_2 capture in 1-alkyl-3-methylimidazolium acetate: Does N-heterocyclic carbene play any role? F. Yan, N.R. Dhumal, **H. Kim**

4:30 44. Solute rotational dynamics in ionic liquids: Insights from fluorescence anisotropy, ^{2}H-T_1 relaxation, and molecular dynamics simulation. **C.A. Rumble**, C. Uitvlugt, B. Conway, M. Maroncelli

4:55 45. Local dynamics and energetic barriers of carbon dioxide and thiocyanate in imidazolium (n = 2, 4, 6) ionic liquids using ultrafast vibrational spectroscopy. **T. Brinzer**, C.A. Johnson, Z. Ren, S. Garrett-Roe

5:20 Concluding Remarks.

Med-Chem Strategies for Chronic Hepatitis B Virus Infection

Magnolia B (Confection Hall Level)
Y. Du, *Organizer*
T. M. Block, B. Dorsey, Y. Du, J. Hu, *Presiding*

1:30 46. Is a cure possible for chronic hepatitis B? Is one necessary? **T.M. Block**

2:10 47. New viral targets for viral hepatitis B drug development. **J. Hu**

2:40 48. Recent advances in drug discovery for chronic hepatitis B virus infection. **Y. Du**, N. Hwang

3:00 49. Exploring combination therapies to cure chronic hepatitis B virus infection. **B.D. Dorsey**

Membrane Structure & Assembly

Magnolia D (Confection Hall Level)
S. Frey, *Organizer, Presiding*

1:30 Introductory Remarks.

1:35 50. Site-directed spin-label EPR spectroscopy of the domain of influenza M2 protein involved in viral budding. **K.P. Howard**

2:00 51. Transmembrane protein design and assembly for voltage sensing. M.J. Iwanicki, C.C. Moser, **B.M. Discher**

2:25 52. Molecular mechanism of temperature-dependent gating of TRPV1. **V. Carnevale**

2:50 Intermission.

3:10 53. Using fluid flow to investigate lipid membranes. **A. Honerkamp-Smith**

3:35 54. Mechanisms of membrane curvature generation. **T. Baumgart**

4:00 Concluding Remarks.

Molecular Modeling in the High School Curriculum

Tower Suite 1 (Tower Level)
K. Range, *Organizer*, *Presiding*

1:30 Introductory Remarks.

1:35 74. Teaching computational chemistry as a formal course at the pre-college level. **R.R. Gotwals**

2:05 75. Molecular modeling for high school students. **K. Range**

2:35 Discussion.

4:25 Concluding Remarks.

Nanoscience: Fundamentals & Applications

Empire B (Confection Hall Level)
M. D. Ellison, *Organizer, Presiding*

1:30 Introductory Remarks.

1:35 55. Green synthesis of uniform ruthenium nanoparticles supported on non-functionalized single-walled carbon nanotube for azo dye degradation. **T. Hemraj-Benny**

1:55 56. Flame synthesis of carbon and metal oxides nanomaterials for energy storage, conversion, and harvesting. **R.L. Vander Wal**

2:15 57. Synthesis and magnetic properties of europium sulfide-europium selenide solid solution colloidal nanocrystals. **N. Rosa**, H.A. Dalafu, D.J. James, S. Omagari, A. Kawashima, T. Nakanishi, Y. Hasegawa, S.L. Stoll

2:35 Intermission.

2:50 58. Phase-effects on cation exchange of metal chalcogenide nanoparticles. R. Kozloski, A. Unruh, **K. Plass**

3:10 59. Virtual design and analysis of Pareto optimal emitter structures for thermophotovoltaic applications. **J.J. Foley**, J. Hernandez, N. Jeon, S.K. Gray, A.B. Martinson

3:30 60. Achieving array spasing from novel configurations: Silver nanoparticles and poly(9,9-di-n-octylfluorenyl-2,7-diyl) polymer films. **J. Tracey**, D. O'Carroll

3:50 Intermission.

4:00 61. Single molecule switching and sensing. **E. Borguet**

4:20 62. Synthesis of 2D nanomaterials by intercalation and exfoliation of layered inorganic solids. M. Strayer, N. Kovtyukhova, T. Senftle, A. Rosas, R. Uppuluri, M.J. Janik, R.M. Rioux, **T.E. Mallouk**

4:40 63. Withdrawn

5:00 Concluding Remarks.

Solid State & Materials Chemistry

Magnolia A (Confection Hall Level)
B. C. Chan, *Organizer*
K. Plass, *Organizer, Presiding*

1:30 64. Retrosynthetic design in the synthesis of inorganic solids and nanostructures. **R.E. Schaak**

1:50 65. Magnetic and electronic studies on magnetic semiconductor solid solutions. **H.A. Dalafu**, S.L. Stoll

2:05 66. Synthetic approaches to samarium chalcogenide nanostructures. **S.E. Ingram**, S.L. Stoll

2:20 Intermission.

2:35 67. Incorporation of polypyridyl osmium, ruthenium, and rhenium complexes into metal-organic frameworks for use as luminescence-based sensors. **J.A. Rood**, K. Kneas

2:55 68. Quantitative analysis of oxidation state in cerium oxide nanomaterials. **C.M. Sims**, R.A. Maier, A.C. Johnston-Peck, J.M. Gorham, V.A. Hackley, B.C. Nelson

3:10 69. Electron doping a kagome spin liquid using soft chemistry techniques. **Z. Kelly**, M.J. Gallagher, T. McQueen

3:30 Intermission.

3:45 70. Understanding and optimizing exploratory hydrothermal reactions. **A.J. Norquist**

4:05 71. Structure-selective nanocrystal cation exchange in the synthesis of metastable zincblende-type MnS and CoS. **J.L. Fenton**, R.E. Schaak

4:20 72. Structure and photoluminescent behavior of lanthanide-doped bismuth organic materials. **K.E. Knope**

4:40 73. Laser annealing of nanoscale carbons. **R.L. Vander Wal**, J.P. Abrahamson, M. Singh

Undergraduate Posters

Red & White Room
L. J. Silverberg, *Organizer*

4:00 - 6:00

76. Reaction of diazonium salts with CdS nanoparticles. **Z. Zeng**, J.W. Kupsky, H. Le, K. Plass

77. pH dependence of imidazole-2-carboxaldehyde tautomeric equilibrium and its implications on potential photosensitization. **J.M. Ackendorf**, M.G. Ippolito, M.M. Galloway

78. Chemical interactions between *Janthinobacterium lividum* and the pathogenic fungus *Batrachochytrium dendrobatidis*. **J.A. Tasca**, T.P. Umile

79. Synergistic antimicrobial effects of aqueous ionic liquids and polymyxin on lipid vesicles. **S. Hanna**, A.J. Swinton, K.J. Cook, G.A. Caputo, T.D. Vaden

80. Distinct roles in caspase inhibition for different domains of the inhibitor of apoptosis protein DIAP1. **S. Kafle**, M. Junker

81. Low temperature EPR studies of cerium nitrate-triphenylphosphine oxide complexes. K. Sestak, **D. Petasis**

82. Interaction between transition metal complexes and substituted indoles. K. Fenner, J. Butkus, **S.M. Basu**

83. Production of His-tagged sfnaD for inhibition studies of the staphyloferrin A biosynthetic pathway. **M.E. Osborne**, E.N. McIntyre, W. Kittleman

84. Design and synthesis of betulinic acid conjugates as anti-cancer agents. P. Suman, A. Patel, L. Solano, A. Indukuri, S.K. Kommineni, R.M. Rutkoski, **S.C. Jonnalagadda**

85. Degradation of Congo red dye in the presence of single-walled carbon nanotube-ruthenium nanoparticles composites. **N.E. Carrero**, R. Sumner, N.F. Tobar, T. Hemraj-Benny

86. *In silico* evaluation of a hydrogen production system with enzyme produced from cell-free protein synthesis. **J. Huang**, D. Hauser

87. Progress towards surface-modified porous silicon. **P.A. Kulyavtsev**, R.P. Spencer

88. Biophysical and structural studies of quadruplex DNA in complex with promising small molecule binders. I. Xiang, **Y. Lin**, L.A. Yatsunyk

89. Effects of Hofmeister ions on particle attachment to surfaces. J. Moser, A. Alghunaim, **B.M. Zhang Newby**

90. Surface immobilization of poly(N-isopropylacrylamide) using silane coupling agents. E.Y. Newby, A. Alghunaim, E. Brink, **B.M. Zhang Newby**

91. Surface immobilization of poly(N-isopropylacrylamide) on polycarbonate. E. Brink, A. Alghunaim, **B.M. Zhang Newby**

92. Mechanically strong protein-based hydrogels from suckerins of the squid ring teeth. Z.T. Benekos, A. Hussein, **B.M. Zhang Newby**

93. Evaluation of guanofuracin as an antibiotic. **J. Trabucco**, T. Owen

94. Unique hot carrier distributions from scattering mediated absorption. **K. Fernando**, N. Eldabagh, J.J. Foley

95. Polysiloxane coated PolyRhodanine (PRd) nanocomposites. M. Chauhan, T. Hong, **E. Esperance**, B.P. Chauhan, A. Patel

96. Functionalizing single-walled carbon nanotubes with [Ru(bpy)2dppz]2+ as a potential mode of drug delivery. S.L. Porello, **L. Lee**, **E. Kim**

97. Treatment of wastewater samples at the New York City-Department of Environmental Protection (NYC-DEP). **J. Leong**, **J. Hwang**, A. Nagatu, F. Jacques, P. Meleties, P.D. Svoronos

98. Density Functional Theory (DFT) calculations of CO2 adsorption to mineral surfaces in the presence of water molecules. R. Bennick, M.D. Kilmer, **L. Tribe**

99. Syntheses of N-hydroxyphenyltrichloroacetamide derivatives by microwave reactor: Possible precursor to polycarbamate. **H. Yun**, J.H. Shin

100. Withdrawn

101. Role of loop 6 in cyclic-di-GMP specific phosphodiesterase in *Shewanella woodyi*. **M. de los Santos**, D. Williams, E.M. Boon

102. Elemental analysis of food using inductively coupled plasma-mass spectrometry at the Food and Drug Administration (FDA), Northeast region laboratories in Jamaica NY. **M. de los Santos**, L. Aleo, D. Stutts, P.D. Svoronos

103. Structural properties of iron in volcanic ash. **K. Wang**, S. Dehipawala

104. Adsorption of phosphate to surfaces for recovery from aqueous environments: Density Functional Theory (DFT) calculations. C. Jakob, D.R. Talham, **L. Tribe**

105. Determination of pesticide residues at the Food and Drug Administration using the QuEChERS extraction method in conjunction with liquid and gas chromatography. **H. Kim**, M. Viner, P.D. Svoronos

106. Conformation and stability of a bacterial regulatory mRNA. **Z. Ndika**, A. Soto

107. Imidazole as a novel and robust gold binding group at STM-BJ method. **X. Yu**, T. Fu, L. Venkataraman, S. Wei

108. Porous microspheres of polyaniline and its derivatives prepared from W/O/W double emulsions. **J. Hwang**, D.M. Sarno

109. Reduction and oxidation of 2,3-diaryl-1,3-thiaza-4-ones. **D.J. Noble**, Z. Yang, L.J. Silverberg

110. Synthesis of tin complexes. **Q. Moyer**, R. Fox, L.J. Silverberg

111. Study of hydrophobic vs. hydrophilic componts of molecules in C_3 to C_{10} acyclic imise synthesis: An undergraduate research project. **K.S. Marshall**

112. Targeted nanoparticles for pathogen-specific drug delivery. **L. Schnorbus**, L.J. Perez

113. Quantification of the dimer formed from the reaction of p-phenylenediamine and 4-amino-2-hydroxytoluene during the hair coloring process with the use of a hair color accelerator. **R. Kazal**, J.M. Fautch

114. S-oxidation of ortho-substituted-2-aryl-3-phenyl-1,3-thiazolidin-4-ones with Oxone®. A. Alkurdi, I. Kurochka, H. Himel, S. Liu, **K.C. Cannon**

115. Photochemistry of biacetyl*water complexes in argon matrices. **D.K. Geremia**, M. Kernan, C.A. Baumann

116. Cation exchange of different phases of copper sulfide with Zn2+. **A. Unruh**, R. Kozloski, K. Plass

117. Assessing G-protein receptor induced cell signaling with dissipation monitoring of the QCM-D. **Y. Pan**, J. Chen, L.S. Penn, J. Xi

118. Investigating the binding properties of green tea polyphenols with pancreatic amylase using UV/VIS spectroscopy. **C.T. Fleming**, A.M. Fedor

119. Rechargeable Zn-based battery: Next-generation (and safer) batteries are here! **M.N. Vila**, J. Ko, C.N. Chervin, J. Parker, P. DeSario, J.W. Long, D.R. Rolison

120. Synthesis and characterization of fluorescent dapoxyl dyes for luminescence-based sensing. **C.A. Ryan**, J.A. MacKay, K. Kneas

121. Reconstruction of ancestral tumor necrosis factor-alpha: Protein activity and primate evolution. **Y. Han**, R. Xiong

122. Effect of montmorillonite on the synthesis of biological polymers RNA surrogates. **E.P. Gordon**, L. Tribe

123. Effect of the bridging ligand on bimetallic asymmetric ruthenium(II) complexes. **T. Heng**, **A. Sona**, **M.T. Mongelli**

124. Investigation of cationic palladium NHC complexes toward Suzuki and Heck coupling. **M. Sebold**, R.J. Swails

125. Chemical and electrochemical reactivity of pyridinium based imidazolium salts. **A. Conner**, R.J. Swails

126. Construction of a His-tagged expression plasmid for production of sfnaB of the staphyloferrin A biosynthetic pathway. **C. Dombroski**, J.R. Cederberg, D.J. Schedler, W. Kittleman

127. Design and synthesis of novel α-(piperazinylmethyl)cinnamates as inhibitors of *Pseudomonas aeruginosa* virulence. P. Suman, A. Patel, B. Patel, P. Mastoridis, L.J. Perez, **S.C. Jonnalagadda**

128. Hantzsch amide for transfer hydrogenation. **R. Palkovitz**, S.A. Van Arman

129. Synthesis and cytotoxicity of Baylis-Hillman template-derived benzoboroxoles. P. Suman, M. Ur Rahman, M. Islam, H. Patel, S. Schwartz, **S.C. Jonnalagadda**

130. Chromatography analysis of flower extract and their application in dye-sensitized solar cells. **L. Warner**, J. Bradley, J. Hu

131. Effect of fatty acids on the binding of bilirubin to human serum albumin. **S. Barriteau**, M. Staretz

132. Targeted genetic mutations to OmpA in *E. coli* and its effect on its susceptibility to the K3 virus. **Y. Ou**

133. Determination of the ionization constant of carboxylic acids using freezing point depression measurements. **E. Mera**, **D. Kwun**, A. Xu, P.D. Svoronos

134. Determination of the total amount of oxygen consumption in effluent via carbonaceous biochemical oxygen demand (CBOD) and biochemical oxygen demand (BOD). **J. Hwang**, J. Leong, F. Jacques, P. Meleties, A. Nagatu, P.D. Svoronos

135. Determination of the total amount of antioxidants present in commercially available beverages via the Folin Ciocalteau microspectrophotometric analysis. **J. Leong**, **M. de los Santos**, S. Svoronos, B. Montalbano, P.D. Svoronos

136. Ultem thermoplastic-based 3D-printed orthoses: A comparative study on the efficacy of using polymer-based 3D-printed orthoses. **V. Joshi**, J. Wee, T. Rahman

137. Determination of the antioxidant gallic acid in commercial beverages via High-Performance Liquid Chromatography (HPLC). **J. Leong**, **M. de los Santos**, S. Svoronos, P. Irigoyen, P.D. Svoronos

138. Aluminum complexes of redox-active ligands. H. Wilson, J. Kirsh, M. Smith, A. Woodside, Z. Hannan, C. Endy, T. Herb, P. Wise, C. Koellner, **C.R. Graves**

139. Novel strategies for amide bond synthesis. **J. Adams**, M. Hammel, S. Philippi, J. Capilato, L.J. Perez

140. Modeling resonant energy transfer in hybrid nanoparticle/molecular systems. **M. Micek**, J.J. Foley

141. Determination of the ionization constant of carboxylic acids in mixed solvents using microscale freezing point depression measurements and the van't Hoff factor. **D. Kwun**, P.D. Svoronos

142. Comparison of iron and zinc distribution within a plant. **L. Clairvil**, S. Dehipawala

143. Investigate iron content and structural properties in *Centella asiatica*. **U. Dewanamuni**, S. Dehipawala

144. Use of x-ray absorption pre edge intensity in structural investigation. **A. Sullivan**, U. Dewanamuni, S. Dehipawala

145. Computational study of the atmospheric decomposition and combustion of 2-Ketohept-n-oxy radical. **C. Protter**, A.C. Davis

146. Development of HPLC lab for undergraduate students to learn instrumental analysis in a research setting. **D. Kraiter**

147. Study of basil growth and nitrate removal at various pH levels in a hydroponic system. **E. Bohn**, L. Lewis, J.A. Graden

148. Development of open source sensor systems for reporting and storing water chemistry readings in an aquaponics laboratory. **L. Lewis**, M. Krause, J.A. Graden

149. Development of stand-alone hydroelectric generation systems capable of supplying energy to water chemistry systems in isolated environments. **R. Temple**, L. Lewis, J.A. Graden

150. Selenium dioxide oxidation of n-alkylated-1-benzazepines to quinoline. **M. Qu**, S. Karimi, S. Ma, G. Subramaniam

151. New synthesis of pyrroles using the Cadogan approach. **M. Lai**, Y. Liu, S. Karimi, S. Ma, G. Subramaniam

152. Examining the interactions of green tea polyphenols with pancreatic lipase using UV/VIS spectroscopy. **P.T. Collins**, A.M. Fedor

153. Scattering mediated absorption in photonic crystals. **N. Eldabagh**, K. Fernando, J.J. Foley

MONDAY MORNING, JUNE 5

History of Chemistry

Cocoa Suite 5 (Main Level)
R. A. Egolf, *Organizer, Presiding*

8:00 Introductory Remarks.

8:05 154. Poster session: Teaching strategies with a window to the history of chemistry. **L.A. Avila**, L.W. Fine, E. Bront de Avila

8:35 155. Chemical technologies in antiquity. **M. Orna**, S.C. Rasmussen

9:05 156. Withdrawn

9:35 Intermission.

9:55 157. Herbal and chemical cures: Where chemistry meets the occult in 17^{th} – 19^{th} century Pennsylvania Dutch cure books. **N.D. Heindel**, R.D. Rapp

10:25 158. Joseph Priestley House: A postal history. **J.B. Sharkey**

10:55 159. Science history: A guide for actual and armchair travelers. **M. Orna**

11:25 Concluding Remarks.

Fluorescence & Luminescence Spectroscopy

Magnolia C (Confection Hall Level)
B. W. Williams, *Organizer, Presiding*

8:30 Introductory Remarks.

8:35 160. Solvation and proton transfer in diethylaminohydroxyflavone. **C.A. Rumble**, J. Breffke, M. Maroncelli

9:00 161. Dynamic fluorescence measurements of Rose Bengal photooxidation. **Y. Zhang**, J. Muthami, S.L. Neal

9:25 162. Whither reduced flavin fluorescence? The case of the disappearing emission quantum yield. **R.J. Stanley**, D. Barnard, R. McBride

9:50 163. Evaluation of effect of gold and silver nanoparticles on luminol chemiluminescence. **C. Kurey**, K. Patel, J. Vossler, M. Grayeski

10:15 Intermission.

10:35 164. Interaction of curcumin with berberine hydrochloride in nanoemulsion. **M.O. Iwunze**

11:00 165. New insights into an old problem: Fluorescence quenching of sterically-graded pyrenes by tertiary aliphatic amines. **M.J. Bertocchi**, A. Bajpai, J. Moorthy, R.G. Weiss

11:25 166. Solvatochromic response of benzo[a]fluorenone in aprotic solvents compared to benzo[b]fluorenone and 9-fluorenone. Y. Kopkalli, T.C. Celius, N.M. Karn, L. Davenport, **B.W. Williams**

Ionic Liquid Bulk & Interfacial Chemistry: Solvation, Polymers & Biological Systems

Cocoa Suite 4 (Main Level)
J. T. Newberg, *Organizer*
M. Maroncelli, *Organizer, Presiding*

8:30 Introductory Remarks.

8:35 167. Ultrafast structure and dynamics of ionic liquid-surfactant complexes as revealed by 2D-IR spectroscopy. **Z. Ren**, T. Brinzer, S. Mitra, C.A. Johnson, S. Garrett-Roe

8:55 168. Influence of alkyl chain length on electronic and structural properties of imidazolium-based cation complexes with free base porphyrin and Fe-porphyrin: Implication for biodegradation of ionic liquids. **J. Shah**

9:25 169. Role of the solvophobic effect in protein-ionic liquid interactions. **T. Greaves**, E. Wijaya, R. Arunkumar, D. Tuncali, F. Separovic, C. Drummond

9:55 Intermission.

10:10 170. Structure and dynamics of ionic liquids in model polyelectrolyte systems. Z. Yu, Y. He, Y. Wang, L.A. Madsen, **R. Qiao**

10:40 171. Self-assembly of block copolymers in ionic liquids: Ultrastretchable iono-elastomers with mechanoelectrical response. **N.J. Wagner**, R. Chen, C. Lopez-Barron

11:10 172. Electrochemical oxidation of metal carbides for double-layer capacitors with ionic liquid electrolytes. D. WalCzyk, D. Mason, B. Palazzo, G. Taylor, N. Zach, J. Hettinger, **L. Yu**

11:40 Concluding Remarks.

Nanoscience: Fundamentals & Applications

Empire B (Confection Hall Level)
M. D. Ellison, *Organizer*
L. B. Thompson, *Presiding*

8:30 Introductory Remarks.

8:35 173. MMP-9 responsive peptide nanocarriers for targeted delivery of metallodrugs. **J. Son**, R. Ulijn, M. Contel

8:55 174. Exploring the toxicity of gold nanoparticles to aquatic amphibians. **L.B. Thompson**, P.P. Fong, G. Carfagno, K. Andresen

9:15 175. Motion of Li^+ and methanol through a 2.25-nm-diameter single-walled carbon nanotube. **M.D. Ellison**, L.M. Nebel, S. Menges, G. D'Arcangelo, A. Kramer, L. Drahushuk, J. Benck, S. Shimizu, M. Strano

9:35 Intermission.

9:50 176. Effects of capping agent and dopant concentration on the quantum yield of ZnS nanocrystals. **A.L. Marsh**

10:10 177. Bimetallic nanocrystal catalysts for hydrodeoxygenation of 5-hydroxymethylfurfural. **J.D. Lee**, J. Luo, H. Yun, C. Wang, M. Monai, P. Fornasiero, R.J. Gorte, C.B. Murray

10:30 178. Electrooptical dynamics of 4-cyano-4'-pentylbiphenyl confined in functionalized zinc selenide nanocavities. E. Rossomme, N. Tay, **A.R. Noble**

10:50 Intermission.

11:00 179. Quantum thermodynamics for nanoscale and molecular systems. **M.A. Ochoa**

11:20 180. High aspect ratio CNT structures produced by energetic ion bombardment. **G. Konesky**

11:40 Concluding Remarks.

Theory & Computation Toward Electronic Properties of Molecular Materials

Empire A (Confection Hall Level)
H. Jaeger, *Organizer, Presiding*

8:30 Introductory Remarks.

8:35 181. π–Stacking pancake bonding. Z. Mou, **M. Kertesz**

9:05 182. Singlet fission and charge transfer quantum dynamics in organic photovoltaic. **P. Huo**

9:35 Intermission.

9:55 183. Theory and computation toward nonadiabatic dynamics of molecular switches and quantum dots. **A.V. Akimov**

10:25 184. Vibrational control of electron-transfer kinetics: A unified theoretical framework and a critical experimental test. **Z. Ma**, P. Antoniou, I.V. Rubtsov, S. Skourtis, P. Zhang, D.N. Beratan

10:40 185. SiR/TiO_2 and GeR/TiO_2 (R = H, Me) heterostructures for photocatalytic applications: Insights from excited-state dynamic simulations. **A. Nijamudheen**, A.V. Akimov

10:55 Concluding Remarks.

Women in Organic Chemistry

Crystal A (Confection Hall Level)
S. Wengryniuk, *Organizer, Presiding*

8:30 Introductory Remarks.

8:35 186. Copper- and nickel-catalyzed oxidative decarboxylative arylation reactions. **J.M. Hoover**

9:05 187. Guaianolide analogs: A valuable testing ground for the allenic Pauson–Khand reaction. **K.M. Brummond**

9:35 188. Discovery of novel selective SYK/ZAP70 kinase inhibitors for rheumatoid arthritis. **S. Lee**

10:05 Intermission.

10:25 189. Application of new methodologies to the synthesis of pharmaceuticals. **M. Garnsey**

10:55 190. Caught red-shifted: Visualizing acyl carrier protein conformational dynamics using a mechanism-based vibrational spectroscopic probe. G. Thiele, C. Friedman, K. Tsai, J. Beld, C.H. Londergan, **L.K. Charkoudian**

11:25 191. Synthesis of diverse oxygen heterocycles via oxidative ring expansions of simple alcohols. **S. Wengryniuk**

11:55 Concluding Remarks.

Active Learning: Strategies for Making It Work in Your Class

Empire C (Confection Hall Level)
F. J. Creegan, D. B. King, *Organizers, Presiding*

9:00 Introductory Remarks.

9:05 192. Leading collaborative and engaging activities in a flipped general chemistry classroom using smart devices. **A.M. Fedor**

9:30 193. Quality by design (QbD) in the classroom and laboratory: Tools for enhancing students' creativity and analytical thinking. **Z.O. Gephardt**

9:55 Intermission.

10:15 194. Second-semester student-centered organic instructional laboratory for non-majors featuring microwave synthesis. C.S. Keenan, J.A. Shick, M.P. Betush, **S. Murphree**

10:40 195. Active learning in the instrumental analysis laboratory with virtual machines. **K. Streu**, N. Lee, A. Zubiria, S. Anderson, S. Gagliardi, R.M. Georgiadis

11:05 196. Using an inquiry-based, research driven approach to design a cross-disciplinary laboratory course. **T. Dwyer**, **J. Burkett**

11:40 Concluding Remarks.

Food Safety

Wild Rose B (Confection Hall Level)
K. M. Morehouse, *Organizer, Presiding*

9:00 Introductory Remarks.

9:10 197. Cold plasma: An emerging antimicrobial intervention to improve food safety. **B.A. Niemira**

9:40 198. Antimicrobial treatments for inactivation of bacteria on produce surfaces and reducing transfer to fresh-cut pieces. **D. Ukuku**

10:10 199. Aqueous inactivation of pathogenic bacteria on fresh produce with a new FDA-approved mixed peroxyacid formula (First Step+ 10). **J. Gurtler**

10:40 Intermission.

11:00 200. Surveys of toxic elements in food. **J. Fong Sam**

11:30 201. ATR-FTIR spectroscopy and chemometrics for the analyses of low levels (0.1%) of dietary trans fat. **S. Karunathilaka**, C. Srigley, S. Farris, M. Mossoba

Lanthanide Chemistry

Magnolia D (Confection Hall Level)
C. E. McDonald, *Organizer, Presiding*

9:00 Introductory Remarks.

9:05 202. Bonding in plutonium siderophore complexes from a FEUDAL perspective. **J.L. Sonnenberg**

9:30 203. Developing the photophysics and photoredox chemistry of molecular cerium compounds. **E.J. Schelter**, H. Yin, Y. Qiao, Y. Jin, K.C. Mullane, J. Hertzog, P.J. Carroll

10:15 Intermission.

10:35 204. Use of ureates as activators for smarium diiodide. **C.E. McDonald**

11:00 205. Mechanistic studies of low-valent samarium reductants. **R.A. Flowers**

11:45 Concluding Remarks.

Med-Chem Strategies for Chronic Hepatitis B Virus Infection

Magnolia B (Confection Hall Level)
Y. Du, *Organizer*
J. Clement, S. D. Kuduk, L. Sepp-Lorenzino, W. Zhu, *Presiding*

9:00 206. SAR studies in the sulfonyl carboxamide class of core protein modulators of the Hepatitis B virus. **S.D. Kuduk**, A. Lam, C. Espiritu, R. Vogel, K. Klumpp, L. Flores, G.D. Hartman

9:30 207. Discovery and pre-clinical characterization of a 3rd generation 4-heteroaryldihydropyrimidine (HAP) analogues as Hepatitis B virus (HBV) capsid inhibitors. **W. Zhu**

10:00 208. ALN-HBV: An investigational RNAi drug for the treatment of chronic hepatitis B. **L. Sepp-Lorenzino**

10:30 209. Screening a natural products library for HBsAg secretion inhibitors. **J.A. Clement**, S. Rawat, D. Solaiman, T. Zhou, M. Goetz, M. Todd

Methods & Applications of Metabolomics

Empire D (Confection Hall Level)
D. Rovnyak, *Organizer*, *Presiding*

9:00 Introductory Remarks.

9:05 210. Orthogonal comparison of GC-MS and ^{1}H NMR spectroscopy for short chain fatty acid quantitation. **J. Cai**, J. Zhang, Y. Tian, L. Zhang, E. Hatzakis, K. Krausz, P.B. Smith, F. Gonzalez, A. Patterson

9:30 211. Through the hills and valleys of time: Quantitative approaches for understanding circadian metabolism. **A. Weljie**

9:55 212. Applications of NMR spectroscopy in food analysis and in health and disease. **E. Hatzakis**

10:20 Intermission.

10:40 213. Differentiation of whole and refined wheat by ^{1}H-NMR spectroscopy. **C. Ridge**, V. Ramakrishnan, D. Luthria, J. Harnly

11:05 214. Withdrawn

11:30 215. Computer-assisted structural elucidation of two natural products. **E.P. Mazzola**, C. Ridge, P. Chen, G.E. Martin

11:55 Concluding Remarks.

Physical Chemistry of Materials

Wild Rose A (Confection Hall Level)
T. S. Snider, *Organizer*, *Presiding*

9:00 Introductory Remarks.

9:05 216. Aligning theory and experiment to design biocompatible nanocluster fluorophores. **Y. Small**

9:35 217. Understanding ultrafast mid-infrared absorptions in TIPS-pentacene during singlet fission. **C. Grieco**, E. Kennehan, J.B. Asbury

10:05 218. Using laser diagnostics and imaging to understand changes in soot nanostructure. **M. Singh**, J.P. Abrahamson, R.L. Vander Wal

10:35 Intermission.

10:55 219. Lighting the way to the "holy grail" of catalysis: Nanoplasmonics as a mechanistic probe for the direct epoxidation of propene on gold. **A.N. Ganguly**, S.L. Bernasek

11:25 220. Controlling morphology: Colloidal covalent organic frameworks and solution-cast freestanding films. **B.J. Smith**

11:55 Concluding Remarks.

Teaching Inorganic Chemistry

Magnolia A (Confection Hall Level)
S. Lin, C. Nataro, *Organizers*, *Presiding*

9:00 Introductory Remarks.

9:05 221. Developing literature discussions for an advanced inorganic chemistry course. **C. Nataro**

9:25 222. Research-based laboratory experiences in the inorganic chemistry curriculum at The College of New Jersey. **A.R. O'Connor**, **B.C. Chan**

9:45 223. Teaching recrystallization in a flipped laboratory. **W.D. Kerber**

10:05 Intermission.

10:20 224. Developing a POGIL-type workbook for inorganic chemistry. **J.M. Keane**

10:40 225. Assessment tools for the foundation-level inorganic chemistry course. **S. Lin**, A.H. Roy MacArthur, W.H. Pearson

11:00 226. IONiC VIPEr: A community of practice for improving the teaching of inorganic chemistry. **C. Nataro**

11:20 Discussion.

11:40 Concluding Remarks.

MONDAY AFTERNOON, JUNE 5

Advances in Organic Chemistry

Empire D (Confection Hall Level)
A. J. Catino, M. W. Fennie, *Organizers*, *Presiding*

1:00 Introductory Remarks.

1:05 227. Synthetic studies toward gephyrotoxin 287C. **S.P. Fearnley**, M.E. Domaradzki

1:30 228. Computational studies of intramolecular Diels–Alder reactions: N-substituted oxazolone trienes. **N. Sizemore**, S.P. Fearnley

1:55 229. Breaking aromaticity: The Wagner-Jauregg reaction. **S.S. Tartakoff**

2:20 230. Manganese-proline derived new catalyst system for the enantioselective synthesis of a-hydroxy phosphonates/a-amino phosphonates. **P. Kaur**, H. Lim, V. Datilus, R. Teriak, P. Chohan

2:45 Intermission.

3:05 231. Progress toward the utilization of *in-situ* generated alkyl hypervalent iodine species for the cross-coupling of sp^3 carbons. **I.D. Hyatt**

3:30 232. Reactions of hypervalent iodonium alkynyl triflates with unsaturated nucleophiles: Fused ring structures through trimethylenemethane intermediates. **T. Li**, K. Pham, D. Hyatt

3:55 233. Displacement of trichloroacetimidates with trimethylaluminum for the synthesis of substituted diarylethanes and related systems. **N. Mahajani**

4:20 234. Catalytic hydroamination of propargyl imidates. **M.W. Fennie**

Bio-Inorganic Chemistry

Magnolia A (Confection Hall Level)
W. D. Kerber, A. J. Reig, *Organizers, Presiding*

1:00 Introductory Remarks.

1:05 235. Modeling nitric oxide signaling chemistry at copper sites. **T.H. Warren**, S. Kundu, S. Zhang, Z. Sakhaei

1:50 236. Different products of hydride attack on five- and six-coordinated ferric heme nitrosyls: A DFT investigation of reaction mechanisms. R. Khade, **Y. Zhang**

2:15 237. Auxiliary ligand binding to divalent metal complexes of DIG_3tren, a tripodal, triguanidine ligand with H-bond donors. **R.C. Scarrow**, K. Gomez, N. Rolfe

2:40 Intermission.

3:00 238. Benefits of biological batteries: A study on the effects of biological templates as a means to enhance lithium-ion batteries. **S.J. Riley**, M.A. Allen

3:25 239. Electrochemical studies of cysteine/zinc interactions. **G.T. Cheek**, M.Y. Doan

3:50 240. Modeling the molybdenum cofactor: Exploring molybdenum pterin-dithiolene reaction chemistry. **S.J. Nieter Burgmayer**, D.R. Gisewhite, B. Willilams, A. Nagelski, N. Nguyen

4:35 Concluding Remarks.

Cosmetic Chemistry: Interdisciplinary Science that Inspires, Imagines & Innovates

Empire B (Confection Hall Level)
S. R. Milstein, *Organizer, Presiding*
H. Kumari, *Presiding*

1:00 Introductory Remarks.

1:10 246. In memoriam: Wayne Wamer. **A. Kornhauser**, S. Milstein

1:40 241. Careers in cosmetic sciences. **D. Wheeler**

1:55 242. University of Cincinnati cosmetic science degree and certificate programs. **H. Kumari**, G. Kasting, G. Kelm, K. Ananthapadmanabhan, N. MacKinnon, R.R. Wickett

2:15 244. Cosmetic ingredient names: The story behind the label. **J. Nikitakis**

2:40 Intermission

2:50 245. Cosmetic and personal care product safety and efficacy claims testing. **C. Weiss**

3:20 243. Anti-aging cream that expands sun care to help protect against infrared damage: The next generation of skincare. **M.S. Goldstein**

3:40 247. Analysis of natural rubber latex proteins in cosmetic products. S.R. Milstein, **A. Brown**, M. Herrmann, A.D. Lucas, E. Miranda-Bermudez, J. Hicks, B. Watson, A. Tebsherani, R. Aziz

4:10 248. Environmental risk assessment of plastic personal care and cosmetic ingredients. **I. Davies**

4:40 Panel Discussion.

4:55 Concluding Remarks.

Current Topics in Bioactive Molecules, both Large & Small

Magnolia C (Confection Hall Level)
K. P. Minbiole, *Organizer, Presiding*

1:00 Introductory Remarks.

1:05 249. New solutions to an old problem: Modernizing quaternary ammonium antiseptics. **K.P. Minbiole**

1:30 250. Bioactive polycationic amphiphiles as novel antiseptics. **K.L. Caran**, K. Seifert, K. Feitosa, J. Marafino, E. Rogers, B. Walsh, S.D. Kendrick, K. McKenna, B. Ashamole, M. Lauer, S.O. Rauer, A. Rister

1:55 251. Carbon dioxide measure with reference to oxygen use in respiration of *Bryophyllum sanctulum*. **C.E. Broderick**

2:20 Intermission.

2:40 252. Pharma: Friend or foe? Development, implementation, and assessment of a cross-disciplinary non-majors course about the pharmaceutical industry. **S.C. Young**, G. Colin

3:05 253. Chemistry on the backs of frogs: Bioactive small molecules from an amphibian-bacterial-fungal ecosystem. **T.P. Umile**

3:35 Concluding Remarks.

Evolving Landscape of Drug Discovery & Development

Magnolia B (Confection Hall Level)
R. W. Lee, R. Wenslow, *Organizers, Presiding*

1:00 Introductory Remarks.

1:10 254. Evolving landscape of drug discovery and drug development: Advances in pediatrics. **K.C. Thompson**

2:00 255. Developability: Bridging the gap between drug discovery and development. **S. Garad**

2:50 Intermission.

3:05 256. Evolution from a failed reaction to spawning a start-up company: Development of a novel pro-drug technology. **F.P. Hollinger**, D. Mahajan, S. Sen, S. Dugar

3:55 Concluding Remarks.

Food Safety

Wild Rose B (Confection Hall Level)
K. M. Morehouse, *Organizer, Presiding*

1:00 Introductory Remarks.

1:10 257. Investigation of sample preparation and acquisition method effects on non-targeted screening using LC/HR-MS. **A. Knolhoff**, C. Kneapler, T.R. Croley

1:40 258. Mass spectrometric analysis of the effects of a proline endopeptidase on gluten in a wheat gluten incurred model sorghum beer. **K.L. Fiedler**, R. Panda, T.R. Croley

2:10 259. Detection and characterization of nanomaterials used in food. **S.A. Khan**, T.R. Croley

2:40 Intermission.

3:00 260. Vanilla authentication using SPME-GC-MS. **W. Young**, S. Genualdi, L. Dejager

3:30 261. Identification of potential neurotoxicants using in vitro enzyme inhibition assays. **M.F. Santillo**

4:00 Concluding Remarks.

History of Chemistry

Cocoa Suite 5 (Main Level)
R. A. Egolf, *Organizer*
M. Orna, *Presiding*

1:00 Introductory Remarks.

1:05 262. Collecting, preserving, and sharing the history of science and engineering at the Chemical Heritage Foundation. **R.S. Brashear**

1:35 263. 19th Century undergraduate chemical education in Pennsylvania's Lehigh Valley. **R.A. Egolf**

2:05 264. 19th Century graduate chemical education in Pennsylvania's Lehigh Valley. **R.A. Egolf**

2:35 Intermission.

2:55 265. Miles Pickering (1943-1991): A mentor, a friend: Primarily a chemical educator. **J.B. Ealy**

3:25 266. Hubert Alyea: Life-long learner. **J.L. Ealy**

3:55 267. Legacy of tetraethyl lead. **J.L. Epstein**

4:25 Concluding Remarks.

Insights into the Chemistry of Protein Function

Magnolia D (Confection Hall Level)
M. Junker, *Organizer, Presiding*

1:00 Introductory Remarks.

1:05 268. Amino acid interaction networks in enzyme catalysis. K.F. O'Rourke, J. Axe, E.M. Yezdimer, N.E. Kerstetter, R.N. D'Amico, **D.D. Boehr**

1:30 269. Lack of folding and yet a function: Structural insights into intrinsically disordered proteins and transcription. **S.A. Showalter**

1:55 270. Investigating the effect of alpha-synuclein tyrosine-39 phosphorylation on synaptic vesicle trafficking. **B. Pan**, E. Petersson, E. Rhoades

2:20 271. DNA-crowded enzyme complex with enhanced activity and stability. **J. Fu**

2:45 Intermission.

3:05 272. Structural and functional analysis of POT1-TPP1 disease mutations in cancer. **E. Skordalakes**

3:30 273. Molecular mechanisms in heme protein function: A thermodynamic perspective from fluoride-binding studies. **J. Cerda**, M. Lockwood, K. Frankenfield, T.S. Nagle, K. Wodzanowski, J. Lopez Garriga

3:55 274. Defining the limits of the solvent dependence of protein dynamics. **N.V. Nucci**, V.R. Moorman, K. Valentine, A.J. Wand

4:20 Concluding Remarks.

Ionic Liquid Bulk & Interfacial Chemistry: Surface Structure & Interactions

Cocoa Suite 4 (Main Level)
M. Maroncelli, *Organizer*
J. T. Newberg, *Organizer, Presiding*

1:00 Introductory Remarks.

1:05 275. Water at the ionic liquid-vapor interface probed by ambient pressure x-ray photoelectron spectroscopy. **A. Broderick**, Y. Khalifa, J.T. Newberg

1:30 276. Molecular and electronic structures of ionic liquids in bulk and interfacial regions. **E. Castner**

2:00 277. Ionic liquid ordered structures near and far from solid surfaces. **S.K. Shaw**, A.J. Lucio, R.S. Anaredy, J. Wrona, A. Hailu

2:30 Intermission.

2:45 278. Uncovering the molecular arrangement of ionic liquids confined to solid surfaces. **L. Li**

3:15 279. Anomalous nanofriction in ionic liquids: The devil is not in the tails. **J.C. Araque**, R. Daly, S. Yadav, M. Shadeck, M. Maroncelli, C.J. Margulis

3:45 280. Insights into the mechanism for CO_2 reduction bismuth-film cathodes in the presence of room temperature ionic liquids. **J. Rosenthal**

4:15 Concluding Remarks.

Physical Chemistry of Materials

Wild Rose A (Confection Hall Level)
T. S. Snider, *Organizer*, *Presiding*

1:00 Introductory Remarks.

1:05 281. Investigation of crosslinker structure in organogels from partially hydrolyzed poly(vinyl acetate). **T. Duncan**, B.H. Berrie, R.G. Weiss

1:35 282. Factors affecting catalytic activity for nitrophenol hydrogenation on colloidal nanocatalysts. **A.L. Marsh**

2:05 Intermission.

2:25 283. Aqueous ionic liquid solutions and their effects on protein structures and lipid bilayers. **T.D. Vaden**

2:55 284. Toward structural design rules for unconventional solar energy conversion in organic conjugated materials. **R.D. Pensack**, G.D. Scholes

3:25 Concluding Remarks.

Revitalizing General & Organic Chemistry Laboratory Experiments

Empire C (Confection Hall Level)
P. F. Martino, *Organizer, Presiding*

1:00 Introductory Remarks.

1:05 285. Analysis of undergraduate student survey on guided-inquiry laboratory activities implemented in a general chemistry laboratory course. **S.E. Ingram**, S. Synnott, L. Winchester, Y. Tong, M. Shahu

1:30 286. Using guided inquiry to study the stoichiometry of carbonate neutralization reactions. **G. Salter**

1:55 287. Taking molecular modeling beyond the ball and stick. **D. Beautreau**

2:20 Intermission.

2:35 288. What is in my shampoo? From active ingredient to active learning. **A.M. Rosan**

3:00 289. Developing two inquiry-based experiments for sophomore organic chemistry teaching laboratory at Drew University. **S.K. Keyser**, A.M. Rosan

3:30 290. Azeotropic preparation of a C-phenyl N-aryl imine: An introductory undergraduate organic chemistry laboratory experiment. **L.J. Silverberg**, D. Coyle, K.C. Cannon, R.T. Mathers, J.A. Richards, J. Tierney

3:55 291. Further explorations of efficient one-pot, three-step reductive amination sequence; and iron (III) chloride catalyzed Friedel-Crafts acylation reaction for the organic laboratory experiments. **X. Fan**, H. Chen, E. Wiggin, C. Zhang

4:25 292. Implementation of an olefin metathesis experiment into the undergraduate organic laboratory course. T. Udumulla, A. Hussain, D. Richiuso, M. McCloskey, M. Romero, K.C. Cannon, **S.L. Carberry**

4:50 Concluding Remarks.

Theory & Computation Toward Electronic Properties of Molecular Materials

Empire A (Confection Hall Level)
H. Jaeger, *Organizer, Presiding*

1:00 Introductory Remarks.

1:05 293. Role of charge transfer excitons in high-mobility polymers. **H. Jaeger**, J. Parker

1:35 294. From molecular electronics to energy storage: Striving for a unified approach to electron transfer in open systems. **R. Jorn**

2:05 295. Spectroscopy of liquids and molecules at metal surfaces: Markovian and non-Markovian electron dynamics. **M. Pavanello**

2:35 296. Development of effective stochastic potential method using random matrix theory for describing electronic excitations in noisy quantum systems. J. Scher, **A. Chakraborty**

3:05 Intermission.

3:25 297. On-the-fly heuristic reordering approach to deterministic optimization for qualitative chemical property prediction. J.M. Elward, **C.B. Rinderspacher**

3:55 298. Toward accurate classical molecular dynamics simulations of molecules on metallic surfaces. Z. Li, A. Tkatchenko, **I. Franco**

4:25 299. Plasmonic hot carriers: Towards material design. **R. Sundararaman**

4:55 Concluding Remarks.

Women in Organic Chemistry

Crystal A (Confection Hall Level)
S. Wengryniuk, *Organizer, Presiding*

1:00 Introductory Remarks.

1:05 300. New stereocontrolled reaction cascades for organic synthesis. **A.J. Frontier**

1:35 301. Harnessing alkyl amines in nickel-catalyzed cross couplings via C–N bond activation. **M.P. Watson**

2:05 302. Catching the frequency: New photochemical and microwave mediated methods for heterocycle synthesis. **E.C. McLaughlin**

2:35 Intermission.

2:55 303. Oxygen driven fragment coupling by activation of C-H, N-H, and O-H bonds. **M. Kozlowski**

3:25 304. Power and perils of high throughput experimentation in process chemistry. **I. Strambeanu**

3:55 305. Keynote address: Madeleine Joullie. **M.M. Joullie**

4:45 Concluding Remarks.

Poster Session

Red & White Room
L. J. Silverberg, *Organizer*

4:00 - 6:00

Biochemistry

306. Logic-gated catalytic circuits for sensing bio-targets. **S. Oh**, **A. Pereira**, T. Zhang, A. Lane, J. Fu

307. Study of the potential antioxidant properties of the reduced form of Nicotinic Acid Adenine Dincleotide (NADPH) using luminometry. **C. Saladino**

308. Study of the potential antioxidant properties of Ascorbic Acid (AA) using luminometry and UV/Vis spectrophotometery. **C. Saladino**

309. Thioamides: Improved incorporation methods and effects on protein stability. **D. Szantai-Kis**, C.R. Walters, Y.J. Wang, T. Barrett, E.M. Hoang, E. Petersson

310. Thioamides suppress dipeptidyl peptidase 4 proteolysis of therapeutic peptide hormones while maintaining bioactivity. **X. Chen**, **T. Barrett**, M.R. Hayes, E. Petersson

311. Positional effects of thioamides on cleavage rates of proteases. **X. Chen**, T. Barrett, E.K. Keenan, **J. Wang**, **C. Liu**, E. Petersson

312. Enhancing fractional ^{13}C incorporation in biosynthetically prepared proteins. **X. Wang**, R.E. Sonstrom, D.S. Rovnyak

313. Purification of hypoxia-inducible factor prolyl-hydroxylases for studies of structure and function. **P. Gallo**, K. Schardien, T. Keagy, N.V. Nucci

314. Novel fluorescently labeled anthraniloyl-m^7G capped RNA as a biomarker for biophysical studies. **A.V. Domashevskiy**, D.J. Rodriguez, D. Gunawardana, D.J. Goss

315. Fluorescent labeling of α-synuclein for studying aggregation, propagation, and strain emergence. **C. Haney**, T.S. Mihaila, R.J. Karpowicz, E. Petersson

316. Characterization studies and activity assay development for sfnaC of the staphyloferrin A biosynthetic pathway. M.V. Muniz, M.K. Callahan, R. Pongdee, **W. Kittleman**

317. Thermodynamics of pHLIP binding and folding is dependent on titration of key acidic residues. **A. Clark**, **Z. Bonham**, **J. Saseen**, **B. Mertz**

318. Effects of a neutral cosolute on the B to Z transition for DNA duplexes incorporating both CG and CA steps. P. Phromsiri, R.R. Gerling, **J.M. Blose**

319. Engineering green fluorescence protein derivatives with cytochrome *c* heme binding sites. **D. Nunez**, **C. Sanders**

320. Efficacy of truncated synthetic analogues of the human antimicrobial peptide salvic against *Escherichia coli* persister cells. **I. Molina**, **S. King**, **M. Kinoian**, C. Fazen

321. Synthesis and effectiveness of antimicrobial peptide temporin F analogues against *Escherichia coli* persister cells. **J. Schwartz**, C. Reiber, C. Fazen

322. Application of fluorescence spectra in the analysis of cocaine samples. **L.E. Felix**

323. Purification of mycobacteriophage terminase and portal proteins in *Escherichia coli*. M. Sperratore, B. Grenyer, **M. Harrison**

324. Study co-aggregations of nucleic acid nanostructures with tetracycline molecules and their potential applications in smart drug delivery. **N. Alzahrani**, F. Jinglin, Z. Wang , D. Yang

325. Probing environments in *Thermoanaerobacter tencongensis* H-NOX. **C. Kearney**, **T. Hirn**, L.T. Olenginski, D. Tariq, S.H. Brewer, C.M. Piro

326. Synthesis and evaluation of copper binding properties and BACE 1 inhibition activity of multi-target compounds. **A. Martinez**, M. Zahran, M. Gomez, C. Cooper, S. Hambleton

327. Conformation of Influenza M2 protein is sensitive to the curvature propensity of membrane lipids. D.S. Arbuckle, A. Holmes, **K.P. Howard**

328. Characterization of the region of the influenza membrane bound M2 protein critical to cholesterol dependent viral budding. A. Herneisen, G. Kim, H. Raymond, **K.P. Howard**

329. Determining chaperone protein requirements for the propagation of heterologous poly-glutamine aggregates in *S. cerevisiae*. **A. Killian**, M. Astor, J.K. Hines

330. Investigating the role of J-proteins in Hsp104-mediated curing of prion [PSI^+]. **S.E. Berger**, E. Kamiya, M. Astor, J.K. Hines

331. Spectrophotometric determination of the binding affinity and computationally determined estimated binding energy of neutral red, riboflavin, and flavin derivatives with riboflavin binding protein. H. Yazgi, N. Abouomar, **J.B. Ealy**

332. Functional and high-affinity binding of dopamine D4 receptor-selective partial agonists as pharmacological tools to study substance use disorders. **H. Hoag**, T.M. Keck

333. Withdrawn

334. Engineering of a protein probe for alpha synuclein detection. **E. Chau**, J. Candreva, J.R. Kim

335. Optimization of a permissive aminoacyl tRNA synthetase for a target unnatural amino acid. **I. Sungwienwong**, E. Petersson

336. Creating peptide hydrazides *via* intein splicing for expressed protein ligation. **O. Ekanayake**, S. Rozovsky, J. Liu

337. Protective function of *Azadirachta indica* (neem) in WI38 lung fibroblast cells subjected to oxidative stress. **A. Wilson**, J. Chen, C. Powell, J. Sekyere, M.C. Abeysiri, M. Benavides

Environmental, Green & Sustainability

338. Matrix effects on equilibria in atmospheric aerosol. **M.M. Galloway**, M.G. Ippolito, J.M. Ackendorf, A. Sager

339. Chemical analysis of water near hydraulic fracturing sites. **T. Milewski**, A. Boland, E. Graham, K.A. Stumpo

340. *In vitro* assays for assessment of estrogenic activity of the novel Bisphenol-A alternative, four Bisguaiacol-F compounds. **Y. Peng**, K. Reno, T.H. Epps, M. Guo, C. Wu

341. Comparison of 1,4-dioxane cometabolism with the amendment of different alkane gases. **M. Li**, Y. Liu, D. Deng

342. Exploring the fate of sulfur in regions of abandoned mine drainage. **K.L. Klein**, K.J. Castle

343. Liquid-phase hydrogenation of furfural and furfuryl alcohol assisted by metal chlorides. **S. Ogozaly**, L.A. Welch

344. Impact of cationic forms of organic matter in natural waters on the nitrogen assimilation processes. I. Povar, P. Spataru, **F. Fernandez**, T. Spataru

345. Withdrawn

346. Detection and cell sorting of cyclic ether degrading *Pseudonocardia* species by fluorescence *in situ* hybridization and flow cytometry using 16S rRNA-targeted oligonucleotide probes. **M. Li**, Y. Yang, P.J. Alvarez

347. Paper-based mercury detection implementing gold nanoparticles and mercury-specific oligonucleotide. **Z. Wu**

348. Tetramethylguanidinidum amino acid-based ionic liquids and their effects on beta sheet proteins. **B.L. Kelsey**, C.C. Christine, B.L. Stinger, C. Wu, G.A. Caputo, T.D. Vaden

Industry & Pharma

349. Withdrawn

350. Investigation of drug delivery options for putative glutaminase inhibitors implicated as cancer therapeutics. **T.W. Mastria**

351. Physical stability of fixed-dose combination tablets: A systematic investigation into the cause of SLS and amorphous API crystallization under conditions of high moisture activity. **E.A. Kemp**, P. Sundararajan, W. Xu, K. Rosenberg, S. Conway, P. Marsac

Organic Chemistry

352. Small-molecule approach to the inhibition of botulinum neurotoxin A. K.M. Recabo, E. Slick, **S.M. Ensel**

353. Metal initiated aggregation induced emission of asymmetric cycloheptatrienylidene substituted fluorophores. **M.E. Medard**, D. Hyatt

354. Stereoselective synthesis of the allo bile acids. **M.R. Krout**, B.N. Nelson, S.P. Kelly, B.J. Huckstep

355. Studies directed towards the synthesis of a sparteine surrogate. **T.F. Higgins**, J.D. Winkler

356. Ter-pyridine derived catalyst system for the cyanation of aldehydes and imines using Et_2AlCN. **D. Moustafa**, P. Kaur

357. Titanium-proline derived system for the asymmetric synthesis of propargyl alcohols. **C. Sweet**, P. Kaur

358. Tropone iron tricarbonyl complex as a platform for the synthesis of bridged nitrogen heterocycles. **D. Griffith**, Z. Huang, D. Sweitzer, R. Tritt, S. Valent

359. Exploring the utility of peptidomimetics as blood-brain barrier shuttles. **S.C. Young**, A. Rice , Y. Kim, A. Wiest, W. Bowman

360. Studying the transmission of substituent effects on comparable ^{1}H and ^{13}C sites in monosubstituted benzenes and pyridines. **M. Malfara**, J. Tierney

361. Synthesis of N-methylarylamines by reduction of isocyanates. **G.D. Mendenhall**

362. Photocycloaddition to aromatic ring: A potential synthetic methodology for ring systems. **A. Barrella**, **H. Kaur**, J.I. Lee, **S. Singh**

363. Metal-catalyzed cross-coupling reactions of functionalized organozinc reagents for the synthesis of β,β-disubstituted enones. **H.R. Rensch**, M.R. Krout

364. Synthesis and characterization of 3-cyclohexyl-2-aryl-1,3-thiazolidin-4-one triphenyltinchloride complexes. **K.C. Cannon**, M. Costa, A. Ongari, J. Tierney

365. There is an absolute zero on the NMR chemical shift scale. **D.D. Clarke**

366. Surface analysis of fibronectin-coated QCM-D sensors by atomic force microscopy. **T.J. Collins**, J.Y. Chen, J. Xi

367. Experimental and DFT computational evidence for new nitrosamine peroxide intermediates generated by photooxidation. A. Ghogare, C. Debaz, M. Silva, I. Abramova, P.P. Mohapatra, K. Kwon, E. Greer, F. Prado, H. Valerio, P. Di Mascio, **A. Greer**

368. Long chain-pterin conjugates with interesting lipophilic and sensitizer properties. M. Vignoni, N. Walalawela, S.M. Bonesi, **A. Greer**, A.H. Thomas

369. Synthesis, photophysics and evaluation of mono-, di-, tri- and hexa-PEG sensitizers for pointsource photodynamic therapy. T. Bornhütter, A. Ghogare, A. Preuß, **A. Greer**, B. Röder

370. Synthesis of α, α, -dibromoketone catalyzed by organosilanes from alkynes. **C. Chong**

371. Design and synthesis of novel lithocholic acid carboxamides with antiproliferative and pro-apoptotic effects on human cancer cells. **S. Ramisetti**, D. Karelia, S. Amin, A.K. Sharma

372. Withdrawn

373. Withdrawn

374. Withdrawn

375. Heterocyclic motifs for natural products synthesis. **S.P. Fearnley**, C. Thongsornkleeb, M.E. Domaradzki, R.C. Lapo, P.M. Lory

376. Soxhlet extraction and analysis of capsaicin from various pepper flesh and seeds. **J. Cawley**, F.C. Mayville

377. Evolution of a manufacturing route to omarigliptin (MK-3102), a long-acting DPP-4 inhibitor for the treatment of type 2 diabetes. **A. Kassim**

TUESDAY MORNING, JUNE 6

Catalysis : Electrocatalysis & Small Molecule Activation

Magnolia A (Confection Hall Level)
J. Rosenthal, R. J. Swails, *Organizers, Presiding*

8:30 Introductory Remarks.

8:35 378. Determination of important catalytic species in heterogeneous layered manganese dioxide materials for water oxidation application. **I. McKendry**, H. Peng, A. Thenuwara, L. Mohammad, R. Remsing, D.R. Strongin, M. Zdilla

9:00 379. Electrocatalytic plasticity: Switching the outcome of CO_2 reduction at post-transition metal cathodes in the presence of room-temperature ionic liquids. **A. Atifi**, J. Rosenthal

9:25 380. Small-molecule activation with metal-organic polyhedra. **E.D. Bloch**

9:50 381. Well-defined chromium catalysts for selective ethylene trimerization. **K.H. Theopold**, W.H. Monillas, J. Young, J. Shen

10:15 Intermission.

10:30 382. Iron polypyridyl complexes for hydrogen generation in aqueous solutions. **W. McNamara**

10:55 383. Electrocatalytic ammonia oxidation with molecular copper catalysts. **T.H. Warren**, M. Raghibi Boroujeni, S. Kundu

11:20 384. Nontraditional porphyrinoid scaffolds as efficient electrocatalysts for the oxygen reduction reaction. **J. Rosenthal**

Organometallic Chemistry

Wild Rose B (Confection Hall Level)
A. R. O'Connor, D. L. Zubris, *Organizers, Presiding*

8:30 385. Development of imino and amino pyridine iron(II) catalysts for Atom Transfer Radical Polymerization (ATRP). **D.L. Zubris**

8:50 386. Leveraging P(III)-P(V) oxide ligands: Enabling polar alkene polymerization by group 10 metals. W. Zhang, M. Tiedemann, C. Padilla, J. Mei, **B.P. Carrow**

9:10 387. Bis(guanidinyl)pyridines as ligands for late first-row transition metals. J.E. Allen, L. Wilkinson, W.S. Kassel, **N.A. Piro**

9:30 388. Sterically reduced design considerations toward the completion of dinitrogen fixation cycles by group 6 Pentamethylcyclopentadienyl, Amidinate (CPAM) complexes. **L.M. Duman**, L.R. Sita

9:50 Intermission.

10:10 389. Synthesis of moderately coordinating anions: Towards the design of organometallic ion pairs. **G. Dobereiner**

10:30 390. Designing ligands for the cluster-surface analogy. P. Cui, Q. Wang, L.M. Thierer, S. Zhang, B.C. Manor, P.J. Carroll, **N.C. Tomson**

10:50 391. Strategies for transition-metal catalyzed, non-directed C-H functionalization. **M. Emmert**

11:10 392. Combined, high-throughput, mechanistic approach to the development of catalytic reactions for the synthesis of active pharmaceutical ingredients. **D. Leitch**

11:30 393. New advances in polydifluoromethylenation reactions. **D.A. Vicic**

Advances in Nanotechnology, Polymers, Terahertz & Analytical Research: Current Applications & Future Direction for the 21st Century

Wild Rose A (Confection Hall Level)
A. Rahman, *Organizer, Presiding*

9:00 Introductory Remarks.

9:05 394. Measurement of resistivity of semiconducting materials via terahertz reflectance route. **A. Rahman**, **A. Rahman**

9:45 395. Terahertz multispectral imaging and other analyses of gold nanoparticles. **W. Ghann**

10:15 Intermission.

10:25 396. Helical polysilane: Conformational study with molecular dynamics simulation. **Z. Muyang**, Y. Zhou

10:55 397. Characterization of cigarette paper by terahertz spectroscopy and multispectral imaging. J.H. Lauterbach, **A. Rahman**, **A. Rahman**

11:25 Concluding Remarks.

Biomarker Synthesis & Clinical Chemistry

Crystal A (Confection Hall Level)
H. F. Sobhi, *Organizer, Presiding*

9:00 Introductory Remarks.

9:10 398. More studies on cyclic six- and seven-membered 2,3-diaryl-1,3-thiaza-4-ones. **L.J. Silverberg**, H. Yennawar, C. Pacheco, A.F. Lagalante, H.F. Sobhi, K. Alemany, J. Bachert, L. Baker, K. Bandholz, A. Bayliff, R. Bendinsky, H. Bradley, M. Buchwalter, A. Cali, O. Cardenas, L. Chen, B. Colburn, A. Cooper, D. Coyle, J. Dahl, M. Felty, R. Fox, J. Islam, E. Kimmel, S. Koperna, M. Lawler, Q. Moyer, C. Mroz, D. Noble, K. Perhonitch, H. Reppert, H. Singh, C. Verhagen, R. Vidal, A. Weisbeck, Y. Xie, Z. Yang

9:45 399. Challenges in the management of pancreatic cancer: How a chemist can help? **C. Boutros**

10:20 Intermission.

10:40 400. Therapeutic relevance of the endocannabinoid system and enzyme-mediated synthesis of 2-arachidonoylglycerol (2-AG). **M.R. Johnston**

11:15 401. Synthesis and characterization of lipophilic acyl: Coenzyme A thioesters for clinical diagnosis of mitochondrial fatty acid oxidation disorder. **H.F. Sobhi**

Chemistry at Interfaces: Living on the Edge

Empire A (Confection Hall Level)
R. Z. Hinrichs, *Organizer, Presiding*

9:00 Introductory Remarks.

9:05 402. Withdrawn

9:30 403. Fabrication of high-resolution OLEDs via contact printing. **J. Li**, L. Xu, C.W. Tang, A. Shestopalov

9:55 404. Topcoats for improved decontamination of painted surfaces. **B.J. Johnson**, B.J. Melde, B.D. Martin

10:20 Intermission.

10:40 405. Coatings with improved performance through the use of polymer pigment composites. **S. Brownell**

11:05 406. Development of modified conducting substrates using on-surface cross-coupling methods with carbon-based electrodes. J. Rosenthal, **R. Pupillo**, A.A. Gietter-Burch, D.A. Watson

Computational Chemistry in the Undergraduate Curriculum: Present & Future

Tower Suite 1 (Tower Level)
J. L. Sonnenberg, *Organizer, Presiding*

9:00 Introductory Remarks.

9:05 407. Roundtable panelist with undergraduate education experience. **B. Albrecht**

9:10 408. Roundtable panelist with a background in undergraduate education. **H.J. Castejon**

9:15 409. Roundtable panelist with experience in pharmaceutical and information technology industries. **W.D. Cornell**

9:20 410. Roundtable panelist with experience in research, education, diversity and policy sectors. **R. Hernandez**

9:25 411. Roundtable panelist: Experienced in undergraduate education. **M.M. Ivey**

9:30 412. Roundtable panelist with experience in undergraduate education, research, and software development. **W.F. Polik**

9:35 413. Roundtable panelist with experience in undergraduate education. **K. Range**

9:40 414. Roundtable panelist with experience in undergraduate education in physical chemistry. **C. Salter**

9:45 415. Roundtable panelist with experience in industry. **V. Shanmugasundaram**

9:50 416. Roundtable panelist with experience in small bio-tech and large pharmaceutical industries. **E.C. Sherer**

9:55 417. Roundtable panelist with experience in undergraduate research and formation of the Molecular Education and Research Consortium in Undergraduate computational chemistRY (MERCURY). **G.C. Shields**

10:00 Panel Discussion.

10:30 Intermission.

10:45 Discussion.

11:55 Concluding Remarks.

Evolving Landscape of Drug Discovery & Development

Magnolia B (Confection Hall Level)
R. W. Lee, R. Wenslow, *Organizers, Presiding*

9:00 Introductory Remarks.

9:10 418. Tweaking our chemical biology platforms to increase the translational potential of the data. **C.J. Thomas**

10:00 419. Overview of US prescription pharmaceutical market and future viability of products approved by 505(b)2 new drug application regulatory pathway. **K. Ostrander**

10:50 Intermission.

11:05 Concluding Remarks.

Fate & Transport of Environmental Contaminants

Empire B (Confection Hall Level)
M. Li, *Organizer, Presiding*
L. A. Welch, *Presiding*

9:00 Introductory Remarks.

9:05 420. Assessing metal contamination and contaminant sources in urban streams. G. Makler, **E.R. McKenzie**

9:30 421. Identifying redox transition zones in the subsurface. **X. Yin**, H. Hua, L. Axe

9:55 422. Distinct effects and molecular basis of inducing and non-inducing auxiliary substrates on 1,4-dioxane biostimulation. **M. Li**

10:20 Intermission.

10:40 423. Self-decontaminating polymer additives for CWA protection. **J. Lundin**, S.L. Giles, B.T. Rasley, R.B. Balow, P. Pehrsson, J.H. Wynne

11:05 424. Characterizing reactive iron mineral coatings in redox transition zones. **H. Hua**, X. Yin, L.B. Axe

11:30 Concluding Remarks.

Innovations in Analytical Chemistry Education

Empire C (Confection Hall Level)
M. Kistler Langston, *Organizer, Presiding*

9:00 Introductory Remarks.

9:05 425. Adapting and extending general chemistry experiments for the analytical chemistry laboratory curriculum. **D. Mencer**

9:30 426. Instrumental analysis at Lafayette College. **M.M. Galloway**

9:55 Intermission.

10:15 427. Incorporation of Laser Induced Breakdown Spectroscopy (LIBS) into analytical chemistry/instrumental analysis and an innovative lab experience for students. **R. Chinni**

10:40 428. Quantitative determination of artemisinin in extracts and supplements using TLC and ImageJ software. **D. Rusak**

11:05 429. Balancing breadth and depth in the design of an analytical course for environmental science majors. **J.A. Palkendo**

11:30 Concluding Remarks.

Life & Times of Joseph Priestley

Empire D (Confection Hall Level)
D. A. Casteel, *Organizer, Presiding*

9:00 430. Joseph Priestley House Museum. **D.A. Casteel**

9:40 431. Priestley residences. **T. Bresenhan**

10:20 432. On being Joseph Priestley. **R.C. Blatchley**

11:00 433. Joseph Priestley House: A National Historic Chemical Landmark. **S. Rovner**

Small Chemical Business

Magnolia D (Confection Hall Level)
A. Rahman, *Organizer, Presiding*
M. Chorghade, *Presiding*

9:00 Introductory Remarks.

9:05 434. Intellectual property protection for small chemical businesses. **A.H. Berks**

9:35 435. Expanding the perspective of drug development: Understanding real world medicine and real world patients. **M.N. Liebman**

10:05 Intermission.

10:15 436. American Horror Story, small business edition: A company possessed by high legal fee demons. **R. Micheletti**

10:45 437. Reverse pharmacology and systems approaches for chemical biology, drug discovery and development: Inspiration from Mother Nature and the wisdom of the Rishis. **M. Chorghade**

11:15 Concluding Remarks.

Structure, Function & Stability: Proteins with Unnatural Amino Acids

Magnolia C (Confection Hall Level)
C. Henkels, *Organizer, Presiding*

9:00 Introductory Remarks.

9:05 438. Optical control of protein function through unnatural amino acid mutagenesis. **A. Deiters**

9:30 439. Exploring protein environments with unnatural amino acids. **S.H. Brewer**

9:55 440. Studying Parkinson's disease using semi-synthetic proteins. **E. Petersson**

10:20 Intermission.

10:40 441. Exploring the solvation state at various sites in proteins. **C.M. Piro**

11:05 442. Designing fluorinated proteins for stability and imaging. **J.K. Montclare**

11:30 443. Examining the fluoro-stabilization effect using *in vivo* unnatural amino acid incorporation. **C. Henkels**

TUESDAY AFTERNOON, JUNE 6

Advances in Chromatography, Mass Spectrometry & Biosensors

Magnolia C (Confection Hall Level)
N. Wittenberg, *Organizer, Presiding*
K. A. Stumpo, *Presiding*

1:00 Introductory Remarks.

1:05 444. Electrografting application toward surface plasmon resonance biosensor. **O. Sathoud**, K.S. Booksh

1:25 445. Influence of brain gangliosides on vesicle adsorption, rupture, and supported bilayer formation determined by quartz crystal microbalance sensing. **L. Jordan**, N. Wittenberg

1:45 446. Sensing and investigating the interactions between small molecule drugs and lipid membranes. **S. Sun**, A.M. Sendecki, S. Pullanchery, D. Huang, T. Yang, P.S. Cremer

2:05 Intermission.

2:20 447. Analysis and comparison of N-linked glycans in *Naja kaouthia* and *Naja mossambica* snake venoms via mass spectrometry. **A. Lara**, K.A. Stumpo, S. Black

2:40 448. N-glycome profile of bird serum using mass spectrometry. **J. Ebeid**, K.A. Stumpo

3:00 449. Gold nanoparticles for laser-desorption ionization mass spectrometry of biomolecules. **C. Sacks**, B. Kelly, K.A. Stumpo

3:20 Intermission.

3:35 450. Gel perm ation chromatography: An analytical tool. **C. Stein**

3:55 451. Investigating the structural and thermodynamics aspect of bile salt enantio-selectivity in MEKC. **T.G. Strein**, D.S. Rovnyak, C. Ouimet, S. Anderson, R. Pirnie, C. Sussman

4:15 452. Monitoring folding and interactions of polyproline peptides using capillary electrophoresis. **A. Holliday**, A.M. Miller, J.D. Barr

4:35 453. Efficient synthetic route to a highly modular turn-on fluorescence probe through regio-selective cross coupling. **J.V. Jun**, D.M. Chenoweth, E. Petersson

4:55 Concluding Remarks.

Bio-Inorganic Chemistry

Empire D (Confection Hall Level)
W. D. Kerber, A. J. Reig, *Organizers, Presiding*

1:00 Introductory Remarks.

1:05 454. Surface functionalized metal-oxo magnetic nanobeads as potential T_1 contrast agents for magnetic resonance imaging. **V. Dahanayake**, W. Hickling, O. Rodriguez, C. Albanese, S.L. Stoll

1:30 455. Synthetically accessible tetrapyrrole metal complexes as efficient photochemotherapeutic agents with remarkably high phototoxicity index. **A.M. Potocny**, M. Martin, J. Rosenthal

1:55 456. Synthetic approaches to novel antibody-gold-based drug conjugates for targeted delivery in cancer chemotherapy. **N. Curado Dianez**, G. Dewaele Le Roi, B. T. Elie, M. Cornejo, M. Contel

2:20 457. Synthesis, DNA binding study, and anticancer activity of organorhenium sulfonato compounds on hormone-dependent MCF-7 and hormone-independent triple-negative MDA-MB-231 breast cancer cells. **T.J. Odebode**, S.K. Mandal, A.J. Winstead

2:45 Intermission.

3:05 458. Mechanism of solar water oxidation in Photosystem II. **K.V. Lakshmi**

3:30 459. Characterization and regulation of weak and strong siderophores by soil nitrogen-fixing *Azotobacter sp.*. **O. Baars**, S.H. Kopf, X. Zhang, F. Morel, M.R. Seyedsayamdost

3:55 460. Interactions of titanium with the siderophore pyoverdine: Ti(IV) complexation, TiO_2 dissolution, and bacterial interactions. **A. Valentine**, K. Jones

4:40 Concluding Remarks.

Catalysis: Mechanistic Elucidation & Method Development

Magnolia A (Confection Hall Level)
J. Rosenthal, R. J. Swails, *Organizers, Presiding*

1:00 Introductory Remarks.

1:05 461. Influences of inorganic additives in organotransition metal catalysis. **G. Dobereiner**

1:30 462. C-H insertion mechanism for heme carbenes. R. Khade, **Y. Zhang**

1:55 463. Mechanistic study and development of catalytic electron transfer reactions. **R.A. Flowers**

2:20 464. Synthesis, characterization, and catalytic activity of aluminum-α-diimine complexes. **C.R. Graves**

2:45 Intermission.

3:00 465. Recent advances in the development of Heck-like reactions using heteroatomic electrophiles. **D.A. Watson**

3:25 466. Zwitterionic N-heterocyclic carbene gold catalyst in a silver-free alkyne hydration reaction with selectivity towards internal alkynes. **K. Weerasiri**, G. Dobereiner

3:50 467. Synthesis of novel phosphine ligands with an imidazolium tether for use in biphasic reaction media. **M.E. Miller**, C.J. Parnell, R.J. Rosso

Chemistry at Interfaces: Living on the Edge

Empire B (Confection Hall Level)
R. Z. Hinrichs, *Organizer, Presiding*

1:00 Introductory Remarks.

1:05 468. Size-dependent morphology of liquid-liquid phase separating aerosol. **M. Freedman**

1:30 469. Role of coating-surface interactions in controlling the mixing state and morphology of soot nanoparticles. **A. Khalizov**, C. Chen, O. Enekwizu

1:55 470. Ions and the ultrafast vibrational spectroscopy and dynamics at mineral-aqueous interfaces. **E. Borguet**

2:20 471. Structure and energetics of the Stern layer at mica-water interfaces. **I.C. Bourg**, S. Lee, P. Fenter, C. Tournassat

2:45 Intermission.

3:05 472. Effect of water on the adsorption of CO2 on kaolinite and montmorillonite. R. Bennick, M.D. Kilmer, **L. Tribe**

3:30 473. Symmetry breaking and photocatalysis of nitrate on TiO_2: Effect of coadsorbed water. **J.G. Navea**

3:55 474. Anthracene and pyrene photolysis kinetics in aqueous, organic, and mixed aqueous-organic phases/interfaces. **J.N. Grossman**, T. Kahan

4:15 475. Heterogeneous ozonolysis of organic adsorbed on mineral aerosol surfaces. **R.Z. Hinrichs**, Z. Coates Fuentes, J. Edziah

4:35 476. Role of the gas-particle interface in the multiphase chemical oxidation of atmospheric organic aerosol. **D.A. Knopf**, J.H. Slade, M. Shiraiwa, J. Wang, H. Su, A. Arangio, U. Pöschl, S. Forrester, J. Li

Chemistry of Materials: Designing Structure

Wild Rose B (Confection Hall Level)
B. J. Smith, *Organizer, Presiding*

1:00 Introductory Remarks.

1:05 477. Polymerization of chloroethyl methacrylates: Chain transfer and the carbon-chlorine bond. **A. Snow**

1:35 478. Chemistry of high-performance waterborne coatings with improved eco-footprint through the use of self-assembled polymer pigment composites: Chemistry that is truly around us. **J. Bohling**

1:55 479. Conformational study of solvated polyethylene glycol 2000: A molecular dynamics study. **D. Sponseller**, E. Blaisten-Barojas

2:15 Intermission.

2:35 480. Rheological and application properties of non-drip paints. **S. Vuong**, T. Cary, K. Alderfer, G. Dombrowski, A. Worrall, A. Ala, V. Telyatnikov, G. Lejeune

2:55 481. Photoactivated shape changing polymer 4D printing system for flexible actuators. **D. Hagaman**, S. Leist, H. Ji, J. Zhou

3:15 482. Withdrawn

3:35 483. Dual affinity solid-binding peptides for nanoscale organization of Li-ion battery cathode materials. **E. Barannikova**, M.A. Allen

3:55 Concluding Remarks.

Chemistry of Molecular Imaging Crystal A (Confection Hall Level)

D. R. Veach, *Organizer, Presiding*

1:00 Introductory Remarks.

1:05 484. Development of fluorescent and ^{18}F labeled PARP targeted molecular imaging agents. **B. Carney**

1:35 485. Bifunctional chelators: The link between radiometals and radiopharmaceuticals. **M.A. Deri**

2:05 Intermission.

2:20 486. More efficient reagent for the site-specific modification of proteins and peptides with radiometal chelators. **M. Davydova**, P. Adumeau, S. Sharma, B. Zeglis

2:50 487. Radiometals in imaging and therapy: The Cardinal Health perspective. **H.C. Padgett**

3:20 488. Impact of FcγRI receptor binding on immunoPET imaging. **C. Rodriguez**, D. Vivier, S. Sharma, P. Adumeau, B. Zeglis

3:50 Concluding Remarks.

Fate & Transport of Environmental Contaminants

Empire A (Confection Hall Level)
M. Li, *Organizer, Presiding*
L. A. Welch, *Presiding*

1:00 Introductory Remarks.

1:05 489. Airport air: What are we breathing? **R.L. Vander Wal**, C. Huang, M. Singh

1:30 490. Salinity effects on metals desorption in urban streams. **M.D. Kilmer**, K. Kramer, E.R. McKenzie

1:55 491. Novel putative propane monooxygenase initiating metabolism of 1,4-dioxane. **M. Li**, D. Deng, F. Li

2:20 Intermission.

2:40 492. CO_2 electrolysis using a 3D-printed flow cell and a bismuth-based electrocatalyst. **S. Velardo**, J. Rosenthal

3:05 493. Analyzing lipid extraction methods for the production of biodiesel from *Rhodotorula glutinis* and *Cryptococcus neoformans*. **S. McGee**, A. Walther, L.A. Welch

3:30 Concluding Remarks.

Innovations in Analytical Chemistry Education

Empire C (Confection Hall Level)
M. Kistler Langston, *Organizer, Presiding*

1:00 Introductory Remarks.

1:05 494. Making connections: High-impact practices for teaching analytical chemistry. **S. Fischer-Drowos**

1:30 495. Early integration of biochemistry into the analytical curriculum: A simple enzyme kinetics lab exercise for a quantitative analysis course. **J.N. Richardson**, T. Miller, T. Frielle, E. Frieben

1:55 496. Encouraging student engagement in a sophomore-level bioanalytical chemistry laboratory course. **U.J. Williams**, **D. Dries**

2:20 Intermission.

2:40 497. Practical use of ^{13}C benchtop NMR spectroscopy in an undergraduate laboratory. **R. Espina**, P. Bowyer, H. Robert, A. Coy

3:05 498. Real world in the undergraduate analytical lab. **G.P. Foy**

3:30 Concluding Remarks.

Medicinal Chemistry & Heterocyclic Synthesis

Cocoa Suite 5 (Main Level)
F. C. Mayville, *Organizer, Presiding*

1:00 Introductory Remarks.

1:05 499. Design, synthesis, and testing of bioisosteres of a topical anti-inflammatory Indomethacin prodrug for treating sulfur mustard burns. **J. Saxena**, C.J. Lacey, C.D. Guillon, L.B. Joseph , G.M. Composto, S.C. Young, C.A. Fianu, J.D. Laskin, D.E. Heck, N.D. Heindel

1:35 500. Anti-inflammatory and thermal behavior of 1,2,4-triazolo-4-amino imines. R.D. Rapp, **C.D. Guillon**, J. Saxena, A. Vetrano, C.A. Fianu, J.D. Laskin, N.D. Heindel

2:05 501. Targeting cancer metabolism using sugar-based small molecules. **F. Ndombera**

2:35 Intermission.

2:55 502. Solithromycin analogs: A click versus *in situ*-click chemistry approaches and antibiotic-resistance benefits. **S. Daher**

3:25 503. Development of betulin-betulinic acid conjugates as anti-cancer agents. **S.C. Jonnalagadda**

3:55 Concluding Remarks.

Opportunities for Academic-Pharma Collaborations

Magnolia B (Confection Hall Level)
B. E. Blass, *Organizer*, *Presiding*

1:00 Introductory Remarks.

1:05 504. SAR development in the start-up and small business environment. **J. Wrobel**

1:30 505. Discovery Partnerships with Academia (DPAc): A collaborative approach to drug discovery. **D. Paone**

1:55 506. The Moulder Center for Drug Discovery Research: An academic research center with an entrepreneurial spirit. **B.E. Blass**

2:20 507. Academia-industry collaborations: Evolution and new models. **S. Kant**

2:45 508. Bristol-Myers Squibb/Princeton University academic research collaboration. **T. Sherwood**

3:10 Concluding Remarks.

Organometallic Chemistry

Wild Rose A (Confection Hall Level)
A. R. O'Connor, D. L. Zubris, *Organizers*, *Presiding*

1:00 509. Progress towards developing a mechanistic understanding of base-free transfer hydrogenation catalyzed by Cp*Ir(pyridinesulfonamide)Cl complexes. **A.R. O'Connor**

1:20 510. Production of secondary phosphines by catalytic cross-coupling reaction. **J.M. Camara**, A.L. Haber

1:40 511. Copper and silver benzoate, aryl complexes, and their implications for oxidative decarboxylative coupling reactions. **J.M. Hoover**

2:00 512. Microwave-assisted copper-catalyzed amidation of aryl chlorides via concurrent tandem catalysis. B.P. Clairmont, S. Lin, **A.H. Roy MacArthur**

2:20 Intermission.

2:40 513. Nickel complexes of primary amido-functionalized N-heterocyclic carbene ligands. **S.E. Kalman**, T.V. Roach, M.D. Miller, M.L. Schmitz

3:00 514. Secondary bonding interactions to facilitate nitrene group tansfer from mid-valent group VI imidos. **R.R. Thompson**, L.R. Sita

3:20 515. Cerium(IV)-imido complexes: Electronic structures and reactivity. **E.J. Schelter**, L. Solola, A. Zabula, W.L. Dorfner, B.C. Manor, P.J. Carroll

3:40 516. Materials for organic light emitting diodes. **N.S. Radu**, N. Herron, G.M. Rossi

4:00 517. Copper(II) aryls in catalytic C-O, C-N, and C-C bond formation. **T.H. Warren**, S. Kundu, C. Greene, T. Cundari

Protein Misfolding & Quality Control

Cocoa Suite 4 (Main Level)
J. K. Hines, *Organizer, Presiding*

1:00 Introductory Remarks.

1:05 518. Ubiquitin receptors mediate proteasomal processivity. M. Cundiff, W.J. Dewey, E.L. Reichard, N.D. Nassif, **D.A. Kraut**

1:35 519. Engineering a self-assembling peptide system derived from beta-amyloid. **J. Candreva**, E. Chau, J.R. Kim

2:05 Intermission.

2:25 520. Exploring a role for the ribosome-associated complex in the interplay between environmental stress and prion formation in yeast. **D. Cameron**, C. Kelly, T. Tessitore, J. Taddeo, O. Elghawy

2:55 521. Defining prion-specific chaperone function in yeast: amyloid diversity as a function of chaperone functional complexity. **J.K. Hines**

3:25 Intermission.

3:45 522. Prion-like transmission of mutant huntingtin aggregates in *Drosophila* brains. **M.M. Pearce**

4:15 523. Biochemical analysis of protein aggregation in animal models of neurodegenerative disease. **R. Fairman**

4:45 Panel Discussion.

4:55 Concluding Remarks.

Synthetic & Biological Catalysis

Magnolia D (Confection Hall Level)
C. Hastings, *Organizer, Presiding*

1:00 Introductory Remarks.

1:05 524. Mechanistic insights into β-lactam formation by a non-ribosomal peptide synthetase condensation domain. **D.H. Long**, C.A. Townsend

1:40 525. New enzyme function enabled by photoexcitation. **T. Hyster**

2:15 Intermission.

2:30 526. Stereospecific nickel-catalyzed cross-coupling reactions of alkyl alcohol derivatives. **M.P. Watson**

3:05 527. Enzyme display on *Bacillus subtilis* spores for protein engineering and optimization. **E.T. Farinas**

3:40 Concluding Remarks.

Poster Session

Red & White Room

4:00 - 6:00

L. J. Silverberg, *Organizer*

Analytical, Bioanalytical & Forensic

528. Validating methanol extraction for the metabolomics of obese patients. **E.J. Robinson**, M.C. Taddeo, X. Chu, W. Shi, C. Wood, C.D. Still, D.S. Rovnyak

529. Development of electrochemical and fluorescence-based tools for nanomaterials characterization. **A. Rao**, **L. Ezra**, K.R. Riley

530. Rapid and sensitive quantification of desmosine in body fluids using a stable-isotope labeling and MALDI MS^2. P. Rathod, M. Kaur, H. Ho, B. Dhital, M. Louis, K. Mark, G. Boutis, J. Lee, **E. Chang**

531. Limits of detection for the spectroscopic analysis of pollutants in water samples. **L.A. Zook-Gerdau**

532. Taurodeoxycholate aggregation and chiral selectivity for binaphthyl compounds with NMR and ITC. **C. Sussman**, R. Pirnie, T.G. Strein, D.S. Rovnyak

533. Progress on NMR metabolomics of Non-Alcoholic Fatty Liver Disease (NA-FLD). **M.C. Taddeo**, E.J. Robinson, X. Chu, W. Shi, C. Wood, C.D. Still, D.S. Rovnyak

534. Comparison of orange fuming method against standard methods for development of latent prints on common substrates. **P.R. Rapalo**, **K. Bauder**, L.A. Welch

535. Chemical measurements in confined liquid films & addressing the urban-rural gap undergraduate research. **S.K. Shaw**

536. LCMS and GCMS determination of extraction products of *Moringa oleifera* leaves. **S.A. Ouassenan**, A.M. Mugweru

537. Reaction of artemisinin with DNA bases: LC-MS analysis of key reaction products. **E. Newton**

538. Electrochemical and chromatographic study of Artemisinin and its metabolites. **Z. Mazzochette**, G. Kamau, A.M. Mugweru

539. Designing tITP stacking for an in-capillary assay for creatinine. **A.F. Kreznor**, T.G. Strein

540. Development of an easy-to-use, paper-based sensing device for colorimetric detection of formaldehyde. **Y. Dai**, Q. Chen

541. Determination of lead in waterways and drinking water samples by ICP-AES. **J. Cawley**

Chemical Education

542. Integrated emission and absorption spectroscopy experiment for general chemistry. **L.A. Zook-Gerdau**, P.S. Szalay, D.V. Perera, E.J. Schurter

543. Comparison of student learning outcomes using mechanism-based and functional group-based approaches in organic chemistry education. **A.R. Szklarski**

544. Get involved with the ACS Division of Chemical Education. **A.E. Martin**

545. Quantitative analysis laboratory: A new look! **S.M. Yochum**

546. Student-created case studies in secondary school science education. **J.K. Berthel**

547. Comparison of Microwave-Assisted Organic Synthesis (MAOS) with Conventionally Heated Over-Pressure Synthesis (CHOPS). **C.S. Keenan**, S. Murphree

548. Authentic chemistry research in high school. **R.P. Spencer**

549. Further explorations of efficient one-pot three-step reductive amination sequence for the organic laboratory experiment. C. Zhang, E. Wiggin, **X. Fan**

550. Extensive studies of iron (III) chloride catalyzed Friedel-Crafts acylation reaction. H. Chen, E. Wiggin, C. Zhang, **X. Fan**

551. Organic chemistry predicting outcomes. **Z.E. Scalyer**

552. Bridging chemistry. R.R. Srinivasan, R. Juarez, D. Meyer, **M. Rowane**, L. Robinson, T. Nicholas

553. Authentic/alternative assessment V: Performance of science majors/non-majors on the categorizing grid. **M. Camacho**

554. Authentic/alternative assessment in chemistry/science education V: The effect of the auto quiz on the achievement of science college students. **M. Camacho**

Computation & MoleCVUE

555. Predicting color appearance of pharmaceutical and cosmetic color additive mixtures using TD-DFT calculations. **J. Mohen**, T.D. Vaden

556. Simulations of soap. **R. VanOsdol**, **R. Rutherford**, S. Faramarzi, B. Mertz, E.L. Harvey

557. Systematic generation of the Dunham coefficients using symbolic mathematics software. **G.G. Hoffman**

558. Unnatural alkanes as models for strained organic compounds. **P.S. Murthy**

559. Controlling the charge carrier dynamics in inorganic chalcogenide perovskites by heteroatom doping. **A. Nijamudheen**, A.V. Akimov

Inorganic Chemistry

560. Development of electrochemiluminescent platforms for high-throughput screening applications. **A. Marangoz**, W. Wu, R.C. Pupillo, G. Andrade, J. Rosenthal

561. Nitric oxide coordination to a high-spin iron (II) complex with H-bond donors. **B.M. Burke**, K. Gomez, R.C. Scarrow

562. Syntheses and structural comparison of $[Co(DIG_3tren)X]BPh_4$ complexes (X = halide). **D. Suryavanshi Magar**, R.C. Scarrow

563. Withdrawn

564. Synthesis, structure, and catalytic activity of pyridinium based M-NHC complexes. **R.J. Swails**, S. Kariofillis, R. Cerbone, A. Conner, M. Sebold

565. *De novo* protein models of binuclear metalloenzymes. **A.J. Reig**

566. Dye molecule-anchored platinum nanocatalysts. **I. Weiss**, B. Yang, E. Galoppini, A.G. Agrios

567. Synthesis of bis(1,10'-phenanthroline)-carbonyl-ruthenium(II) complexes with varying pyridine ligands. **A. Seitllari**

568. Synthesis of bis-(2,2'bipyridine)-carbonyl-ruthenium(II) complexes with varying imidazole ligands. **S. Collins**

569. Green synthesis of gold nanoparticles using red azalea plant: An anti-microbial study. **A.M. Greene**, V. Fusco, L. Bechdel, M. Devadas

570. Characterizing the dimerization of N-methyl mesoporphyrin IX *via* fluorometric and UV-vis analysis. **A. Gao**

571. Synthesis and characterization of metallospiroligomers toward the design of artificial metalloenzymes for catalytic oxidation reactions. **T.M. Keller**, M.A. Pham, M. Zdilla, .E. Schafmeister

572. Characterization studies of an ionic conducting soft-solid electrolyte LiCl:DMF. **M. Van Vliet**, P.R. Chinnam, M. Zdilla, S.L. Wunder

573. Anti-cancer activity of ruthenium-gold and titanium-gold bimetallic complexes bearing N-heterocyclic carbene ligands. **N. Gimenez**, Y. Fung Mui, B. T. Elie, M. Contel

574. Transition metal complexes with n-heterocyclic ligands for MRI and MRS application. **P.J. Burns**, J.R. Morrow

575. Biochemical and spectroscopic characterization of phylogenetically diverse homologs of the antibiotic resistance protein Cfr. **J. Gumkowski**, R. Martinie, C. Krebs, A.K. Boal

576. Nonaromatic tetrapyrrole complexes for the electrochemical and photochemical activation of dioxygen. **Q. Cai**, **M. Martin**, J. Rosenthal

577. Performance comparison of metal oxide-graphite anodes in the electrochemical oxidation of ethanol, acetaldehyde, and acetic acid. **A.T. Poulos**, R. Furman, M. Namer, V. Patel, P. Poulos, M. Sahni

578. Inorganic microwave synthesis: From quadruple bonds to metal-organic frameworks. **C. Reed**, C. Feeney, M. Merritt

579. Modeling the molybdenum cofactor: Synthesis and reactivity of molybdenum quinoxalyldithiolenes. **D.R. Gisewhite**, A. Nagelski, S.J. Nieter Burgmayer

580. Synthetic models of Fe/Mn discrimination by proteins in the ferritin-like superfamily. **W.D. Kerber**

581. Withdrawn

Physical Chemistry

582. Surface chemistry of zinc bromide deliquescence. **C. Arble**, S. Rani, J.T. Newberg

583. Measuring the electron scattering cross-section of water vapor using a hydrophobic ionic liquid and lab-based ambient pressure XPS. **Y. Khalifa**, A. Broderick, J.T. Newberg

584. Tetramethylguanidinium amino acid-based ionic liquids: Synthesis, characterization, and evaluation for biochemical applications. **J. Tomlin**, **K.G. DeFrates**, **B.L. Stinger**, **R.A. Nanfara**, T.D. Vaden

585. Conductivity, viscosity, and thermodynamic properties of propylene carbonate solutions in ionic liquids. **P.H. Lam**, **A. Tran**, **L. Yu**

586. Various isomers of ketenylidene cation investigated using ab initio methods. **R.C. Mayrhofer**

587. Simultaneously measuring trapped and free carriers using time-resolved infrared spectroscopy. **K.T. Munson**, C. Grieco, E. Kennehan, J.B. Asbury

588. Synthesis of ZnSe:Mn-doped quantum dots for tuning charge carrier lifetimes. **K. Schlegel**, J.B. Asbury

589. Carbon dioxide self-quenching rates. **L.V. Eckermann**, K.J. Castle

590. Decrease in activation energy and frequency factor for the intramolecular isomerization reaction of azobenzenes when anchored to ZrO_2 nanocrystalline semiconductor thin films. **D.C. Achey**, C. Pointer

591. Without barrier methyl radical transfer from methylco(II)balamin cofactor of vitamin B12 to cysteine in the methionine synthase process. T. Spataru, **F. Fernandez**, P. Spataru, I. Povar

592. Photochemistry and infrared spectra of biacetyl*water complexes. **M. Kernan**, D.K. Geremia, C.A. Baumann

593. Luminoprobes study of intramolecular dynamics in kappa-carrageenan-B-type gelatin. **T. Erickson**, S.S. Bollinger, B.H. Milosavljevic

594. Intermolecular electron transfer in neat pyridinium ionic liquids. **M. Saladin**, C.A. Rumble, B. Wu, E. Castner, M. Maroncelli

595. Synthesis, characterization, and evaluation of CoNiP as an electrocatalyst for the hydrogen evolution reaction. **C. Lesniak**, **N. Thatcher**, S. Wahl, A.M. Mugweru, T.D. Vaden

596. Ultrafast vibrational dynamics of perylene diimide solutions during excimer formation. **E. Kennehan**, C. Grieco, G. Doucette, J.B. Asbury

597. Rotational dynamics of ionic liquid/acetonitrile mixtures. **C. Uitvlugt**, B. Conway, C.A. Rumble, M. Maroncelli

598. Visualizing the trimethylamine-N-oxide induced compacted structural ensemble of α-synuclein. **J.J. Ferrie**, C. Haney, B. Pan, J. Yoon, E. Rhoades, A. Nath, E. Petersson

599. Mechanism of $Ru(bpy)_3^{2+}$ luminescence quenching by oxygen in water-isopropanol binary system is mixture composition-dependent. E. Brand, **L. Gadila**, B. Knepp, L. Krynski, B.H. Milosavljevic

600. Pseudobinary mixture comprising (50mol% CH_3CN and 50 mol% 1-butanol) and water: A DSC and photophysical study involving PRODAN luminophore. **M. Alzarooni**, L. He, J. Sutyak, Q. Tran, B.H. Milosavljevic

Polymer, Colloids, Nano & Materials

601. Dendrimer-glutaminase inhibitor conjugates for the treatment of Rett syndrome. **R. Rami Reddy**, E. Smith, S. Kambhampati, M. Johnston, B.S. Slusher, M. Blue, S. Kannan, K. Rangaramanujam

602. Structure and energetics of solvated lactic-co-glycolic acid oligomers. **J. Andrews**, M. Namazi, E. Blaisten-Barojas

603. Development of borinic acid polymers as new supported catalysts and multi-stimuli responsive materials. **M.K. Baraniak**, F. Jaekle

604. Ozone uptake on kaolinite as a function of relative humidity and organic coating. **Z. Coates Fuentes**, R.Z. Hinrichs

605. LbL-deposited polyelectrolyte layers as barriers for sustaining release of hydrophilic drugs from hydrogel matrices. Q. Wang, **B.M. Zhang Newby**

606. Effect of microstructure on alkaline hydrolysis of poly(3-hydroxybutyrate) films. **N. Vasanthan**

607. Development of thermometric titration to characterize catalyst supports: Advantages in process control and fundamental understandings of support. **R.M. Supkowski**

608. Polymer analysis applications of Thermo Fisher Scientific picoSpin NMR spectrometers. **D. Frasco**

609. Investigations of the impact of tetramethylcyclosiloxanes on generation and self-assembly of silver nanoparticles. B.P. Chauhan, **D. Artiga**, G. Nkak, S. Chaudhry, A. Patel

610. Optical and electronic properties of magic number, mixed ligand gold clusters. **A.C. Meola**, M. Devadas, K.P. Reber, V.D. Thanthirige

611. Synthetic deconvolution of interfaces and materials components in hybrid nanoparticles. **J.L. Fenton**, R.E. Schaak

612. Surface effects of accelerated degradation on pigmented barrier coatings. **N. Weise**, I. Long, A.E. Mera, J.H. Wynne

613. Metalloporphyrins nanoparticles as an efficient catalyst for olefinic oxidation. **M. Tuz Cordova**

MARM 1

Authentic/alternative assessment V: Classification of organic compounds, reactions/mechanisms by science majors

***Moises Camacho**, juancamachorn@gmail.com. Extension Division, University of Puerto Rico Mayaguez Campus, Mayaguez, Puerto Rico, United States*

The purpose of this study was to investigate the ability to complete, identify and classify common organic reactions, the mechanisms by which they take place and the major organic reactants/products. A pilot study was made with majors/non-majors to observe their classification skills with a sample of 50 reactions which were taken from well known organic chemistry texts like Mc Murry Organic Chemistry. The instrument was administrated to about 60 chemistry majors and non-majors (Biology) who had approved from 16 to 40 chemistry semester hours. The results demonstrated that 98.0% of the subjects had forgotten almost 100% of the type of classes (e.g. compounds, reactions, mechanisms involved in the reactions). Only about 2% remembered very few concepts. The study was repeated for several semesters with the purpose of reproductibility. The results were very similar. There was no significant statistical difference between the mean scores of majors and non-majors. These findings have been observed in several classification studies (e.g. compounds, reactions, equations, problems) of the author and others. The implications for chemical education, science and mathematics in general are relevant since these findings reflected rote-memorization not genuine understanding, permanent learning, nor long term memory (LTM).

MARM 2

Use of a PLTL variant to increase student engagement in large enrollment Organic Chemistry recitation sections

***Suzanne M. Stanley Fernandez**, smf314@lehigh.edu. University, Lehigh University, Reading, Pennsylvania, United States*

Large enrollment introduction classes are commonplace in many colleges and universities. Administrators and faculty alike struggle with the idea of increasing the number of lecture/recitation sections to reduce class size, but the logistical and financial issues associated with increasing the number of sections make the idea impractical. Large lecture/recitation settings are often passive learning environments; many students are reluctant to ask and answer questions in the large classroom, and discussions are simply not practical with large numbers of students. Additionally, it is difficult for an Instructor to gauge student learning during a lecture, which means the Instructor misses the opportunity to clarify key concepts as needed. There is little argument that a more meaningful learning experience is one in which an active learning environment is employed, and small group problem solving sessions are an effective means of creating such a learning environment. In this presentation you will learn how a variant of the Peer-Led Team Learning model was introduced into two recitation sections, each with enrollments of greater than one hundred Organic Chemistry I students, held in a large lecture hall. This model helps reconcile the logistical issues of large classes with current pedagogy by creating an active learning environment within the large lecture hall setting. The Instructor of the course is also provided with meaningful and timely feedback to gauge student understanding through post-recitation commentary from the peer leaders. Further, this model provides the peer leaders an opportunity to review course content, serve in leadership positions, and work on communication and interpersonal skills.

MARM 3

Finding time for active learning in the organic chemistry classroom with Just-in-Time-Teaching (JiTT)

***Thomas P. Umile**, umile.t@gmercyu.edu. Natural & Computational Sciences, Gwynedd Mercy University, Gwynedd Valley, Pennsylvania, United States*

A version of Just-in-Time Teaching (JiTT) was implemented in a two-semester organic chemistry course at Gwynedd Mercy University. Before every class session, students prepare with assigned readings, learning objectives, instructor-developed YouTube videos, and a reflection quiz. Typically, approximately 30 minutes of class are spent addressing concepts that were identified in the reflection quiz as most challenging. The remaining 60 minutes of class involve work in small groups on instructor-designed practice problems. Essentially, the course was “semi-flipped.” After two years, the initial success of these implementations is evidenced by increases on exam scores and overall class grades. Additionally, student comprehension of specific content improved, and student motivation, confidence, and interest in course content increased. These outcomes can all be assessed using specific examples from exams, course evaluations, class surveys, and anecdotal student and faculty feedback.

MARM 4

Enhancing learning by using muddiest point cards with international students

***Junyang Xian**, xianjym@gmail.com, Daniel B. King. Chemistry, Drexel University, Philadelphia, Pennsylvania, United States*

Active learning is a way to engage students in the classroom. Active learning is becoming a more popular pedagogical approach due to the increased evidence that it enhances students' learning and benefits the students. One example of an active learning technique is the muddiest point card. The use of this technique in an entry-level chemistry course for international students at Drexel University will be presented. At the end of each lecture, the instructor hands out a 3 x 5 card to each student. The students are required to write down questions they have about the lecture and/or something they've learned during the lecture. This study analyzed student exam performance as a function of muddiest point responses. Student responses were divided into three groups based on different learning levels: remembering, understanding, and applying. The results indicate that students who got higher grades tended to give more responses at higher learning levels.

MARM 5

Seeding your future initiative: STEM outreach for grades 5-12

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The Seeding Your Future Initiative started in Fall 2014 with the goal of providing STEM outreach in the Eastern Panhandle of WV and the surrounding four-state area. The Initiative began with the Seeding Your Future Conference, which will be in its fourth year next October. This Conference targets middle school age girls, with the goal of the girls gaining or maintaining an appreciation for STEM fields and their abilities within them. The conference features a plenary by a woman in STEM, a speed-dating style panel, and a series of ~1hr hands-on STEM workshops. In September 2015, the Seeding Your Future Workshop Series began for high school students. Workshop Series events are held monthly during the academic year and feature a two-hour hands-on STEM activity. This talk will include details of the Seeding Your Future Initiative, discuss its novel aspects, and showcase data from the past few years highlighting the program's successes. All program activities are free of charge thanks to generous grant funding.

MARM 6

In-class experiments in a liberal arts chemistry course

***Daniel B. King**, daniel.king@drexel.edu. Drexel Univ, Philadelphia, Pennsylvania, United States*

Liberal arts chemistry courses create a number of challenges, including students with a wide range of backgrounds, students who aren't interested in the content, and the lack of an associated lab. We have created a course called Why Things Work: Everyday Chemistry, which is open to students of all majors and all years. Rather than just serving as an easier version of general chemistry, this course teaches enough chemistry to explain an everyday application and then moves on to the next application. This course doesn't have a lab component, which means that any experiments must be done in a lecture classroom. Instead of just having the lecturer do a series of demonstrations, we wanted students to have the opportunity to do experiments themselves. To accomplish this, a set of experiments have been created and/or modified to allow students to perform them in small groups in their seats. Each experiment has been chosen to illustrate a particular chemistry concept. In many cases the experiments also help connect the chemistry content to the corresponding everyday application. These experiments are all hands-on and self-contained, using safe materials. Results of each experiment can be determined visually or by touch. In this presentation several of the experiments will be described, as well as how they connect to the content. Features of the experiments that enable them to be performed by small groups in a lecture setting will also be presented.

MARM 7

Synthesis and characterization of a series of tris(3-phenylpyrazolyl)borato zinc(II) oxocyclohexadienolate complexes derived from in situ oxidation of parent catecholate complexes

Diane Isaacs[1], Mark Bezpalko[4], Nicholas A. Piro[3], William S. Kassel[3], ***William G. Dougherty[2]****, doughertyw@susqu.edu. (1) Susquehanna University, Selinsgrove, Pennsylvania, United States (2) Department of Chemistry, Susquehanna University, Selinsgrove, Pennsylvania, United States (3) Department of Chemistry, Villanova University, Villanova, Pennsylvania, United States (4) Chemistry, Villanova University, Villanova, Pennsylvania, United States*

The synthesis of three different (tris(3-phenylpyrazolyl)borato)Zn(oxocyclohexadienolate) complexes, $Tp^{Ph}Zn(OCHD)$, was achieved through independent, one-pot reactions of $Na[Tp^{Ph}]$, $Zn(BF_4)_2 \bullet xH_2O$, NaOH and either catechol, 4-*t*-butylcatechol or 3,5-di-*t*-butylcatechol in methanol. Ambient dioxygen was used to oxidize the catechol substituent to the semiquinonate radical anion in solution. The substitution pattern on the semiquinonate determined the fate of the radical anion in each case. The unsubstituted semiquinonate (SQ) produced a green $[Tp^{Ph}Zn(OCHD)]_2$ dimer (**1**) through *in situ,* radical coupling of two $Tp^{Ph}Zn(SQ)$ complexes. The 4-*tert*-butylsemiquinonate radical complex was unable to dimerize due to the bulky *t*-butyl substituent and decomposed via solvent interaction producing a red, dimethoxy substituted $Tp^{Ph}Zn(OCHD\text{-}(OMe)_2)$ complex (**2**). The 3,5-di-*tert*-butylsemiquinonate radical (3,5-DBSQ) is stabilized by the additional bulk of the second *t*-butyl substituent and was isolated, intact, as blue, $Tp^{Ph}Zn(3,5\text{-}DBSQ)$ (**3**). All complexes were characterized by ^{1}H-NMR spectroscopy, single crystal X-ray diffraction, infrared spectroscopy and UV-visible spectroscopy. Complexes **1** and **2** exhibited diamagnetic ^{1}H-NMR spectrum consistent with radical decomposition while the spectrum of **3** was significantly broadened supporting the presence of the stabilized semiquinonate radical. Structural analysis of **1-3** revealed bidentate oxocyclohexadienolate ligand coordination to zinc within the pocket formed by the planar phenyl substituents on the Tp^{Ph} ligand. Two different C-O bond lengths averaging 1.248(3) and 1.314(3) Å, across the series, is consistent with partial oxidation of the catechol starting material. The electrochemical properties of each complex were analyzed using cyclic voltammetry and **1-3** exhibited similar voltammograms in methylene chloride. The voltammogram of **1-3** contained a pseudo reversible one-electron reduction and an irreversible one-electron oxidation assigned to the redox activity of the oxocyclohexadienolate moiety. There were slight changes in the redox potentials across the three complexes consistent with the inductive effects of substitution on the oxocyclohexadienolate ligand.

MARM 8

Synthesis and reactivity studies of nickel aryl chalcogenolate complexes

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Nickel-oxygen and nickel-sulfur complexes have been widely studied due to their relevance in enzymatic and industrial systems. However, less is known about the heavier chalcogen atoms, selenium and tellurium. In an effort to provide a direct comparison of nickel chemistry throughout the chalcogen series, a variety of aryl chalcogenolate nickel complexes have been synthesized. Two series of coordination complexes, each consisting of either the hydrotris(pyrazolyl)borate (Tp) ligand or the macrocyclic tetramethylcyclam (tmc) ligand, are explored. The oxidative addition of various dichalcogenides, E_2R_2 (E = S, Se, Te; R = Ph) to a monovalent nickel precursor provided the corresponding nickel (II) chalcogenolate species. X-ray crystal characterization and spectroscopic studies have established the geometric and electronic structures of these complexes. The observed spectroscopic and structural effects reveal distinct trends in accordance with the variation of the atom in the aryl chalcogenolate substituent.

MARM 9

Phosphorus-31 NMR spectroscopy of molybdenum carbonyl phosphine complexes: Correlations with bond enthalpies, bond lengths, and infrared spectra

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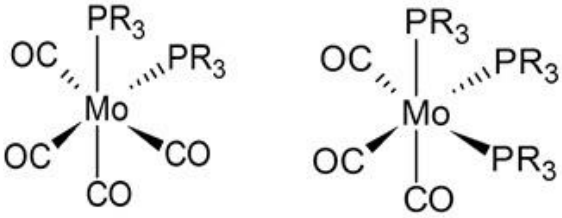
We have previously found strong correlations between the P-31 Nuclear Magnetic Resonance coordination chemical shift and the enthalpy of metal-phosphorus bond formation, as well as the metal-phosphorus bond length for a series of ruthenium phosphine complexes. These include $CpRuCl(PR_3)_2$, $Cp^*RuCl(PR_3)_2$, Grubbs' first- and second-generation catalysts, and related complexes.
Here we report P-31 NMR spectra, which have been measured for a series of $Mo(PR_3)_2(CO)_4$, and $Mo(PR_3)_3(CO)_3$ complexes. Interestingly, it is the P-31 chemical shifts of these complexes which show correlations with their known Mo-P bond distances as well as with bond enthalpies. The Mo-P complexes' coordination chemical shifts do correlate with the metal-carbonyl infrared stretching frequencies for some of these compounds. In both the ruthenium and molybdenum phosphine complexes, P-31 data correlates with other properties of the metal-phosphorus bond, offering new insights into their bonding.



MARM 10

Synthesis and characterization of aluminum complexes of nitroxide-based ligands: A new family of redox-active aluminum complexes

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The preparation of aluminum complexes supporting new functionalities and reactivity profiles is very desirable and serves as an important challenge significant to green and sustainable chemistry. The development of metal complexes supported by redox-active ligands has resulted in new classes of compounds for use in multi-electron transformations that have expanded the reaction profiles of various main group, transition, and f-block metal complexes. Our work has focused on the development of aluminum complexes of redox-active ligands.

Herein we report the synthesis of aluminum coordination complexes implementing redox-active nitroxide-based ligands. Reaction of two equivalents of a *N*-*tert*-butyl-*N*-(2-R-pyridyl)hydroxylamine (2-(*t*BuNOH)py-R, R = H, 4-CH_3, 4-CF_3) with $AlMe_2Cl$ gives the corresponding $[\kappa^{2}\text{-}N_{py},O\text{-}(2\text{-}^{t}BuNO)py\text{-}R]_2AlCl$ complexes in excellent yields. The R = H complex was also prepared via salt metathesis between Na[2-(*t*BuNO)py] and $AlCl_3$ in good yield. Salt metathesis of $[\kappa^{2}\text{-}N_{py},O\text{-}(2\text{-}^{t}BuNO)py]_2AlCl$ with alkali metal salts gives new $[\kappa^{2}\text{-}N_{py},O\text{-}(2\text{-}^{t}BuNO)py]_2AlX$ complexes. All of the complexes where characterized using ^{1}H and ^{13}C NMR spectroscopies, X-ray diffraction, UV-vis spectroscopy, and DFT. The redox behaviour of the complexes was investigated using electrochemistry, with the cyclic voltamograms of all three complexes displaying quasi-reversible processes attributed to $N\text{-}O^{-}/N\text{-}O^{\cdot}$ couples. In general, these features are shifted to a more positive potential in the aluminum complexes relative to the free ligands, indicating that the reduced state of the ligand is stabilized with coordination to the Al^{3+} ion. The potentials are also dependent on both the substitution pattern of the $^{R}pyNO^{-}$ ligands and the anion that completes the aluminum coordination sphere.

MARM 11

Spectroelectrochemical studies of ruthenium complexes with the 4,4'-dihydroxy-2,2'-bipyridine ligand

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Designing metal complexes with ligands that can stabilize high oxidation states has significant implications in catalyst development. The 4,4'-dihydroxy-2,2'-bipyridine ligand (4,4'bpy$(OH)_2$) is a pH dependent ligand that alters the electronic properties of the metal to which its coordinated. Specifically, upon deprotonation, the 4,4'bpy$(OH)_2$ ligand becomes more electron-donating and has the ability to stabilize these higher oxidation states. Numerous structural, electronic and spectroscopic studies have been carried out on Ru^{II}complexes with the 4,4'bpy$(OH)_2$ ligand. We report here, studies on the Ru^{III} oxidation state with the metal complexes $[Ru(bpy)_2(4,4'bpy(OH)_2)]^{3+}$ and $[Ru(phen)_2(4,4'bpy(OH)_2)]^{3+}$ (bpy = 2,2'-bipyridine; phen = 1,10-phenanthroline) and the effects of pH on the electronic properties of these complexes. The technique of spectroelectrochemistry was utilized to obtain the Ru^{III} species in solution by oxidizing the corresponding Ru^{II} complex. In all cases, a decrease of the MLCT bands in the 400 to 500 nm region occurred and the appearance of a broad new band was observed in the 600 to 1000 nm region of the spectrum. Computational analysis reveals that these bands are due to multiple types of charge transfer bands, many involving a mixture of the ruthenium center mixing with the deprotonated 4,4'bpy$(O^{-})_2$ ligand. In addition, Pourbaix Diagrams will be reported to relate the reduction potentials to pH and protonation state of the complexes.

MARM 12

Reactions of palladium compounds containing 1,1'-bis(diphenylphosphino)ferrocene

***Nicole Wamser**, wamsern@lafayette.edu, Chip Nataro. Chemistry, Lafayette College, Easton, Pennsylvania, United States*

The ligand 1,1′-bis(diphenylphosphino)ferrocene (dppf) is commonly employed in compounds that are catalytic precursors in a variety of reactions. The dppf is typically coordinated in a κ^2-bonding mode through the two phosphorus atoms in compounds such as $[Pd(dppf)Cl_2]$. However, the κ^3-binding mode through the two phosphorus atoms and the iron atom has also been observed in compounds such as $[Pd(dppf)(PR_3)]^{2+}$. Of current intrest is the reaction of these κ^2 and κ^3 compounds with more electron donating 1,1′-bis(phosphino)ferrocene ligands. The reaction of $[Pd(dppf)Cl_2]$ with 1,1′-bis(di-*iso*-propylphosphino)ferrocene (dippf) or 1,1′-bis(dicylohexylphosphino)ferrocene (dcpf) results in clean replacement of the dppf ligand by the more donating ligand. The related compound $[Pd_2(dppf)_2(\mu\text{-}Cl)_2]^{2+}$ is prepared by reacting $[Pd(dppf)Cl_2]$ with Na[BArF] (BArF = tetrakis(3,5-trifluoromethyl phenyl)borate). The reaction of $[Pd_2(dppf)_2(\mu\text{-}Cl)_2]^{2+}$ with a more donating 1,1′-bis(phosphino)ferrocene ligand results in cleaving the dimer and giving a monopalladium species containing both dppf and the more donating 1,1′-bis(phosphino)ferrocene ligand. The reactions of the $[Pd(\kappa^3\text{-}dppf)(PR_3)]^{2+}$ with more donating 1,1′-bis(phosphino)ferrocene ligands results in a mixture of products that typically display coordination of the more donating ligand in a κ^3-coordination mode. The product distribution is dependent on the donor ability of the PR_3 ligand relative to dppf. The synthesis, NMR spectroscopy, electrochemistry and structures of these compounds will be presented.

MARM 13

Towards neutral mixed-valence copper cyanide polymers

***Peter W. Corfield**, pwrc@earthlink.net, Joseph Dayrit, Christina Sheedy, Thomas Stavola. Chemistry, Fordham University, Briarcliff Manor, New York, United States*

Two- and three-dimensional CuCN networks are well known. Those that involve 3- and 4-coordinated Cu atoms linearly bridged by CN groups are anionic, with neutrality provided by cationic guest moieties in cavities in the network. Our goal is the rational syntheses of mixed-valence copper cyanide frameworks where incorporation of Cu(II) could lead to a neutral CuCN network, which could then accommodate neutral guest molecules. We report here the synthesis, X-ray structural analysis and properties of several CuCN compounds, including three inorganic compounds, $Cu_n(CN)_{n+1}.xH_2O$, where n=3, 4, and 5, and x= 3 or 4. We also present details of a green compound with composition $Cu_2(CN)_3L$, where L is N-methylethanolamine. The crystal structure appears to contain Cu(I) atoms only, with charge neutrality occurring from the non-coordinated, protonated base, LH^+. However, esr analysis indicates the presence of Cu(II). In another compound with the same composition, but with L=1,3-diaminopropane, the network clearly contains only Cu(I), and the cationic guest appears to be a protonated ligand that has undergone chemical reaction to form a guanidinium cation. Further studies on these compounds are ongoing.

MARM 14

Coordination chemistry of rare earth elements to address problems in their separations and sustainability

***Eric J. Schelter**[2], schelter@sas.upenn.edu, Justin Bogart[2], Bren E. Cole[2], Michael Boreen[1], Connor Lippincott[2], Brian C. Manor[2], Patrick J. Carroll[2]. (1) University of California, Berkeley, Berkeley, California, United States (2) Dept of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania, United States*

Rare earth elements are essential in renewable energies technologies including in permanent magnets used in smartphones and wind turbines, and other applications in hybrid and electric vehicles, energy efficient lighting phosphors and many others. The separations chemistry used to obtain pure rare earth materials relies on scalable but inefficient liquid-liquid extraction, which presents a severe environmental burden. We have identified mono- and multi-dentate hydroxylamines as superior ligands for exploring new directions the separations chemistry of rare earth elements. We developed a tripodal ligand H_3TriNOx and established its coordination chemistry. The RE(TriNOx)(THF), RE = La–Lu and Y, series demonstrated an unusual solubility dependence of the resulting complexes. These observations afforded a new method for separating RE elements, in particular, for their targeted recycling from consumer materials. Variation of the coordination chemistry in this conceptual framework is expected to improve the targeted separations of technologically important rare earth elements.

MARM 15

Total syntheses of nannocystins and homodimericins

*Jun Huang, Donghui Ma, Yangbin Liu, **Zhang Wang**, zwang9@albany.edu. Chemistry, University at Albany, SUNY, Albany, New York, United States*

Total synthesis of natural products plays a key role in synthetic organic chemistry. In this talk, the total synthesis of depsipeptides nannocystins A and A0 will be presented. Key features in this synthesis include an amide bond formation via acyl chloride and a macrocyclic ring-closing metathesis. The synthetic strategy is a general one for nannocystin analog synthesis. In the second part, the biomimetic total synthesis of homodimericin A will be discussed. The route features an oxidative cascade reaction and an intramolecular Diels-Alder cascade reaction. Our results validate the biosynthetic proposal by the Clardy group.

MARM 16

Synthesis of icetexane anti-cancer natural products

*Daniel J. Moon[1], Mohammad Al-Amin[1], Robert Lewis[2], Glenn P. Yap[1], Kimberly Arnold[1], Jennifer Sims-Mourtada[1], **William J. Chain**[1], wchain@udel.edu. (1) University of Delaware, Newark, Delaware, United States (2) Chemistry, University of Hawaii, Honolulu, Hawaii, United States*

Premnalatifolin A is a dimeric icetexane diterpene containing an interesting 6-7-6 tricyclic structure. The icetexane diterpene natural products have myriad anticancer activity, and we set out to develop synthetic pathways for the various tricyclic monomers based on the manipulation of our enolate–*ortho*-quinone methide Michael addition reaction. We have successfully developed approaches to both the ketone and tertiary alcohol monomeric units of premnalatifolin A, as well as a small library of analogues based on highly diastereoselective classical enolate alkylation and aldol reactions, and we are learning about the biological activities of simplified analogues.

MARM 17

Total synthesis of natural products enabled by N-sulfinyl metallodienamines

***Rodrigo B. Andrade**, randrade@temple.edu. Temple Univ, Philadelphia, Pennsylvania, United States*

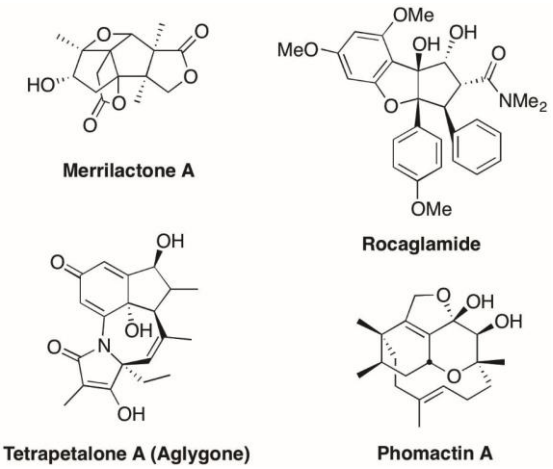
In 2013, our laboratory developed the use of *N*-sulfinyl metallodienamines (NSMDs) for the concise asymmetric total syntheses of *Aspidosperma* alkaloids (–)-aspidospermidine, (–)-tabersonine, and (–)-vincadifformine. We showed that these chiral synthetic intermediates can engage electrophilic olefins (e.g., acrylates) in a domino Michael-Mannich sequence to afford tetrahydrocarbazoles in high yield and diastereoselectivity. Our application of NSMDs toward the total synthesis of several natural products will be highlighted.

MARM 18

How natural product structures drive synthetic innovation

***Alison J. Frontier**, frontier@chem.rochester.edu. Chemistry Dept, University of Rochester, Rochester, New York, United States*

The presentation will describe how our group has been compelled to innovate in response to challenges offered by natural product structures. The ways in which synthetic strategies targeting complex polycycles evolved as a result of unexpected reactivity will be described, as well as how these projects have advanced our understanding of cyclization reactions and spurred the development of new multistep cascades.



MARM 19

Total synthesis of neurologically active natural products

***Timothy R. Newhouse**, timothy.newhouse@yale.edu. Chemistry, Yale University, New Haven, Connecticut, United States*

This poster will present recent work towards the synthesis of diverse natural products that are known to attenuate the production of reactive oxygen species by unknown mechanisms of action.

MARM 20

Some efforts in natural product synthesis design

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Complex molecule synthesis benefits from both methodological advances and strategic innovation. With the belief that a quality synthesis requires a solid strategy, our group focuses largely on synthesis design. In this lecture, I will describe some successes and some ongoing attempts to devise and execute concise syntheses of complex secondary metabolites. Often, the targets are potentially valuable for their biological activities, in which case general applicability to a range of family members and/or unnatural analogues is incorporated into the design. Our current interests, from which the lecture will draw, include polycyclic terpenoids, alkaloids, and polyhalogenated natural products.

MARM 21

Investigation into the analysis of narcotic analgesics from postmortem blood using Biocompatible Solid-Phase Microextraction (BioSPME)

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Forensic toxicology laboratories are responsible for analyzing postmortem samples, such as bile, vitreous humor, urine, blood, liver, gastric contents, brain, and kidney, for common drugs or poisons. For criminal investigations, analysis of these postmortem samples may be time consuming and cause delays. The application of in-vivo solid-phase microextraction (SPME) has grown due to its ability to be directly injected into a biological matrix without the physical removal of sample. Biocompatible SPME (BioSPME) fibers have been developed to absorb any drugs that may be present within the sample, leaving behind any substances that may cause interference, such as macromolecules. The aim of this study is to provide a new procedure for postmortem toxicology testing that is faster than current toxicology testing methods. The use of BioSPME coupled with gas chromatography-mass spectrometry (GC-MS) and liquid chromatography-tandem mass spectrometry (LC-MS/MS) allows for minimal sample collection, preparation, and analysis for illicit substances in a shorter time frame.
In this study, an extraction, screening, and quantitation method has been developed which has been used to analyze fentanyl in a blood matrix. Two types of BioSPME fibers have been investigated when developing this method, C-18 and mixed-mode coated fibers. These fibers are conditioned, directly injected into a biological matrix (blood) for extraction of possible drugs, desorbed into solution, screened by GC-MS, and finally analyzed and quantified by LC-MS/MS. The procedure utilized a screening method, which was comprised of an Agilent 7890A Series GC system using a Rxi-5sil MS (29.0 m x 0.25 mm x 0.25 mm) column, coupled with an Agilent 5975C Mass Selective Detector. The confirmation method of this procedure was comprised of a Shimadzu® LC system using an Ascentis® Express Biphenyl Column (50 mm x 2.1 mm, 2.7 *m*m) with the weak mobile phase consisting of 0.1% (v/v) formic acid in water and the strong mobile phase consisting of 0.1% (v/v) formic acid in acetonitrile along with a AB SCIEX™ 3200 Qtrap® triple quadrupole mass spectrometer with an electrospray ionization (ESI) source operated in the positive-ion mode. The method was applied to postmortem blood samples provided by the Lehigh County Coroner's Office of Allentown, Pennsylvania.

MARM 22

Elemental analysis of oil paints using Laser Induced Breakdown Spectroscopy (LIBS)

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Laser induced breakdown spectroscopy (LIBS) is a useful method of analysis for cultural heritage objects. In LIBS, a laser is focused onto the sample; the laser heats, ablates, atomizes, and ionizes the surface material causing the formation of a plasma. The light from the plasma is spectrally resolved and detected. The resulting spectrum can

be used for various qualitative and quantitative analyses.

Oil paint pigments from a range of traditional to modern palettes were used for this study. The pigments were analyzed by themselves and in mixtures. LIBS was able to distinguish the pigments by comparing the characteristic elements present in the individual spectra. The ease and accuracy of such identification is essential in deciphering an artist's palette, especially for dating and authentication purposes. For example, identifying a pigment such as *mars black* or *titanium white* would indicate the artwork could not be dated earlier than the 19th century when these synthetic pigments first became available. It could also indicate that an older painting containing a modern pigment is either a forgery or has been conserved in the past. These inferences are made by referring to characteristic emission lines in LIBS spectra and to the historical background of the associated pigments.

MARM 23

Assessment and optimization of chemical-based contrast enhancement techniques on mammalian pelts for shooting distance estimation

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Gunshot residue (GSR) is produced from the discharge of a firearm, and for the purpose of this research includes any material originating from the propellant, primer, projectile, cartridge case, residue from previous discharges, and cleaning agents or lubricants present in the barrel that exit the muzzle upon discharge. When the range-of-fire is close, these residues can create a pattern on the target that circumscribes the bullet hole. Examination of these patterns may permit an estimation of muzzle-to-target distance to aid in reconstruction of firearm-related events. In cases involving animals, visualization of GSR is complicated by fur color and length. Thus, the visual and chemical techniques typically used for fabric targets must be modified.

Initial photography of the pattern permits visualization, but alone provides little contrast. Contrast can be increased with the application of various visual techniques. High-intensity, tunable-wavelength light sources, also known as "alternate" light sources, and infrared illumination (IR) can be used to enhance GSR patterns. Radiography may also be employed to detect radiopaque metallic particles, which may surround the entrance hole.

After visual enhancement methods are complete, chemical detection of nitrites, which are formed by the combustion of smokeless powder, is achieved with the Modified Griess test (MGT). This test is usually performed with desensitized photographic paper, but unlike most textiles, animal hides do not permit the permeation of acetic acid; thus, a reverse MGT is performed instead. This method involves the application of acetic acid and heat to a porous substrate, in the same manner as a Bashinksi transfer. Transfer techniques are often used in the sodium rhodizonate test to detect the presence of lead on dark targets. The sequential use of these tests allows both to be performed on the same analytical substrate, with results being photographed at each step.

Chemical enhancement becomes increasingly crucial as the animal coat becomes darker and longer, as less visual contrast is observed. Results of the MGT are consistent with the visual enhancement methods: both show an increase in pattern size and dispersal with an increase in firing distance. Detection of elemental lead with sodium rhodizonate exhibits better sensitivity than the visual enhancement and radiographic methods.

MARM 24

Application of FTIR microscopy to microcrystalline tests for drugs

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Microcrystalline tests have long been used both as preliminary and confirmatory tests for the analysis of seized drugs. Tests for substances like cocaine and amphetamines have been well-documented. A microcrystal representative of the substance being studied results from the formation of a temporary complex between the precipitating reagent and the substance. The crystal shape, habit and optical activity are often used as parameters to identify the substance. The subjectivity associated with this and the lack of tangible instrumental data has steered analysts away from using these tests in their protocols. Some studies have demonstrated the use of infrared microscopy and raman microscopy for microcrystals of known substances to gather information about molecular structure. The primary challenge lies in obtaining good quality spectra from the microcrystals.
This presentation discusses a study that evaluates microcrystal tests for thirty emerging psychoactive substances

belonging to cathinones, piperazines, amphetamines, piperazines and opioids.Several of these substances form reliable and recognizable microcrystals with traditional microcrystalline test reagents. Analogs of substances form microcrystals that are microscopically distinguishable. The presentation dicusses the application of FTIR microscopy in obtaining molecular information for microcrystals of analogs of novel psychoactive substances and the challenges associated with the technique. The shifts in vibrational bands observed for the microcrystal when compared to the drug alone are discussed. The role of a combined protocol that uses microcrystalline tests in association with FTIR microscopy was evaluated in this study for its practicality and application in routine forensic casework.

MARM 25

Analysis of stimulants extracted from dried blood spots via LC-MS/MS

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In this study, a liquid chromatography tandem mass spectrometry method was developed for the analysis of various stimulant-type drugs from 30 µL dried blood spots (DBS). FTA DMPK-C cards were used as the medium to collect and store the blood spots. The extracted samples were analyzed using a Shimadzu LC system coupled to an AB Sciex 3200 QTRAP triple quadrupole mass spectrometer operating in positive-ion mode. The extraction procedure used for the DBS was optimized through testing various solvent systems, mixing techniques, reconstitution solvents, and DBS drying time. The most favorable extraction conditions involved the use of a 1:1 ratio of methanol and acetonitrile as the extraction solvent after the DBS were allowed to dry for three hours. This developed method has the potential of being used by forensic laboratories as a road side method for driving under the influence of drugs (DUID) cases because it is less invasive and due to its ability to decrease the amount of time between the time of stop and the time of sample collection.

MARM 26

Method development and quantification of lisdexamphetamine and amphetamine in hair

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Since 2007, lisdexamfetamine dimesylate (LDX) has been on the market as a schedule II prescription substance known as Vyvanse®, a prodrug for amphetamine. LDX is metabolized into amphetamine and L-lysine in hepatic metabolism and/or the first pass intestinal metabolism. Since LDX is metabolized quickly, we investigated the use of hair to determine the presence of lisdexamphetamine in an attempt to discriminate LDX from amphetamine use. Aliquots of pubic and head hair from an individual that takes 30mg of Vyvanse® daily were weighed into Eppendorf tubes with β-glucuronidase and pH6 phosphate buffer. The tube were incubated at 40 degress Celsius and agitated at 400rmp for two hours. Solid phase extraction was carried out using Bond Elute columns followed by derivatization with TFAA:EtOAc (1:1) for ten minutes at room temperature. Analysis of the samples was carried out on a PerkinElmer Gas Chromatography (Clarus® 680)/Mass Spectrometer (Clarus® SQ 8 T). The ions looked at for LDX where m/z 364, 321, and 180, 91, 119, and 140 for amphetamine. LDX-D4 and amphetamineD-11 were used as internal standards. The hair growth rates were determined by waxing for pubic hair and cutting for head hair. Pubic hair growth rate was 0.414mm/day±0.1830, while the head hair growth rate was 0.288mm/day. Lisdexamphetamine was not detected in any of the samples. Amphetamine was detected in both head and pubic hair with concentrations being greater in pubic hair.

MARM 27 Withdrawn

Impairment testing: An alternative to workplace drug testing for cannabis

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As more and more states legalize cannabis for either medical or recreational use, the need to assure workplace safety has resulted in widespread drug testing of job applicants and employees. Since cannabis can remain in the body for up to three to four weeks after use but the effects only last a few hours, drug testing is not an accurate assessment of the current state of an individual's physiological or psychological condition. Impairment testing may be the answer to this dilemma, since it can determine if a worker can safely perform job functions. This paper will explore the currlent options for both drug & impairment testing.

MARM 28

When just knowing isn't enough: Turning unknowns into quantitative knowns in Non-Targeted Analyisis (NTA)

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Non-targeted analysis (NTA) has recently been adopted and adapted by the environmental and analytical chemistry fields to greatly enhance trace analysis and forensic chemistry mass spectrometry applications. Whilst being able to identify vast numbers of molecular features in samples, NTA is inherently a qualitative technique, and thus, generally unable to provide quantitative information on contaminants in the absence of a standard. Here, we introduce new techniques and methodology that allow for quantitation of unknowns (those for which we can put forth a tentative candidate or probable structure) in samples without the need for conventional standards. Concentration calibration curves have been generated for hundreds of chemicals prepared as synthetic mixtures as part of a larger NTA round robin trial. Structural similarity indexes have been implemented in order to relate postulated structures to previous chemicals' calibration curves. This allows for semi-quantitation of newly-discovered unknowns, which provides exposure/dosage information to be considered in support of 21st century chemical screening programs

MARM 29

Using HILIC-MS/MS for the simultaneous determination of GHB and its glucuronide

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GHB is an endogenous compound that is classified as a Schedule I controlled substance in that is highly addictive with low medicinal properties and has been abused in health clubs, raves, and in DFSA cases. It is rapidly eliminated from the body after its absorption making it difficult to detect. GHB-Gluc is a recently discovered metabolite of GHB whose role in the metabolism of GHB still requires investigation and is not well understood. There is currently no method to detect GHB and its metabolite, GHB-Gluc, simultaneously in biological fluids using hydrophilic interaction liquid chromatography (HILIC).

A Macherey-Nagel NUCLEODUR HILIC column (100 x 2 mm, 3 µm) connected to a tandem mass spectrometer with an electrospray ionization (ESI) source operated in the negative ion mode was used for all analyses. Mass spectrometric analysis was performed in the multiple reactions monitoring (MRM) mode using appropriate collision energy for each selected precursor ion. MRM transitions monitored for GHB included m/z of 103 to 101, 103 to 85, and 103 to 85 for quantitation. The MRM transitions monitored for quantitation of GHB-Gluc were m/z of 279 to 113, 279 to 103, and 279 to 113. Chromatography was performed at 50°C using a binary flow method with mobile phases of 0.1% (v/v) formic acid in water (pH=7) as the strong phase and 0.1% (v/v) formic acid in acetonitrile for the weak phase. GHB and GHB-Gluc eluted at approximately 2 and 9 minutes, respectively. The spiked urine samples were diluted 1:4 with 0.1% (v/v) formic acid in acetonitrile, filtered and then 5 µL was injected into the HILIC column.

The method was validated in urine samples following SWGTOX guidelines. It has the potential to be used in forensic laboratories for victims of Drug Facilitated Sexual Assaults (DFSA), driving under the influence (DUI) suspects, and postmortem investigations.

MARM 30

Utilizing deconvolution reporting software with retention time locking to improve GC/MS analysis of fire debris evidence

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Identifying the presence or absence of ignitable liquids in fire debris evidence can provide critical information to fire scene investigators. However, there are various challenges with the recovery of potential accelerants from fire scene evidence. Due to the volatility of petroleum-based liquids, residues may be undetectable or compositionally different by the time of analysis. Other factors that complicate the analysis of fire debris evidence include matrix interferences and the presence of pyrolysis or combustion products. At present, fire debris analysis is done by evaluating extracted ion profiles (EIP) for characteristic hydrocarbon classes and by comparing chromatographic

patterns with reference ignitable liquids, making analysis inherently subjective. This research investigates the use of deconvolution reporting software (DRS) with retention time locking to improve the accuracy of fire debris analysis.
This research is being conducted using an Agilent GC/MS 5975 with a Phenomenex ZB-1ms column that is 30m x 0.25mm x 1.00µm. GC/MS parameters were optimized using neat standards of gasoline, kerosene, and diesel fuel diluted to 1:1000 in carbon disulfide. The method is locked to decane (C_{10}) because it is present in the ASTM E1618 Test Mix, which is used by many forensic laboratories, and because it is a mid-range hydrocarbon. A DRS database was created for specific use with fire debris evidence to make the identification of target compounds possible. Charred samples were prepared by spiking wood, rug, and linoleum with ignitable liquids and lighting with matches. Results demonstrate that retention time locking coupled with DRS software improves the identification of patterns with the ability to consistently overlay chromatograms with reference liquids as well as identifying components of diagnostic patterns commonly seen in ignitable liquids. This research provides a supplemental method for the traditional analysis of fire debris evidence using instrumentation and techniques that are readily available to most forensic laboratories.

MARM 31

Invisible ink: The history and chemistry associated with it

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Espionage cases have been known in history for a very long time and invisible ink has served as a significant tool in transferring information across enemy territory. Many of the reactions associated with it are simple and several of them can be understood at the college freshman level. Cases involving invisible ink will be discussed and the historical and chemical details will be presented.

MARM 32

Tracking the sexual assault kit backlog

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The backlog of untested sexual assault kits is a national problem. Numerous federal funding opportunities offer the forensic science and law enforcement communities valuable resources needed to test the kits, but issues still remain. The majority of resources are focused on the collection and testing of sexual assault kits, but the tracking of the kits has not been a primary focus. This research highlights improvements that can be made to better understand the current backlog and improve the future processing and tracking of kits. Given the lack of a universal evidence tracking database among agencies, tracking sexual assault kits seems impossible. In Allegheny County, over 100 different law enforcement agencies exist, each with their own policies and procedures. As a result, the number of untested kits is unknown. Through a comprehensive review of improved practices in proactive jurisdictions, including Ohio, Houston, and Detroit, valuable data was gathered about improved tracking mechanisms. Additionally, interviews with key stakeholders identified issues in Pennsylvania. This information led to the development of a survey that will aid in data collection related to sexual assault tracking practices across the country. A multidisciplinary, collaborative approach is needed to better understand the true sexual assault kit backlog in order for agencies to more effectively use grant funding aimed at testing the kits. The results of this research will provide valuable information to enhance sexual assault kit tracking methods.

MARM 33

Multistep synthesis of 2-arachidonoylglycerol (2-AG) in undergraduate organic laboratories

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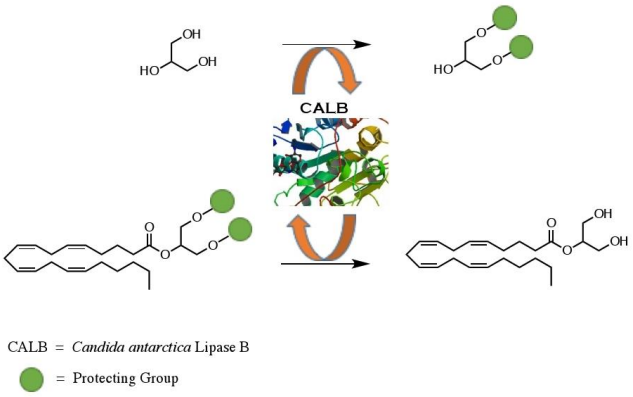
In order to introduce the concepts of biocatalysis and its utility in synthesis to organic chemistry students, a multistep synthesis of endogenous cannabinergic ligand 2- arachidonoylglycerol (2-AG) was tailored for use as a laboratory exercise. Over four weeks, students successfully produced 2-AG, purifying and characterizing products at each stage of the reaction series. This synthetic series also reinforces the importance of executing reactions under inert atmosphere, the strategic placement of protecting groups, and regioselectivity.



MARM 34

Combining computational chemistry with vibrational spectroscopy to increase insight into selection rules

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A laboratory project for the upper-division physical chemistry laboratory is described combining IR and Raman spectroscopies with Gaussian electronic structure calculations to determine the spectra of saturated and unsaturated hydrocarbons with different symmetries. The main difference between the molecules of interest is the presence or absence of an inversion center. Students measure the IR and Raman spectra of a variety of hydrocarbons and carry out Gaussian calculations to predict the vibrational wavenumbers and use the results to assign the spectra. By considering their results for the four samples, they assign specific vibrations to those observed in the experimental spectra and explain differences between computational and experimental as well as IR vs. Raman. The complexity of the project immerses the students in vibrational spectroscopy so that they learn the subject at a deeper level.
In summary, students complete a more thorough investigation of vibrational selection rules using Raman spectroscopy, computational chemistry, and infrared spectroscopy in combination because they provide complementary insight into the molecular structure.

MARM 35

Grant writing practice in an undergraduate laboratory

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At some point in their careers, most chemists will need to convince others of the value of their work. As a capstone laboratory in Analytical Chemistry, students were tasked with persuading their peers and instructor by writing an experiment proposal modeled after the National Science Foundation Grant Proposal Guidelines. Over three weeks, students practiced developing hypotheses, drafting budgets, and using the chemical literature. They also considered potential hazards and safety needs before carrying out their experiments and writing a formal lab report.

MARM 36

Integrating far-infrared spectroscopy into the physical chemistry laboratory

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Far-Infrared spectroscopy is a useful tool in understanding large scale intermolecular and intramolecular vibrations. Density functional theory calculations combined with experimental techniques, including mid- and far-infrared spectroscopy, can interpret important intermolecular interactions. This presentation will discuss two laboratories that integrate far-infrared spectroscopy and computational chemistry into a second semester physical chemistry course in quantum mechanics. The first study analyzed the hydrogen bonding of phenol and para-substituted phenol derivatives, including p-cresol, 4-isopropylphenol, and 4-fluorophenol, in solution in the mid and far-IR region. The intermolecular hydrogen bonding nature of these derivatives were compared. The second study examined various ionic liquids including 1-ethyl-3-methylimidazolium ethyl sulfate, 1-butyl-3- methylimidazolium tetrafluroborate, and 1-butyl-3-methylimidazolium hexaflurophosphate in the far-IR and assigned intermolecular

cation/anion vibrational motions using density functional theory. Sampling accessories, instrumentation, and computational chemistry software used to carry out these studies will be discussed in detail.

MARM 37

Development and evaluation of a team-taught online course in medicinal chemistry

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Medicinal chemistry generates increasing interest among students pursuing careers in the biological and medical sciences. Bioorganic faculty from the Lehigh Valley's six private colleges and universities created a 27-module fully online course in medicinal chemistry geared towards advanced undergraduate and beginning graduate-level students. Professors handled topical areas drawn from their own professional expertise, including drug discovery, development, metabolism, manufacturing, and marketing. All lectures, which ranged in length from 16 to 120 minutes, were recorded in a TV studio classroom with closed-caption lines for the hearing impaired. Lehigh University's Distance Education staff then digitized, edited, and mounted the lectures. Modules feature a common structure: title template, online readings, learning objectives, study questions, and pedagogical content, including close-up videos of test tube experiments. This course has been offered as an entire course, an abbreviated mini-course, or as selected individual modules. Although student evaluations are still underway, preliminary results will be reported.

MARM 38

Pressure effects on ion dynamics in Imidazolium based ionic liquids

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Imidazolium based ionic liquids (ILs) have found applications in energy conversion and storage devices such as lithium ion batteries and electrochemical double layer capacitors because of their unique transport properties and tunability. As a result, they have been extensively studied using various techniques mainly as a function of temperature, but less has been done using variable pressure. In this monologue, we present variable pressure multi-(^{1}H, ^{2}H and ^{19}F) Nuclear Magnetic Resonance (NMR) inversion recovery and pulsed gradient spin echo techniques. NMR has been instrumental in the study of ion conductors with potential applications in energy storage and conversion devices. Through measurements of spin-lattice relaxation times (T_1) and self-diffusion coefficients (D), both short and long range dynamics which can correlate with material performance, can be probed. When coupled with selective deuteration of the materials and investigated as a function of pressure, we can get site specific dynamical information as well as details about the interactions taking place. In collaboration with James Wishart (Brookhaven National Laboratory, NY) and Stefano Passerini (Helmholtz Institute, Ulm), we present variable pressure NMR T_1 and D data on selectively deuterated imidazolium (EMIM and BMIM), and pyrrolidinium based cations, coupled with TFSI, FSI and BF_4 anions. The goal of both studies was to determine the effect of cation chain length on both cation and anion dynamics. Additionally, the effect of anion type on the imidazolium based system was also a goal.

MARM 39

Structure & nanostructure in ionic liquids

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More than one hundred years after their discovery by Walden, ionic liquids (ILs) have become important, tuneable chemical solvents in many scientific fields. Key to their emergence is pronounced solvent (nano)structure, which has been driving interest in ILs even before it was widely appreciated. In this talk, the present state of understanding of structure in ILs comparison to conventional solvents will be discussed. Whilst historically ILs were thought to be structurally homogeneous systems, recent theoretical and experimental evidence suggests they highly structured solvents, particularly at interfaces. The signature of structure in ILs is the capacity for ions to *self-assemble*; often into bicontinuous morphologies of polar and apolar domains. Many examples of self-assembly of ILs in bulk phase, near solid surfaces as well as the effect of variables will be highlighted.

MARM 40

Structural comparisons of homologous zwitterionic and ionic liquids

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We will discuss the structural features of a pair of homologous liquids: one is a zwitterion, and the second is a more typical ionic liquid (IL). These two liquids differ only by a single C-C bond that is present in the zwitterion and absent in the IL. The structures of the two liquids are given below. The zwitterion is 1-[2-(2-methoxyethoxy)ethyl]-3-(3-carboxypropyl)-imidazolium (Zw-IL) and the homologous IL is 1-[2-(2-methoxyethoxy)ethyl]-3-ethylimidazolium acetate (IL). The structure factors for this pair of liquids are obtained from X-ray scattering and molecular dynamics simulations. Our analysis shows that the charge ordering is still a significant figure in zwitterionic liquid. We observed a first sharp diffraction peak in both of these ionic liquids, which indicates the presence of intermediate range order arising from intermolecular hydrogen-bonding interactions between the imidazolium ring protons and the carboxylate oxygen atoms.

MARM 41

Role of geometrical shape and basicity of aprotic heterocyclic anions (AHAs) in 1-ethyl-3-methylimidazolium-based ionic liquids on molecular structure and interactions

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Ionic liquids with aprotic heterocyclic anions (AHAs) have been developed for CO_2 separation applications, but have also been investigated for use as electrolytes. Here, we synthesized selected AHAs with various geometries and basicities in combination with 1-ethyl-3-methylimidazolium ($[emim]^+$) cations. The microscopic local structures of each IL was studied with deuterium exchange reaction kinetics and equilibrium, ^1H NMR chemical shifts, and IR spectra. When the anions are sufficiently basic, deuterium exchange occurs not only with the acidic proton on the C2 of the cation, but also with the less acidic C4 and C5 protons. IR spectra and ^1H NMR chemical shifts of the pure ILs and mixtures with D_2O give insight into the strength of the interionic interaction and the proximity between the cations and anions. Steric hindrance plays a significant role in these hydrogen bonding interaction. Finally, we show how the hydrogen bonding strength affects physiochemical properties.

MARM 42

Domain disturbing effects of asymmetric fluorinated anions

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In the study of ionic liquids (ILs) bulk structures, several components are known to be domain disturbing, such as ethyl chains, silicon atoms and fluorinated alkyl tails. Both ethyl chains and silicon atoms are polar and flexible, causing the tails to bend rather than organize into nanoscale domains. The fluorinated tails, on the other hand, are very nonpolar. Being so, they are not compatible with the carbonyl tails and thus can serve as domain disturbing structures. Our study of ILs with asymmetric fluorinated anions provides evidence of domain disturbing. The total structure functions S(q) is depressed for these ILs. They also show features of triphilic systems when the anion is large. We believe that ILs with domain disturbing structures tend to have low viscosities compared with their carbonyl analogues. Therefore, the fluorinated ILs are promising low-viscosity materials. Fluorous materials are also important to make batteries. The combination makes them better ILs to study.

MARM 43

CO_2 capture in 1-alkyl-3-methylimidazolium acetate: Does N-heterocyclic carbene play any role?

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Ionic liquids provide a promising medium for CO_2 capture. Recently, it was found that the family of ionic liquids comprising 1-alkyl-3-alkyl'-imidazolium cations and acetate anions, such as 1-ethyl-3-methylimidazolium acetate (EMI^+OAc^-), react with CO_2 and form carboxylate compounds. It is widely assumed that N-heterocyclic carbene (NHC) is responsible by directly reacting with CO_2. However, this is controversial in that NHC has not been detected experimentally in this ionic liquid family. In this presentation, we address this issue by presenting our recent computational study of CO_2 capture in EMI^+OAc^-. Quantum chemistry calculations with the self-consistent reaction field theory method predict that NHC becomes unstable in solution as the solvent polarity increases, suggesting that NHC is not formed in EMI^+OAc^-. Ab initio molecular dynamics simulations with the constrained dynamics method indicate that an EMI^+ ion activated by the approach of a CO_2 molecule can donate its acidic proton to a neighboring OAc^- anion and form a carboxylate compound with the CO_2 molecule. Analysis of this termolecular process indicates that the EMI^+-to-OAc^- proton transfer and the formation of 1-ethyl-3-methylimidazolium-2-carboxylate occur essentially concurrently. Based on these findings, a novel concerted mechanism that does not involve NHC is proposed for CO_2 capture. Its implications for other reactions in the 1-alkyl-3-alkyl'-imidazolium acetate ionic liquid family are briefly discussed.

MARM 44

Solute rotational dynamics in ionic liquids: Insights from fluorescence anisotropy, ^2H-T_1 relaxation, and molecular dynamics simulation

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Ionic liquids (ILs), salts which are molten below 100 degrees C, exhibit structural and dynamical heterogeneity, phenomena not commonly encountered in conventional solvents. These features of the IL environment can significantly impact solute rotational dynamics through observation of non-hydrodynamic friction and non-diffusive motion. Using a combination of experiments and molecular dynamics (MD) simulations we will show that heterogeneous dynamics, non-hydrodynamic friction, and large-amplitude jump motions are observed in the rotation dynamics of solutes of comparable size to the constituent IL ions.

The first solute to be examined is benzene, whose oblate shape is known to manifest in strongly anisotropic rotations. Using NMR ^2H-T_1 relaxation measurements in the extreme narrowing limit we show that integral rotation times are much shorter than predicted by hydrodynamics, indicating weak coupling between benzene and the IL. The use of a novel fitting technique based on MD simulated rotational correlation functions is then used to interpret T_1 times outside of the motionally narrowed limit. Good agreement between the experiment and simulation allows us to use the MD results to analyze the mechanism of rotational relaxation of benzene in detail. Using angular mean square displacements, angular trajectories, and orientational van Hove distributions we will show that benzene rotations in the IL environment are characterized by highly non-diffusive motions illustrated by large 180 degree jumps and orientational caging dynamics.

In addition to rotations of benzene, we will also discuss the effects of solute charge and charge distribution on small molecule rotation in ILs using the neutral/dipolar/cationic triplets *p*-xylene/tolunitrile/4-methyl-N-methylpyridinuim and 9,10-dimethylanthracene/9,10-cyanomethylanthracene/9,10-dimethylacridinium using NMR T_1 relaxation and fluorescence anisotropy measurements, respectively. As in the case of benzene, we employ MD simulations of rotational dynamics to aid in interpretation of the experimental observations. The results of this work show that molecular charge has only a modest effect on the friction on a small rotating solute. Large amplitude motions and caging dynamics are also observed for both sets of solutes and are described in detail using results from the MD simulations.

MARM 45

Local dynamics and energetic barriers of carbon dioxide and thiocyanate in imidazolium (n = 2, 4, 6) ionic liquids using ultrafast vibrational spectroscopy

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We have studied the temperature-dependent ultrafast dynamics of CO_2 and $[SCN]^-$ in $[Im_{n1}][Tf_2N]$ ionic liquids with varying alkyl chain lengths (n = 2, 4, 6) using two-dimensional infrared (2D-IR) spectroscopy. 2D-IR spectroscopy reports vibrational frequency fluctuations on a femtosecond to picosecond timescale, which is associated with local structural reorganization of the solvent or reorientation of the vibrational probe. We compare the local dynamics of a small, uncharged molecule (CO_2) with those of a relatively hard anion ($[SCN]^-$). We expect CO_2 to be mostly associated with $[Tf_2N]^-$ anions and $[SCN]^-$ to be mostly associated with $[Im_{n1}]^+$ cations in the charge-ordered domains of the ionic liquid. Varying the alkyl chain length allows us to see how these dynamics change with the advent of heterogeneous polar and non-polar domains, while the temperature-dependent results allow us to interrogate the energetic barriers associated with local structural relaxation. We analyze the results using the Vogel-Fulcher-Tamman (VFT) equation from mode-coupling theory, and compare these with the results from an Arrhenius model, specifically using the Eyring equation to extract qualitative trends in entropy and enthalpy of activation.

MARM 46

Is a cure possible for chronic hepatitis B? Is one necessary?

***Timothy M. Block**, tim.block@bblumberg.org. Baruch S. Blumberg Institute, Doylestown, Pennsylvania, United States*

Now that hepatitis C is routinely “cured” with direct acting antiviral agents, there is a growing excitement and expectation for a cure for hepatitis B. But is it possible? More than 240 million world wide, and as many as 2 million people, in the United States, are chronically infected with the hepatitis B virus (HBV). Chronic hepatitis B is a leading cause of death due to liver cirrhosis and liver cancer. The currently used drugs do not “cure”, require life long use and are useful in only limited subsets of those infected. So, a need would seem obvious. This presentation will address the remaining needs, discuss the first in class direct acting antiviral approaches being taken experimentally which range from entry, cccDNA to morphogenesis inhibitors, and offer opinion as to the likelihood of their success.

MARM 47

New viral targets for viral hepatitis B drug development

***Jianming Hu**, juh13@psu.edu. Microbiology and Immunology, College of Medicine, Penn State, Hershey, Pennsylvania, United States*

Current antiviral chemotherapies for chronic Hepatitis B virus (HBV) infection are limited to nucleoside analogs that inhibit the viral reverse transcriptase (RT) (i.e., nucleoside RT inhibitors or NRTIs), which can suppress HBV replication but rarely eliminate the infection, due to the persistence of the viral covalently closed circular DNA (cccDNA) even after years of treatment. Therefore, efforts to develop a cure for chronic HBV infection are ultimately aimed at clearing cccDNA, either by blocking its generation or accelerating its removal. Existing NRTIs can decrease cccDNA by depleting the precursor to cccDNA, the viral relaxed circular DNA (rcDNA), but the suppression of rcDNA production is likely incomplete even with the most potent NRTIs currently available. Thus, approaches to achieving more complete inhibition of rcDNA production, either by targeting additional viral factors such as the viral capsid protein required for rcDNA production, or by developing ways to inhibit RT activities that are distinct from existing NRTIs, should complement current therapies. Approaches to directly blocking rcDNA to cccDNA conversion or accelerating cccDNA degradation are also been explored, by degradingcccDNA directly or inducing host mechanisms to stimulate cccDNA turnover. In addition, it may be possible to silence cccDNA so as to suppress viral gene expression and replication, without complete elimination of cccDNA, thus achieving a “functional” cure. Finally, convenient markers need to be developed that can accurately reflect functional intrahepatic cccDNA levels to guide antiviral treatment.

MARM 48

Recent advances in drug discovery for chronic hepatitis B virus infection

***Yanming Du**, yanmingd@yahoo.com, Nicky Hwang. Baruch S. Blumberg Institute, Doylestown, Pennsylvania, United States*

To address the unmet medical need for the complete cure of chronic hepatitis B patients, non-nucleos(t)ide small molecules have been extensively pursued. This presentation will give a synopsis of progress in the areas of capsid assembly modulators, surface antigen inhibitors, and immunotherapy. New chemical structures that were discovered over the last few years will be outlined and discussed.

MARM 49

Exploring combination therapies to cure chronic hepatitis B virus infection

***Bruce D. Dorsey**, brucedorsey11@gmail.com. Chemistry, Arbutus Biopharma, Inc., Ambler, Pennsylvania, United States*

Global chronic hepatitis B virus infection (cHBV) remains a significant cause of morbidity and mortality. Therapy with single antiviral agents or immune modulators provides some relief; however, eradication of the virus in most chronically infected patients continues to prove a challenge. With a handful of approved medications available, and several potential drugs targeting unique mechanisms of viral replication now in clinical development, it is possible to consider combination therapy for the treatment of cHBV. Precedence for an antiviral combination approach can be found in the successful treatments for patients infected with HIV and chronic hepatitis C. At Arbutus, we are developing a portfolio of drug candidates with multiple mechanisms of action to treat cHBV. This presentation will highlight some recent results in our approach toward achieving this objective.

MARM 50

Site-directed spin-label EPR spectroscopy of the domain of influenza M2 protein involved in viral budding

***Kathleen P. Howard**, khoward1@swarthmore.edu. Chemistry and Biochemistry, Swarthmore College, Swarthmore, Pennsylvania, United States*

Influenza M2 protein is a 97 residue homotetrameric protein that plays critical roles during the viral infection cycle. While a variety of high-resolution biophysical techniques have been used to characterize the transmembrane domain (residues 22-46), less is known about the conformation and dynamics of the C-terminal domain that is critical to viral budding. We have used site-directed spin label electron paramagnetic spectroscopy (SDSL-EPR) experiments to probe the conformation, dynamics and membrane topology of the M2 protein reconstituted into membrane bilayers.

MARM 51

Transmembrane protein design and assembly for voltage sensing

*Martin J. Iwanicki, Christopher C. Moser, **Bohdana M. Discher**, bohdana@mail.med.upenn.edu. Biochemistry and Biophysics, University of Pennsylvania, Philadelphia, Pennsylvania, United States*

One of the most critical technological needs for deciphering the functional connectome of the brain are bright action potential probes suitable for sub-ms timescale imaging with high spatial resolution and selectively targetable to cells of choice. Inorganic probes developed for this purpose proved to be fast enough to detect neuronal action potentials with sufficient time resolution. However, these probes non-selectively partition into membranes other than plasma membranes and they cannot be targeted to specific cells. Protein-based optical voltage-sensing probes can address this problem, but current genetically encoded voltage indicators (GEVIs) lack behind the inorganic probes in speed and amplitude. We will present the design and characterization of *de novo* designed proteins (maquettes) that are the core of emerging protein-based sensors that will operate on electron transfer based mechanism. These designed membrane maquettes contain four membrane-spanning α-helices and bind redox-active cofactors to form electron transfer chain within a lipid bilayer. To facilitate *in vitro* characterization, they have been expressed in high yields in inclusion bodies of *E. coli*, purified and refolded in charged and uncharged detergent micelles, as well as in lipid vesicles. Circular dichroism studies revealed 70% α-helicity in SDS and no melting in high temperatures and common denaturants, indicating their strong structural stability. The maquettes assemble in different membrane environments and bind 3 hemes upon assembly in vesicles (two hemes strongly with 150 nM affinity and third one more weakly with k_d ~ 1 μM). The redox midpoint potentials of the three hemes at pH = 8.0 are -38, -150, and -203 mV, suggesting that they will be in mixed oxidation states when incorporated in resting plasma membranes. We are currently expressing these maquettes together with fluorescent proteins to enable fast electron and energy transfers that will lead to strong fluorescent signal deltaF/F as a function of transmembrane voltage.

MARM 52

Molecular mechanism of temperature-dependent gating of TRPV1

***Vincenzo Carnevale**, vincenzo.carnevale@temple.edu. Temple University, Philadelphia, Pennsylvania, United States*

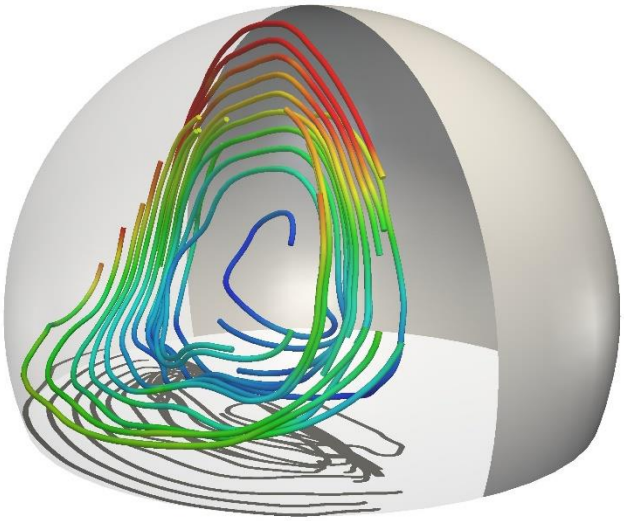
TRPV1 is a channel involved in nociception that promotes cationic currents across cellular membranes in response to multiple stimuli such as increased temperature or pressure, binding of chemicals, low pH and voltage. The molecular underpinnings of TRPV1 gating, in particular the mechanism of temperature sensitivity, are still largely unknown. I will discuss molecular simulations and electrophysiology experiments that shed light on the closed to open transition. Specifically, I will show that gating of TRPV1 relies on the motion of an evolutionarily conserved amino acid (N676) in the middle of the S6 pore helix. On rotation, the side chain of this asparagine faces either the central pore or four small nonpolar cavities. I will thus discuss a model for TRPV1 gating involving the dynamic dehydration/hydration of the central pore and of these four cavities. This gating mechanism is markedly temperature dependent, thereby offering a possible explanation for TRPV1 temperature sensitivity.

MARM 53

Using fluid flow to investigate lipid membranes

***Aurelia Honerkamp-Smith**, auh216@lehigh.edu. Physics, Lehigh University, Bethlehem, Pennsylvania, United States*

While most life takes place in an aqueous environment, the physics of micro-scale movement in fluid environments can be counterintuitive. I will discuss recent experiments with the theme of building up a three-dimensional, microscopic picture of motion. Multi-component lipid membranes act like two-dimensional whose flow can be observed to couple closely to that of the surrounding water. This fluidity can be used to ask questions about the physical properties of lipids and membrane proteins.



MARM 54

Mechanisms of membrane curvature generation

***Tobias Baumgart**, baumgart@sas.upenn.edu. University of Pennsylvania, Philadelphia, Pennsylvania, United States*

Membrane curvature has developed into a forefront of membrane biophysics. Numerous proteins involved in membrane curvature sensing and membrane curvature generation have recently been discovered, including proteins containing the crescent-shaped BAR domain as membrane binding and shaping module. Accordingly, the structure of these proteins and their multimeric complexes is increasingly well-understood.
Substantially less understood, however, are the detailed mechanisms of how these proteins interact with membranes in a curvature-dependent manner. New experimental approaches need to be combined with established techniques to be able to fill in these missing details. Here we use model membrane systems in combination with a variety of biophysical techniques to characterize mechanistic aspects of BAR domain protein function. This includes a characterization of membrane curvature sensing and membrane generation. We present

a new approach to investigate membrane curvature transitions, and introduce membrane shape stability diagrams as a powerful tool to enhance the mechanistic understanding of membrane trafficking phenomena, including endocytosis, with molecular detail.

MARM 55

Green synthesis of uniform ruthenium nanoparticles supported on non-functionalized single-walled carbon nanotube for azo dye degradation

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The integration of carbon nanotubes with nanoparticles into hybrid structures often possess unique structural and catalytic properties that are not available to the respective components alone, and thus, have been envisioned for many applications. Studies have shown that SWNTs offer superior electrical, mechanical and catalytic performance over MWNTs due to their smaller and more homogeneous diameter, higher surface area and less defect densities. Herein, single-walled carbon nanotubes (SWNTs) reinforced with uniform distribution of ruthenium nanoparticles (~5 nm) were synthesized by microwave irradiation in ethanol without the presence of additional reducing agents. A comparative study was done to determine the mechanism of metal nanoparticle formation. The Ru nanoparticle-SWNT composites were characterized by High Resolution Transmission Electron Microscopy (HR-TEM), Energy Dispersive X-ray Spectroscopy (EDS), and UV-Vis Spectroscopy. The efficiency of using this synthesized SWNT-Ru nanoparticle catalyst in the degradation of Congo red was also studied for future waste-water contaminant removal applications.

MARM 56

Flame synthesis of carbon and metal oxides nanomaterials for energy storage, conversion, and harvesting

***Randy L. Vander Wal**[2,1], ruv12@psu.edu. (1) Dept. of Energy and Mineral Engineering, Penn State University, University Park, Pennsylvania, United States (2) The EMS Energy Institute, Penn State University, University Park, Pennsylvania, United States*

With energy at the forefront of the national economy and security energy-directed applications are of particular interest. Not surprisingly, energy and materials are intimately related. Many forms of energy utilization, conversion and storage and generation are dominated by interfacial chemistry. Therein nanomaterials as an interfacial modifier can play a critical role in these processes.

Specific energy applications we have explored include the following:
Storage: Increased energy density in Li ion batteries and supercapacitors using carbon nanotubes
Efficiency: Reduced friction using nanolubricants between moving parts
Transfer: Improved thermal management using nanofluids in heat transfer applications
Conservation: Lightweight polymeric composites incorporating nanotubes, nanoclays and graphene oxide for vehicle composites
Control: Gas sensors based on nanoscale metal oxide semi-conductors for process control and monitoring
Generation: Catalysts and photocatalysts using nanostructured oxides for accelerated charge transfer and minimal recombination losses
Highlights in each application will be presented.

Though synthesis of a host of carbon and metal oxide nanomaterials has been demonstrated, their integration into practical applications remains highly challenging. This talk will provide an overview of their synthesis, integration and value in energy storage, conservation, transfer, efficiency, control and generation. Alternative, scalable synthesis approaches such as flame synthesis and associated laser-based optical diagnostics will be touched upon.

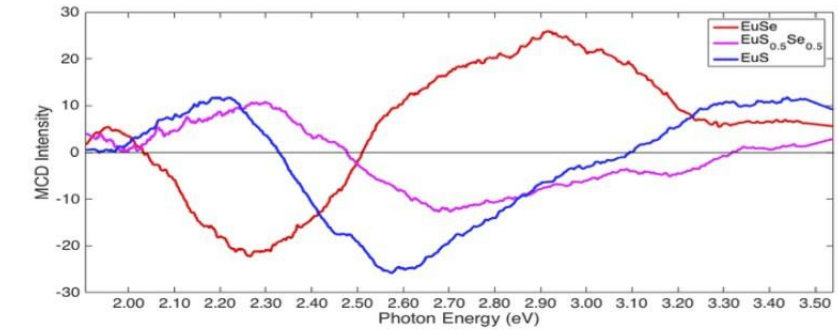
Picture of pre-mixed flame and chimney for material flame synthesis of nanomaterials.

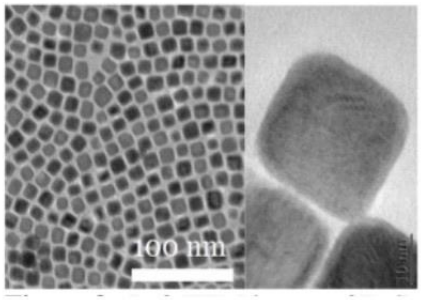
MARM 57

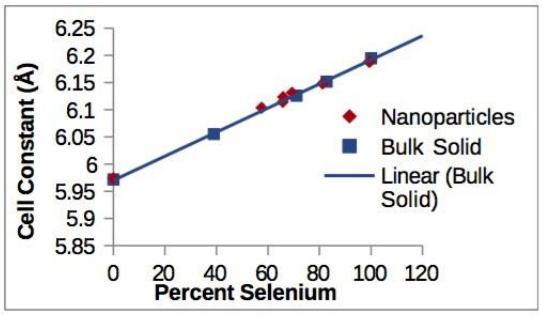
Synthesis and magnetic properties of europium sulfide-europium selenide solid solution colloidal nanocrystals

Nicholas Rosa[2], *nr252@georgetown.edu, Haydee A. Dalafu*[2], *Derak J. James*[2], *Shun Omagari*[3], *Akira Kawashima*[3], *Takayuki Nakanishi*[3], *Yasuchika Hasegawa*[3], *Sarah L. Stoll*[1]. *(1) Georgetown University, Washington, District of Columbia, United States (2) Chemistry, Georgetown University, Washington, District of Columbia, United States (3) Hokkaido University, Sapporo, Hokkaido, Japan*

The europium chalcogenides are all magnetic semiconductor materials that display a range of magnetic behavior from ferromagnetic to antiferromagnetic. The highly coupled electronic, magnetic, and optical properties give rise to phenomena that are of particular interest in magneto-optical and spintronic devices. Using this as a model system to investigate these phenomena and the principles governing them, solid solutions of ferromagnetic europium sulfide (EuS) and metamagnetic europium selenide (EuSe) nanocrystals have been synthesized by solution-phase thermolysis. The resulting nanomaterials of composition EuS1-xSex have been characterized by powder X-ray diffraction (PXRD), transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDS), UV-visible spectroscopy, magnetic circular dichroism (MCD), Farady rotation spectroscopy, and superconducing quantum interference device (SQUID) magnetometry. These materials obey Vegard's law and ferromagnetism has been found to persist well into the selenium-rich portion (>85%) of the phase diagram. As composition changes, smooth changes in ordering temperature (Tc), UV-VIS absorbance, and MCD and Faraday effect signal wavelength and intensity were observed. Additionally, there are dramatic changes that occur in the magnetic and magneto-optical behavior near the ferromagnetic-metamagnetic transition composition. The synthesis has been monitored over time and suggests the initial nucleation particles have a different composition than the final materials which form over the course of the reaction. The MCD has been studied as a function of the applied field to investigate f-d exchange mechanism and its role in the magnetism.







MARM 58

Phase-effects on cation exchange of metal chalcogenide nanoparticles

*Ryan Kozloski, Angus Unruh, **Katherine Plass**, kplass@gmail.com. Chemistry, Franklin Marshall College, Lancaster, Pennsylvania, United States*

Ion exchange can transform nanostructures, generating particles with morphology and phase that is difficult to obtain through direct synthesis. When performing cation exchange, copper chalcogenides are common precursors for cation exchange due to the high mobility and easy exchange of copper ions. The copper chalcogenides, however, are a complex system representing a large variety of phases and compositions and which can be chemically altered to even greater complexity. It has already been established that variations in copper vacancy concentration can alter amenability of particles toward cation exchange. Here we present studies on the effect that variation in the phase of precursors has on the resultant exchanged product.

MARM 59

Virtual design and analysis of Pareto optimal emitter structures for thermophotovoltaic applications

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The ability to shape the absorption and emission profile of nanostructures by exploiting various resonant phenomena that arise in nanoscale structures has garnered significant interest in designing nanostructured selective emitters for thermal energy conversion applications such as thermophotovoltaics.

In this work, we focus on composite planar structures that leverage the interaplay between two resonant phenomena that can be realized in simple planar nanostructures: resonant absorption in weakly-absorbing thin films and reflection resonances in multi-layer dielectric stacks (Bragg Reflectors). The interplay between these resonances enables spectral tunability of the composite nanostructures, and yields structures whose thermal emission properties approach the ideal limit of a step-function emitter.
We combined rigourous electrodynamics calculations with a virtual screening technique based on Pareto optimality to identify a small number of promising structures from a search space of more than 5 million structures, and we have begun experimentally realizing and characterizing structures from this small subset. The results we will report on are an important step towards realizing efficient and robust structures for solar and thermal energy conversion.

MARM 60

Achieving array spasing from novel configurations: Silver nanoparticles and poly(9,9-di-n-octylfluorenyl-2,7-diyl) polymer films

Jill Tracey[1]*, jtracey@ramapo.edu, Deirdre O'Carroll*[1,2]*. (1) Chemistry and Chemical Biology, Rutgers, The State University of New Jersey, Piscataway, New Jersey, United States (2) Materials Science and Engineering, Rutgers, The State University of New Jersey, Piscataway, New Jersey, United States*

Current demonstrations of spasers (Surface Plasmon Amplification by Stimulated Emission of Radiation) have used gold for the nanoparticle cavity and either laser dyes or inorganic semiconductors as the active gain medium. If other materials were implemented the efficiency of spasers could be improved. In addition, using different constituents would allow for accessing a wider range of wavelengths which could lead to more applications of spasers. For example, silver has a surface plasmon resonance which is tunable across blue wavelengths. These wavelengths are inaccessible using gold due to gold's interband electronic absorptions at wavelengths below about 550 nm. Silver's tunability across lower wavelengths also allows for the implementation of different gain media such as organic semiconducting conjugated polymers which have higher chromophore densities, superior synthetic tuneability, strong room-temperature excitonic emission, biocompatibility, and more facile processing compared to inorganic semiconductors.

The goal of this research project is to fabricate thin film nanoparticle/polymer composites which will then be utilized to demonstrate functioning spasers. To verify spasing is occurring two tests are performed, first, utilizing photoluminescence spectroscopy to observe spectral narrowing, and, second, power dependent spectroscopy, to observe nonlinear (specifically; linear to superlinear) intensity behavior. Both of these are used to observe stimulated emission which is characteristic of spasing. This presentation will focus on the fabrication and characterization of planar thin film array configurations of spasers. Many variables have been investigated to achieve functioning spasers, including silver nanoparticle size, silver nanoparticle density, and polymer layer thickness. Our results indicate that spasing is achievable utilizing 60 nm silver nanoparticles and poly(9,9-di-n-octylfluorenyl-2,7-diyl) as the gain media. However all three of these variables (size, density, thickness) play a key role in the functionality of the spasers.

MARM 61

Single molecule switching and sensing

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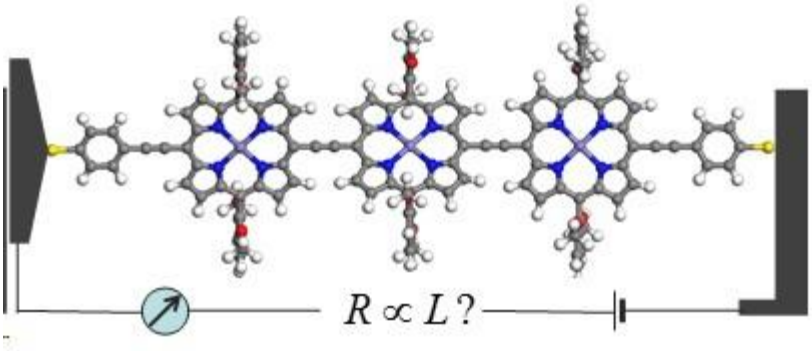
Charge transport through and between molecules is central to many important processes in nature. In particular, studying the conductivity of single molecules can contribute to a better understanding of charge transport, and also help develop better molecular wires and other building blocks of molecular electronics, light harvesting devices, etc. We will discuss the results of different experiments designed to understand these processes at the single molecule level. We measure the conductivity of molecules using the Scanning Tunneling Microscope break-junction (STM-BJ) method that utilizes repeatedly formed circuits where one or a few molecules are trapped between two electrodes, at least one of which has nanoscale dimensions. The statistical analysis of thousands of measurements yields the conductance of single molecules.

One particular interest has been the role of the molecule-electrode contact in charge transport. In the simplest analysis this contact can present a substantial barrier to charge injection, which can have important consequences in devices such as dye sensitized semiconductor nanoparticle solar cells. We have demonstrated that carbodithioate termination of molecules can enhance conductivity by an order of magnitude. We have also shown how the sensitivity of the electrical conductivity of single molecules to external perturbations can allow for switching and sensing, as well as the use of single molecule conductance for the discovery of novel materials.



MARM 62

Synthesis of 2D nanomaterials by intercalation and exfoliation of layered inorganic solids

*Megan Strayer[1], Nina Kovtyukhova[1], Thomas Senftle[1], Alyssa Rosas[1], Ritesh Uppuluri[1], Michael J. Janik[1], Robert M. Rioux[2], **Thomas E. Mallouk**[1], tom@chem.psu.edu. (1) Pennsylvania State University, University Park, Pennsylvania, United States (2) Dept of Chemical Engineering, Pennsylvania State University, University Park, Pennsylvania, United States*

Layered solids – which have strong bonds in two dimensions and weaker links in the third - are interesting building blocks for composite materials and devices because they potentially offer control over structure at the molecular level. Many layered oxides consist of negatively charged sheets interleaved by exchangeable cations. These oxides are particularly amenable to exfoliation (and to other topochemical reactions) by simple ion-exchange and acid-base reactions. Recently we have found that van der Waals solids such as graphite, hexagonal BN, and MoS_2 can also be intercalated and exfoliated without incurring damage to the sheets by means of acid-base and redox reactions.

Layer-by-layer assembly of 2D nanomaterials is enabled by sequential adsorption reactions that overcompensate the surface charge of nanosheets. This effect can be exploited to invert the layer charge of nanosheets (which is typically negative for sheets derived from early transition metal oxides) and enable the intercalation of negatively charged molecules and nanoparticles. While studying these reactions, we observed surprisingly strong bonding between late transition metal oxide nanoparticles and early transition metal oxide nanosheets. Calorimetric measurements and electronic structure calculations suggest that d-acid/base interactions – originally proposed by Leo Brewer to explain the anomalous stability of early-late transition metal alloys – contribute to the strength of nanoparticle/nanosheet covalent bonding. This finding helps us understand the strong metal support interaction (SMSI) in catalysis and provides a prescription for stabilizing catalytically active late transition metal nanoparticles.

MARM 63 Withdrawn

Nanoscale interface directs alignment of a cell-assembled extracellular matrix to template neurite outgrowth

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Tissue regeneration requires directing the assembly of cells and their extracellular matrix (ECM) into arrangements that possess native physical and mechanical properties. We have prepared an interface that templates aligned cell spreading to yield confluent layers of cells across an entire two-dimensional surface. Here, a volatile zirconium alkoxide complex is vapor deposited onto a surface pattern prepared by a novel shadow masking process; the substrate is then heated to form surface-bound, 10-70 nm thick zirconium oxide patterns, which are treated with 1,4-butanediphosphonic acid to give monolayer patterns of the zirconium phosphonate. NIH 3T3 fibroblasts attach to these patterns, spread, and form aligned, confluent monolayers across the entire surface; they assemble an ECM in which the fibronectin fibrils are highly aligned. Decellularization yields spatially aligned matrix attached to the polymer surface. Biologic function is illustrated by oriented neurite outgrowth along the aligned matrix fibrils, which supports the goal of developing a platform for integrating spatially directed cell behavior with a device for nerve regeneration. In this context, shadow mask patterning in 20-micron wide stripes has been applied to the inside surface of polymeric “nerve conduit” tubes.

MARM 64

Retrosynthetic design in the synthesis of inorganic solids and nanostructures

***Raymond E. Schaak**, schaak@chem.psu.edu. Pennsylvania State University, University Park, Pennsylvania, United States*

When approaching the synthesis of a material that requires rigorous control over multiple features (e.g. composition, crystal structure, shape, size), it is helpful to understand how the material forms, including how each variable influences its formation. Realistically, though, this is not always possible, particularly for inorganic solids that form at high temperatures and colloidal nanoparticles that form in solution. We have been studying the reaction pathways that lead to the formation of inorganic solids and nanostructures with the goal of developing retrosynthetic capabilities for target-oriented materials synthesis. This talk will emphasize recent efforts in elucidating the reaction pathways that produce complex hybrid nanoparticles, including new insights into chemoselective growth and the development of reactive solid-state synthons that lead to new classes of multi-functional nanostructures. This talk will also include the design and synthesis of new bulk and nanostructured solid-state materials with useful catalytic properties and crystal structures that are not routinely accessible using traditional methods.

MARM 65

Magnetic and electronic studies on magnetic semiconductor solid solutions

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Magnetic semiconductors are of great interest because of their coupled magnetic, electronic, and optical properties. Due to this coupling, europium chalcogenides exhibit spin filtering effects, giant magnetoresistance, large magneto-optical Kerr rotations, and giant magnetocaloric effects at the ferromagnetic ordering temperature. These properties are highly desirable for many applications like memory devices, where magnetic, optical and electrical signals can be interconverted.

Europium selenide is a particularly interesting magnetic semiconductor because it is metamagnetic, meaning it is antiferromagnetic at low- and ferromagnetic at high-magnetic fields. We have prepared bulk powders of $EuS_{(1-x)}Se_{(x)}$ solid solutions by solid-state reactions. Varying the composition at the anion site was used to control the band gap (E_g). ICP-MS and pXRD were used to confirm composition and structure of the alloys. SQUID measurements were then used to study the relationship between the composition (and therefore E_g) and the magnetic ordering temperature.

Another system we are interested in is the $Eu_{(1-x)}Sm_{(x)}Se$ solid solution. By changing the composition at the cation site we can study the how the metal environment can be tuned to control the lanthanide valence. Measurements using pXRD show that the cell constant follows a non-linear trend with the increase in x, which can be explained by the change in the oxidation state of Sm as it is doped into EuSe. Doping Sm^{3+} at low doping levels results to a decrease in cell constant, and as the doping level increases the cell constant also increases approaching that of SmSe. X-ray absorption experiments are used to probe the oxidation states of the cations and their relative composition in the alloys.

MARM 66

Synthetic approaches to samarium chalcogenide nanostructures

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The synthesis of lanthanide chalcogenide nanostructures has been explored for a variety of precursors and reaction conditions. In particular, our group has extensively studied the synthesis of EuS and EuSe because of the novel properties and highly coupled electronic, magnetic, and optical phenomena that are of particular interest in magneto-optical and spintronic devices. Our goal is to study the resulting properties of solid solutions of $Eu_{1-x}M_xY$ systems where $M=Sm^{+2}$ and $Y=S^{-2}$ or Se^{-2}. However, we have found that the samarium chalcogenide materials have differing reactivities than their europium counterparts. By investigating various precursors and reaction conditions via solid state and solution phase routes for particle growth, we hope to control both the phase and morphology of samarium sulfide and samarium selenide nanomaterials.

MARM 67

Incorporation of polypyridyl osmium, ruthenium, and rhenium complexes into metal-organic frameworks for use as luminescence-based sensors

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Metal-organic frameworks continue to receive interest in the fields of small molecule storage and sensing, owing to their highly tunable, porous structure. Luminescent metal-organic frameworks (LMOFs) can be created by incorporating a luminescent transition metal complex into the framework structure via the organic ligands on the transition metal complex. Such an approach holds great potential for the development of sensors and should result in good sensor-to-sensor reproducibility and uniform response due to the regular, extended structure. The LMOF should retain the luminescent properties of the transition metal complex and allow for interactions with analytes of interest within the pores of the MOF. In the current work, small amounts of luminescent polypyridyl rhenium, ruthenium, or osmium complexes are incorporated into the MOF, $Zn_3(bpdc)_6(bpy)$ (where bpdc = biphenyldicarboxylate and bpy = 4,4'-bipyridine). Highlighted here are approaches for both oxygen sensing and polarity-based sensors. Prototype LMOFs for oxygen sensing incorporate $[M(L)_2(dc\text{-}L)]$ into the framework structure, where M is Ru or Os and L is 2,2'-bipyridine or 1,10-phenanthroline and dc-L is 2,2'-bypyridine-4,4'-dicarboxilic acid or 1,10-phenanthroline-4,7-dicarboxylic acid. Photophysical characterization of the LMOFs includes acquisition of luminescence excitation and emission spectra and Stern-Volmer oxygen quenching plots. Polarity-based LMOF sensors incorporate $[Os(CO)_2Cl_2(dc\text{-}L)]$ or $[Re(CO)_3Cl\ (dc\text{-}L)]$ due to their large dipole moments within the excited state as demonstrated by anisotropy measurements performed on the complexes. These complexes in the LMOF show sensitivity to solvents of different polarities, which is detected by changes in emission wavelength.

MARM 68

Quantitative analysis of oxidation state in cerium oxide nanomaterials

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Of the many engineered nanomaterials being incorporated into our society, cerium oxide (ceria, CeO_{2-x}) based nanomaterials (NMs) are receiving increased attention due to their unique chemical properties and vast number of current and potential applications (e.g., automotive catalysts, UV filters, agricultural treatment agents, antioxidant therapeutics.). Previous research designed to understand the potential environmental and toxicological effects of ceria NMs have yielded conflicting results, with ceria NMs found to be both toxic and non-toxic to cells and organisms. As the overall environmental and toxicological outcomes of ceria NMs are not yet fully understood, it is imperative to develop a comprehensive understanding of their physicochemical properties since these properties will influence the interactions of ceria NMs with biological and environmental systems.

Here, we describe the development of an analytical procedure designed to measure the cerium oxidation state in ceria NMs using orthogonal approaches. Preparation of materials for control measurements *and* methods for optimizing data acquisition and processing were developed to efficiently analyze and objectively interpret the distribution of Ce^{3+} vs. Ce^{4+} oxides. Our results demonstrate a high degree of agreement between the utilized techniques (electron energy loss spectroscopy (EELS), X-ray photoelectron spectroscopy (XPS), and annular dark field scanning transmission electron microscopy (ADF-STEM)) when stable control materials are employed. The methodology is applied to thoroughly characterize a suite of commercial ceria NMs. In agreement with previous research, our results suggest the primary particle size has a large influence on the oxidation state of the ceria particles, with smaller particles having increased Ce^{3+}/Ce^{4+} ratios compared to their larger counterparts.

MARM 69

Electron doping a kagome spin liquid using soft chemistry techniques

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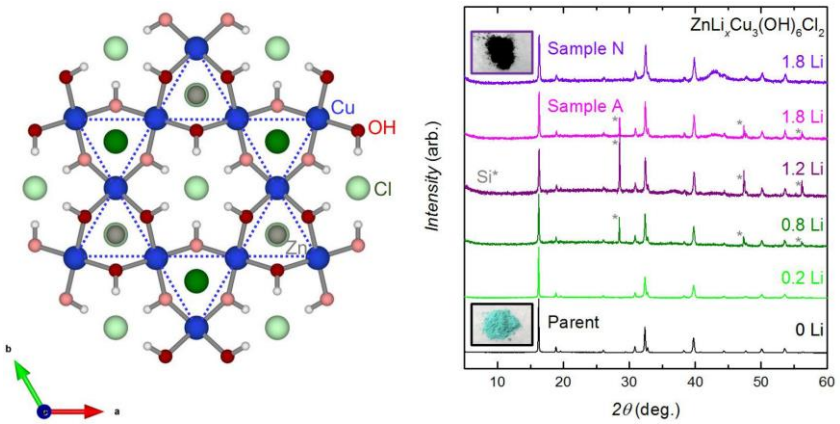
In 1987, Anderson proposed that charge doping a material with the "resonating valance bond" (RVB) state would yield a superconducting state. Ever since, there has been a search for these RVB containing spin liquid materials and their charge doped counterparts. Studies on the most promising spin liquid candidate, Herbertsmithite, $ZnCu_3(OH)_6Cl_2$, a two dimensional kagome lattice, show evidence of fractionalized excitations and a gapped ground state. In this work, we report the topochemical synthesis and characterization of a newly synthesized

electron doped spin liquid, $ZnLi_xCu_3(OH)_6Cl_2$ from x = 0 to x = 1.8 (3/5th per Cu^{2+}). Despite heavy doping, the series remains insulating and the magnetism is systematically suppressed. We have done extensive structural studies of the doped series to determine the effect of the intercalated atoms on the structure, and whether these structural differences induce strong localization effects that suppress the metallic and superconducting states. Other spin liquid candidates are also being explored to understand if this localization is system dependent or systemic to all doped spin liquid systems.



MARM 70

Understanding and optimizing exploratory hydrothermal reactions

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Inorganic–organic hybrid materials such as organically templated metal oxides, metal–organic frameworks (MOFs) and organohalide perovskites have been studied for decades, and hydrothermal and solvothermal syntheses have produced thousands of new materials that collectively contain nearly all the metals in the periodic table. The development of new compounds relies primarily on exploratory syntheses because their formation is not fully understood, Simulation- and data-driven approaches (promoted by efforts such as the Materials Genome Initiative) provide an alternative to experimental trial-and-error. In this work, an alternative approach that uses machine-learning algorithms trained on reaction data to predict reaction outcomes for the crystallization of templated vanadium selenites is demonstrated. Archived ‘dark’ reactions, both failed and successful attempts at hydrothermal syntheses, were used to create a database. Physicochemical property descriptions to the raw notebook information using cheminformatics techniques, and the resulting data were used to train a machine-learning model to predict reaction ‘success.’ When carrying out hydrothermal synthesis experiments using previously untested, commercially available organic building blocks, the machine-learning model outperformed traditional human strategies, and successfully predicted conditions for new organically templated inorganic product formation with a success rate of 89 percent. Inverting the machine-learning model reveals new hypotheses regarding the conditions for successful product formation.

MARM 71

Structure-selective nanocrystal cation exchange in the synthesis of metastable zincblende-type MnS and CoS

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The arrangement of atoms in inorganic crystals has a significant impact on the properties of the material. While organic chemists have established pathways towards target products, solid-state chemists are often limited to obtaining thermodynamic phases, as the high-temperature synthetic methods used to generate solid materials are not as well understood or rationally manipulated to yield arbitrary structural targets. Nanoscale cation exchange, which proceeds quickly under mild conditions and low temperatures, can alter the elemental composition of a nanocrystal while preserving key structural features of the template, and can yield unexpected crystal phases. However, the predictive power of this chemistry has not been well established, and it has been previously restricted to compounds of late- and post-transition metal systems. In this presentation, we will highlight the transformation of digenite $Cu_{2-x}S$ nanoparticles to zincblende MnS and CoS, crystal structures that are metastable in bulk, through a low-temperature cation exchange process. Importantly, these products retain both the cubic

closest packed arrangement of anions and the tetrahedrally coordinated cation coordination environment characteristic of the digenite starting material. When combined with analogous exchange chemistry that transformed a roxbyite $Cu_{2-x}S$ nanotemplate to metastable wurtzite MnS and CoS with similar structural retention, we demonstrate the rational, predictive power of cation exchange for targeting arbitrary structural features otherwise inaccessible to direct synthetic methods.

MARM 72

Structure and photoluminescent behavior of lanthanide-doped bismuth organic materials

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Lanthanides play an important role in many energy-related, electronic, environmental, and military applications due to their f-electron configurations and resulting unique magnetic and optical properties. However, due to recent concerns over lanthanide global supply vulnerability, the development of photoluminescent compounds that address our energy, lighting, and security needs, while also reducing our dependence on rare earth resources, remains an on-going challenge. To address this challenge, our group has begun an investigation into the development of bismuth-based compounds into which lanthanide metal ions may be incorporated. Our choice of bismuth based compounds stems from bismuth's attractive materials properties (availability, low cost, and low toxicity) that collectively may be harnessed towards achieving more effective use of our rare earth supply.Presented here will be an overview of the synthesis and characterization of a bismuth-organic material (BiOM) that exhibits promising PL behavior and structural features that have not been observed in other main group, d-, or f-block systems. Upon incorporation of lanthanide (Ln) ions via doping, this material exhibits intrinsic visible or NIR metal-based luminescence. Structure-property relationships in this and other recently isolated bismuth-organic complexes, as well as the luminescent behavior of the lanthanide doped phases, will be discussed.

MARM 73

Laser annealing of nanoscale carbons

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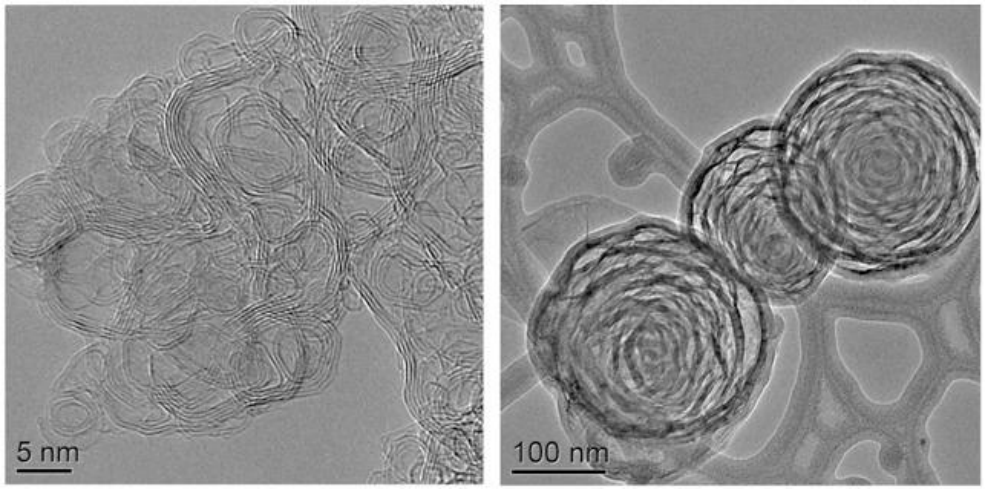
An investigation of the structural changes due to the different time scales of high temperature treatment on nanoscale carbons is presented, using pulsed laser annealing. To resolve detailed nanostructural changes, high-resolution transmission electron microscopy was used to examine the carbon before and after heating. Pulsed laser annealing process led to graphitization of lamellae and also accentuated the recognizable structural differences between the different carbons. Several structures are reported here, such as partial graphitization, formation of hollow particles, rosette structures, and multi-compartmented nanospheres.



HRTEM images of the laser annealed carbons showing nanostructure of particles with the differences due to original starting material – accentuated by the transient heating action by the pulsed laser irradiation.

MARM 74

Teaching computational chemistry as a formal course at the pre-college level

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The need for formal education in the technologies, techniques, and tools of computational chemistry is of critical importance for tomorrow's chemistry professionals. This education can and should start before students matriculate to the undergraduate level. This session describes the efforts of the North Carolina School of Science and Mathematics to teach computational chemistry as a formal chemistry elective to pre-college students. In addition, this session will address how computational chemistry is integrated into honors and AP chemistry courses and into the research in chemistry program at NCSSM. Finally, this session will describe the development of a distance learning program in computational chemistry and the development of a textbook in computational chemistry specifically for high school educators and students.

MARM 75

Molecular modeling for high school students

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Pedagodical applications of molecular compuation and visualiztion approriate for high school students will be presented, followed by an opportunity for hands-on time with some of the technologies.

MARM 76

Reaction of diazonium salts with CdS nanoparticles

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Surface ligands control many aspects of nanocrystal behavior and are generally based on Lewis acid/base interactions between molecules or ions and the surface species of the particle. This results in facile ligand exchange, which is useful for attachement of a variety of surface species but which may not always be desireable. We hypothesized that a less-reversible surface ligand attachment process could proceed through a radical mechanism. For example,n aryl radical could be attached to a semiconductor nanoparticle surface by reducing a diazonium salt through photo-excitation. To test this, we examined the interaction of CdS nanoparticles and the diazonium salt, 4-nitrobenzenedazoium tetrafluoroborate, under various conditions.

MARM 77

pH dependence of imidazole-2-carboxaldehyde tautomeric equilibrium and its implications on potential photosensitization

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Recent study of atmospheric aerosol growth has identified the photosensitized oxidation reaction of volatile organic compounds as a potentially significant contributor to secondary organic aerosol mass. Several studies have used imidazole-2-carboxaldehyde (IC) as a model compound to investigate growth, due to the prevalence of IC as a product of the reaction of glyoxal and the ammonium cation. One characteristic of IC that most of these studies has not accounted for, however, is the tautomeric equilibrium between IC and its hydrated diol form. This equilibrium is pH-dependent, yet few studies in aerosol growth account for differences in pH. To further investigate these conditions, aqueous solutions of ammonium sulfate, succinic acid and IC were analyzed at varying pH levels using UV-Visible spectroscopy and NMR spectrometry. The aldehyde form absorbs at a maximum wavelength of 287 nm, and the hydrated form absorbs at a maximum wavelength of 212 nm. Additionally, a dramatic pH-dependence is evident, shifting the concentration of IC almost completely to the hydrated form at pH<5. Atmospheric aerosol are estimated to exist at a pH between 1 and 3; therefore, a minimal amount of IC would be present in atmospheric aerosol in the aldehyde form. Most importantly, wavelengths of both 287 nm and 212 nm fall within the UV-C spectrum, most of which is blocked out of the troposphere by the ozone layer. *This evidence calls into question the study of IC as a model photosensitizer for applications in aerosol growth*, considering that this compound absorbs insignificant amounts at both atmospherically relevant pH and within the tropospheric solar spectrum.

MARM 78

Chemical interactions between *Janthinobacterium lividum* and the pathogenic fungus *Batrachochytrium dendrobatidis*

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The fungal pathogen *Batrachochytrium dendrobatidis* (Bd) causes the amphibian disease chytridiomycosis, which has been linked to worldwide amphibian population declines. Bd inhibits the amphibian immune system using compounds such as methylthioadenosine and kynurenine. The bacterium *Janthinobacter lividum* provides protection to amphibians by producing the antifungal compound violacein. Using HPLC and cell growth assays, we investigated how compounds produced by Bd affect *J. lividum's* growth and metabolite production.

MARM 79

Synergistic antimicrobial effects of aqueous ionic liquids and polymyxin on lipid vesicles

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Ionic liquids (ILs) have recently been seen to function as antibiotics by inserting themselves into lipid membranes. Traditional antibiotics such as Polymyxin B (PMB) function by disrupting bacterial cell membranes. We hypothesize that PMB and ILs ($BMIBF_4$ and BMICl) may work together synergistically to function as more efficient antibiotics than PMB alone. Synthetic lipid vesicles were used as a model for bacterial cell membranes. Absorbance shrinkage studies demonstrated a vesicle size change when ILs were added, and a negligible size change was observed when PMB was added. However, the addition of both ILs and PMB resulted in a greater vesicle size change. DLS measurements supported these observations and showed that aggregation of vesicles may occur at high concentrations of ILs (specifically $BMIBF_4$) in the presence of PMB. FRET analysis suggested that aggregation may be due to possible fusion of vesicles. The fluorescent probe, Bis (2,2'-bipyridyl) ruthenium (II) chloride hexahydrate (Rubipy), was also used to assess vesicle disruption by ILs and PMB. Since Rubipy's fluorescence lifetime changes with environment, Rubipy was trapped within lipid vesicles, and lifetime measurements were used to determine lipid vesicle disruption. Lifetime data indicated that high concentrations of ILs (especially $BMIBF_4$) in the presence of PMB disrupt vesicle membranes.

MARM 80

Distinct roles in caspase inhibition for different domains of the inhibitor of apoptosis protein DIAP1

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Programmed cell death (apoptosis) is a process required for normal development and tissue regeneration in animals. By removing potentially harmful cells, apoptosis also protects against cancer and the spread of a viral infection. At the cellular level, apoptosis requires the activation of caspase proteases which are kept inhibited in living cells by inhibitor of apoptosis proteins (IAPs). Binding of certain apoptosis-promoting proteins to IAPs relieves the caspase inhibition to enable apoptosis to occur. IAPs typically contain 2-3 BIR (baculovirus IAP repeat) domains with intervening "linkers". In previous studies with recombinant *Drosophila* proteins, we found that an IAP fragment from DIAP1 containing the BIR1 domain and adjacent C-terminal linker (BIR1-linker) was minimally required to effectively inhibit the caspase DCP-1, as the BIR1 alone or the linker and BIR2 were each ineffective. Based on X-ray crystal structures of IAP-caspase complexes, we propose that the linker functions by directly blocking the caspase active site but binds with low affinity while the BIR1, which binds outside the active site, does not inhibit the caspase but provides the necessary affinity for the linker. We tested this by competing BIR1 and BIR1-linker fragments for inhibiting DCP-1. In an *in vitro* kinetic assay, 1.5 μM BIR1-linker caused a 42 ± 3% reduction in DCP-1 activity while 1.6 μM BIR1 caused no inhibition. However, adding 1.5 μM BIR1 before adding the BIR1-linker reduced the BIR1-linker's inhibition of DCP-1 by 45 ± 3%, and doubling the BIR1 concentration reduced the inhibition by 91 ± 4%. This is consistent with the BIR1 functioning to bind but not inhibit DCP-1, which enables it to prevent the binding and inhibition by the BIR1-linker. Corroborating this, increasing the BIR1-linker concentration progressively reversed the BIR1 interference. Experiments are underway to independently test the protein binding interactions among the BIR1, BIR1-linker, and DCP-1 proteins.

MARM 81

Low temperature EPR studies of cerium nitrate-triphenylphosphine oxide complexes

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Complexes of lanthanide ions with phosphine oxides have been known for many years. Variable temperature EPR measurements of a Ce(III) nitrate complex with triethylphosphine oxide have been carried out in order to gain a better understanding of the electronic properties of Ce in this compound. The complexes $Ce(NO_3)_3(Ph_3PO)_4(Me_2CO)$ (1) and $Ce(NO_3)_3(Ph_3PO)_2(EtOH)$ (2) have been synthesized using established methods such as the reaction of cerium(III) nitrate hexahydrate and triphenylphosphine oxide in acetone (1) or ethanol (2) in air. Single crystals of these complexes were grown under a variety of conditions to ensure that the crystals were free of defects and inclusions. EPR spectra of the crystals were collected at liquid helium temperatures to allow the determination of the order and energy separation of the three Kramers doublets $|J=5/2; J_z=\pm1/2\rangle$, $|J=5/2; J_z=\pm3/2\rangle$ and $|J=5/2; J_z=\pm5/2\rangle$ in the $^2F_{5/2}$ ground state manifold of Ce(III). The EPR spectra as well as the crystal synthesis techniques will be presented along with potential applications of these crystals.

MARM 82

Interaction between transition metal complexes and substituted indoles

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The interactions between various transition metal (zinc and nickel) complexes and the indoles melatonin, serotonin, tryptamine, and tryptophol were characterized using UV-vis and fluorescence spectroscopy. Both the metal complexes and indoles fluoresce independently, and in certain cases, the fluorescence of the indole is quenched in presence of the metal complex. Fluorescence quenching was measured as a function of quencher concentration and was characterized as static or dynamic using Stern-Volmer analysis. Stern-Volmer constants (K_{SV}) were determined from dynamic quenching plots, and the binding constant (K_A) and binding site number (n) were determined from static quenching plots. The thermodynamic parameters for changes in entropy (ΔS), enthalpy (ΔH), and Gibb's free energy (ΔG) were calculated using Van't Hoff plots for trials in which static quenching occurred. Lifetime measurements for each series were obtained via fluorescence decay analysis in order to observe any changes in lifetime with increasing quencher concentration. Several metal complexes displayed interaction with the indoles through dynamic or mixed quenching, and there were no notable lifetime changes.

MARM 83

Production of His-tagged sfnaD for inhibition studies of the staphyloferrin A biosynthetic pathway

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SfnaD is the second enzyme of the biosynthetic pathway for staphyloferrin A in *Staphylococcus aureus*. This enzyme catalyzes amide bond formation between citrate and D-ornithine forming a δ-citryl-D-ornithine intermediate. This intermediate is subsequently used by the third enzyme, SfnaB, to produce staphyloferrin A. Staphyloferrin A is one of two, iron-binding siderophores produced by *S. aureus*. The overall goal of this research is to produce inhibitors of SfnaD thereby reducing iron uptake. If successful, these inhibitors could serve as new drugs to battle bacterial infections caused by methicillin-resistant *S. aureus* (MRSA). A His-tagged expression plasmid is currently being constructed to produce SfnaD for *in vitro* inhibition studies. Progress towards this goal, along with results of small-scale overexpression and purification studies is presented. The results of preliminary activity studies and a proposed transition state inhibitor are also reported.

MARM 84

Design and synthesis of betulinic acid conjugates as anti-cancer agents

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Betulinic acid is a bioactive pentacyclic lupane type triterpenoid, which can be isolated from the bark of yellow and white birch trees. Betulinic acid derivatives show diverse range of pharmacological activity including their use as anti-tumor, anti-inflammatory, antiparasitic, and anti-HIV agents. Previously, we have reported the synthesis of chalcones, α-acetoxyamide and amine based derivatives of betulin via aldol condensation, Passerini reaction, and

reductive amination respectivley. We have also prepared novel betulinic acid-triazole derivatives employing Baylis-Hillman reaction and click chemistry as the key steps in our synthesis. All the compounds were evaluated for their potential as anti-cancer agents on murine breast cancer (4T1) and human pancreatic cancer (MIA PaCa-2) cell lines. Based on these results, we were able to identify two series of betulinic acid-triazole cojugates for further SAR analysis. In an effort toward increasing their water solubility and potency, we have synthesized a series of quaternary ammonium salts starting from our most potent analogs. This poster will focus on our more recent results on the preparation and anti-cancer activity of our second-generation betulinic acid triazole conjugates.

MARM 85

Degradation of Congo red dye in the presence of single-walled carbon nanotube-ruthenium nanoparticles composites

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Congo red dyes are often used in textile industries which are lost in waste water during the dyeing procedure and causes great threats to aquatic life. Herein, a comparative study of the catalytic degradation of Congo red dye by single walled carbon nanotubes-ruthenium nanoparticle composites was performed. The composites catalytic properties were characterized by UV-Vis Spectroscopy.

MARM 86

***In silico* evaluation of a hydrogen production system with enzyme produced from cell-free protein synthesis**

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Producing hydrogen from carbohydrates economically requires efficient and long-endurance catalytic reformers. Limited endurance is the main challenge of traditional synthetic pathway biotransformation (SyPaB) reformers. Using a cell-free transcription-translation system (TX-TL) and inverted membrane vesicles (IMVs) to divert some of the energy to produce new enzymes for the SyPaB can enhance the endurance of the pathway. Before the system can be assessed experimentally, I developed a computational optimization to approximate the parameters with data from previous literature.

MARM 87

Progress towards surface-modified porous silicon

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Progress towards synthesis of a small-molecule functionalized p-type porous silicon is discussed. Historically, porous silicon (pSi) is a mesoporous semiconductor with high surface area, and customizable pore morphology that has been used for optical sensing. pSi is biocompatible, readily decomposing to orthosilicic acid ($Si(OH)_4$) in vivo without adverse side-effects, and its use for subcutaneous drug delivery is currently being explored. Herein, a small molecule mannose binding lectin-mimic is synthesized and attached to pSi to evaluate the practicality of a biomedical device to clean blood or deliver drugs with minimal side effects.
pSi was prepared via stain etching of Si-100 wafers using potassium permanganate or sodium nitrite in sulfuric acid/hydrofluoric acid. Post-etching, surface silicon-hydride bonds were observed by attenuated total reflection infrared (ATR-IR) spectroscopy, pores were evident by atomic force and scanning electron microscopy, and visible photoluminescence was seen when illuminated at 254 nm. A wafer etched with sodium nitrite/hydrofluoric acid/sulfuric acid solution could be modified with biphenyldiazonium salts by direct covalent coupling. Synthesis of variably substituted biphenylamino compounds by Suzuki coupling of an arylboronic acid and diazotizations was investigated for attachment to the pSi surface.

MARM 88

Biophysical and structural studies of quadruplex DNA in complex with promising small molecule binders

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G-quadruplexes (GQ) are non-canonical tetra-stranded DNA structures implicated in cancer and aging. The ability of small molecule ligands to bind to the GQ structures and alter their stability is of special interest especially for the development of anticancer therapeutics. In this project, we aim to perform biophysical and structural (X-ray) characterization of select GQ DNA from oncogenes promoters (Bcl-2) and telomeres (THM) with a variety of

promising and well-studied GQ ligands, e.g. RHPS4, NMM, PDS, and Braco-19. We used UV-vis and fluorescence titrations, Job plot, and CD melting studies to determine both the stabilizing ability and the affinity of the ligands. NMM is found to stabilize Bcl-2 by 21.1 ± 0.5 °C at 2 equivalents and bind with a 1:1 stoichiometry and K_a of (0.45 ± 0.13)×10^6 M^{-1}. RHPS4 was found to somewhat decrease the parallel character of GQ formed by THM and to stabilize it by 14.6 ± 0.5 °C at 2 equivalents. Native PAGE gel electrophoresis study suggests that THM forms a homogeneous and well-folded structure both alone and with RHPS4. Initial crystallization trials for the THM-RHPS4 complex have been completed and yielded small cubic and hexagonal crystals. Optimization screens are underway. The results from this study will be valuable in the future design of anticancer agents.

MARM 89

Effects of Hofmeister ions on particle attachment to surfaces

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Attachment of particles and bacteria to surfaces, an early stage of fouling, could normally be explained by thermodynamic interactions. Recently, we have observed that the behaviors, in the presence of some salts, deviate from the predicted results. The deviation appears to be associated with the hydrophobic interactions between the particles and the surfaces. The presence of salts could amplify or reduce such interactions; an effect was discovered by Hofmeister in 1888 for protein precipitations. The attachment of positively and negatively charged particles to both hydrophobic and hydrophilic surfaces in the presence of monovalent Hofmeister ions, halides and alkalis, was studied using flow chambers. With an ion concentration of 0.1 M or higher, the attachment followed the prediction of the Hofmeister effects, but such effect was not obvious when the ion concentration was 0.01 M. These results provide some additional insights in fouling to allow the development of effective fouling control strategies, which will have implications in areas from bioprocesses, disease control, to membrane separation/filtration.

MARM 90

Surface immobilization of poly(N-isopropylacrylamide) using silane coupling agents

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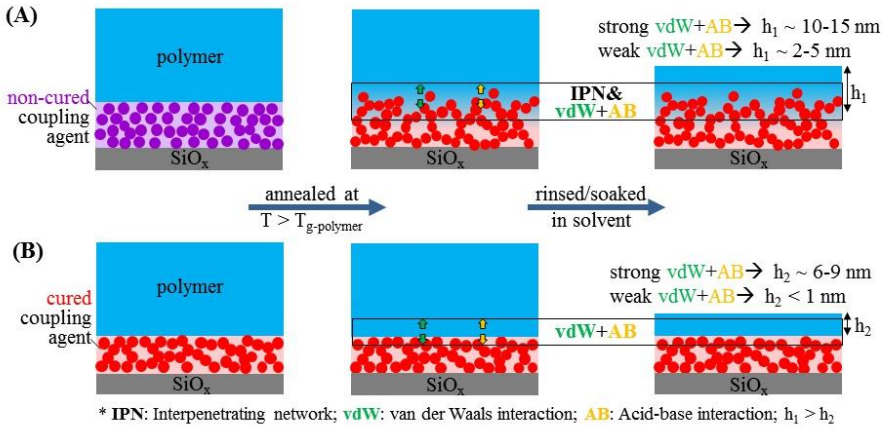
Silane coupling agents are commonly employed to link an organic polymer to an inorganic substrate. One of the widely-utilized coupling agents is 3-aminopropyl-triethoxysilane (APTES). In this study, we investigated the ability of APTES to immobilize thermo-responsive poly(N-isopropylacrylamide, pNIPAAm) on hydroxylated surfaces such as glass. For comparison purposes, polystyrene (PS), which has lower van der Waals and acid-base (contributed by hydrogen-bonding) interactions with APTES, and two other silane coupling agents, which have similar structures to that of APTES but exhibiting less interactions with pNIPAAm, were utilized. Under our processing conditions, the stronger interactions, particularly hydrogen bonding, between pNIPAAm and APTES were found to contribute substantially to the retention of pNIPAAm on the APTES modified surface, especially on the cured APTES layer when the interpenetration was minimal or non-existent. On the non-cured APTES layer, the formation of APTES-pNIPAAm interpenetrating network (IPN) resulted in the retention of thicker pNIPAAm films. The retained pNIPAAm layer (6-15 nm), on both non-cured and cured APTES, exhibited thermo-responsive behavior, as demonstrated by water contact angles (i.e., 7 – 15° higher at 40°C, the temperature above the lower critical solution temperature or LCST of 32°C for pNIPAAm, as compared to those at 25°C) and cell attachment and detachment behaviors (i.e., attached/spread at 37°C, above LCST; detached at 20°C, below LCST).



MARM 91

Surface immobilization of poly(N-isopropylacrylamide) on polycarbonate

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Immobilizing thermo-responsive polymers on a substrate has attractive applications in tissue engineering, drug delivery, and fouling/antifouling controls. Due to the practicality of polymeric substrates (inexpensive, ease of processing), there is a great interest of generating thermo-responsive polymeric surfaces that would allow cell attachment/growth and subsequently cell/cell sheet detachment. In this study, we investigated the possibility of immobilizing thermo-responsive poly(N-isopropylacrylamide, pNIPAAm) on polymeric substrates, such as polycarbonate (PC), utilizing the interpenetration between pNIPAAm and PC as well as van der Waals and acid-base interactions. The approach was much simpler than e-beam or plasma based grafting approaches. Thin pNIPAAm films were spin-coated on untreated and plasma treated PC, and the assembly was annealed at 160°C, 10 and 25°C greater than the glass transition temperature (Tg) of PC and pNIPAAm, respectively, for 3 days. Most of the films, especially those on the plasma treated PC, exhibited the thermo-responsive behaviors based on water contact angle, but the pNIPAAm film retained on non-treated PC (< 5 nm) was much thinner than those retained on plasma treated PC (13 – 45 nm, depending on the film thickness of pNIPAAm and PC). Also, by blending a coupling agent, such as 3-aminopropyl-triethoxysilane (APTES), with pNIPAAm, a thicker pNIPAAm layer could be retained; however, cell attachment/proliferation was not as good as that on a thinner pNIPAAm layer (15 – 30 nm).

MARM 92

Mechanically strong protein-based hydrogels from suckerins of the squid ring teeth

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Biomaterials have given rise to novel technologies that are renewable and readily compatible with living tissues. The squid ring teeth (SRT) protein, or suckerin, found in the suckers of squid tentacles is one such biomaterial with impressive mechanical (having a mechanical strength of 4.5 – 7.5 GPa in its dry state) and thermoelastic (reversible solid to melt transition, but only thermally degrades at a temperature > 250°C) properties. By simply mixing suckerin into gelatin, hydrogels with a higher compressive modulus was generated. With 0.01 to 0.1 wt.% of suckerin added to gelatin, 5 – 20 x increase in modulus was achieved, and the modulus increased almost linearly with the amount of suckerin added. Suckerin could also be cross-linked with gelation to form even stronger hydrogels. These enhanced mechanical properties could allow protein hydrogels for applications in the biomaterial, orthopedic, orthodontic, and even civil engineering fields.

MARM 93

Evaluation of guanofuracin as an antibiotic

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Antibiotics are substances made by one microorganism to kill another microorganism. Humans have adapted these natural substances to inhibit the growth of or kill bacteria which cause many infections. However, many pathogenic bacteria are showing increased resistance to commonly used antibiotics, forcing scientists to search for novel ones that may not be naturally occurring. This research project is aimed at further characterizing the

potential of one of these compounds, the hydrazone gunaofuracin, as an antibiotic. Typically, the concentration of an antibiotic needed to inhibit the growth of specific bacteria is determined using a minimal inhibitory concentration (MIC) protocol. In a traditional MIC test, serial 1:2 dilutions of drug are made in tubes and then bacteria are added to each tube. Following a period of growth, the extent of cell growth is determined by measuring the absorbance (600 nm) on a spectrophotometer, one tube at a time. In order to optimize space, time, and materials, the MIC assay was miniaturized to a 96-well format. The compound dilutions were performed more quickly using a multichannel pipette and more replicates of the dilutions were able to be performed with less materials. Instead of using a traditional spectrophotometer, a 96-well plate reader was used to take the absorbance measurements of all 96 wells in less than 10 seconds. This miniaturized system was tested using a common antibiotic, ampicillin, which was tested against a lab strain of *Staphylococcus aureus* known to be ampicillin sensitive. The issues of chemical solubility and stability for guanofuracin are currently being studied while subsequently determining the MIC for guanofuracin against both Gram-positive and Gram-negative species.

MARM 94

Unique hot carrier distributions from scattering mediated absorption

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Scattering mediated absorption (SMA) is a phenomenon that occurs in hierarchical nanoparticles that consist of a dielectric nanosphere which is decorated with small metal nanoparticles. Metals nanoparticles have broad absorption, whereas dielectric nanospheres have narrow scattering features; by combining both of these materials, an emergent property is observed which only arises in hierarchical nanoparticles. The interaction between the dielectric nanoparticles causes certain frequencies of light to slow down and be encapsulated for a prolonged period of time. The light trapped in the dielectric core causes strong absorption in the metal nanoparticles, which is observed through absorption features that mimic the dielectric scattering features. This leads to the excitation of hot electrons in the small metal nanoparticles. The hot electrons generated by this SMA can be used in a variety of applications ranging from medical applications such as photodynamic therapy, to energy applications such as solar energy conversion. In this research, a multi-scale modeling approach was developed in order to understand the hot electron dynamics and approximate the electrons in the metal nanocubes. This methodology will allow characterization of the electric field at these hierarchical nanostructures and also will yield knowledge about the excitations of the electrons in the metal in response to SMA. Our results convey that the SMA in hierarchical nanoparticles causes continual generation of hot electrons over longer periods of time in comparison to absorption of lone metal nanocubes. Results also show that, by changing the size of the dielectric core, one can exercise control the generation of hot electrons. This exciting phenomenon may improve upon applications, such as solar energy conversion and photocatalysis.

MARM 95

Polysiloxane coated PolyRhodanine (PRd) nanocomposites

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Conducting polymers and polysiloxanes are used as chemical barriers to the corrosion process and loading them with metal nanoparticles improve their protecting properties. *1,3,5,7-TetramethylCyclotetrasiloxane* and *Polymethylhydrosiloxane* (PMHS) are the byproduct of the silicone industry and are widely used as adhesion promoters between metal surfaces and organic resins**.** They are environment friendly reducing agents, biocompatible and have economic advantages. Rhodanine(Rd) and PolyRhodanine(PRd) nanofibers possess heteroatom centers: N,S and O are excellent for coating on metal surfaces and have a wide variety of biological activities such as anticonvulsant, antibacterial, antidiabetic, antiviral, antimicrobial and antihistaminic agents. In this research, a strategy of synthesizing Polysiloxane coated polyRd/Silver Nanoparticles composite will be presented. Rd first forms a one dimensional complex with the Silver cation due to coordination. Consecutively, silver ions are reduced to silver nanoparticles which catalyze the polymerization on the surface of the complex due to the surface adsorption and electron transporting effect, eventually resulting in siloxane coated AgNP/Poly-Rd nanotubes. The size of the nanotubes can be manipulated by changing the ratio of the solvents.

MARM 96

Functionalizing single-walled carbon nanotubes with [Ru(bpy)2dppz]2+ as a potential mode of drug delivery

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Recent studies have demonstrated the potential of carbon nanotubes in a variety of applications due to their structural, mechanical and electronic properties. Single-walled carbon nanotubes (SWCNTs) are made of a single graphene sheet rolled into a cylindrical structure. The large surface area and delocalized electron system allow for non-covalent adsorption of cargo molecules through extended π systems on the nanotube surface, making them promising candidates as drug carriers for the delivery of therapeutic agents. Evidence suggests that SWCNTs protect their "cargo" drug from degradation, reduce side effects, and enables targeted delivery. In addition, SWCNTs have been shown to enter eukaryotic cells with no significant toxicity. In this research, we describe the attachment of [Ru(bpy)2dppz]2+, a DNA intercalator, to SWCNT to form a composite. The characterization of such a composite and its interaction with dsDNA *in vitro* is reported. The long term goal is the delivery of [Ru(bpy)2dppz]2+ to the nucleus of *S. cerevisiae* using SWCNT as carrier, and its binding to nuclear DNA. Modification of SWCNT surfaces was achieved through successive rounds of sonication and centrifugation of an aqueous solution of SWCNTs and [Ru(bpy)2dppz]2+. This procedure dispersed the aggregated SWCNTs to allow π- π interactions to occur between the dipyridophenazine (dppz) ligand and the nanotube surface. Evidence for the formation of the Ru-SWCNT composites was provided by UV/Visible and fluorescence spectroscopy, which, when compared to the spectra of pristine SWCNTs, revealed the appearance of an MLCT band characteristic of the Ru(II) complex and enhanced fluorescence at 609 nm. The capacity of SWCNT to transfer the [Ru(bpy)2dppz]2+ to dsDNA was examined *in vitro* through gel electrophoresis and fluorescence spectroscopy of samples containing Ru-SWCNT composites and ctDNA. Studies of the effect of SWCNT/Ru-SWCNT composites on yeast cultures are underway in our laboratory.

MARM 97

Treatment of wastewater samples at the New York City-Department of Environmental Protection (NYC-DEP)

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The New York City Department of Environmental Protection (NYC-DEP) is responsible for cleaning the wastewater and protecting the environment in New York City. The Newtown Creek wastewater treatment plant in Brooklyn tests the treated wastewater from all 14 plants every day via its chemistry and microbiology research laboratories. When samples arrive in the lab they are separated into four different groups – acidified, non-acidified, processed solids and total solids. After they are tested for their pH value samples are composited according to an established flow sheet. Details of this procedure and examples of cases encountered daily will be described. The difference in the processing of Total Suspended Solids (TSS) and Total Solids (TS) using primary and secondary digesters that reduce the degree of pathogens during the treatment process will also be highlighted.

MARM 98

Density Functional Theory (DFT) calculations of CO2 adsorption to mineral surfaces in the presence of water molecules

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Shale formations present a natural environment for the sequestration of CO2 from coal-burning energy plants and other sources. The composition of the shale, as well as the degree of humidity of the supercritical CO2, has a significant effect on the interaction of the adsorbate with the mineral surfaces. In this study the change in Gibbs' free energy of the adsorption process is determined. Models of CO2 and clusters representing both Kaolinite (a non-swelling clay) and Montmorillonite (a swelling clay) were developed and energy minimized. In addition to the dry surfaces, models with a progressively increasing number of water molecules were prepared until a monolayer of hydration was achieved. Clusters were set up with varying distances between the CO2 molecules and the models mentioned above, and also energy minimized. The infrared vibrational frequencies of all the proposed models were calculated, and the ΔGads were established by subtracting the free energies of the complexes from those of the initial components. The results were analyzed to determine trends based on the degree of humidity, and to contrast the differences due to the nature of the clays.

MARM 99

Syntheses of N-hydroxyphenyltrichloroacetamide derivatives by microwave reactor: Possible precursor to polycarbamate

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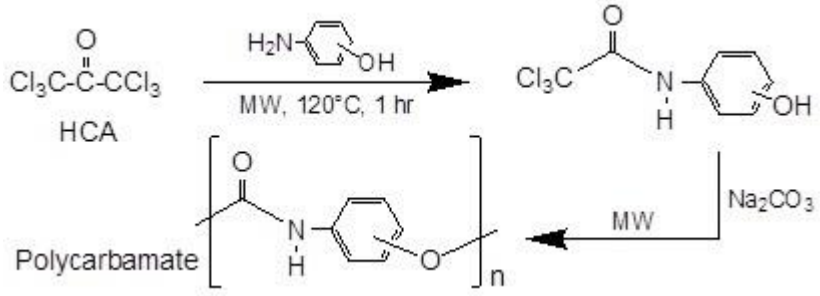
Microwave reactor is a new technology and has become an invaluable tool adopted in many areas of science laboratories due to the convenience including temperature, pressure and power controls. In the previous report, N-4-hydroxyphenyltrichloroacetamide was prepared from the reaction between hexachloroacetone (HCA) and 4-aminophenol after refluxing overnight in $CHCl_3$. However, the same result was obtained after heating the reaction mixture for 1 hour at 120°C using a microwave reactor. 2- and 3-hydroxy derivatives were also similarly obtained using a microwave reactor in one hour instead of refluxing overnight. The prepared three derivatives were spectroscopically characterized, and the molecular structures were also determined by X-ray diffraction. Further reactions to convert them to the corresponding polycarbamate using a microwave reactor are under investigation.



MARM 100 Withdrawn

Refractive index of oxalic acid measured by zoom-In method and extension method

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The refractive index of oxalic acid was measured by a refractometer using two different methods: zoom-in and extension methods. The zoom-in method requires two solvents which satisfy the following conditions: (i) a solid should have reasonable solubility in two solvents (10%), and (ii) the refractive index of the solid should be between those of two solvents. Two sets of solvents (i) DMSO and THF, and (ii) DMSO and n-PrOH were selected to determine the refractive index of oxalic acid, and the average value of 1.428(1) was obtained as its refractive index. The extension method, on the other hand, needs only one solvent to determine the refractive index of a solid, however, better solubility of a solid in the solvent was required compare to the zoom-in method. The refractive index of oxalic acid was measured indirectly from the linear relationship obtained between the % mass concentration of oxalic acid solution and its refractive index obtained by a refractometer. The refractive index of oxalic acid was determined in six different organic solvents, and the values were in the range of 1.409 and 1.427. It is noteworthy to mention that oxalic acid showed very good solubility in DMSO and MeOH (up to 52% by mass), and a good linear plot between the % mass concentration and its refractive index were observed over 50% solution which may clearly support the assumption of the extension method that the straight line would be extended to 100% solution.

MARM 101

Role of loop 6 in cyclic-di-GMP specific phosphodiesterase in *Shewanella woodyi*

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Biofilms are matrix encapsulated microbial colonies which usually adhere to moist surfaces. Though beneficial to the survival of bacteria, biofilms can carry potentially harmful pathogens which can compromise one's heath. Cyclic di-GMP is a bacterial second messenger molecule that has a hand in the formation ofis well documented in biofilm regulations. In general, high concentrations of cyclic-di-GMP cause biofilm formation, and in low concentrations they cause biofilm dispersal of biofilms. Nitric oxide (NO) has also been implicated in biofilm regulation. Like many other bacteria Shewanella woodyi's cyclic di-GMP processing, bifunctional enzyme has both phosphodiesterase (PDE) and cyclase ability (DGC). Certain bacterial heme proteins have been known to behave as nitric oxide (NO) sensors, such as H-NOX (heme nitric oxide/oxygen binding) proteins. Indeed, H-NOX proteins

have been known shown to regulate HaCE cyclic-di-GMP synthesis and hydrolysis activity in some bacteria. For example, in Shewanella woodyi, when nitric oxide is bound to H-NOX, PDE cyclic-di-GMP hydrolysis activity increases, leading to decreased cyclic-di-GMP concentration causing biofilm dispersal. This project focuses on uncovering the role of amino acid residues in the loop 6 region of the S. woodyi H-NOX-associated cyclic-di-GMP hydrolysis enzyme (HaCE), which is responsible for binding substrate and magnesium ions, of the cyclic di-GMP specific phosphodiesterase in the HaCE. Two different mutants were made, S543A and D535A. Unlike the wild-type, enzyme activity of both mutants displayed relatively no activity, confirming the importantce of these residues in enzyme activity. S. woodyi H-NOX was also characterized by UV-visible spectrophotometry. Future studies will focus on investigating the activity of the mutants in the presence of H-NOX protein in its reduced, unligated and NO- bound states. Understanding the roles of the different parts of the proteins in these complex bacterial signaling pathways may aid in the development of novel therapeutic intervention methods and antimicrobial treatments to prevent and alleviate biofilms.

MARM 102

Elemental analysis of food using inductively coupled plasma-mass spectrometry at the Food and Drug Administration (FDA), Northeast region laboratories in Jamaica NY

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The Food and Drug Administration (FDA) mission is to protect the public health by ensuring the safety and security of human and veterinary drugs, biological products, and medical devices and by ensuring the safety of our nation's food supply, cosmetics, and products that emit radiation. The Regional Field Office, Northeast Region, in Jamaica, NY includes the elemental analysis lab, which monitors the amounts of toxic elements in foods. Through the inductively coupled plasma-mass spectrometric technique the determination of elements such as arsenic, cadmium, chromium, lead and mercury is performed using a microwave assisted digestion. The details of the experimental procedure and cases studies will be presented.

MARM 103

Structural properties of iron in volcanic ash

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Synchrotron X-ray absorption was used to investigate structural properties of iron species in volcanic ash. X-ray absorption near edge structure and pre-edge feature that appears before the main absorption edge provides useful information such as oxidation state and bonding properties of iron species. For example, only iron-oxygen compounds exhibit pre-edge feature due to 1s – 3 d transition in atomic orbitals. This transition is forbidden by selection rules but become allowed due to mixing of iron 3d and oxygen 2p orbitals. The normalized intensity of the pre-edge feature was used to extract bonding properties of iron. The results of ash and other iron standards will be presented.

MARM 104

Adsorption of phosphate to surfaces for recovery from aqueous environments: Density Functional Theory (DFT) calculations

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Phosphorous is a finite resource required in large quantities for fertilization. Ultimately, phosphorous is dispersed in the environment where it both disrupts the biological balance and destroys aquatic ecosystems. Receptors to detect phosphorous in aquatic media and to recover it from solution are not easy to develop due to the interaction of the phosphate anion with water molecules forming hydrogen bonds, and because of the polyprotic nature of the anion. In this work we begin to study the affinity of dissolved phosphorous for surfaces with phosphate and phosphonate moieties. Electronic structure calculations were performed with Density Functional Theory to establish the change in Gibbs' free energy of the systems with free vs. bonded phosphates at pH 7. Both HPO_4^{2-} and $H_2PO_4^-$ were considered, and the surface was represented by phosphate species with and without methyl groups.

MARM 105

Determination of pesticide residues at the Food and Drug Administration using the QuEChERS extraction method in conjunction with liquid and gas chromatography

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The Food and Drug Administration (FDA) Regional Field Office, Northeast Region in Jamaica, NY includes a division that tests for the presence of pesticide residues in any food sample. The ReQuEChERS (Quick Easy Cheap Effective Rugged Safe) extraction process is combined with liquid chromatography/mass spectrometry (LC-MS/MS), gas chromatography/mass spectrometry with a mass selective detector (GC-MS/MSD) and gas chromatography mass spectrometry with triple quadrupole (GC-MS/QQQ) to serve this purpose. The procedure involves a series of selective acetonitrile extractions and centrifugations before the instrumental analysis that emphasizes linearity, precision and an estimate of the detection limit. The description of the experimental procedure and case studies will be presented.

MARM 106

Conformation and stability of a bacterial regulatory mRNA

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MTS2282 is a non-coding RNA, also known as B11, whose sequence is highly conserved throughout many pathogenic and non-pathogenic mycobacteria such as *Mycobacterium tuberculosis*. It is suspected that B11 acts as a regulatory RNA, possibly using a “small RNA” mechanism to mediate gene expression. However, due to its predicted conformation, it has been proposed that B11 may use a “riboswitch” mechanism to mediate gene expression. In a riboswitch mechanism, the presence of a ligand promotes a conformational change that enchances or inhibits gene expression. In order to understand how B11 contributes to gene expression, we want to characterize its conformation and stability, and subsequently test the effects of its presence in the expression of model genes.

In this work, we have used various spectroscopic techniques to characterize the conformation of B11. It is predicted that B11 forms a 6C motif, characterized by the presence of two cytosine rich hairpin loops. Our unfolding experiments (UV melts) show that B11 unfolds in three or four stages, depending on the conditions. This unfolding pattern suggests that B11 conforms to the predicted 6C motif (which should produce 2 transitions) with additional interactions between the stems or loops that result in the production of additional transitions. Our unfolding experiments also reveal that the RNA stability is increased in the presence of MgCl2 and NaCl, with the presence of Mg2+ ions producing one additional transition. Hence, our results suggest that B11 may adopt two different conformations, depending on the conditions. These results support the possibility that B11 may act as a riboswitch, in which the presence of a ligand promotes a switch from one conformation to another.

MARM 107

Imidazole as a novel and robust gold binding group at STM-BJ method

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Recent technological advances allow for the fabrication of single molecule electronic circuits. In particular, the Scanning Tunneling Microscopy based Breaking Junction method (STM-BJ) developed in 2003 provides reliable, reproducible generation and measurement of electronic properties of molecular circuits. In order to complete the circuit with gold electrodes, special gold atom binding groups are installed at the both terminals of organic compound of interest. Typical gold binding groups include amino, thiol, methyl sulfide, thiochroman and pyridine. To expand this toolbox, we plan to investigate the imidazole as a potential candidate for the first time. We have quickly synthesized a series of bis(imidazole) alkane compounds (Im-n-Im) by a one-step reaction. Their initial conductance measurements by STM-BJ method are very promising.

MARM 108

Porous microspheres of polyaniline and its derivatives prepared from W/O/W double emulsions

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We have developed a method to prepare highly porous microspheres of the conducting polymer polyaniline (PANI) and a selection of its ring-substituted derivatives. Briefly, a water-in-oil-in-water (W/O/W) double emulsion is generated when excess ammonium hydroxide is rapidly added to an acidic dispersion of the preformed polymer that contains a monomer such as *o*-toluidine or *m*-toluidine. These monomers are soluble in acidic solutions, but spontaneously form immiscible droplets in sufficiently alkaline solution. Spheres are formed when the granular polymer dissolves in the monomer droplets, and pores are formed by water droplets trapped in the polymer matrix. The amphiphilic monomer serves as a single small molecular surfactant that stabilizes both the oil-water and water-oil interfaces of the double emulsion, which is rare among W/O/W systems. The granular and spherical forms have nearly identical FTIR and UV-Vis spectra, indicating no differences in the molecular or electronic structure. However, SEM images reveal that the morphology is highly sensitive to the monomer concentration. Too little yields only granular particles and too much yields an oily product. The monomer may be unconsumed reactant from the polymer synthesis (e.g. *o*-toluidine in poly(*o*-toluidine)), or specifically added to a polymer dispersion (e.g. *o*-toluidine in PANI). We have investigated PANI and poly(*o*-toluidine) with a variety of monomers. Poly(*m*-toluidine), poly(2-ethylaniline) and poly(3-ethylaniline) are the subject of ongoing study. The simplicity and convenience of this method in combination with the unique electronic properties of the polymers suggest applications including electroactive microreactors, scaffolds for catalysis, and encapsulants for payload delivery.

MARM 109

Reduction and oxidation of 2,3-diaryl-1,3-thiaza-4-ones

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The products of the syntheses of 2,3-diaryl-1,3-thiaza-4-ones were used and elaborated upon by reduction and oxidation. Imines were created and recrystallized; the imines along with thioacids were used to make 2,3-diaryl-1,3-thiaza-4-ones. Oxidations of 2,3-diaryl-1,3-thiaza-4-ones were done with oxone to make the sulfoxides. Reductions were attempted to make 2,3-diaryl-1,3-thiazinanes. All results found to date will be presented.

MARM 110

Synthesis of tin complexes

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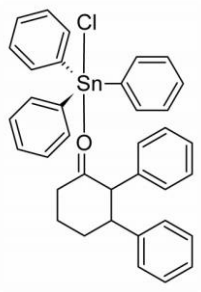
Complexes of triphenyltin chloride and a cyclic amide can theoretically be prepared by stirring the two in the presence of acetone under inert conditions such as gaseous nitrogen. The tin atom typically bonds to the amide oxygen and trigonal bipyrimidal geometry results. The sole sigma bond between the amide and triphenyltin chloride permits free axial rotation of the three phenyl groups. A complex of 2,3-diphenyl-3,4,5,6-tetrahydro-2H-1,3- thiazin-4-one and triphenyltin chloride was confirmed with x-ray diffraction but complications were encountered in subsequent attempts with 2,3-diphenyl-2,3-dihydro-4H-1,3-benzothiazin-4-one; x-ray crystallographic data indicated oxidation of the compound at the sulfur. The complexes also appear to degrade rapidly during heating and when migrated via thin layer chromatography, making crystallization and analysis particularly difficult. A new synthetic protocol has been employed in which the heterocyclic compound and triphenyltin chloride are stirred in cyclohexane under reflux. The procedure eliminated technical complications associated with previous attempts, in which reactants were dissolved in acetone separately and combined dropwise over a twenty-minute interval. Syntheses by this method with several 2,3-diphenyl-1,3-thiaza-4-ones have been completed, with crystals readily developing from the reaction solvent at room temperature. Nuclear magnetic resonance and x-ray diffraction results will confirm or deny the presence of tin complexes.



Generalized structure of the tin complexes. Synthesis results in a 1:1 adduct of Ph_3SnCl and the chosen compound.

MARM 111

Study of hydrophobic vs. hydrophilic componts of molecules in C_3 to C_{10} acyclic imise synthesis: An undergraduate research project

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The purpose of this research was a study to determine when the hydrophobic portion of molecules overrode the hydrophilic portion during symmetrical acyclic imide synthesis. Experiments were carried out from C_3 to C_{10}. The corresponding alkyl nitrile and alkyl carboxylic anhydrides were used. Reactions were catalyzed by silica sulfuric acid and were carried out at 80° C. The study used percent yield of the solid imide as a measure of whether the reaction went or not. The imide products were confirmed by a GC-MS comparison of the m/z value of the molecular ion to the molar mass of the imide. C_3 to C_6 had poor to moderate yields, ranging from 7.8 to 54.1% [C_3 19.0; C_4 50.2; C_5 7.8; C_6 54.1]. However, C_7 to C_{10} were at or near zero. The data clearly indicated the reactivity wall was at C_7. There results were consistent with previous work using a different set of reagents (amide, acid anhydride and acid chloride).

MARM 112

Targeted nanoparticles for pathogen-specific drug delivery

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We propose to encapsulate broad-spectrum antibiotics into pathogen-targeted polymeric nanoparticles to facilitate targeted drug delivery. Pathogen specific targeting is achieved by application of sugar-functionalized nanoparticles as drug carriers targeted for species-specific lectin binding. The *Pseudomonas aeruginosa* lectins, LecA and LecB, are two sugar-binding proteins distinct in structure, binding preference and involvement of biofilm formation in this pathogen. We will describe the presentation of LecA and LecB binding motifs on a series of polymeric nanoparticle cores and preliminary investigations of biological activity.

MARM 113

Quantification of the dimer formed from the reaction of p-phenylenediamine and 4-amino-2-hydroxytoluene during the hair coloring process with the use of a hair color accelerator

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Hair coloring is a very popular service in salons worldwide. Typical processing time for permanent hair color is at least thirty minutes, however, total processing time can be decreased with the addition of a hair color accelerating product. Hair color accelerating products are not frequently used as they are not required to process the color and increase the cost of supplies, but could potentially increase a salons revenue if the desired hair color could be achieved in less time. The effects an accelerating product can have on the coloring material itself, after being applied to the hair, were investigated. The major organic component of the dye (i.e. dimer compound) that is formed after coloring human hair was quantified using analytical techniques, including chromatography. Understanding more about the coloring process and the resulting organic components of the dye could progress hair dye formulations to be more efficient without sacrificing results.

MARM 114

S-oxidation of ortho-substituted-2-aryl-3-phenyl-1,3-thiazolidin-4-ones with Oxone®

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S-oxidation of *ortho*-substituted-2-aryl-3-phenyl-1,3-thiazolidin-4-ones with Oxone® was investigated and compared to *ortho*-substituted-2-aryl-3-cyclohexyl-1,3-thiazolidin-4-ones. For all eight compounds evaluated, selective oxidation to the corresponding sulfoxide was realized in high yields using 3 equivalents of Oxone® at room temperature. The corresponding sulfone was first prepared by oxidation with potassium permanganate. These novel sulfoxides and sulfones were then characterized by 1H and 13C NMR. Finally, the attempted preparation of sulfones using the "greener" oxidant Oxone® at high temperature was evaluated. The extent of sulfone versus sulfoxide formation was not only affected by the substituent of the C2 aromatic ring, but also varied significantly in many cases based on N3 substitution. Selectivities of the product sulfoxides and sulfones were quantified by isolation using thin layer chromatography.

MARM 115

Photochemistry of biacetyl*water complexes in argon matrices

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Complexes of water and biacetyl were isolated in argon matrices under vacuum. Infrared spectra of water, biacetyl, biacetyl*water complexes, and respective deuterated forms were then obtained. The matrices were irradiated using the filtered output of a mercury vapor lamp with short and long pass filters of varying wavelengths. Density Functional Theory (DFT) calculations of water, biacetyl, biacetyl*water complexes, and possible transition states were optimized with an aug-cc-pVTZ basis set and uM06-2X method. Frequency calculations were then computed on optimized geometries, and excited state (time-dependent DFT) calculations were performed on stable molecules and complexes. Frequencies of possible isotopomers were also completed for comparison with experimental data. The theoretical infrared spectra were then compared to experimental infrared spectra in order to further understand the transition and product species resulting from photochemical reactions of biacetyl and water.

MARM 116

Cation exchange of different phases of copper sulfide with Zn2+

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Cation exchange is an exciting tool for the production of new nanoparticle structures, including complex multicomponent structures through partial exchange. The rate of ion replacement for copper selenides has been found to vary with the degree of copper deficiency. We have been exploring the affect of copper sulfide nanocrystal structure (monoclinic and tetragonal Cu_2S) and degree of copper deficiency on the extent of ion replacement by carrying out slow, room temperature exchange reactions monitored by light absor. By doing such a long and slow exchange the progress of the exchange could be halted at different times thus producing particles with varying Cu:Zn ratios.

MARM 117

Assessing G-protein receptor induced cell signaling with dissipation monitoring of the QCM-D

***Yue Pan**, yp87@drexel.edu, Jennifer Chen, Lynn S. Penn, Jun Xi. Drexel Univ Chemistry Dept, Phila, Pennsylvania, United States*

G-protein receptor (GPCR) pathway has broad pharmaceutical and biological application due to its involvement in many cellular processes such as survival, differentiation and migration in many types of cell. The development of GPCR screening assays and understanding the mechanism of the GPCR pathways are the major focus of drug discovery research. We have developed a non-invasive real-time method using the quartz crystal microbalance with dissipation monitoring (QCM-D) to quantitatively monitor such cellular processes using the dissipation factor Δ*D*. Previously, we have successfully tracked real-time changes in cell adhesion due to induction of the EGFR pathway using the QCM-D. In this study, we monitored the GPCR pathway induced response using the QCM-D and to qualitatively and quantitatively assess GPCR induced cellular responses we utilized immunofluorescence microscopy.

MARM 118

Investigating the binding properties of green tea polyphenols with pancreatic amylase using UV/VIS spectroscopy

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Green tea has numerous benefits including the prevention of certain types of cancer and cardiovascular disease, but one benefit that has really peaked our interest is its role in weight loss. Green tea polyphenols are the main component behind the correlation of green tea and weight loss. This investigation studied the binding of green tea polyphenols with pancreatic amylase, a digestive enzyme released into the small intestine which breaks down starch into sugars. The binding was observed using a combination of UV/VIS spectroscopy and Autodock Vina. This docking software pinpoints the active sites in which binding occurs. Polyphenols were extracted from green tea leaves soaked in a 70/30% ethanol/water solution using supercritical CO2. After the ethanol was evaporated, polyphenol crystals were isolated and added to solutions of pancreatic amylase prepared in a pH 7.4 phosphate buffer. A detailed UV/VIS spectral analysis combined with docking results will be presented to confirm and characterize the interactions between pancreatic amylase and green tea polyphenols.

MARM 119

Rechargeable Zn-based battery: Next-generation (and safer) batteries are here!

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Rechargeable zinc–air batteries counter the disadvantages of Li-ion power sources (flammability, toxic components) by using an aqueous alkaline electrolyte while offering the potential of high power and energy density performance. For future success, these batteries have to overcome (*i*) dendritic growth at the zinc anode that prevents extended cycling and (*ii*) under-performing O_2-evolution during the charge step. At the NRL, we have solved the first by fabricating monolithic 3D zinc sponge architectures to uniformly distribute currents throughout the electrode structure and are addressing the second by synthesizing nanometric nickel-iron oxides of varying $Ni_yFe_{1-y}O_x$ composition and in different pore–solid architectures. We exhibit bifunctional O_2-evolution and O_2 reduction by incorporating cryptomelane MnO_x and $Ni_yFe_{1-y}O_x$ aerogels into a carbon powder–composite electrode to demonstrate rechargeability in air-breathing cells.

MARM 120

Synthesis and characterization of fluorescent dapoxyl dyes for luminescence-based sensing

***Christopher A. Ryan**, ryanch4334@gmail.com, James A. MacKay, Kristi Kneas. Department of Chemistry & Biochemistry, Elizabethtown College, Harrisburg, Pennsylvania, United States*

Dapoxyl dyes are environmentally sensitive fluorophores with unique electronic properties ideally suited for luminescence-based sensing. Electron-donating and electron-withdrawing groups conjugated through a 2,5-diphenyloxazole core afford a solvatochromic shift in emission wavelength in environments capable of stabilizing the triplet internal charge transfer excited state (TICT). Recently, a dapoxyl sulfonic acid (DSA) based relative humidity sensor utilizing an analyte-sensitive hydrogel scaffold with DSA suspended in its pores was reported. As the gel expands or contracts based on analyte concentration, the environment around the dye changes, altering its emission wavelength. While DSA worked well in the gas phase sensor, leaching of the dye from the hydrogel prevents its use in the aqueous phase. To overcome this limitation, we envisioned dapoxyl dyes with functionalized termini for polymerization into an acrylamide hydrogel.

Two dapoxyl dye analogues have been synthesized. These analogues contain an *N*-acrylamido attached to the dye via an electron-donating piperazine. Various electron-withdrawing groups were explored. The oxazole core was constructed using a Robinson-Gabriel oxazole cyclization. Piperazine was then coupled with an aryl-bromide via a Buchwald-Hartwig amination. Finally, the piperazine was acryloylated to give the polymerizable DSA analogues. Synthesis of a dapoxyl nitrile dye (DND) has been accomplished in 62% yield over 3 steps and the synthesis of polymerizable DSA analogues is being optimized.

The solvatochromic response of DND has been established in various solventsAt higher solvent polarity, solvatochromic sensitivity was decreased relative to solvents with lower polarity. This decreased solvent-sensitivity may be the result of the piperazine substituent preventing the molecule from entering the TICT excited state or the lower withdrawing effect of the nitrile compared to the sulfonate. To investigate, a diethylamino analogue of DND was synthesized. The solvatochromic response will be investigated and compared to DND. DND will be co-polymerized into a hydrogel to determine if its luminescent properties are retained.

MARM 121

Reconstruction of ancestral tumor necrosis factor-alpha: Protein activity and primate evolution

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Ancestral protein reconstruction aims to resurrect ancestral proteins from now-extinct species to directly measure protein functions *in vitro*. Tracking the changes in amino acid sequences along a phylogenetic tree, in addition to measurements of protein functions, can potentially reveal rich information about protein evolution. This study focuses on tumor necrosis factor-alpha (TNF-α), a pleiotropic pro-inflammatory cytokine. Abundant evidence suggests that TNF-α plays a key role in inducing several immune-mediated diseases that involve chronic inflammation; however, more knowledge about this protein is required in order to explain the pathogenesis of these diseases. Using gene sequences from 19 extant primate species (and a rabbit outgroup), we estimated TNF-α sequences for 19 ancestral nodes ranging in age from 10-60 million years before present, including the common ancestor of all primates. Ancestral sequences were inferred using Phylogenetic Analysis by Maximum Likelihood (PAML). In terms of the number of amino acid changes in TNF-α, we found out 1) overall, most putative changes in TNF-a occurred in terminal taxa, with significantly less evolution change occurring at ancestral nodes; 2) very little evolution of TNF-α happened during the first two bifurcations in primate history; 3) the amount of evolutionary change among all primates was largest (12-21 putative changes) at terminal branches in the *Ceboidea* and *Strepsirrhini*; 4) within the *Cercopithecoidea* and the *Hominoidea*, few amino acid changes (0-2) occurred at most ancestral nodes, whereas between 5 to 12 changes occurred on each terminal branch (extant species). Expression of ancestral TNF-α protein from the common ancestor of all primates using a cell-free transcription-translation system (TX-TL) was completed and the TX-TL product was purified. Ongoing work includes confirmation of the existence of the reconstructed ancestral TNF-α protein and functional assays for testing functional differences between select ancestral and extant TNF-α proteins. Results from this research study will offer insights into the evolution of the structure-function relationship of TNF-α and could expand our knowledge about cytokine activities in the complex immune system.

MARM 122

Effect of montmorillonite on the synthesis of biological polymers RNA surrogates

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This research focuses on the Origins of Life the hypothesis known as the RNA World. In this scheme RNA was present before proteins and DNA. One of the issues with this theory is the instability of RNA in an aqueous environment, which has led to the use of montmorillonite as a catalyst or scaffold for the assembly of the oligomers of the biological macromolecule. A computational approach was used here to explore the effects of the presence of the clay mineral using molecular mechanics implemented by the software package Spartan. A poly-adenosine chain was modified by replacing ribose with simpler sugars that have been shown to be more likely to be present in primordial conditions. The model was used to study both the periodicity of the structure, to determine matching features in the exposed montmorillonite surface, and the potential for bonding to occur between the chain and the surface through specific complexes.

MARM 123

Effect of the bridging ligand on bimetallic asymmetric ruthenium(II) complexes

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Complexes of the form, $[(bpy)_2Ru(BL)Ru(Cl)(tpy)]^{3+}$,where bpy is a bidentate terminal ligand 2,2'-bipyridine, tpy is the meridonal tridentate terminal ligand 2,2':6',2"-terpyridine and BL is a bridging ligand (i.e. 2,3-bis(2-pyridyl)pyrazine (dpp) or 2,2'bipyrimidine (bpm)), have been synthesized and purified. The complexes have been characterized with respect to their absorbance and electrochemical properties. Ideally, these complexes will also be screened for their ability to bind and photocleave DNA.

MARM 124

Investigation of cationic palladium NHC complexes toward Suzuki and Heck coupling

***Melissa Sebold**, seboldm@lafayette.edu, Roxy J. Swails. Chemistry, Lafayette College, Easton, Pennsylvania, United States*

A variety of cationic imidazolium complexes have been synthesized and utilized to form charged palladium complexes. These complexes were then examined as potential catalysts for Suzuki and Heck coupling reactions in aqueous and mixed solvent systems.

MARM 125

Chemical and electrochemical reactivity of pyridinium based imidazolium salts

***Allyssa Conner**, connera@lafayette.edu, Roxy J. Swails. Chemistry, Lafayette College, Easton, Pennsylvania, United States*

Cationic imidazolium salts were created in an effort to utilize them as ionic NHC supporting ligands and subsequently synthesize water stable and soluble organometallic complexes. Unlike related imidazolium salts these compounds did not readily form stable metal complexes. Their unique chemical and electrochemical reactivity will be discussed and compared to related pyridinium based ligands.

MARM 126

Construction of a His-tagged expression plasmid for production of sfnaB of the staphyloferrin A biosynthetic pathway

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Staphyloferrin A is one of two, iron-binding siderophores produced by *Staphylococcus aureus*. It is synthesized in three steps using SfnaC, SfnaD and SfnaB. SfnaB catalyzes the final reaction in the pathway and combines a citryl-D-ornithine intermediate with citrate to produce staphyloferrin A. The long term goal of this research is to develop SfnaB inhibitors thus preventing the production of staphyloferrin A resulting in reduced iron uptake. If successful, these inhibitors could be new therapeutic agents to battle bacterial infections caused by methicillin-resistant *S. aureus* (MRSA). The *sfnaB* gene has been amplified by polymerase chain reaction (PCR) and progress towards the construction of a His-tagged expression plasmid is presented. The structures of two proposed competitive inhibitors, a mono-citryl ornithine intermediate and a novel cyclic-citryl ornithine are also presented.

MARM 127

Design and synthesis of novel α-(piperazinylmethyl)cinnamates as inhibitors of *Pseudomonas aeruginosa* virulence

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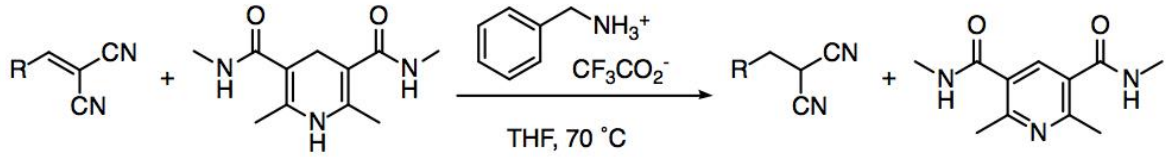
Baylis-Hillman reaction provides allylic alcohols and amines in a one-step transformation and it can lead to the generation of a large library of structurally diverse scaffolds. Piperazine derivatives display a wide array of biological activities and are recognized for their use as anti-parasitic, anti-depressant, anticancer and antimicrobial agents. Accordingly, we envisioned the synthesis of α-(piperazinylmethyl)cinnamate derivatives via Baylis-Hillman reaction. All the synthesized derivatives were screened for their *in vitro* anti-cancer efficacy as well as their antimicrobial activity against *P. aeruginosa*, *E. coli* and *S. aureus*. While most of the compounds tested did not show any significant cytotoxicity or antibiotic activity, some of these compounds exhibited potent inhibition of LasR quorum sensing in *Pseudomonas*. The poster will detail our synthetic and biological efforts in this project.

MARM 128

Hantzsch amide for transfer hydrogenation

***Robert Palkovitz**, rpalkovi@fandm.edu, Scott A. Van Arman. Franklin Marshall Coll, Lancaster, Pennsylvania, United States*

We have recently demonstrated that Hantzsch amides are effective transfer hydrogenation reagents for α,β-unsaturated ketones. Use of the Hantzsch amide is advantageous *vs* the well-known Hantzsch ester because it can be removed simply by extraction. Here we report the extension of this process to α,β-unsaturated propanedinitriles.



MARM 129

Synthesis and cytotoxicity of Baylis-Hillman template-derived benzoboroxoles

*Pathi Suman, Md. Ashiq Ur Rahman, Md. Reazul Islam, Heena Patel, Steven Schwartz, **Subash C. Jonnalagadda**, jonnalagadda@rowan.edu. Chemistry and Biochemistry, Rowan University, Glassboro, New Jersey, United States*

Boronic acids find applications in synthetic, medicinal, and materials chemistry because of their unique electronic and physicochemical properties. Benzoboroxoles are a sub-category of cyclic boronic acids and they have received wide attention owing to their structural stability and synthetic utility. Recently, a topical solution of 5-fluorobenzoboroxole (Kerydin®) was approved by the FDA for treatment of onychomycosis. Our long-standing interest in developing novel functionalized boron based compounds as therapeutic agents prompted us to further explore the utility of these scaffolds as potential anti-cancer agents. We have synthesized densely functionalized benzoboroxoles utilizing Baylis-Hillman reaction, Passerini reaction, aldol condensation, and reductive amination protocols as the key steps. The synthesized compounds were evaluated for their biological efficacy. Based on the initial SAR, we have identified few benzoboroxoles for further investigation as *anti*-cancer agents. The poster will describe our recent efforts on the development of benzoboroxole conjugates as therapeutic agents.

MARM 130

Chromatography analysis of flower extract and their application in dye-sensitized solar cells

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This study aims to characterize flower pigments that can be used to harvest solar energy. Natural pigments were extracted with acidified ethanol from various flower petals including Redbud, Cherry Blossom, Crabapple, and Peony . The pigments were purified with solid phase extraction (SPE) and characterized by UV-vis absorption spectroscopy, paper chromatography, thin layer chromatography-mass spectrometry (TLC-MS), and high performance liquid chromatography (HPLC). Our results showed that the flowers contained multiple anthocyanins such as Malvidin, Delphinidin, and Pelargonidin. The plant pigments were used to construct dye-sensitized solar cells (DSSCs). The voltage and current output of the DSSCs were measured. The correlations between the composition of plant pigments and the power output of DSSCs was investigated.

MARM 131

Effect of fatty acids on the binding of bilirubin to human serum albumin

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The current study utilizes fluorescence spectroscopy to investigate the effect of fatty acids binding of bilirubin to human serum albumin. Human serum albumin is an important protein in the blood which helps transport endogenous and exogenous compounds that have limited solubility in the blood. Bilirubin is an endogenous compound that is a byproduct of hemoglobin breakdown. It is a waste product that is normally transported in the blood by albumin to be excreted in bile or urine. Infants often experience jaundice which is associated with high levels of bilirubin in the blood. Bilirubin in infants can cause brain damage due to an underdeveloped blood brain barrier and the ability of bilirubin to cross that barrier because of its lipid solubility. Bilirubin when bound to albumin is less toxic because only free bilirubin is able to cross the blood brain barrier. Fatty acids are known to also bind to albumin and many infant fromulas are supplemented with fatty acids. Given that both bilirubin and fatty acids can bind to albumin, there is the potential for fatty acids to cause displacement of bilirubin from albumin leading to increased toxicity in jaundiced infants. The binding of bilirubin to albumin can be studied using fluorescence quenching. Binding of bilirubin to albumin leads to a quenching of tryptophan related fluorescence in the protein. The effect of the presence of the fatty acids, eicosapentanoic acid, docasahexanoic acid, and arachidonic acid on

the binding of bilirubin to albumin was examined using fluorescence quenching. The results of these studies will be presented.

MARM 132

Targeted genetic mutations to OmpA in *E. coli* and its effect on its susceptibility to the K3 virus

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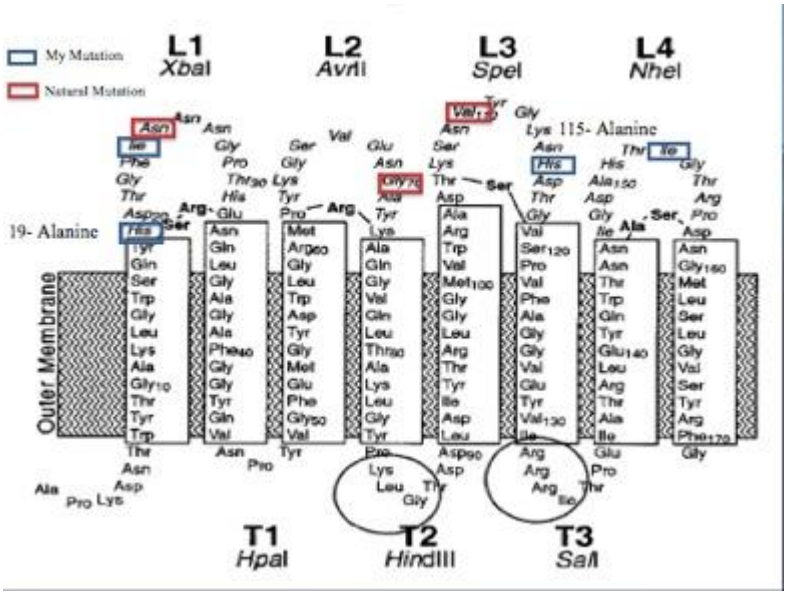
The outer membrane protein A (OmpA) in *E. coli* serves many function, including selective binding to sugars and small molecules, as well as serving as a phage receptor. OmpA has two domains, with the N-terminal domain (170 aa) made up of an antiparallel -barrel transmembrane region that forms four hydrophilic, surfaced-exposed loops. Extra-membranous loops often serve important functions in proteins. Earlier studies in the structure and function of OmpA explored the effects of deleting one or more of these transmembrane loops, particularly with regards to their interaction with several bacteriophages. One study demonstrated that the removal of loops 1, 2, or 3 was sufficient to prevent infection by the K3 virus, presumably because the virus interacts with the loops for entry. Another study demonstrated that naturally occurring mutations in loop two was sufficient to make E. coli resistant to K3 (naturally occurring mutations in the remaining loops had not effect). The aim of this study is to make specific, targeted mutations of single amino acids in loops one, two, and three in order to identify the specific amino acids in each loop that interact with the K3 virus. Mutations are induced using the FRUIT method (Flexible Recombineering Utilizing Integration of thyA).



MARM 133

Determination of the ionization constant of carboxylic acids using freezing point depression measurements

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Freezing point depression is a colligative property that is directly related only to the number, but not the nature, of particles (ions and molecules) in solution. For the first time, the ionization constant of a carboxylic acid is determined in a non-traditional method that does not require the titration of the acid with a standardized base solution. This project involves the use of thermal probes to determine the ionization constant of a carboxylic acid using the experimentally obtained value of the van't Hoff factor of their aqueous solutions as long as the K_a value is above 10^{-3}. The ionized portion of the solute is measured through a derived equation that corresponds to the freezing point depression temperature. The measured K_a values of various carboxylic acids were determined at various concentrations. The experiment is fast, uses extremely low concentrations of the solute, and the results are easily and infinitely reproducible leaving very little waste.

MARM 134

Determination of the total amount of oxygen consumption in effluent via carbonaceous biochemical oxygen demand (CBOD) and biochemical oxygen demand (BOD)

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Water from showers, rain, melted snow, and sidewalk washing travels into a whole new world through a remarkable series of pipes in the New York's City sewer system, the DEP (Department of Environmental Protection). This is a wastewater treatment plant system that removes most of the pollutants from wastewater before being released. One of the most commonly measured constituents of wastewater is the **Biochemical Oxygen Demand (BOD) which** is the amount of dissolved oxygen required for aerobic microorganisms (found in sewage) to decompose the organic matter in the wastewater. It measures the degree of pollutants by identifying the decrease of dissolved oxygen the bacteria need. If more oxygen is consumed than produced, the DO (dissolved oxygen) value will decrease and some aquatic life forms will either weaken, migrate to a different location or die. This test is used by government agencies to determine how efficient their plants are and how effluent (released water from treatment plant) will affect receiving water. The Carbonaceous Biochemical Oxygen Demand (CBOD) follows the same procedure as the BOD but measures the inhibition of the nitrifying bacteria in the sample. Nitrifying bacteria consume nitrogenous materials (compounds with reduced forms of nitrogen) and add to the oxygen demand of the wastewater. The methods and procedures will be presented along with the importance of testing BOD/CBOD in the wastewater treatment facility.

MARM 135

Determination of the total amount of antioxidants present in commercially available beverages via the Folin Ciocalteau microspectrophotometric analysis

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Antioxidants are nutrients whose mission is to quench the formation of cell impairment by neutralizing free radicals in our bodies. They are found in various fruits, vegetables, plants and juice beverages and perform a role in the prevention of several illnesses and potential acceleration delay of the aging process. Free radicals are electron deficient species that fulfill their octet by seeking an electron from neighboring atoms. Antioxidants come into play by donating electrons to satisfy this process, thus avoiding the possibility of cell damage. The wine industry uses the Gallic Acid Equivalent method to determine the total amount of antioxidants present in an aliquot. The technique uses the Folin Ciocalteau method whereby a phosphomolybdate/phosphotungstate complex oxidizes gallic acid, which is used as a reference, into the corresponding quinone. The preparation of a standardized gallic acid calibration curve allows the microspectrophotometric (visible light) determination of the total amount of antioxidants present in any liquid sample. The data obtained for various types and brands of tea and juice beverages will be presented and the semi-quantitative measurement of gallic acid decomposition with time will be evaluated.

MARM 136

Ultem thermoplastic-based 3D-printed orthoses: A comparative study on the efficacy of using polymer-based 3D-printed orthoses

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Individuals with neuromuscular disorder face serious limitations in performing basic functions such as eating and picking up small objects. Exercise and the use of orthoses are the common remedies for such conditions. Recent technological developments have dramatically improved the effectiveness of the orthosis treatment.
The objective of this study was to determine if the 3D-printed custom orthoses based on the Ultem thermoplastic material were as effective as the traditional orthoses and if they can be produced for a lower cost. Ultem thermoplastic is a polymer material and the 3D-printing runs on FDM technology which allows the building of parts layer-by-layer from the bottom up by heating and extruding thermoplastic filament.
Six subjects (ages 40-72) participated in the study. The subjects' dominant hand was scanned using the 3D laser scanner and the images were processed using Autodesk MeshMixer software and 3D-printed using a FORTUS 3D printer. The subjects performed 11 timed assessments for manual and finger dexterity using both types of

orthoses. An average of three trials was taken for data analysis and was followed by an immediate comparative questionnaire that was administered to the subjects.
Results show that the order in which the dexterity assessments were performed (3D-printed first or traditional first) had an impact on the time taken to perform the tests ($p<0.05$). The subjects performed the tests faster with the orthosis they tested later perhaps because they became more familiar as the assessments progressed. However, the time taken to perform the tasks was comparable for both orthosis types ($p>0.05$). Subjects reported a greater comfort with the 3D-printed orthoses emphasizing the greater wrist support. Therefore, 3D printed orthoses were at least as effective as traditional orthoses. The material cost to print each 3D orthosis, on average, was $39.52 compared to the $26.99 for the commercially available brace.

MARM 137

Determination of the antioxidant gallic acid in commercial beverages via High-Performance Liquid Chromatography (HPLC)

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Oxidative processes in our bodies produce free radicals, which may cause harm to our otherwise good health. Phenolics have potent antioxidant properties that can help prevent diseases that are related to oxidative stress. Juices with high levels of antioxidants can serve this purpose. Gallic acid has the ability to quench radicals by providing radicals with electron(s) that will convert them to species that obey the octet rule thus, inhibiting the oxidation of biomolecules. As a result it is used as the standard measure of antioxidants in the wine industry. High Performance Liquid Chromatography (HPLC) is employed to separate, identify and quantitatively measure components present in a liquid sample using a particle packed column and solvent(s) under high pressure of up to 400 atmospheres. Several known standard concentrations of gallic acid are first tested via HPLC to create a calibration curve that helps measure the exact quantity of monomeric gallic acid present in commercial juices. A gallic acid content comparison of several beverages will be presented.

MARM 138

Aluminum complexes of redox-active ligands

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Aluminum is a highly abundant and inexpensive metal. The development of aluminum complexes supporting new functionalities and reactivity profiles is therefore desirable and serves a significant challenge to green and sustainable chemistry. However, the use of aluminum coordination complexes for the activation *and* redox transformation of small molecules has not been well developed. This is because aluminum chemistry has been defined by the stability of the +3 oxidation state. The lack of readily accessible multi-electron redox states for common aluminum complexes has limited their applicability for processes that depend on oxidative and reductive chemistries. The development of aluminum coordination complexes implementing redox-active and non-innocent ligands aims to expand the reaction portfolio of aluminum compounds. We have been developing families of coordination complexes of aluminium with redox-active ligands and have studied their electronic structures using spectroscopy, X-ray diffraction, electrochemistry, and theory. We will present our newest results in this area focusing on two ligand platforms: a-diimines and nitroxides.

MARM 139

Novel strategies for amide bond synthesis

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The coupling of a carboxylic acid to an amine to form an amide bond is a powerful and widely used methodology for the construction of complex molecules. Here we describe our research focused on the development of two novel strategies for the synthesis of amide bonds. The first involves the application of a novel organoboron catalyst to aid in amide bond formation from traditional starting materials. In the second project, we describe the synthesis of amide bonds from methyl ketones, a non-traditional starting material for this bond construction.

MARM 140

Modeling resonant energy transfer in hybrid nanoparticle/molecular systems

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Hybrid nanoparticles that include noble metal nanoparticles have been a main focus for light initiated generation of energetic carriers for solar energy conversion since the noble metal nanoparticles can accommodate localized plasmon resonances, oscillations of conduction electrons along the surface of the nanoparticle, which makes them ideal for manipulating light flow. We will describe hybrid nanoparticles that are comprised of a dielectric core, which can trap light along the surface, and is surrounded with noble metal particles that can absorb thr light that is trapped by the dielectric core. The properties from the dielectric core slows down the light in the nanoparticle which can induce the phenomena of scattering mediated absorption. Scattering mediated absorption occurs when the dielectric core traps some of the light which propagates in the structure instead of simply passing through the particle. The trapped light can then be utilized to generate hot carriers even in the absence of plasmon resonance, even in low intensities of light.
Rigorous electrodynamics calculations were performed to elucidate the relationship between the size and position of the noble metal nanoparticles on the energy and intensity of scattering mediated absorption. A new model will be developed to solve the Time Dependent Liouville Equation using a density matrix that replicates the energy transport between hybrid nanoparticle donors and small molecule acceptors over time. We will describe our use of this model to understand what conditions maximize energy transfer between the nanoparticles and will allow for other uses of the energy harvested by the light scattering in the hybrid nanostructure.

MARM 141

Determination of the ionization constant of carboxylic acids in mixed solvents using microscale freezing point depression measurements and the van't Hoff factor

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The ionization constant (K_a) is a constant value used to determine the strength of an acid. The traditional method of calculating it involves titration with a strong base and an indicator. A new method has been established using microscale freezing point depression measurements and the van't Hoff factor (*i*). This alternate method involves a newly derived formula that correlates *i* to the ionization constant. The calculation of a newly derived K_f value for mixed solvents enables the calculation of K_a in such media. The project has involved four carboxylic acids ($K_a > 10^{-3}$) using various concentrations in several aqueous/organic solvent mixtures. This method is easily reproducible and produces little waste.

MARM 142

Comparison of iron and zinc distribution within a plant

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Both iron and zinc are important mineral humans need. Green leafy plants provide both these minerals. However, amount and distribution of these two minerals depend on the type of plant. We used synchrotron X-ray absorption to investigate distribution of iron and zinc within a plant leave. Tissue samples from different areas of a plant leave were collected and prepared for X-ray absorption experiment. The absorption coefficient of X rays was measured at the vicinity of iron and zinc k edges. The main absorption peak height is proportional to the amount of the specific element and energy position depends on the charge state of the compound. The results obtained for both iron and zinc will be presented.

MARM 143

Investigate iron content and structural properties in *Centella asiatica*

***Udya Dewanamuni**, udya29@gmail.com, Sunil Dehipawala. Physics Dept, Queensborough Community College, Bayside, New York, United States*

Centella asiatica is considered as very nutritional leafy vegetable in countries such as Mynamar, Sri Lanka, Bangladesh, Vietnam, and Thailand. It contains essential minerals such as iron and zinc. We used synchrotron X-ray absorption to investigate properties of iron in Centella asiatica. The X ray absorption spectra were collected in fluorescence from several different samples and standards for comparison. The height of main absorption edge provide relative amount of iron presence in a sample and edge is sensitive to the electronic environment of iron atoms. The amount of iron present is compared to the other iron containing plants.

MARM 144

Use of x-ray absorption pre edge intensity in structural investigation

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In typical x-ray absorption spectra of iron containing compounds exhibit small absorption feature before the main absorption edge. This feature provides valuable structural information about the absorbing atom. It is well known that this feature is due to electronic transition from 1s to 3d. Under normal conditions this transition is forbidden but allowed when iron atoms exists next to oxygen atoms. We explored this pre edge in several different iron compounds with different site symmetries and use outcomes to extract structural properties of iron in plant tissue samples.

MARM 145

Computational study of the atmospheric decomposition and combustion of 2-Ketohept-n-oxy radical

***Connor Protter**, cprotter@fandm.edu, Alexander C. Davis. Chemistry, Franklin and Marshall College, Lancaster, Pennsylvania, United States*

Ketoalkoxy radicals are an important intermediate in both the combustion and atmospheric oxidation of volatile organic carbons (VOC). They are produced by successive oxygen addition to alkyl and alkoxy radicals in the presence of HO_x and NO_x. In this study, the unimolecular isomerization and bond scission reactions of 2-Ketohept-n-oxy radical (where n=1, or 3-7) are investigated using the Gaussian 09 suite of programs. Initial geometries are determined by optimizing all possible configurations at the B3LYP/6-31+G(d,p) level. The lowest energy structures are then refined with geometry optimizations and frequency calculations at B3LYP/6-311++(3df,3pd). Finally, the CBS-QB3, G3 and G4 composite methods are use for their reported accuracies of ~4 kJ mol^{-1}. Initial results suggest that intramolecular H-bonding and the presence of the ketone group have a significant impact on the kinetic and thermodynamic parameters for these reactions, as compared to alkoxy radicals.

MARM 146

Development of HPLC lab for undergraduate students to learn instrumental analysis in a research setting

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Students tendency to compartmentalize knowledge and skills prevents them from drawing from then when needed outside the environment they acquired the knowledge from. This phenomenon is well observed among chemistry student. In this report we created a series of laboratory project based on problem based learning to help students improve their critical thinking and also decompartmentalize the information acquired throughout their academic career. We created three rotation experiments using a single sample type. Each rotation required the student to understand the instrumentation available to them prior to drafting a procedure and performing the experiment. The different experiment were created around GCFID, UV-HPLC, UV-VIS, H-NMR, ATR-FTIR, Redox titration All using edible oil as the analyte

MARM 147

Study of basil growth and nitrate removal at various pH levels in a hydroponic system

***Emily Bohn**[2], emilybhn6@gmail.com, Lochlain Lewis[2], Janet A. Graden[1]. (1) Chemistry, Montgomery County Community College, Pottstown, Pennsylvania, United States (2) Sustainability Hub, Montgomery County Community College, Pottstown, Pennsylvania, United States*

Over the course of the setup and stabilization of an aquaponics system many systems show varying pH levels in the system due to the growth of a nitrification cycle as well as variations in source water and system temperature. The purpose of this study was to more fully understand the effects of various pH levels in aquaponics systems though the measurement of basil growth and nitrate levels in a hydroponic system using aquaponics source water. In the study aquaponics source water was maintained in four different growing systems with pH levels ranging from 5.5 to 8.5. Basil productivity was measured through plant growth, root health observation, root weight, and nitrate levels. The results discussed will serve as the basis for determining the pH requirements for optimal plant growth in hydroponics and aquaponics systems.

MARM 148

Development of open source sensor systems for reporting and storing water chemistry readings in an aquaponics laboratory

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Polling of regional academic programs in aquaponics and hydroponic research reveals a reluctance to adequately track and record water chemistry data. It is likely that managers, researchers, and students involved in studying sustainable growing systems overlook recording water chemistry data as a tedious and insignificant parameter of sustainable growing techniques. A hardware and software design for collecting and recording water chemistry using low cost, reliable open source hardware will be presented. When combined with adequate database support the system offers the development of a comprehensive, reliable database that can be used in the classroom in cross-discipline study and analysis of current and historic system specific events. The system can be used to assist researchers in developing solutions to current problems and predicting outcomes of experiments where water chemistry plays a critical role.

MARM 149

Development of stand-alone hydroelectric generation systems capable of supplying energy to water chemistry systems in isolated environments

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A need exists for an isolated water chemistry testing system that derives power from the river that is being monitored. The placement of the water quality system and its generator should be located beneath the surface of the river. This placement allows the system to function while remaining unobtrusive to boating traffic, river visitors, and wildlife. The design for a low cost low maintenance hydroelectric generation system will be presented. The data collected from such a system can be used to further the understanding of the water quality and health of river ecosystems.

MARM 150

Selenium dioxide oxidation of n-alkylated-1-benzazepines to quinoline

Michelle Qu[2]*, mqu74@tigermail.qcc.Cuny.edu, Sasan Karimi*[2]*, Shuai Ma*[1]*, Gopal Subramaniam*[1]*. (1) Department of Chemistry and Biochemistry, Queens College CUNY, Flushing, New York, United States (2) Department of Chemistry, Queensborough Community College, Bayside, New York, United States*

We are investigating the oxidation of several N-alkylated and 3-alkylated 1-benzazepines in order to make functionalized derivatives that can be tested for their pharmacological potential. In this quest, we recently reported oxidation of 3*H*-1-benzazepine and its 3-methylated derivative using NBS and selenium dioxide. In the case of NBS, initial oxidation was always at C3, but selenium dioxide gave products resulting from oxidation at either C3 or C5. Using the strategy reported for converting 3*H*-1-benzazepine to N-alkylated and 3-alkylayted 1-benzazepine, we plan to subject N-methyl, N-benzyl, and 3-benzyl 1-benzazepines to oxidation with selenium dioxide to understand the mechanistic aspects of the oxidation.

MARM 151

New synthesis of pyrroles using the Cadogan approach

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The Cadogan-Sundberg synthesis of indoles and carbazoles involves deoxygenation/cyclization of *o*-nitrostyrenes or *o*-nitrostilbenes with trialkyl phosphite. For example, *o*-nitrostyrenes and beta-nitrostyrenes are converted to indoles and 2-nitrobiphenyls to carbazoles using a reducing agent which produces either a nitrene or a nitroso intermediate. This method of indole synthesis is similar to that of the Leimgruber-Batcho approach except there is no need to prepare a dinitrostyrene before reduction, thus avoiding an extra step. The aim of this research project is to investigate if the available methods for preparing indoles and carbazoles, from nitro compounds, are also applicable to the synthesis of pyrroles. We were able to prepare substituted pyrroles from nitrodienes using triphenylphosphine in one step. The yields are low, but can be enhanced using an Mo catalyst, bis(acetylaceto)dioxomolybdenum (VI). DFT calculations show that the reaction probably goes through a nitrene intermediate.

MARM 152

Examining the interactions of green tea polyphenols with pancreatic lipase using UV/VIS spectroscopy

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Green tea leaves and supplements are thought to have beneficial health effects and have been used for the treatment of certain cancers, for the prevention of cardiovascular disease, and to promote weight loss. In this study, the anti-obesity properties of green tea and green tea supplements were studied by examining their binding properties with pancreatic lipase, an enzyme found in the human body involved in the breakdown of fats. Extracted polyphenols from green tea leaves and green tea supplements were combined with pancreatic lipase in a phosphate buffer and UV/VIS spectra were acquired. Spectra of pancreatic lipase, combinations of lipase and the contents of various green tea supplements, and lipase and extracted polyphenols from green tea leaves were compared. Solutions of extracted polyphenols (2.00 X 10^-5 M) and lipase had the most enhanced absorption when compared with solutions of lipase (λmax =273 nm). Results from this study will be used to develop an instrumental analysis lab protocol which will involve the extraction, characterization, and binding properties of green tea polyphenols.

MARM 153

Scattering mediated absorption in photonic crystals

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Scattering mediated absorption is a phenomena that occurs in hierarchical nanoparticles with a dielectric core nanosphere decorated with metal nanoparticles on the surface. Due solely to the physical properties of this composite nanoparticle, metals have sharp absorption peaks that they otherwise would not outside of this composite structure. This phenomena occurs regardless of whether the metal undergoes resonant absorption inherently. This allows one to use any type of metal in this hybrid nanoparticle for applications that otherwise were dependent upon the use of plasmonic metals.

Our recent research has also shed light on the fact that these hierarchical nanoparticles continue to produce hot electrons over longer periods of time compared with a metal nanoparticle alone. This is because the dielectric nanosphere causes light to travel in modes dependent upon its diameter, whereas a solitary metal nanoparticle has no mechanism of keeping the light in its vicinity. It was also discovered that by simply changing the diameter of the dielectric core, one can alter the duration of generation of hot electrons, and the probability of exciting the hot electrons in the metals.

Our current research aims to continue by creating a photonic crystal of these hierarchical nanoparticles, which potentially may allow for more control over the hot electrons generated and the duration of their generation. It may also allow us more freedom in the selection of materials to use in the photonic crystal, by using different metals, plasmonic and non-plasmonic for instance, to be used in tandem, or perhaps even different dielectrics in the same photonic crystal.

This presentation will address how arranging hierarchical nanoparticles into photonic crystals can allow control over the lifetimes of hot electrons generated in the metal of the hybrid nanoparticles. This presentation will also discuss the opportunity to design new structures that allow us to more easily and with more control generate hot electrons that can be transferred to nearby molecules to illicit chemical reactions.

MARM 154

Poster session: Teaching strategies with a window to the history of chemistry

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This presentation focuses on how poster sessions can be used to teach undergraduates awareness of the history of chemistry and the importance of precise reporting scientific facts to preserve the integrity of science history. At Columbia University we have created a student-centered laboratory course that involves nine weeks of verification experiments and a three-lab period independent research project. We have substituted the traditional final examination by a poster session that takes place at the end of classes. Originally, the poster session was intended to raise awareness of the history of chemistry; therefore, we selected themes according to particular events related

to twentieth century chemists. Gradually, we introduced the discovery of new materials and their relation to national historic chemical landmarks. Within these sessions, we have commemorated 75 years of Nylon industrial production, twenty years of fullerene research, and twenty-five years of carbon nanotubes. Last semester poster session highlighted the debate that arose when the 2010 Physics Nobel Prize Scientific Background authors were prompted to review inaccuracies regarding the discovery of graphene.

MARM 155

Chemical technologies in antiquity

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Chemistry was so intimately involved in the rise of civilization of that a whole range of chemical technologies that had their roots in antiquity are still part of modern civilized societies. A symposium on this topic was sponsored by the Division of the History of Chemistry (HIST) at the Spring, 2015 ACS National Meeting in Denver, and recently published as an ACS Symposium Series Volume. This paper will highlight topics from the book dealing with the development of ceramics and glass, organic and inorganic pigments, metals and alloys, soaps and perfumes, and fermented beverages. It was this purposeful manipulation of matter that developed out of the need to survive and thrive that ran parallel to, and indeed supported, human achievement. Shifts from small hunter-gatherer communities to agrarian societies to the rise of full-fledged empires all owe their origins to concomitant shifts in the way that natural materials were chemically transformed into more and more useful items.

MARM 156 Withdrawn

History of the dyes through the centuries

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Ever since the early stages of human civilization the addition of color was involved in defining status and embellishment. The first dyes after charcoal, were isolated from natural sources, such as vegetables, fruit, shells and animals. The development of both inorganic and organic chemistry has exponentially increased the variation of both natural and artificial dyes. A survey of the history of dyes through the centuries starting from several millennia BC up to today will be presented in a date sequence and will be correlated to the various dynasties and cultures. A series of related books and sources will also be available.

MARM 157

Herbal and chemical cures: Where chemistry meets the occult in 17th – 19th century Pennsylvania Dutch cure books

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Recipes using freshly prepared lead acetate from gunshot as a styptic to staunch bleeding exist side-by-side with the recital of magic words or the oft-repeated reading of *Ezekiel 16:6*. Copper sulfate douches treat bacterial infections of the skin but so does the use of mystic sing-song charms…"Wildfire and dragons fly over my wagon…" Roasted raw zinc carbonate ore yields zinc oxide which is then suspended in wine and used as an eyewash to treat vision problems in horses. However, at the same time the farmer is advised that the best days to administer this cure are the third, fifth, and seventh days after the new moon. Extract of periwinkle disinfects the bite of a mad-dog but "Put thy nose to the ground, hound!" prevents the bite from happening in the first place. Pocket-sized texts – most having Old World roots – became commonly available to Pennsylvania German farmers beginning about 1700. The English called such books *domestic physicians* but to the German community they were *Pferd Artz* and *Haus Artz* and in some cases mere ownership of the book blessed its user with occult powers. The consolidation of chemistry, charms, cures, and culture for healing man and beast in the early Pennsylvania German immigrant community will be reviewed as will the specific texts which are part of that tradition.

MARM 158

Joseph Priestley House: A postal history

John B. Sharkey*, johnbsharkey@me.com. Chemistry, Pace University, New York, New York, United States*

The correspondence of Joseph Priestley, a prolific letter writer, survives in various collections throughout the United States and England. Although Priestley lived in his house in Northumberland PA for a mere ten years, his legacy lives on with the many scientific meetings that have taken place there over the past century and a half. This paper will review these meetings, and will investigate the philatelic documentation for many of these meetings,

including some of Priestley's early correspondence. As a chemist, philatelist and postal historian, the author has found this topic to be a very interesting area of exploration.

MARM 159

Science history: A guide for actual and armchair travelers

***Mary Virginia Orna**, maryvirginiaorna@gmail.com. Chemistry, The College of New Rochelle, New Rochelle, New York, United States*

This talk will highlight a newly-published ACS Symposium Volume that is a science travelogue designed and narrated by experts. Travel to London and walk its alleyways in the expert hands of Peter Morris, long-time curator of chemistry at the London Science Museum. Learn how the Scots invented oh! so many things such as the steam engine and television, as told by former Director of the Royal Scottish Museums and present Director of the Chemical Heritage Foundation, Robert Anderson. Travel on to science sites in Germany, Italy, France, Scandinavia, Russia, and farther afield to China, Peru, and Mexico. There's plenty of bang for the buck in this book!

MARM 160

Solvation and proton transfer in diethylaminohydroxyflavone

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4'-N,N-diethylaminohydroxyflavone (DEAHF) is a fluorophore which undergoes an excited-state intramolecular proton transfer (tautomerization) reaction following absorption in the visible. The progress and equilibrium state of this reaction can be probed by examining its fluorescence spectrum, consisting of 'normal' and 'tautomer' bands, using time-resolved and steady-state fluorescence methods. Prior studies of DEAHF have indicated that the equilibrium constant and proton transfer rates are highly sensitive to both solvent polarity and hydrogen bonding, which has made DEAHF promising candidate as a ratiometric sensor of such solvent properties. The separation of the effect of solvation dynamics and solvent polarity on the fluorescence of DEAHF has been difficult, since simply changing the solvent will change both polarity and solvation time.

Here we report on steady-state and femtosecond Kerr-gated emission measurements of DEAHF in mixtures of acetonitrile and propylene carbonate. This mixture was chosen due to having nearly constant polarity across all mixture compositions while having solvation times that differ by approximately and order of magnitude. We find that the proton transfer rate is retarded by fast solvation, suggesting an unusual coupling between solvation dynamics and proton transfer in DEAHF. This curious result has been explained based on the placement of the Franck-Condon state on the excited-state potential energy surface. For solvents in which electrostatic coupling between the solvent and solute is minimized, such as *n*-alkanes, we find no dependence of reaction time on viscosity, indicating that the effect is due to solvation dynamics and not solvent friction.

MARM 161

Dynamic fluorescence measurements of Rose Bengal photooxidation

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Rose Bengal (RB) is a halogenated fluorescein dye that is an efficient absorber that has a high intersystem crossing quantum yield. Consequently, it is an efficient photosensitizer and is the focus of extensive research to work out the kinetic details of the reactions that occur during photodynamic therapy [PDT]. Since RB is readily excited to the triplet state, a typical reaction is the generation of singlet oxygen [$^1O_2$] by energy transfer from the photosensitizer in the first excited triplet state to molecular oxygen in the triplet ground state. While RB photosensitization has been studied in homogeneous solvents and buffers, it has not been studied as extensively in bio-relevant, microheterogeneous media.

In this investigation, the light-induced degradation of RB in octanol is monitored using wavelength- and frequency-resolved fluorescence spectroscopy. Octanol is a solvent that is commonly used to model the hydrophobicity of biological systems in experimental and computational studies. Fluorescence emission-decay (time- and frequency domain) measurements are amenable to numerical analysis and show great potential to provide greater insight into complex systems than their steady-state counterparts. The evolution of the spectra and emission decays of RB and its fluorescent photooxidation products during photoirradiation are described.

MARM 162

Whither reduced flavin fluorescence? The case of the disappearing emission quantum yield

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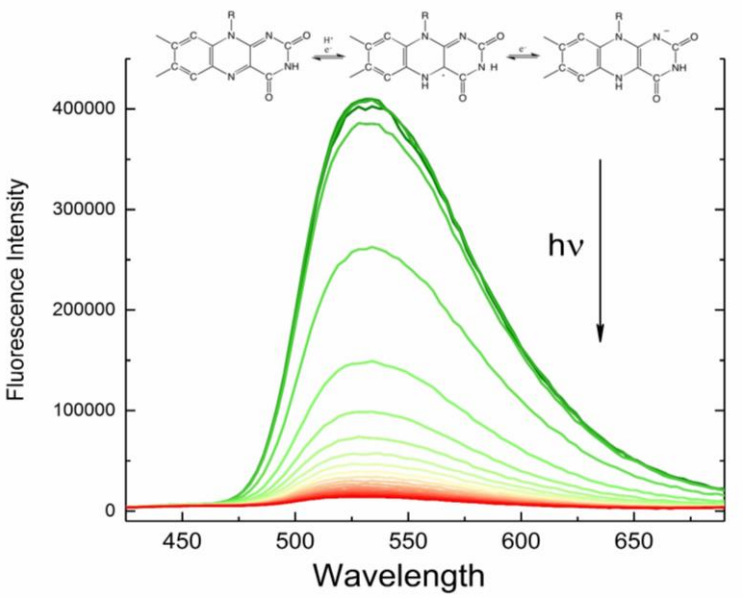
Flavins are ubiquitous enzyme cofactors. They are also highly fluorescent and have been used as endogenous fluorophores in bioimaging. While the emission quantum yield of the oxidized form is relatively high, the one electron-reduced semiquinone is non-fluorescent. Flavins commonly undergo two electron reduction (e.g. FAD → $FADH_2$ or $FADH^-$, the hydroquinone or hydroquinone anion respectively) in the presence of substrates or the coenzyme NADH. In particular, this combination of cofactor and coenzyme is a common motif in metabolic proteins found in mitochondria. The question about whether the hydroquinone form is emissive is of significance because of the power to image the "redoxosome" in real time. Generally, the hydroquinone forms are considered non-emissive, but there is no real measure of the emission quantum yield for $FADH_2$ or $FADH^-$. Here, we report on accurate upper limits of these yields and elaborate on the prospects of imaging changes in flavoprotein redox states in cells.



Photoreduction of FAD in the presence of EDTA.

MARM 163

Evaluation of effect of gold and silver nanoparticles on luminol chemiluminescence

***Caitlin Kurey**, ckurey@m.marywood.edu, Kuntal Patel, Jordan Vossler, Mary Lynn Grayeski. Science Department, Marywood University, Scranton, Pennsylvania, United States*

The effect of silver and gold nanoparticles on the chemiluminescent reaction of oxidation of luminol by hydrogen peroxide is evaluated for potential development of analytical measurements. Both gold and silver strongly enhance the chemiluminescence. Consistency of the effect varies based on the types of nanoparticles and added metal catalysts. This is primarily due to the differences in the kinetic profiles observed for different conditions. This enhancement can be explained due to a catalytic effect. This effect is examined in the presence of various metal ions for changes in chemiluminescence intensity and kinetics. Enhancement is observed in the presence of cobalt, iron, and copper with cobalt exhibiting high initial intensities but the use copper resulting in high average intensities. Kinetic characteristics will be discussed as they relate to analytical measurement implications.

MARM 164

Interaction of curcumin with berberine hydrochloride in nanoemulsion

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Curcumin, a phytochemical, has various pharmacological uses so also is berberine hydrochloride, a phytochemical alkaloid. These chemicals are extensively used in many bodily ailments, ranging from cancer to anti-inflammation. However, these compounds are quite insoluble in aqueous systems but are liberally soluble in nanoemulsion. Nanoemulsion is a nano-sized oil droplet this is dispersed in water using a surface active agents (surfactants). An investigation of the interaction between these pharmacologically important compounds was carried out in this medium using a steady-state fluoresce spectroscopy. Based on the observed data it was observed that the interaction led to the quenching of curcumin fluorescence with a quenching constant of 2.9 x 10-11/s and an interaction constant of 2.14 x 1103. Using Forster equation, the interaction distance between these reacting molecules is calculated as about 40.0 Å

MARM 165

New insights into an old problem: Fluorescence quenching of sterically-graded pyrenes by tertiary aliphatic amines

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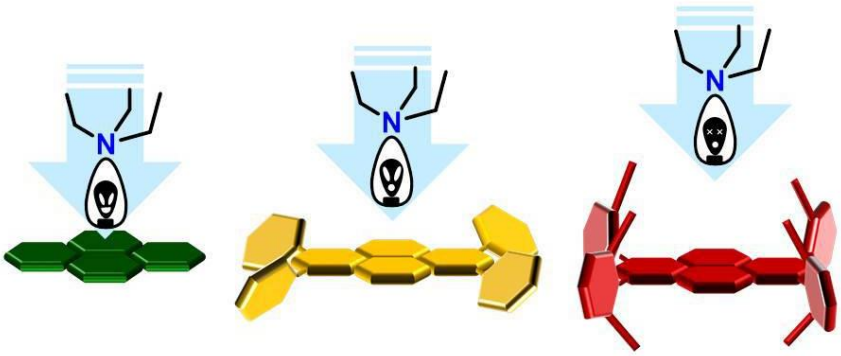
Steric interference and conformational mobility are known to influence directly charge- and electron-transfer reactions. However, judicious analyses of these effects based on experimental data have been unable to discriminate between competing steric and electronic factors. To unravel some of the complexities, fluorescence from three electronically related aromatic molecules—pyrene, 1,3,6,8-tetraphenylpyrene (TPPy), and 1,3,6,8-tetrakis(4-methoxy-2,6-dimethylphenyl)pyrene (PyOMe) which differ in accessibility to the pyrenyl core—was quenched by a structurally diverse set of tertiary aliphatic amines. Correlations among the quenching rate constants have been explored in terms of both steric factors and electronic properties of the amines and the pyrenes (e.g., sizes, shapes, conformational labilities, excitation energies, and oxidation or reduction potentials). By employing sterically graded pyrenes with similar electronic properties, it has been possible to separate steric and electronic influences more clearly and make quantitative assessments of the orientation of and distance between the lone-pair of electrons of an amine and the π-system of an aromatic singlet-excited state.



MARM 166

Solvatochromic response of benzo[a]fluorenone in aprotic solvents compared to benzo[b]fluorenone and 9-fluorenone

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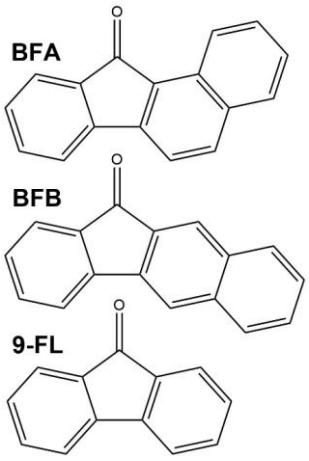
The fluorescence of 9-fluorenone (9-FL) and its mono-substituted derivatives are known to show polarity dependent solvatochromism. Previously, fluorescent solvatochromism has also been observed in the structurally related compound benzo[b]fluorenone (BFB). The current study extends this work to benzo[a]fluorenone (BFA),

and compares its solvatochromism to 9FL and BFB. Initially, the steady-state solvatochromic response of BFA the structural isomer benzo[a]fluorenone (BFa) (Figure 1) was measured in a series of aprotic solvents. The fluorescence lifetime and quantum yields for BFA in cyclohexane and acetonitrile were also determined, permitting quantitative comparison with the solvatochromic response of BFB and 9-FL. Finally, TD-DFT calculations on the ground and lowest energy excited singlet states for BFA, BFB and 9-FL using an accessible solvent model were carried out in order to extend and improve the existing conceptual model accounting for the effect of increasing polarity on 9-FL emission to BFA and BFB. These calculations included the structural isomer benzo[c]fluorenone (BFC) in order to predict its solvatochromic response in the absence of measurements. Experimentally, this work demonstrates that changing the aromatic structure from BFB to BFA greatly affects the solvatochromic response to increasing polarity in aprotic solvents. Theoretically, this work helps rationalize the different solvatochromic response observed for BFA compared to BFB and 9-FL to changing polarity in terms of differences in the relative possibilities for intersystem crossing (ISC) and internal conversion (IC).



MARM 167

Ultrafast structure and dynamics of ionic liquid-surfactant complexes as revealed by 2D-IR spectroscopy

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Ionic liquids have been found to form micro-structures with surfactants in organic solvents. These complexes are a couple of nanometers in size, possessing special properties, such as decreased viscosity, and could be used as “nano-reactors”. The current research on these systems is hindered by a lack of fundamental understanding of the structure and dynamics of these complexes.

We report, by the polarization-controlled two-dimensional infrared (2D-IR) spectroscopy of CN stretch of $[SCN]^-$, the structure and dynamics of 3-butyl-1-methyl imidazolium thiocyanate ([bmim][SCN]) as a function of surfactant type, the choice of organic solvent, relative concentration of ionic liquid-to-surfactant (W value).

The ionic liquid and surfactants form micro-structures in the solvent because the observed dynamics is independent of the absolute concentration of both ionic liquids and surfactants and has a negative correlation with the W value. Different surfactants yield very different dynamics of $[SCN]^-$ compared to the bulk [bmim][SCN]: while an anionic surfactant slows down the dynamics, a cationic surfactant maintains a similar dynamics, and a non-ionic surfactant accelerates the dynamics. This suggests that the ionic liquid is strongly interacting with the surfactant. Increasing the viscosity of the oil phase slows down the dynamics of the complex: keeping other conditions the same, the dynamics measured in chlorobenzene is more than two times slower than in dichloromethane. The polarization-controlled 2D-IR reveals that $[SCN]^-$ exhibits faster reorientation than in the bulk for all surfactants, and the environment is very anisotropic which is detected by a significant discrepancy between the 2D-IR spectra of two different polarization configurations.

The results together show that 2D-IR could be a promising tool to understand the structure and dynamics of the ionic liquid-surfactant complexes.

MARM 168

Influence of alkyl chain length on electronic and structural properties of imidazolium-based cation complexes with free base porphyrin and Fe-porphyrin: Implication for biodegradation of ionic liquids

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Ionic liquids have long been considered environmentally benign solvents due to their negligible vapor pressure. However, aqueous solubility of ionic liquids and resulting ecotoxicity present substantial challenges to the aquatic environment. It is, thus, crucial to design ionic liquids that are inherently biodegradable or that they can be biodegraded in water and wastewater treatment plants. In order to incorporate biodegradability aspects while designing an ionic liquid requires that the pathways by which biodegradation takes place be known. Research in this direction has suggested that cytochrome P-450 may be involved in the oxidation of the imidazolium-based ionic liquids. However, no definite evidence has yet been presented.

In an effort to evaluate the feasibility of biodegradation of imidazolium-based ionic liquids by cytochrome P-450 and elucidating the molecular level mechanism of biodegradation of ionic liquids, we have carried out, as the first step, ab initio calculations of homologous series of 1-n-alkyl-3-methylimidazolium cations $[C_nmim]^+$ (n=2,4,6,8, and 10) in the presence of free base porphyrin (FBP) and iron substituted porphyrin (FeP) – the catalytic site of cytochrome P-450 to elucidate the electronic coupling between these molecules. Various aspects of the composite systems such as location of frontier orbitals (highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO)), HOMO-LUMO energy gap, and intermolecular charge transfer were determined in order to assess the influence of the pophyrin molecules on the ionic liquid electronic properties.

Our results indicate that, although the locations of HOMO and LUMO do not change significantly in the complexes in comparison to those in the gas phase, the energies of the frontier orbitals are perturbed to a significant extent: both HOMO and LUMO energies are upshifted; the shift in the energies, however, was found to be dependent on the orientation of the cation with respect to FBP and FeP as well the length of the alkyl chain. The charge transfer, indicative of the electronic coupling between the porphyrin molecule and the cations, was observed to be higher for FBP than that for FeP. In addition to these results, we will also present the results of the Gibbs free energy of formation for these complexes.

MARM 169

Role of the solvophobic effect in protein-ionic liquid interactions

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Biological applications which utilise enzymes, or other proteins, require the tertiary structure of the protein to be retained. However, many proteins readily undergo aggregation or denaturation when outside their native environment, and/or over longer timescales. The stability of proteins in solvents other than water is usually considered unappealing due to an assumption that the protein will be insoluble or denatured. However, a few solvents, such as glycerol and dilute alcohols have been shown to have protein stabilising properties, such as in cryopreservation.

Previously we have developed extensive structure-property relationships between the chemical structures and mesostructures of non-aqueous solvents and the solvophobic effect experienced by amphiphiles for molecular solvents and protic ionic liquids (PILs). Here we have extended this to develop a greater understanding of what solvent features are important for protein stability. We have utilised a series of small polar non-aqueous molecular solvents and protic ionic liquids consisting of acid-base combinations of alkyl- and alkanolammonium cations paired with formate or nitrate. Solutions were prepared of these PILs combined with water, and with added formate or nitrate to explore a broad range of pH from 0 to 11.2 and ionicity from 0 to 11 M. For this initial work egg white lysozyme (HEWL) was used. These solvent systems enabled us to explore the effect of pH, solvent concentration (ionicity), solvent cohesive energy density and polarity towards protein stability. The activity of the lysozyme was assessed based on its lytic activity towards Micrococcus lysodiekticusce using UV-Vis spectroscopy. The secondary and tertiary structures of the lysozyme were determined using Small angle X-Ray scattering (SAXS) and IR spectroscopy. Protein crystallisation studies have been successfully conducted for many of these protic ionic liquid solvent systems, with significant differences in the crystal structures formed.

This work extends our understanding of protein stability in a wide variety of solvent environments, and has enabled

structure-property relationships to be developed for a protein in concentrated molecular solvent and protic ionic liquid solvent systems. This work has the potential to lead to the development of tailored solvent systems to optimise protein stability.

MARM 170

Structure and dynamics of ionic liquids in model polyelectrolyte systems

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A new class of ion gels, in which rigid-rod polyanions are aligned within room-temperature ionic liquids, has been fabricated recently. These ion gels exhibit an unusual combination of properties such as high ionic conductivity and large elastic modulus, and they open up exciting new avenues for engineering ion conducting materials. To understand the formation of these gels and their unusual mechanical and transport properties, we investigate the structure and dynamics of ionic liquids in these gels using molecular dynamics simulations. We show that the ion distribution in the interstitial space between rod-like polyanions exhibits the hallmarks of the ionic liquid structure near charged surfaces, i.e., cations and anions form alternating layers around the polyanions and the charge on the polyanions is over-screened by the ionic layer surrounding them. The distinct ordering of ions suggests the formation of a long-range “electrostatic network” in the ion gel, which may contribute to its mechanical cohesion and high modulus. The dynamics of both cations and anions slow down due to the fact that some cations become associated with the sulfonate groups of the polyanion on nanosecond time scales, which hinders the dynamics of all ions in the gel. Cation and anion diffusion in the gel are only 2 to 10 times slower than in bulk RTILs, which is still much faster than, e.g., Li+ ions in the typical ion conducting polymers.

MARM 171

Self-assembly of block copolymers in ionic liquids: Ultrastretchable iono-elastomers with mechanoelectrical response

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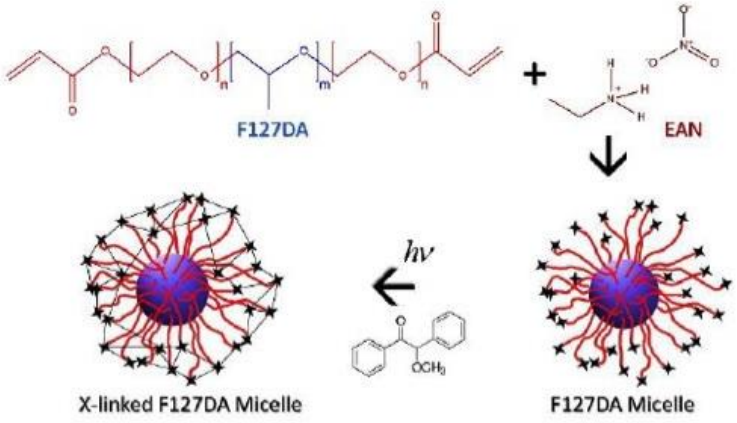
Self-assembly of amphiphilic block copolymers can impart desired discrete or continuous nanostructures, such as micelles utilized as drug delivery vehicles in aqueous solvents, or cross-linked micelles for stretchable electronics fabrications in ionic liquids. These appealing applications have motivated significant research efforts to understand the nano- and microstructure as well as the structure-property relationships underlying such self-assembled systems, with the ultimate goal being effective formulation. To take full advantage of the bottom-up self-assembly approach, a comprehensive understanding of the factors that govern the self-assembly behavior of dilute, concentrated and functionalized system of non-ionic block copolymers self-assembly in ionic liquids, as well as robust characterization methods for quantifying the microstructure and properties relationship arereviewed.

The emerging technologies involving wearable electronics require new materials with high stretchability, resistance to high loads, and high conductivities. We report a facile synthetic strategy based on self-assembly of concentrated solutions of end-functionalized PEO_{106}–PPO_{70}–PEO_{106} triblock copolymer in ethylammonium nitrate into face-centered cubic micellar crystals, followed by micelle corona cross-linking to generate elastomeric ion gels (iono-elastomers). These materials exhibit an unprecedented combination of high stretchability, high ionic conductivity, and mechanoelectrical response. The latter consists of a remarkable and counterintuitive increase in ion conductivity with strain during uniaxial extension, which is reversible upon load release. Based on in situ SAXS measurements of reversible crystal structure transformations during deformation, we postulate that the origin of the conductivity increase is a reversible formation of ion nanochannels due to a novel microstructural rearrangement specific to this material.

Iono-Elastomer in EAN



MARM 172

Electrochemical oxidation of metal carbides for double-layer capacitors with ionic liquid electrolytes

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Vanadium carbides and Niobium carbides thin films with the textured cubic crystal structure (NbC, VC) or hexagonal crystal structure (Nb_2C, V_2C) are prepared by a reactive magnetron sputtering approach on sapphire substrates. The metal carbides coated sapphire substrates are used as working electrodes and investigated in aqueous neutral, basic, or acidic electrolyte solutions. Cyclic voltammetry results demonstrate that the carbides can be oxidized in all of these electrolyte solutions and produce niobium or vanadium ions. In basic solutions, the oxidation potentials are lower than the potentials in acidic or neutral solutions. Nb_2C and V_2C are oxidized at lower potentials, compared with NbC and VC, in all of these solutions. Raman spectra demonstrate that after the oxidation carbide-derived (CDC) carbon produced on the surface of the electrodes except for the Nb_2C electrode. Scanning electron microscope images demonstrated that the surface morphology of the electrodes depends on the oxidation conditions such as potential, the electrolyte solution, and the metal carbides. The so-produced porous carbon electrodes are also tested in ionic liquid solutions with various cations, anions, and ionic solutes. The performance of the electrodes includes the double layer capacitance depend on the structures and properties of the molecular ions in the ionic liquids.

MARM 173

MMP-9 responsive peptide nanocarriers for targeted delivery of metallodrugs

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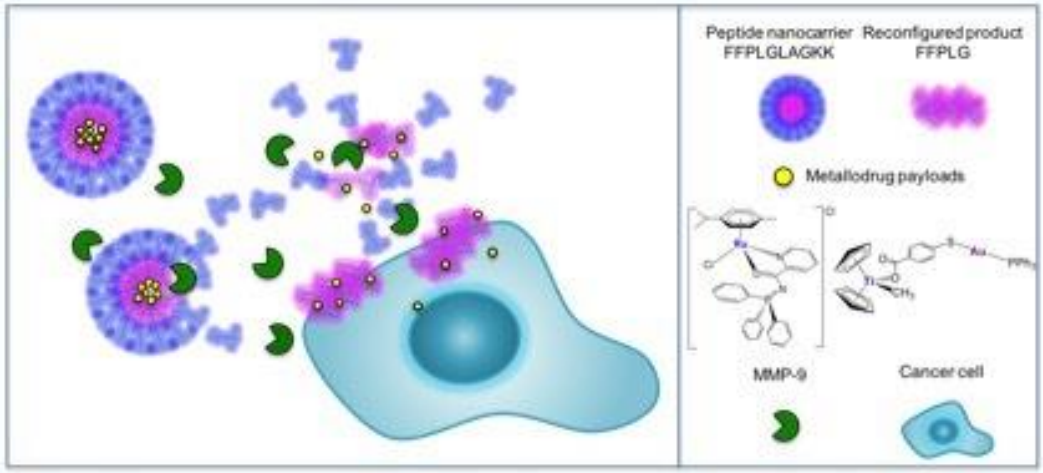
Drugs such as, cis- platin, oxaliplatin, and carboplatin have limitations including poor solubility, quick clearance, lack of selectivity, and limited therapeutic activity. These limitations can be addressed by peptide nanotechnology, which offer unique design space for developing safer and more effective medicines. Here we report on the development of peptide nanocarriers that target matrix metalloproteinase-9 (MMP-9) and use highly active unconventional metallodrugs as the payloads. The up-regulation and the roles of MMPs have been associated with cancer invasion and metastasis. Therefore, MMP-9 is a suitable cancer specific bio-target and the enzyme action can be exploited to produce a desirable response in the peptide nanocarriers: 1) formation of fibers that stay localized near the cancer cells and 2) site specific release of payloads. Scheme 1 shows the structures of two metallodrugs synthesized by the Contel group that were cytotoxic *in vitro* and displayed impressive tumor reduction *in vivo* in MDA-MB-231 and Caki-1 cells and xenografts. We will present on the characterization of novel peptide amphiphiles with tunable MMP-9 cleavage kinetics and desired self-assembly properties, as well as preliminary studies on the entrapment of the metallodrugs. Using unconventional metallodrugs that are highly active against MMP-9 overexpressing cell lines as payloads in the MMP-9 targeting peptide nanocarriers will provide a minimally invasive method to kill cancer cells that are resistant to current chemotherapy.



Scheme 1. Schematic representation of the drug-loaded peptide nanocarrier. Upon enzymatic action by MMP-9 which are overexpressed and secreted by cancer cells, the amphiphilic nanocarrier breaks down. The hydrophobic portion of the peptide re-configures into less mobile fibers that accumulate on the cell surface to slowly release the metallodrug payloads.

MARM 174

Exploring the toxicity of gold nanoparticles to aquatic amphibians

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The discharge of pollutants such as pharmaceuticals, personal care products, heavy metals, and other toxicants into freshwater streams and oceans is a growing environmental problem. Nanoparticles, a new class of environmental pollutants, have attracted much attention in recent years because of our ability to readily synthesize particles of controlled size, shape, and surface chemistry. The control over these properties has enabled new applications in electronic, biomedical, and pharmaceutical applications. Despite their increasing use, our knowledge of the environmental consequences of released nanoparticles in air, soil, and water, is wanting. We have explored the influence of cetyltrimethylammonium bromide capped gold nanoparticles exposed to wood frog and bullfrog tadpoles. A variety of endpoints have been measured including time to metamorphosis, uptake, localization, and species specific uptake. We also measured depuration time of gold in wood frogs. Gold was largely depurated from the tadpole within 5 days, in gold free water, indicating that the nanoparticles may be a transient toxicant. Our finding of differential uptake between closely related species living in similar habitats with overlapping geographical distributions argues against generalizing toxicological effects of nanoparticles for a large group of organisms based upon measurements in only one species.

MARM 175

Motion of Li^+ and methanol through a 2.25-nm-diameter single-walled carbon nanotube

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Carbon nanotubes present an important molecular-sized conduit because of their hydrophobic interiors and enahnced flow for water and other species. We have compared the the ionic transport of Li^+ and the molecular transport of methanol through a 2.25-nm-diameter, 200-µm-long single-walled carbon nanotube. As the applied electric field was increased, the Li^+ pore-blocking current was found to generally increase in the range of 1–6 pA. Likewise, above the observed threshold voltage of 700 mV, methanol exhibited pore blocking and the pore-blocking current also increased with applied field in the same range as for Li^+, 1–6 pA. This similarity is explained by a simple model comparing the volumes of methanol and hydrated Li^+. The dwell times for Li^+ transport varied linearly with inverse electric field from 200 and 1200 ms for applied voltages between 200 and 1000 mV, indicating an electrophoretic mobility of 1.6×10^{-7} m^2 V^{-1} s^{-1}, in agreement with previous studies of alkali metal ions in SWNT nanopores. Conversely, the dwell times for methanol remained relatively constant at an average of 88 ms. The average velocity of the methanol molecules was found to be 2.3×10^{-3} m/s, which is too fast for diffusion and in

agreement with predictions of a model developed for the electro-osmotic flow of neutral molecules through a small-diameter nanopore. This work is the first to measure the transport properties of neutral molecules through narrow-diameter nanopores and potentially useful information for systems such as fuel cells, in which motion through nanoconfined environments is very important.

MARM 176

Effects of capping agent and dopant concentration on the quantum yield of ZnS nanocrystals

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Quantum dot sensitized solar cells show promise in improved efficiency of these devices. Most of the research has focused on cadmium selenide nanocrystals as the quantum dots, but these two elements are of concern from environmental and toxicological standpoints. Zinc sulfide nanocrystals doped with manganese could serve as possible replacements for cadmium selenide nanocrystals. The main goal of this research was to determine the effects of capping agent molecular structure and dopant concentration on the fluorescence quantum yield of these colloidal nanocrystals. Undoped and doped zinc sulfide nanocrystals were prepared by reacting aqueous solutions of zinc acetate, a known amount of a selected capping agent, and a chosen percentage of manganese acetate ranging from 0% to 2% with aqueous solutions of sodium sulfide. Particle sizes were determined to be around 4 nm using UV/Vis absorption spectroscopy, and the emission properties were studied using fluorescence spectroscopy. The quantum yield of the doped nanocrystals will be determined by comparing results with those from the fluorescence standard quinine. Future work will involve the fabrication of solar cells using manganese doped nanocrystals in order to correlate quantum yield with solar cell performance.

MARM 177

Bimetallic nanocrystal catalysts for hydrodeoxygenation of 5-hydroxymethylfurfural

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In order to reduce the demand on using fossil fuels for the production of liquid fuels and chemicals, lignocellulosic biomass is providing us a sustainable solution for alternative carbon resources. The 2,5-dimethylfuran (DMF), as a promising candidate for biofuel application, is obtained by the hydrodeoxygenation (HDO) of 5-hydroxymethylfurfural (HMF). A suitable catalyst is the keystone for realizing this process with high yield, in which bimetallic catalysts are emerging as one of the most promising materials with enhanced activity and selectivity. The synthesis and characterization of Pt-based and transition metal-based colloidal nanocrystals (NCs) as high performance catalysts for DMF production will be discussed. A high degree of control over size, shape and composition of NCs were achieved via solvothermal method and the composition-dependent HDO performance were examined using a continuous flow reactor system over carbon-supported NC catalysts.

MARM 178

Electrooptical dynamics of 4-cyano-4'-pentylbiphenyl confined in functionalized zinc selenide nanocavities

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The electooptical properties of zinc selenide (ZnSe), a semiconductor transparent in the infrared region of the electromagnetic spectrum, have been exploited in the development of a variety of scientific technologies. Additional studies have demonstrated the facility of this substrate for the adsorption of alkanethiolate self-assembled monolayers (SAMs) and the support of nematic liquid crystals (LCs), such as 4-cyano-4'-pentylbiphenyl (5CB). We have investigated the influence of the ZnSe morphology on the electrooptical dynamics of nanoscale 5CB liquid crystalline films supported on both the bare substrate and a surface functionalized with hexadecanethiol (HDT) SAMs. Infrared spectra indicate that the introduction of an HDT monolayer between the ZnSe surface and the liquid crystalline film reorients the director of the liquid crystalline film with respect to a film mounted on bare ZnSe. Furthermore, the attenuation of the electronic effects of the ZnSe surface by the SAM led to a notable decrease in the threshold voltage required to induce the Fréedericksz transition in the 5CB film. This feature of SAM functionalized ZnSe suggests the possibility of fine-tuning the dynamics of 5CB, allowing for additional applications of the substrate. In conjunction with this study, we also report a new bi-layer positive resist

methodology for the fabrication of a gold interdigitated electrode microarray on ZnSe—a methodology that can be readily generalized for the fabrication of other microscale structures.

MARM 179

Quantum thermodynamics for nanoscale and molecular systems

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Nanoscale devices, trapped atoms in cavities, molecular motors and plasmonic nanoparticles are the subject of current intense research efforts, motivated by the ultimate goal of understanding and controlling motion, energy and electron transfer as well as chemical reactions at this scale. During my talk, I will describe the results of our recent theoretical investigations in the thermodynamics of these systems, with particular emphasis in the concepts of energy distribution, efficiency, heat and work rates among others. I will introduce the main challenges in the field and will also explain the main differences with classical systems. The conclusion of these investigations will be illustrated for several model systems, and the relevance of the quantum mechanical properties of nanoscale and molecular systems in the characterization their thermodynamic quantities will be presented.

MARM 180

High aspect ratio CNT structures produced by energetic ion bombardment

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Cross-linking of randomly oriented MWCNT thin films into an interpenetrating network has been demonstrated using energetic argon ion bombardment with an ion energy of 4 keV and a fluence on the order of 10^{17} ions/cm^2. However, at higher energies and fluence, a surprising transformation takes place. High aspect ratio structures that consist of vertically aligned CNTs are produced at energies of 11.5 keV and fluence on the order of 10^{19} ions/cm^2 from the original randomly oriented MWCNT film. We discuss potential mechanisms for this transformation, and possible applications of this high surface area structure in energy storage and sensors.

Earlier research has sought to utilize the exceptional thermal conductivity of CNTs to produce a heat spreader by bulk cross-linking the CNTs into an interpenetrating network. An isotropic thermal conductivity of 2150 W/m-K was measured in a 5 μm thick MWCNT film which had been subject to argon ion bombardment with an ion energy of 4 keV and a fluence on the order of 10^{17} ions/cm^2. While energetic ions will randomly bombard the entire CNT network, on occasion, one will strike a junction where two or more CNTs are touching, momentarily disrupting them. CNTs have the remarkable ability to self-heal, and in doing so, the disrupted junction self-heals into a new interpenetrating junction. However, practical heat spreader applications require films at least 100 times thicker than this initial demonstration. In an attempt to achieve this, substantially higher ion energies and fluence were applied. But rather than forming interpenetrating junctions deeper into the bulk of a CNT thick film, an interesting new form of high aspect ratio structure results, where groups of CNTs are now vertically aligned, even though the original CNT thick film was randomly oriented. There is also a sharp transition at the base of these structures from the new aligned form to the original randomly oriented form. We consider various aspects of ion-induced sputter dynamics coupled to the growth processes of CNTs to account for these new aligned high aspect ratio structures. The role of ion channeling within and between CNTs is also considered.

MARM 181

π–Stacking pancake bonding

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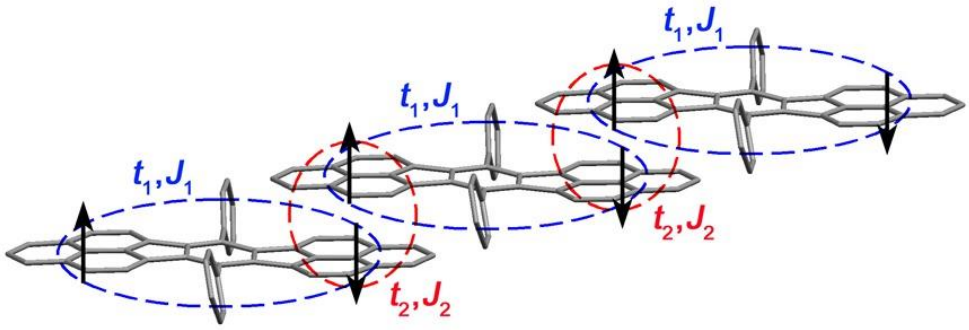
π–stacking geometries between molecules are quite common in systems as diverse as conducting organic materials and DNA. Is there a specific π–stacking interaction that favors face-to-face packing? It has been argued that a specific π to π stacking interactions *per se* do not exist as a form of intermolecular interaction between closed shell molecules. However, there is a category of molecular radicals, many of which are non-Kekule types, that strongly favor π to π stacking geometries with short contact distances and enhanced charge carrier transport properties. This enhancement is the result of uniquely short contacts due to the overlap of the singly occupied molecular orbitals, SOMOs. These unusual intermolecular contacts occur between (1) conjugated molecules or ions, showing (2) good face-to-face atom-over-atom stabilizing π-π stacking overlap with (3) shorter than van der Waals (vdW) contact distances with larger than vdW interaction energies. This intermolecular interaction termed “pancake bonding” has wide ranging applications in organic conductors. Pancake bonding can affect reaction mechanisms: transition structures and intermediates can be stabilized by pancake bonds. Computationally these

aggregates are challenging because of the multireference nature of their ground states, their low lying triplet states and the importance of van der Waals interactions. While multireference methods, such as MR-AQCC are successful in dealing with these systems, there are also a few select density functionals with good accuracy that can be applied for larger pancake bonded systems. We show pancake bonding and its special features for triangular shaped graphene flakes that are multiradicals.



MARM 182

Singlet fission and charge transfer quantum dynamics in organic photovoltaic

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We apply a real-time path-integral approach to investigate the charge-transfer mediated singlet fission quantum dynamics in a model pentacene dimer, as well as charge-transfer dynamics in model organic photovoltaic. Our path-integral method gives accurate fission dynamics across various reactions regimes as well as a broad range of reorganization energies and temperatures. With this method, we investigate the destructive interference between the two charge-transfer (CT) mediated fission pathways, and discovered two mechanisms that can suppress this deleterious effect. First, increasing the energy gap between two CT states effectively shuts down the high-lying CT pathway, leaving a better functioning low-lying CT pathway with a minimum amount of destructive interference. Second, intermolecular vibrations induce electronic-coupling fluctuations, such that the destructive cancellations due to the different signs in static electronic couplings are suppressed. Further, combined with a scalable yet accurate electronic structure method, such as self-consistent charge Density-Functional Tight-Binding (SCC-DFTB) approach we use the ab-initio partial linearized path-integral dynamics to simulate the charge-transfer process in model organic photovoltaic systems. These findings reveal promising design principles for more efficient singlet fission materials.

MARM 183

Theory and computation toward nonadiabatic dynamics of molecular switches and quantum dots

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Nonadiabatic effects are ubiquitous in nature and play essential role in many chemically interesting processes, such as charge transfer and chemical transformations. Nonadiabatic molecular dynamics (NA-MD) methodology aims to model such processes by describing a coupled electron-nuclear evolution. Modeling NA-MD processes in solid-state and molecular systems is a challenging topic, both conceptually and pragmatically. In simulations of realistic systems, one is bound to make certain approximations, which limit the scope of the methodology. In this presentation, I will focus on the accuracy of utilized approximations and the methods that can help addressing these concerns.

One of the limitations of the approximate NA-MD technique is the lack of electron-nuclear back reaction. The approximation restricts the range of systems to which the approach can be applied. I will present the delta-SCF-NA-MD approach that allows to overcome this limitation, opening the opportunities for computationally-efficient modeling of photoinduced isomerization in molecular switches.

The accuracy of the quantities used in NA-MD simulations, such as nonadiabatic couplings (NAC), depends on the level of electronic structure calculation. Practical NA-MD modeling often relies on computationally efficient pure

density functionals, despite the known intrinsic problems of the latter. The hybrid functionals are significantly more expensive, but are often more reliable. I will showcase how the choice of the density functional affects the magnitudes of the computed NACs, as applied to small silicon clusters. The role of the correct asymptotic of electronic exchange will be emphasized and the implications of the incorrect behavior of pure density functionals on the computed NACs will be discussed.

MARM 184

Vibrational control of electron-transfer kinetics: A unified theoretical framework and a critical experimental test

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We present a theoretical framework to describe how transient infra-red (IR) excitation perturbs electron transfer (ET) rates in donor-bridge-acceptor systems. We also present the development of non-equilibrium molecular dynamics (NEqMD), a powerful approach to study IR-excitation induced geometry perturbation and coupling modulation effects. Recent experiments find that IR excitation can change ET rates and can even change the relative dominance of ET and competing reactions. We formulate a comprehensive theoretical framework to describe IR-perturbed ET kinetics, including non-equilibrium initial state populations and IR-perturbed bridge-mediated couplings. We find that these effects can produce either rate slowing or acceleration. The model is used to understand the experimentally observed rate slowing in a donor-bridge-acceptor structure, and to predict the influence of IR excitation on the recombination rate. The predictions were validated experimentally.

MARM 185

SiR/TiO_2 and GeR/TiO_2 (R = H, Me) heterostructures for photocatalytic applications: Insights from excited-state dynamic simulations

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Photocatalysis provides green and renewable methods for the synthesis of fine chemicals, degradation of pollutants, and production of clean fuels. The efficiency of currently used photocatalysts is too low for their large-scale applications. The knowledge of excited-state dynamics of photogenerated charge carriers can provide useful guidelines for the design of novel photocatalysts with improved efficiency. With the aim of predicting novel photocatalysts, we have investigated the electronic structure and excited-state dynamics of heterostructures composed of 2D silicane- and germanane-based materials (SiR, GeR; R = H, Me) and anatase or rutile polymorphs of TiO_2. Our calculations indicate that the band gaps of these heterostructures can be tuned appreciably: from 2.28 eV in SiH/a-$TiO_2$to 0.16 eV in GeMe/r-TiO_2. Nonadiabatic molecular dynamic (NA-MD) simulations predict electron-hole recombination timescales of 46.0, 3.6, and 1.2 ns in SiH/a-TiO_2, SiH/r-TiO_2, and GeH/a-TiO_2, respectively. These timescales are notably longer compared to other well-known 2D/3D heterostructures such as graphene/TiO_2 and BP/TiO_2 (BP = black phosphorous). The methyl functionalization of Si or Ge monolayers and the use of rutile TiO_2 increase the nonadiabatic coupling and accelerate the recombination. We have devised an accelerated NA-MD technique to evaluate the time scales for slow electronic transitions. Unlike slow electron−hole recombination, “hot” electrons thermalization occurs within ultrafast time scales, whereas some hot holes thermalize slower, on the order of 20.5 ps in SiH/a-TiO_2 and 65.3 ps in GeH/a-TiO_2. The high band gap tunability, suitable electron and hole localization, and long recombination time scales indicate that SiH/a-TiO_2, SiH/r-TiO_2, and GeH/a-TiO_2 heterostructures may be promising candidates for photocatalytic applications.

MARM 186

Copper- and nickel-catalyzed oxidative decarboxylative arylation reactions

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Decarboxylative coupling reactions are emerging as efficient routes to access a diverse array of substituted arenes from inexpensive and readily available precursors. Unfortunately, most methods require pre-functionalized aryl halide coupling partners. An oxidative transformation enabling the direct decarboxylative coupling with an arene C-H bond is an attractive alternative, but current methodologies suffer limitations of substrate scope. This talk will focus on our recent efforts to overcome these substrate limitations with a focus on our recently developed copper- and nickel-catalyzed oxidative decarboxylative C-H arylation reactions.

MARM 187

Guaianolide analogs: A valuable testing ground for the allenic Pauson–Khand reaction

***Kay M. Brummond**, kbrummon@pitt.edu. Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania, United States*

The allenic Pauson–Khand reaction has enabled efficient access to [5,7]-ring systems. This is expected to be of great value for preparing guaianolides and related compounds, a class of richly bioactive natural products. For this presentation we will discuss: 1) the synthesis of guaianolide isosteres possessing a thiol reactive, tunable α-methylene-γ-lactam, 2) the electrophilic reactivity of this hetero-Michael acceptor towards sulfhydryl nucleophiles, and 3) their inhibitory activity against the NF-κB signaling pathway, a key contributor to carcinogenesis.

MARM 188

Discovery of novel selective SYK/ZAP70 kinase inhibitors for rheumatoid arthritis

***Sandra Lee**, sandra_lee2@merck.com. Discovery Chemistry, Merck Research Laboratories, Kenilworth, New Jersey, United States*

The discovery and development of highly selective Spleen Tyrosine Kinase (SYK) inhibitors for the treatment of rheumatoid arthritis showcases the optimization of early leads and the key insights from structure-based drug design and metabolic characterizations that led to clinical candidates MK-8457 and MK-8449.

MARM 189

Application of new methodologies to the synthesis of pharmaceuticals

***Michelle Garnsey**, michelle.garnsey@pfizer.com. Pfizer, Groton, Connecticut, United States*

The development of novel methodologies is critical to the continued advancement of medicinal chemistry. The discovery of innovative approaches for the divergent synthesis of small molecule libraries accelerates the drug discovery process and facilitates the elucidation of novel targets. This talk will describe recent efforts in our group for the functionalization of pharmaceutical scaffolds and how new reaction development greatly facilitated those investigations.

MARM 190

Caught red-shifted: Visualizing acyl carrier protein conformational dynamics using a mechanism-based vibrational spectroscopic probe

*Grace Thiele[1,2], Connie Friedman[1,2], Kathleen Tsai[1,2], Joris Beld[3], Casey H. Londergan[1], **Louise K. Charkoudian**[2], lcharkou@haverford.edu. (1) Department of Chemistry, Haverford, Pennsylvania, United States (2) Haverford College, Haverford, Pennsylvania, United States (3) Department of Microbiology and Immunology, Drexel University, Philadelphia, Pennsylvania, United States*

Acyl carrier proteins (ACPs) are central hubs in polyketide and fatty acid biosynthetic pathways, but the fast motions of the ACP's phosphosphopantetheine (Ppant) arm make its conformational dynamics difficult to capture using traditional spectroscopic approaches. In this talk, I will present how the synthetic modification of the terminal thiol of ACP's Ppant arm into a thiocyanate group transforms the ACP's reactive site into a vibrational spectroscopic probe that can report on the local environment of the Ppant arm. We leveraged this probe to resolve Ppant conformations on the picosecond time scale and visualize ACP complex formation with functional catalytic partners. Given the practical, generalizable, and scalable nature of our approach, it is anticipated that these methods will be valuable in future structural and biosynthetic engineering studies.

MARM 191

Synthesis of diverse oxygen heterocycles via oxidative ring expansions of simple alcohols

***Sarah Wengryniuk**, sarahw@temple.edu. Chemistry, Temple University, Philadelphia, Pennsylvania, United States*

Oxygen heterocycles are ubiquitous motifs in bioactive natural products, appearing with diverse substitution patterns and in a variety of ring sizes. As a result extensive efforts have been made towards their synthesis, however challenges remain, particularly in the area of medium-sized ring construction. Our laboratory has discovered that the unique reactivity of (poly)cationic lambda-3 iodane reagents can enable numerous synthetic approaches to these scaffolds. A chemoselective oxidative ring expansion of simple alcohols allows facile access to medium-ring ethers, and key mechanistic insights have facilitated the extension to late stage scaffold diversification of natural products and therapeutic lead compounds. Additionally, these reagents have enabled a facile approach to aryl ether synthesis via a proposed electrophilic alcohol cyclization pathway.

MARM 192

Leading collaborative and engaging activities in a flipped general chemistry classroom using smart devices

***Anna M. Fedor**, afedor@misericordia.edu. Misericordia University, Dallas, Pennsylvania, United States*

Students use mobile technology to communicate and access information quickly. Although students are generally competent with their devices for these purposes, their work often shows that they have difficulty when trying to collect, organize, and apply information. This talk is centered on integrating well-established hardware and software technologies with the flipped classroom pedagogy to improve student engagement in a general chemistry course. This was done by redirecting the use of smart devices from detached texting and social media channels to face-to-face group collaboration using Google Docs and Google Sheets. Prior to the activities, students were required to watch recorded lectures and complete short quizzes on course material. Groups worked through activities and shared information in real-time and were monitored by the instructor. Two activities will be discussed in depth including analyzing data using Beer's Law in Google Sheets, and comparing energies in the electromagnetic spectrum using Google Docs. Effective leading and time management of these activities will also be discussed with a focus on reviewing information in real time. A partial demonstration of one of the activities will be included in the oral presentation.

MARM 193

Quality by design (QbD) in the classroom and laboratory: Tools for enhancing students' creativity and analytical thinking

***Zenaida O. Gephardt**, gephardtzo@rowan.edu. Chemical Engineering, Rowan University, Glassboro, New Jersey, United States*

Quality by Design (QbD) has become prevalent in many laboratories because its strategic methodology allows for better conclusions and continuous improvement. Application of QbD tools in the classroom and laboratories can serve to guide students in developing optimal ways of solving problems and of obtaining measurements. QbD helps to minimize the deterministic thinking that can limit creativity and options in problem solving. Thinking in terms of design spaces, ranges and probabilities enhances students' analytical thinking and creativity. Students familiar with QbD applications are more likely to seek innovative solutions and are better prepared for the marketplace. The teaching and application of QbD techniques will be discussed in the context of undergraduate classrooms and laboratories. Specific examples with experimental results will be discussed.

MARM 194

Second-semester student-centered organic instructional laboratory for non-majors featuring microwave synthesis

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A standalone second-semester non-majors instructional organic laboratory has been revised to embrace a student-centered design. Individual modules include a Grignard synthesis; extraction, quantification, and NMR characterization of fats in crackers; electrophilic aromatic substitution; and a multi-step synthesis of benzocaine that begins with an optimization study of esterification using microwave-assisted synthesis. Practical and pedagogical aspects are discussed.

MARM 195

Active learning in the instrumental analysis laboratory with virtual machines

***Kristina Streu**[1], streu@bu.edu, Norman Chih-Yih Lee[1], Alexi Zubiria[2], Shawn Anderson[2], Steve Gagliardi[2], Rosina M. Georgiadis[1]. (1) Chemistry, Boston University, Boston, Massachusetts, United States (2) Agilent Technologies, Santa Clara, California, United States*

Many advanced undergraduate laboratory courses are structured using round robin rotations, where small groups of students work on a different sequence of experiments and up to six or more different types of instruments are utilized in a single laboratory period. At Boston University we have implemented the use of virtual machines (VMs) into our undergraduate instrumental analysis laboratory curriculum to keep student groups small while performing the same sequence of experiments and in the same order. By utilizing vendor cloud-hosted and BU local-hosted VMs students can access instrument interface software and data analysis software on their own personal laptops or university computers, allowing the entire class to be 'virtually' sitting at the same single instrument. VMs facilitate a more meaningful hands-on laboratory experience for students that is fully integrated with all aspects of the course curriculum. Pre-laboratory lecture meetings take place in a computer classroom where students explore

instrument or data analysis software with peer and instructor guided input to master authentic research questions before entering the laboratory. Students begin the laboratory period with a well-developed familiarity of the instrument software, and therefore utilize laboratory time to perform preliminary data analysis and to make experimental or instrumental method adjustments. Our students experience hands-on, realistic, and comprehensive data analysis that often includes a library search and is performed off-instrument by accessing VMs during or after the laboratory period has ended. Most significantly, the VMs help the instructor to promote active learning by implementing more open-ended, investigative experiments that require the students to problem solve in the laboratory. Student feedback reveals that integrating VMs allowed them to develop a deeper understanding of the instrumentation, which translated into confidence in the lab, success in the course, and potential benefits in their future careers.

MARM 196

Using an inquiry-based, research driven approach to design a cross-disciplinary laboratory course

***Timothy Dwyer**, tdwyer@stevenson.edu, **Jeremy Burkett**, jburkett2@stevenson.edu. Chemistry, Stevenson University, Owings Mills, Maryland, United States*

Pedagogical advancements, like the development of High Impact Practices, have been successfully used to deepen student's engagement with courses over a wide variety of disciplines. Here we describe the design, implementation, and assessment of a cross-disciplinary, inquiry-based lab course built around the proven success of these deeply engaging practices. Our Biochemistry/Inorganic chemistry lab course allowed students to engage in novel research that drew upon both currently emerging molecular sensing techniques as well as long-standing, thoroughly understood cancer treatments. Students designed and tested their own analogs to an industry standard (cisplatin) and, using the data they collected, were able to draw substantive conclusions about the relative success of their attempts. In conclusion, we will also present any practical difficulties or unavoidable limitations that were encountered as well as the numerous benefits of this approach to offering laboratory-based courses.

MARM 197

Cold plasma: An emerging antimicrobial intervention to improve food safety

***Brendan A. Niemira**, brendan.niemira@ars.usda.gov. ERRC, USDA-ARS, Wyndmoor, Pennsylvania, United States*

Contamination of fresh and fresh-cut fruits and vegetables by foodborne pathogens has prompted research into novel interventions. Cold plasma is a nonthermal food processing technology which uses energetic, reactive gases to inactivate contaminating microbes. This flexible sanitizing method uses electricity and a carrier gas such as air, oxygen, nitrogen or helium; conventional antimicrobial chemical agents are not required. The primary modes of action are via reactive chemical products of the cold plasma ionization process and UV light. Current research has developed a wide array of cold plasma systems which operate at atmospheric pressures or in low pressure treatment chambers. Multi-log reductions of *Salmonella*, *Escherichia coli* O157:H7, *Listeria monocytogenes*, norovirus and other pathogens have been demonstrated, but further optimization is needed. This presentation will summarize the science behind this class of devices and describe recent advances in this promising area of technology. Finally, key areas of future research will be described that will facilitate commercialization.

MARM 198

Antimicrobial treatments for inactivation of bacteria on produce surfaces and reducing transfer to fresh-cut pieces

***Dike Ukuku**, dike.ukuku@ars.usda.gov. ERRC- ARS-USDA, Wyndmoor, Pennsylvania, United States*

There are many reports of disease due to consumption of fruits and vegetables that were contaminated on the surface with enteric pathogens. Therefore, the safety of fresh-cut fruits and other produce available in salad-bar operations and supermarkets is a concern. Physical and chemical treatments are used in food processing to eliminate, or at least reduce, the population of pathogenic and spoilage microorganisms. The objective here is to summarize some of the work we have done on produce safety and quality research in my laboratory at Eastern Regional Research Center using our own in house antimicrobial processing technologies. The efficacy of these technologies on bacterial inactivation on produce surfaces will be elucidated and recommend processing techniques that eliminated/ drastically reduced transfer of bacterial pathogens to fresh-cut pieces during fresh-cut preparations.

MARM 199

Aqueous inactivation of pathogenic bacteria on fresh produce with a new FDA-approved mixed peroxyacid formula (First Step+ 10)

***Joshua Gurtler**, joshua.gurtler@ars.usda.gov. Food Safety and Intervention Technologies, USDA-ARS, Wyndmoor, Pennsylvania, United States*

First Step+ 10 is a newly developed mixed peroxyacid antimicrobial produce wash resulting from collaboration between NatureSeal, Inc. (a division of Mantrose-Haeuser, Inc.) and the USDA. A study was undertaken to examine the effects of FirstStep+ 10 on inactivating pathogens in rinse water and on fresh produce. The BS EN 1276 method was used to assess survival of *Salmonella, E. coli* O157:H7 and *Listeria monocytogenes* in a quantitative suspension test with product concentrations of 0.5, 0.6, 0.8, 1.0, 1.2, and 1.6 percent. An organic interference substance (bovine albumen) (BA) was added to the suspensions to create “CLEAN” conditions (0.03 percent BA) or “DIRTY” conditions (0.30 percent BA). The diluted produce wash solutions were tested against *E.coli* O157:H7 using the EN 1276 under both “CLEAN” and “DIRTY” conditions. In 5 min contact time, the produce wash inactivated more than 5 log CFU of *E.coli* O157:H7 under both CLEAN and DIRTY conditions. Various concentrations of diluted produce wash were inoculated with four *Salmonella* serovars (*viz*., Stanley, Montevideo, St. Paul and Newport). Following BS EN 1276, the produce wash achieved a greater than or equal to 6.6 log inactivation of four strains of *Salmonella* in 5 minutes contact time under both CLEAN and DIRTY conditions for all dilutions tested. A cocktail of five *Listeria monocytogenes* strains was used to test the efficiency of the produce wash. Using BS EN 1276, under CLEAN conditions, 0.5 percent to 1.0 percent produce wash achieved greater than 6 log reduction of *Listeria monocytogenes* in 5 minutes contact. Under DIRTY conditions, 0.8 percent and 1.0 percent produce wash achieved more than a 5 log reduction, and 0.5 percent and 0.6 percent produce wash inactivated greater than 4.0 log CFU/ml. Wash waters also inactivated up to 3.59 log CFU of pathogens on fresh cut produce.

MARM 200

Surveys of toxic elements in food

***Jennifer Fong Sam**, jennifer.ysseldyke@fda.hhs.gov. Center for Food Safety and Applied Nutrition, Food and Drug Administration, College Park, Maryland, United States*

At the U.S. Food and Drug Administration’s (FDA) Center for Food Safety and Applied Nutrition (CFSAN), research in the elemental analysis group focuses on the detection of toxic and nutritional elements in a variety of food products. Levels of toxic elements such as lead (Pb), cadmium (Cd), mercury (Hg), and arsenic (As) in food are routinely monitored, with particular emphasis on foods consumed by vulnerable populations such as children. Recent surveys for toxic elements in foods have focused on Cd and Pb in cocoa and chocolate products and Pb in a variety of foodstuffs. These surveys focused on commodities where the Codex Committee on Contaminants in Foods is considering setting or revising maximum levels. Additional surveys for the determination of inorganic As in infant rice cereals and toxic elements in dietary supplements will be discussed. Total elemental concentrations in foods are determined using microwave assisted digestion techniques followed by inductively coupled plasma mass spectrometry (ICP-MS). Inorganic arsenic determination is accomplished using anion exchange high performance liquid chromatography (HPLC) coupled with ICP-MS. These validated methodologies, which are rugged, sensitive, and yield dependable data, are routinely used in CFSAN and other FDA field laboratories. By monitoring toxic elements, FDA is able to evaluate the extent and significance of these analytes in the food supply and aid CFSAN and other organizations to take steps to reduce the concentrations of toxic elements in domestic and imported foods.

MARM 201

ATR-FTIR spectroscopy and chemometrics for the analyses of low levels (0.1%) of dietary trans fat

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In June 16, 2015, the U.S. Food and Drug Administration issued its final determination that partially hydrogenated oils (PHOs), the major dietary source of industrially-produced *trans* fat (TF), were no longer “generally recognized as safe (GRAS)” for any use in human food. However, small amounts of *trans* fat (i.e., <2%) continue to be present in refined, bleached, and deodorized (RBD) edible fats and oils due to the *cis*-to-*trans* isomerization of double bonds during high temperature processing. Accurate and rapid analytical methods for quantifying low concentrations of total *trans* fat are needed for verifying label claims, such as “zero grams of *trans* fat.” Consequently, the objective of the present study was to develop a rapid screening tool, using attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy in conjunction with partial least squares regression (PLSR) for the prediction of low concentrations of TF. PLSR calibration models were developed separately for

samples of neat edible oil/fats and lipid extracts of fast foods using a PLSR approach. Predicted concentrations of TF for edible oils/fats and fast food extracts showed good correlation (R^2>0.99), relative to the gas chromatography primary reference data, and high accuracies. For benchtop and portable devices, low root mean standard error of cross-validation (RMSECV) values of 0.05 and 0.04 % (edible oils/fats) and 0.14 and 0.07 % (fast food extracts), respectively, were obtained. TF contents as low as 0.12% for edible oils/fats and 0.39 % for processed foods were accurately predicted. Also, for the first time, a calibration model developed on the benchtop spectrometer was successfully transferred to a portable FTIR device for the prediction of TF concentrations of edible oils/fats as low as 0.13%. This simple, non-destructive, and rapid methodology has the potential to be used as an alternative to time-consuming chromatographic methods for screening of TF contents for quality control of raw material and processed food and nutritional labeling.

MARM 202

Bonding in plutonium siderophore complexes from a FEUDAL perspective

***Jason L. Sonnenberg**, sonnenberg.11@osu.edu. Gaussian Inc., Wallingford, Connecticut, United States*

Siderophores are organic chelating groups secreted by grasses, microbes and marine organisms to gather iron. In the presence of plutonium and other actinides, these chelators can bind and transport those metals as well. Understanding the metal ligand binding in these complexes is the first step to harnessing siderophores for environmental phytoremdiation or microbial remediation. The FEUDAL description of actinide bonding was one of the first qualitative models for actinide complexes but is still relevant today. Results from scalar-relativistic density functional theory calculations on a variety of actinide siderophore complexes will be presented.

MARM 203

Developing the photophysics and photoredox chemistry of molecular cerium compounds

***Eric J. Schelter**[1], schelter@sas.upenn.edu, Haolin Yin[1], Yusen Qiao[1], Yi Jin[1], Kimberly C. Mullane[1], Jerald Hertzog[2,1], Patrick J. Carroll[1]. (1) Dept of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania, United States (2) Chemistry, Washington & Jefferson College, Butler, Pennsylvania, United States*

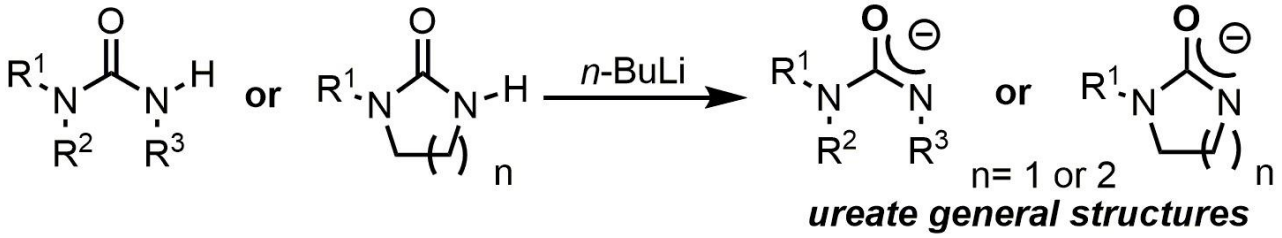
Cerium phosphors are an important class of solid state luminescent materials but only a small number of the related luminescent molecular compounds have been described. The luminescent characteristics of compounds in the solid- and molecular states derive uniquely from 4f-5d electronic transitions. Cerium is similarly the only member of the lanthanides to have extensive molecular chemistry in the +4 oxidation state. We have recently shown that visible light provides a useful handle to interrogate and develop Ce(III/IV) redox cycling through associated photoredox processes, a new direction in lanthanide chemistry. We also demonstrated this photoredox cycling can be leveraged into new stoichiometric and catalytic chemistry on organic substrates. The results of these studies, including coordination chemistry, structure property relationships photophysics and their implications for new one-electron chemistry with cerium will be presented.

MARM 204

Use of ureates as activators for smarium diiodide

***Chriss E. McDonald**, mcdonald@lycoming.edu. Chemistry, Lycoming College, Williamsport, Pennsylvania, United States*

Simple ureates have proven to be easy to construct and to be more effective activators for samarium(II) iodide than the traditional yet mutagenic activator, HMPA. It will be shown that SmI_2/ureate complexes can reduce radical precursors of quite low reactivity including aryl fluorides. It will also be shown that SmI_2/ureate complexes are excellent choices for effecting halo-alkene cyclizations.

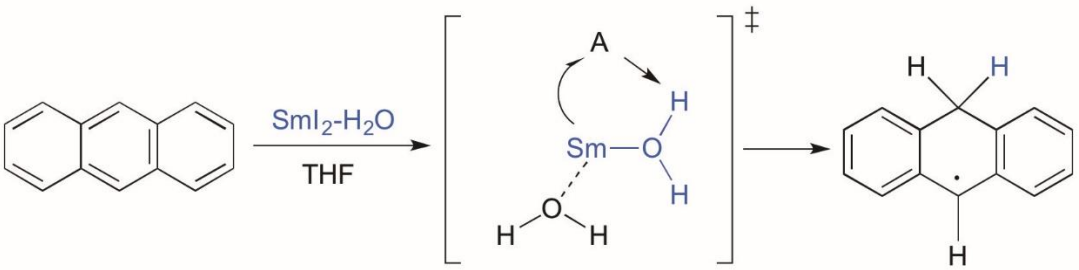


MARM 205

Mechanistic studies of low-valent samarium reductants

***Robert A. Flowers**, rof2@lehigh.edu. Chemistry, Lehigh University, Bethlehem, Pennsylvania, United States*

Interconversion of carbon-centered cations, radicals, and anions through single-electron transfer (SET) provides a powerful tool in organic synthesis. The ability of chemists to interconvert these species through the use of metal-based oxidants and reductants has led to the development of tandem reactions that utilize one or more reactive intermediates in bond-forming events to synthesize complex molecules of great societal importance. Among reagents that initiate these types of processes, low valent Sm has played a prominent role in the development of single electron reductions. Despite the utility of these reagents, chemists have a limited understanding of the fundamental steps in the electron transfer process, especially when coordinating ligands and proton donors are employed in reactions. The studies presented in this lecture will focus on recent mechanistic studies designed to improve and develop efficient methods that utilize low-valent Sm reagents as single electron and hydrogen atom transfer reagents in organic synthesis.



MARM 206

SAR studies in the sulfonyl carboxamide class of core protein modulators of the Hepatitis B virus

***Scott D. Kuduk**, skuduk@its.jnj.com, Angela Lam, Christine Espiritu, Robert Vogel, Klaus Klumpp, Lalo Flores, George D. Hartman. Novira Therapeutics, a Janssen Pharmaceuticals Company, Doylestown, Pennsylvania, United States*

Hepatitis B virus infection is a common cause of severe liver disease and liver cancer. Current treatment options cannot fully suppress viral replication in the majority of patients and only show very low cure rates. Accordingly, the identification of antivirals with a new mechanism of action should allow for the intensification of HBV suppression towards fully blocking HBV production in the liver and thus improve treatment outcomes toward the identification of a cure. The HBV core capsid protein has multiple essential functions in the HBV life cycle to enable chronic HBV infection. It is therefore an important target for antiviral drug development. Herein we describe the identification and SAR of a series of sulfonyl carboxamide-based HBV core protein modulators and propose a mode of binding at the core protein dimer-dimer interface.

MARM 207

Discovery and pre-clinical characterization of a 3rd generation 4-heteroaryldihydropyrimidine (HAP) analogues as Hepatitis B virus (HBV) capsid inhibitors

***Wei Zhu**, zhuweisioc@hotmail.com. Roche RD Center (China) Ltd., Pudong Shanghai, China*

HBV capsid is formed by the assembly of HBV core proteins and it protects the enclosed viral genome and creates the environment for reverse transcription of pre-genomic RNA (pgRNA) to DNA. The assembly and disassembly of HBV capsids are essential steps in the HBV life cycle and interruption of the normal capsid assembly process will block the HBV replication. This presentation will describe the discovery and structure-activity relationship (SAR) studies of the 3rd generation 4-H heteroaryldihydropyrimidines (4-H HAPs) featuring the introduction of a C6 carboxyl group as novel HBV capsid inhibitors. This new series of 4-H HAPs shows improved anti-HBV activity and better drug-like properties compared to the 1st and 2nd generation 4-H HAPs. X-ray crystallographic study clearly elucidated the role of C6 carboxyl group played for the increased binding affinity. The representative analogue HAP_R10 was extensively characterized in ADMET (absorption, distribution, metabolism, excretion and toxicity), HDI (hydrodynamic injection) mouse model and MoA studies, and was selected for further development as oral anti-HBV infection agent.

MARM 208

ALN-HBV: An investigational RNAi drug for the treatment of chronic hepatitis B

Laura Sepp-Lorenzino, *lsepplorenzino@alnylam.com. Alnylam Pharmaceuticals, Cambridge, Massachusetts, United States*

ALN-HBV is a subcutaneously administered, investigational RNAi therapeutic, in clinical development for the treatment of chronic hepatitis B (CHB). CHB infection is the most common serious liver infection in the world. Worldwide, two billion people have been infected with HBV and 240-290 million people have become chronically infected. Nearly 25% of chronic HBV patients develop serious liver diseases such as cirrhosis, fibrosis and hepatocellular carcinoma (HCC). An estimated one million people die each year from HBV infection and its complications worldwide; about 5,000 of those are in the United States. Despite the use of nucleoside analog inhibitors of viral DNA synthesis and interferon therapies, the cure rate for chronic HBV infection is less than ten percent. Reduction in HBV surface antigen, or HBsAg, levels of over 0.5 log10 is the single best predictor of immunologic cure. We believe an RNAi therapeutic inhibiting all steps of the HBV life cycle and silencing tolerogenic viral antigens has the potential to achieve a “functional cure.” Pre-clinical study results in rodent HBV models showed that subcutaneous administration of ALN-HBV led to potent and durable knockdown of HBsAg. Single doses of ALN-HBV in mice resulted in an up to 3.6 log10 and a mean of 1.6 log10 reduction of HBsAg 15 days after a single dose. Further, multiple doses of ALN-HBV in rats showed highly durable knockdown, with effects lasting up to 4 months following three weekly doses of ALN-HBV at 3 mg/kg. In addition, ALN-HBV was generally well tolerated in 13-week GLP toxicology studies in rat and non-human primates. Phase 1/2 randomized, single-blind, placebo-controlled study is ongoing. The primary objective of the study is to evaluate safety and tolerability of single and multiple subcutaneous doses of ALN-HBV. Secondary objectives include evaluation of pharmacokinetics and clinical antiviral activity for ALN-HBV as measured by its effects on serum HBsAg levels in hepatitis B envelope antigen (HBeAg) positive and negative chronic HBV patients.

MARM 209

Screening a natural products library for HBsAg secretion inhibitors

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The inhibition of hepatitis B virus S-antigen (HBsAg) secretion is a potentially useful target for the development of therapeutic agents for the treatment of chronic HBV infection. We have recently developed an assay for screening for HBsAg secretion inhibitors with several improved features over previous assays. Using this assay and selected follow-up assays, we have identified several extracts derived from actinomycete fermentations with HBsAg secretion inhibitory activity. We will present our results in the isolation and identification of the compounds responsible for this activity.

MARM 210

Orthogonal comparison of GC-MS and ^{1}H NMR spectroscopy for short chain fatty acid quantitation

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Short chain fatty acids (SCFAs) are important regulators of host physiology and metabolism, and when in excess, may contribute to the pathogenesis and progression of obesity and its associated metabolic diseases. Interest in SCFAs has increased in part due to the recognized importance of the gut microbiota and how production or metabolism of SCFAs by the microbiota may signal to the host. Therefore, reliable and affordable methods for SCFA profiling are required for accurate identification and quantitation. In the current study, four different methods for SCFA (acetic acid, propionic acid, and butyric acid) extraction and quantitation were compared using two independent platforms including gas chromatography coupled with mass spectrometry (GC-MS) and ^{1}H nuclear magnetic resonance (NMR) spectroscopy. Sensitivity, recovery, repeatability, matrix effect, and fecal SCFAs were determined across all methods. The GC-MS propyl esterification method exhibited superior sensitivity and recovery accuracy. NMR methods by either quantitation relative to an internal standard or quantitation using a

calibration curve, yielded better repeatability and minimal matrix effects compared to GC-MS methods. All methods generated good calibration curve linearity (R-square>0.991) and comparable measurement of fecal SCFA concentration. Lastly, these methods were used to compare fecal SCFAs obtained from conventionally-raised (CONV-R) and germ free (GF) mice. Results from global metabolomic analysis of feces generated by ^{1}H NMR and bomb calorimetry were used to further validate these approaches.

GC-MS Propyl Esterification Method					
Compounds	Spiked amount (μg/ml)	Amount recovered (μg/ml)	%Recovery	%RSD	%Matrix effect
Acetic Acid	10	6.7±1.0	66.9	14.9	76.3
	100	108.3±15.0	108.3	13.9	94.4
	250	254.5±16.3	101.8	5.9	92.7
Propionic Acid	10	7.2±1.2	72.3	16.9	74.2
	100	100.2±17.6	100.2	17.5	84.2
	250	244.5±36.6	97.8	15.0	92.7
Butytic Acid	10	6.7±1.1	67.0	11.2	77.7
	100	99.4±20.4	99.4	20.6	88.2
	250	249.7±38.1	99.8	15.3	97.4
GC-MS Acidified Water Method					
Compounds	Spiked amount (μg/ml)	Amount recovered (μg/ml)	%Recovery	%RSD	%Matrix effect
Acetic Acid	10	7.5±1.9	74.8	25.1	116.8
	100	108.7±14.9	108.7	13.7	95.7
	250	226.1±19.2	90.4	8.5	76.2
Propionic Acid	10	7.5±1.2	75.4	16.0	95.1
	100	106.3±10.7	106.3	10.1	80.3
	250	297.2±23.1	118.9	7.8	76.2
Butyric Acid	10	5.2±0.4	52.2	6.8	89.6
	100	87.6±17.0	87.6	20.6	76.2
	250	291.7±24.3	116.7	8.3	79.7
^{1}H NMR Quantitation Relative to TSP Method					
Compounds	Spiked amount (μg/ml)	Amount recovered (μg/ml)	%Recovery	%RSD	%Matrix effect
Acetic Acid	10	8.4±0.4	83.7	4.2	90.6
	100	97.7±4.3	97.7	4.4	118.5
	250	271.7±16.0	108.7	5.9	111.7
Propionic Acid	10	10.1±0.6	101.4	6.0	107.2
	100	116.6±5.5	116.6	4.7	116.1
	250	332.1±15.3	132.8	4.6	104.8
Butyric Acid	10	5.4±0.8	54.2	14.7	64.1
	100	92.9±4.6	92.9	5.0	118.1
	250	263.2±14.7	105.3	5.6	106.8
^{1}H NMR Quantitation with Calibration Curve Method					
Compounds	Spiked amount (μg/ml)	Amount recovered (μg/ml)	%Recovery	%RSD	
Acetic Acid	10	8.6±0.4	85.6	4.2	
	100	98.7±5.1	98.7	5.2	
	250	277.9±16.3	111.2	5.9	
Propionic Acid	10	8.0±0.48	80.2	6.0	
	100	91.4±4.6	91.4	5.0	
	250	262.7±12.1	105.1	4.6	
Butyric Acid	10	5.4±0.8	54.1	14.7	
	100	92.0±4.7	92.0	5.1	
	250	263.0±14.7	105.2	5.6	

Recovery and matrix effect of SCFAs from fecal extracts spiked with different concentration of SCFAs standards by different quantitation methods. Values are expressed as mean ± sd. n=6 per group.

MARM 211

Through the hills and valleys of time: Quantitative approaches for understanding circadian metabolism

***Aalim Weljie**, aalim@upenn.edu. Systems Pharmacology and Translational Therapeutics, University of Pennsylvania, Philadelphia, Pennsylvania, United States*

Almost all organisms have a molecular clock which is responsive to external circadian cues, such as light:dark and temperature cycles. Recently, time-dependent changes in metabolism and metabolic function have come to the fore due to implications in various disease pathologies such as cancer and other metabolic diseases. Metabolite measurement through the circadian day requires reliable and quantitative methods to ensure temporal differences are accurately captured. Appropriate study design and data processing measures essential for detecting rhythmicity in metabolomics data are also required. Here a combination of analytical approaches based on nuclear magnetic resonance spectroscopy (NMR) and liquid chromatography-mass spectrometry (LC-MS) will be presented. These included COLMeD, an LC-MS optimization strategy based on design of experiments methods, and NMR targeted profiling. Application of these tools to novel biological questions in the circadian field, such as interactions of the molecular clock with oncogene function will also be considered. Future developments in these

technologies are anticipated vis-à-vis validating these early findings, given that metabolomics has only recently entered the ring with other systems biology assessments in chronobiology studies.

MARM 212

Applications of NMR spectroscopy in food analysis and in health and disease

***Emmanuel Hatzakis**, euc15@psu.edu. Department of Food Science and Technology, Ohio State University, Columbus, Ohio, United States*

In the last decade, Nuclear Magnetic Resonance (NMR) spectroscopy has emerged as a rapid, efficient and reliable analytical method for the screening of multi-component matrices, such as pharmaceutical products, foodstuffs and dietary supplements. In addition, NMR spectroscopy can be a robust tool for the analysis of biofluids and tissues, such as serum, urine and liver. NMR is quantitative, has a non-destructive nature and allows minimal or no sample preparation. When combined with statistical analysis (metabolomics), NMR spectroscopy can be used for the comparison of spectral patterns and the identification of metabolic biomarkers and thus provide invaluable information for the evaluation of food products. It can also provide a deeper understanding of disease pathogenesis and help scientists to develop advanced strategies for the early disease diagnosis/prognosis and therapy.
Our results indicate that multinuclear (1H, 13C, 31P) NMR spectroscopy can be a valuable tool for the determination of several bioactive compounds in fish oil and coffee and revealed that dietary 2,3,7,8-tetrachlorodibenzofuran (TCDF) exposure induced liver dysfunction and significant alterations in several metabolic pathways, including hepatic lipogenesis, perturbed TCA cycle, and inhibition of de novo fatty acid biosynthesis. Interestingly, the mild liver injury and the subsequent metabolic disorders induced by TCDF exposure were found to be Aryl Hydrocarbon Receptor (AHR) dependent.

MARM 213

Differentiation of whole and refined wheat by ^{1}H-NMR spectroscopy

***Clark Ridge**[1], clarkridge@gmail.com, Venkatesh Ramakrishnan[2], Devanand Luthria[2], James Harnly[2]. (1) CFSAN, US FDA, Berwyn Heights, Maryland, United States (2) ARS, USDA, Beltsville, Maryland, United States*

The differentiation of products made with whole grain from those made with refined grain presents an analytical challenge that is of interest due to the commercial success of whole grain products. Here we present the application of an NMR fingerprinting method on two types of wheat as a step toward the goal of differentiation of whole and refined grain end products. A principal component analysis (PCA) of the 1D-proton spectrum was used. We analyzed the three different fractions of the two wheat varieties: bran, germ and refined wheat. In addition, a whole wheat sample containing all three fractions was included. Results show that the 1D, proton-NMR spectrum provides a unique spectral fingerprint for the bran, germ, refined, and whole wheat flours. The contribution of phenolic acids to the difference was investigated by limiting the spectral window that was analyzed. Reconstituted whole grain was also studied at several ratios of the germ, bran and refined grain. PCA analysis on ^{1}H-NMR data with four different bin sizes (0.02, 0.04, 0.08 and 0.16 ppm) was used as a proxy for data quality and NMR field strength to test the robustness of the analysis. A comparison to results from near-infrared (NIR) spectroscopy will also be presented.

MARM 214 Withdrawn

Compositional analysis of grass and hay using NMR: TD-NMR as a practical tool

***Istvan Pelczer**, ipelczer@princeton.edu. Chemistry, Princeton University, Princeton, New Jersey, United States*

The composition of grass and hay is a very important information both for obvious nutritional reasons, but particulalry for identification and quantification of soluble sugars. Excess of the small molecular sugars can cause insulin resistance and diabetes-like symptoms in horses. Usually there is limited information available about grass and hay, especially when purchased in bulk.
There are analytical methods available for analysis, including relatively expensive and complicated conventional wet-chemistry approaches, also NIR, etc.
We have been testing the capabilities of time-domain NMR (TD-NMR) as a fast and easy to implement technology for this purpose. TD-NMR is widely popular in agriculture for simple analyses, such as measuring moisture content. However, using appropriate calibration sets, one can use this technique to measure relative concentrations of several components in the mixture, as long as their relaxation properties are different enough. We have been studying dried ground grass samples, which were analyzed by wet-chemistry methods, and compared the results both using the statistical engine built into the native software of the Bruker MiniSpec, as well as using SIMCA (Umterics/MKS). TD-NMR has proven to be a valuable and cost-effective alternative, although the populations characterized by the different methods don't fully overlap.

Next to TD-NMR we have been testing a variety of other methods to analyze the composition of grass and hay, including extraction methods and HR-MAS technology, which will also be discussed in this talk.

MARM 215

Computer-assisted structural elucidation of two natural products

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Approximately 50 years ago NMR spectroscopy was recognized as a chemist's most powerful tool, aside from X-ray crystallography, for identifying the structure of organic compounds. Computer programs that would permit the automatic determination of such structures soon became the dream of organic and natural products chemists. With the advent of a variety of 2D NMR experiments to establish direct and long-range homo- and heteronuclear connectivity, computer-assisted structure elucidation (CASE) techniques have become a major tool in the arsenal of chemists. CASE methods will be illustrated for two natural products, one very complex and another of surprising simplicity.

MARM 216

Aligning theory and experiment to design biocompatible nanocluster fluorophores

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Nanoclusters of noble metals have emerged as promising fluorescent markers in nanomedicine applications, due to their high brightness, low toxicity and tunability. Our group has investigated a series of single-stranded DNA sequences bound to silver nanoclusters in various solution environments. Uncertainties remain about the mechanism of stability of the fluorescent clusters and the structure property relationships for size selected silver nanoclusters. We couple an experimental and computational approach to probe both factors, leveraging the experience in our group in applying quantum mechanical/molecular mechanical (QM/MM) methods to a variety of soft matter systems.

MARM 217

Understanding ultrafast mid-infrared absorptions in TIPS-pentacene during singlet fission

Christopher Grieco*, griecoceg@hotmail.com, Eric Kennehan, John B. Asbury. Chemistry, The Pennsylvania State University, University Park, Pennsylvania, United States*

Singlet fission is an exciton multiplication reaction that occurs in organic molecules, which can potentially be used to improve solar cell efficiency. To this point, the reaction mechanism has been studied using electronic spectroscopy to track the formation of the product triplet excitons. However, the precise mechanism remains controversial because it is challenging to spectroscopically distinguish these products states from any intermediate intermolecular states. To clarify the reaction mechanism, we probed the intermediate species occurring during singlet fission using time-resolved vibrational spectroscopy since it has been shown in the past to be very sensitive to the structure of intermolecular electronic states. We have chosen the highly efficient singlet fission molecule, 6,13-bis(triisopropylsilylethynyl) pentacene (TIPS-Pentacene), since it contains alkyne bonds that serve as useful vibrational probes. In addition to observing vibrational features, we also discovered interesting electronic absorptions in the mid-infrared region that decay on the timescale of singlet fission. In this talk, I will focus on the assignments of these mid-infrared transitions and how they add unexpected insights into the singlet fission reaction.

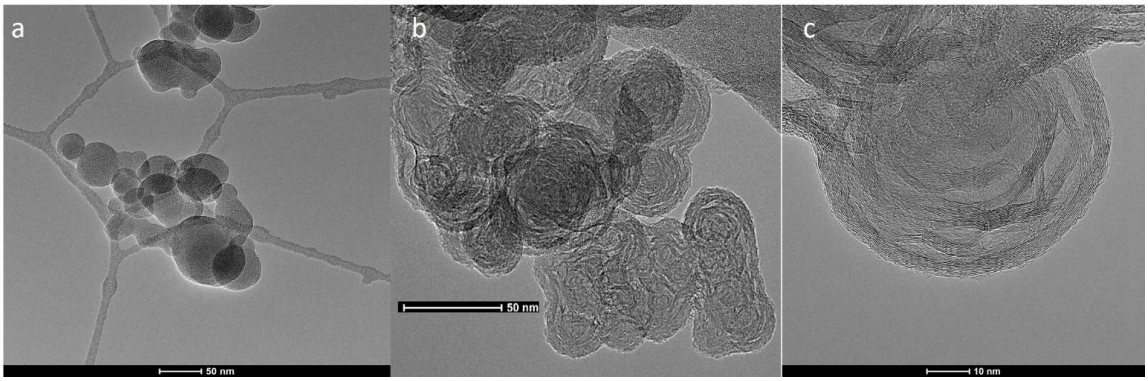
MARM 218

Using laser diagnostics and imaging to understand changes in soot nanostructure

Madhu Singh*, mus374@psu.edu, Joseph P. Abrahamson, Randy L. Vander Wal. Dept. of Energy and Mineral Engineering, The Penn State University, University Park, Pennsylvania, United States*

Particulate matter such as soot derived from vehicle emissions or other combustion processes is detrimental to human health. Deteriorating air quality due to particulate emissions has been linked to high risk of heart and lung diseases and also contributes to climate change. Thus, to establish global air quality guidelines, it is important to measure the concentration of soot in the atmosphere. Laser-induced incandescence (LII) is one such diagnostic that measures soot concentration and primary particle size. This technique can be used in-situ and has high sensitivity, providing accurate measurements even with low concentrations of soot. In order to interpret the LII signal for these measures requires reference to models for LII based on an energy balance. These models predict soot primary particle size and concentration, each with a set of assumptions about soot physical parameters –

often leading to discrepancies between simulated and experimental results. This work uses carbon black as soot surrogate and highlights some such differences by comparing experiments with model predictions. For instance, transmission electron microscopy (TEM) from this work shows significant changes in carbon black nanostructure upon laser heating, analogous to annealing, an aspect overlooked by LII models. UV-Vis spectroscopy of laser annealed carbon black shows that its emissivity can be approximated by that of a black-body with unit emissivity. This makes the analysis of the LII signal more straightforward than with presumed initial properties. By not accounting for such changes models often over- or under-predict soot primary particle size when compared to particle sizes directly measured by TEM imaging. Concentration determination is similarly skewed. Thus refinement of model parameters by comparison to experimental results is required to better predict these quantities – as shown by the presented results.



TEM images of (a) nascent and (b,c) laser heated carbon black

MARM 219

Lighting the way to the "holy grail" of catalysis: Nanoplasmonics as a mechanistic probe for the direct epoxidation of propene on gold

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The structure and pressure gap between industrial materials and laboratory models in heterogeneous catalysis has proved to be the primary obstacle to the rational design of industrial catalysts. Gold based catalytic systems epitomize a class of systems that require the development of simplified, yet representative, model systems of oxide supported nanoparticles, due to the discrepancy between the inert nature of bulk gold and the unique chemical activity of oxide supported nanoparticles of gold for heterogeneous oxidative reactions at low temperatures.

Nanoplasmonics-based sensing and spectroscopy provides a potential means to bridge both the structure and pressure gaps simultaneously. It allows the study of chemical interactions on nanoparticulate catalyst surfaces under *in situ* conditions of high temperature and pressure that mimic industrial conditions. The core of this experimental technique is the use of the plasmonic properties of sensor nanostructures (commonly gold) to probe changes on the surfaces of model catalyst-support films deposited on top of the sensing particles, using both refractive index sensitivity of peaks in the UV-visible spectra and surface enhancement of Raman signal for vibrational spectroscopy. We demonstrate the design of an experimental platform based on nanoplasmonics for the study of surface dynamics in oxide-supported gold catalysts by addressing three different aspects; design and construction of suitable experimental apparatus such as a flow reactor, preparation of model catalyst-support architectures on the sensor surfaces, and the design of an optimized nanoplasmonic sensor.

We demonstrate that simple rationally designed sensing experiments on gold surfaces lead to important mechanistic insight into complex, yet intriguing, reactions such as the direct epoxidation of propene on gold. Our experimental platform elucidates how the unique nature of light-matter interactions at the nanoscale can become an invaluable tool in the hands of a materials chemist or chemical engineer.

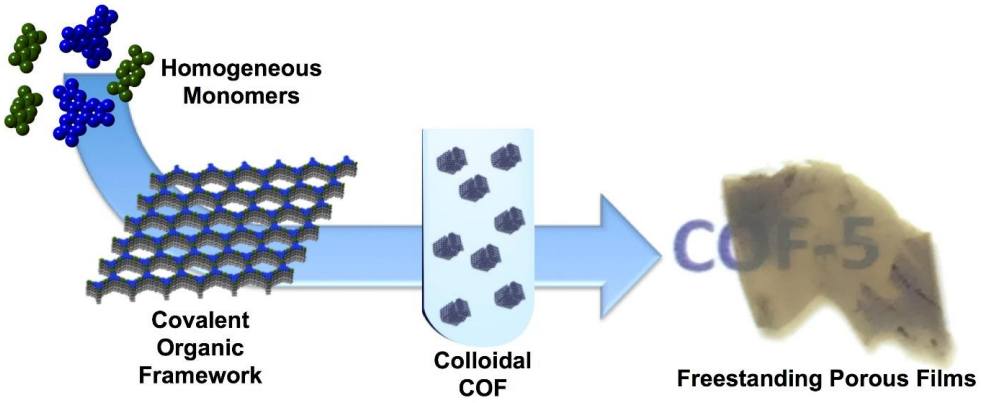
Direct Epoxidation of Propene on Gold

MARM 220

Controlling morphology: Colloidal covalent organic frameworks and solution-cast freestanding films

***Brian J. Smith**, brianjsmith@gmail.com. Bucknell University, Lewisburg, Pennsylvania, United States*

Designing materials based on molecular self-assembly achieves a structural precision and complexity unachievable with traditional top-down techniques. Covalent organic frameworks (COFs) are crystalline, polymer networks with designed topology and chemical functionality, permanent porosity, and high surface areas. These features are useful for a broad range of applications, including catalysis, optoelectronics, and energy storage devices. Despite this potential, current COF syntheses offer poor control over the material's morphology and final form, generally yielding insoluble and unprocessable microcrystalline powder aggregates. This is due, in part, to our limited understanding of COF nucleation and growth mechanisms. By controlling the synthesis conditions, we stabilize colloidal boronate ester COFs, which provide further characterization insight into COF growth and allow for post-synthetic processing into free standing, transparent porous films.



MARM 221

Developing literature discussions for an advanced inorganic chemistry course

***Chip Nataro**, nataroc@lafayette.edu. Lafayette Colg, Easton, Pennsylvania, United States*

Recent workshops run by the Interactive Online Network of Inorganic Chemists (IONiC) leadership council have focused on developing literature discussion learning objects (LOs). In those workshops, expert speakers were brought in to give presentations on a recent publication and assist the workshop participants in the development of their LOs. The workshops were very beneficial to the participants, and since the LOs are published on the Virtual Inorganic Pedagogical Electronic Resource (VIPEr www.ionicviper.org) they benefit the greater inorganic community. However, the greater community does not get to share in the lessons learned of how to develop a literature discussion suitable for their classroom and publication on VIPEr. The process of developing a literature discussion LO, from selecting the paper to publishing on VIPEr, will be presented using an example from the recent organometallic chemistry literature. The impact on student learning and their confidence in reading the chemical literature will also be discussed.

MARM 222

Research-based laboratory experiences in the inorganic chemistry curriculum at The College of New Jersey

***Abby R. O'Connor**, oconnora@tcnj.edu, **Benny C. Chan**, chan@tcnj.edu. Chem Dept, College of New Jersey, Ewing, New Jersey, United States*

The chemistry department at The College of New Jersey (TCNJ), a public, highly selective primarily undergraduate institution (PUI) considers undergraduate research a critical component of chemistry education. In addition, this department views research as a crucial piece in the development of a student's chemistry major identity. The TCNJ chemistry department offers ACS-certified and non-ACS certified chemistry degrees, with most students pursuing a research-based ACS-certified degree. The chemistry department at TCNJ has 13 research active tenure-track faculty members and approximately 130 chemistry majors. About 75% of these students participate in traditional undergraduate research projects, however more students want to participate in research than available lab positions and others are unsure about the research process, as it can be intimidating and barriers exist for participation. In order to lower the barriers for students to participate in research activities and engage more students, the laboratory experience for the inorganic curriculum, which is part of the core chemistry courses taught

at TCNJ, has been transformed over the past four years to incorporate original hypothesis driven research projects. Students work in collaborative teams to write research proposals and conduct original experiments during about half of the 3-hour per week semester long lab course. The experience is concluded by ACS-style oral presentations along with an American Chemical Society style written article summarizing all findings. Professors Chan and O'Connor have actively involved ~35 undergraduates/year in the TCNJ Inorganic courses (CHE 451 and CHE 452) in X-ray crystallography and analysis, synthetic inorganic research, bioinorganic chemistry assays and catalytic applications, which has resulted in publications with undergraduate co-authors. We describe our best practices and trajectory in developing methods to incorporate research activities into the advanced level inorganic chemistry curriculum to provide all chemistry majors with unique research opportunities and to enhance the chemistry major identity.

MARM 223

Teaching recrystallization in a flipped laboratory

***William D. Kerber**, will.kerber@bucknell.edu. Bucknell University, Lewisburg, Pennsylvania, United States*

Flipping a classroom is the inversion of traditional lecture and homework elements in a course. Students learn introductory material on their own so that class time may be devoted to advanced concepts and/or problem solving. We have used this pedagogy in introductory inorganic chemistry labs to teach recrystallization techniques. Students watched a short video and completed an assignment in advance, which seemed to improve performance and comprehension during the laboratory period.

MARM 224

Developing a POGIL-type workbook for inorganic chemistry

***Joseph M. Keane**, keane@muhlenberg.edu. chemistry, Muhlenberg College, Macungie, Pennsylvania, United States*

A workbook consisting of thirty-three actitivites has been drafted for POGIL-type instruction of undergraduate inorganic chemistry courses. Roughly half of these activites have undergone formal review by The POGIL Project. Topics addressed include formation of the elements, atomic and molecular structure, symmetry, acid-base reactions, solids, and coordination compounds. Suggestions generally applicable to POGIL-type instruction, regardless of discipline, are included. The challenges involved in developing general POGIL-type materials for inorganic chemistry include both those inherent in addressing topics that seem less amenable to guided-inquiry instruction and concerns directly related to undergraduate inorganic courses, namely the wide variability in level, content, and credit hours among courses at different institutions. The workbook continues to be revised and is available for review by faculty familiar with POGIL-type instruction.

MARM 225

Assessment tools for the foundation-level inorganic chemistry course

***Shirley Lin**, lin@usna.edu, Amy H. Roy MacArthur, Wayne H. Pearson. United States Naval Academy, Naval Academy, Maryland, United States*

The US Naval Academy offers an ACS-accredited BS degree in chemistry, graduating 30-40 students per year. Inorganic chemistry is taught in the major through a one-semester, four-credit hour foundation-level course in inorganic chemistry and an accompanying integrated laboratory course that includes inorganic chemistry experiments. This presentation will highlight some of the assessment tools used in these courses to measure student learning. Analysis of recent results will be shared and implications on curriculum and instruction discussed.

MARM 226

IONiC VIPEr: A community of practice for improving the teaching of inorganic chemistry

***Chip Nataro**, nataroc@lafayette.edu. Lafayette Colg, Easton, Pennsylvania, United States*

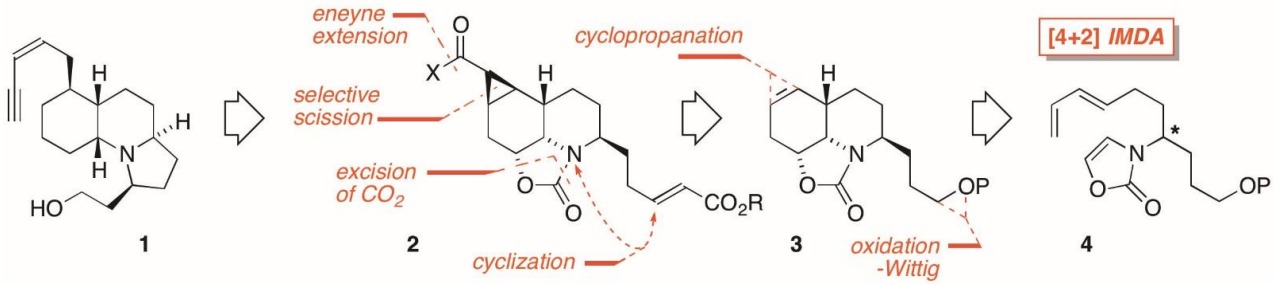
The Interactive Online Network of Inorganic Chemists (IONiC) has worked to improve teaching and learning in inorganic chemistry for over ten years. The foundation of this community is the Virtual Inorganic Pedagogical Electronic Resource (VIPEr, www.ionicviper.org). With over 1000 registered faculty users from around the world, VIPEr is a vibrant community of committed educators who have developed over 850 learning objects (LOs) for use in the classroom. This talk will highlight the ways that faculty can use the IONiC network and VIPEr resources to incorporate current research and active learning strategies in their inorganic chemistry course(s). Ways to leverage the community to teach inorganic courses and recent innovative ways that people have used VIPEr to crowdsource assessment data, collaboratively develop classroom materials, share what they are doing and incorporate new methods of teaching into their classes will be presented. VIPEr: come for the content, stay for the community.

MARM 227

Synthetic studies toward gephyrotoxin 287C

Stephen P. Fearnley[1,2]*, fearnley@york.Cuny.edu, Maciej E. Domaradzki*[2]*. (1) Dept of Chemistry, York College, the City University of New York, Jamaica, New York, United States (2) Ph.D. Program in Chemistry, The Graduate Center of the City University of New York, New York, New York, United States*

Gephyrotoxin 287C (GyTX) **1** is a tricyclic neuroactive alkaloid first isolated from the skin of the Columbian poison arrow frog *dendrobates histrionicus.* Following our successful completion of 2-*epi*-pumiliotoxin, we recently embarked on its total synthesis. The key step – an intramolecular oxazolone Diels-Alder reaction of **4** – yields the decahydroquinoline AB core **3**, fully functionalized for further embellishment. Studies toward regio- and stereospecific installation of the C6 side chain and the pyrrolidine C-ring will be presented.



MARM 228

Computational studies of intramolecular Diels–Alder reactions: N-substituted oxazolone trienes

Nicholas Sizemore[2]*, nicholas.sizemore@scranton.edu, Stephen P. Fearnley*[1]*. (1) Chemistry, York College CUNY, Jamaica, New York, United States (2) Chemistry, University of Scranton, Scranton, Pennsylvania, United States*

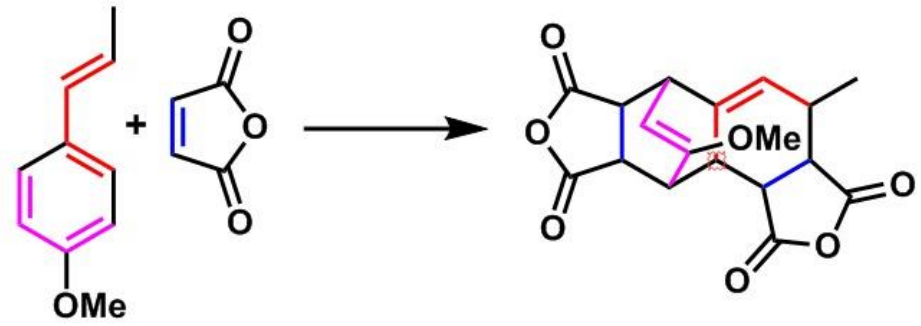
Octahydroquinoline heterocycles are useful intermediates in the synthesis of alkaloid natural products. The intramolecular Diels–Alder reaction of N-substituted oxazolone trienes has found synthetic utility for the rapid construction of such motifs. Factors affecting the diastereoselectivity of cyclization have been investigated using computational methods. These results will be reported in the context of the divergent synthesis of a decahydroquinoline family of natural products.

MARM 229

Breaking aromaticity: The Wagner-Jauregg reaction

Samuel S. Tartakoff*, startakoff@stlawu.edu. Chemistry, St. Lawrence University, Canton, New York, United States*

The two primary functions of synthetic organic chemistry, as a discipline, are making small molecules of known importance more efficiently and making potentially useful, previously inaccessible molecules. The Diels-Alder reaction serves as an ideal tool in the synthetic chemist's toolbox because it enables both of these goals. Since its discovery in 1928, the mechanism of the Diels-Alder reaction has been investigated, the synthetic scope has been expanded, and the reaction has been applied to a vast number of challenging synthetic problems. By contrast, the analogous Wagner-Jauregg reaction, discovered only two years after the Diels-Alder reaction was first reported, has received very limited attention. Long considered a special type of Diels-Alder reaction, in which a styrenyl diene is utilized, very few attempts to apply the Wagner-Jauregg reaction to the synthesis of complex small-molecules have been reported. I will present on preliminary studies to support or refute the proposed reaction mechanism and will showcase efforts towards expanding the scope of the Wagner-Jauregg reaction.

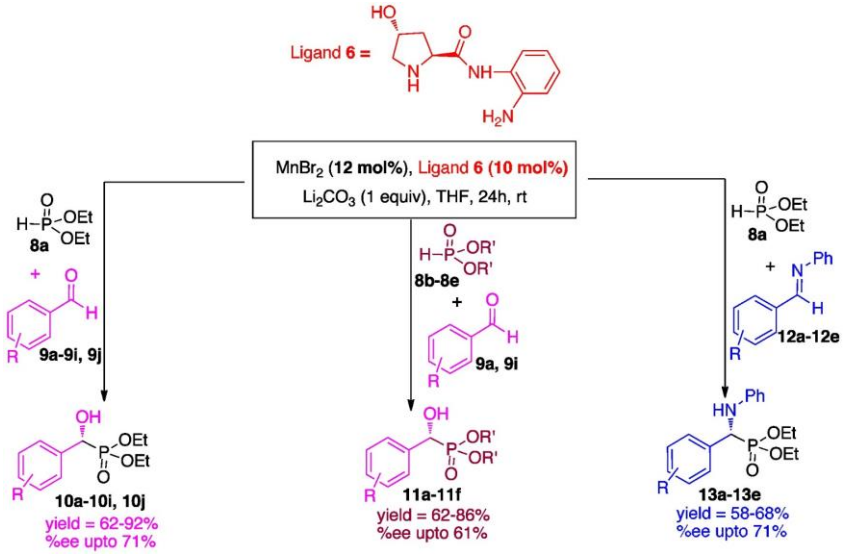


MARM 230

Manganese-proline derived new catalyst system for the enantioselective synthesis of a-hydroxy phosphonates/a-amino phosphonates

***Parminder Kaur**, kaurp6@wpunj.edu, Hyun Lim, Vicklyn Datilus, Rania Teriak, Prianka Chohan. Chemistry, William Paterson University, Wayne, New Jersey, United States*

A novel manganese/proline-derived catalyst system is reported for the stereoselective synthesis of *a*-hydroxyphosphonates and *a*-aminophosphonates. The reaction proceeded smoothly under mild reaction conditions with efficient reaction times. The resulting products were obtained with high yields and good enantioselectivities (up to 83% ee).

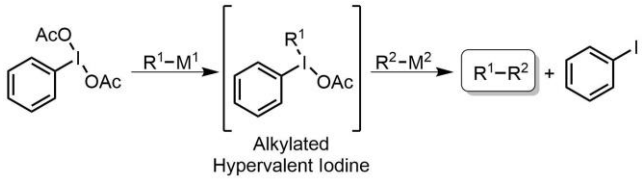


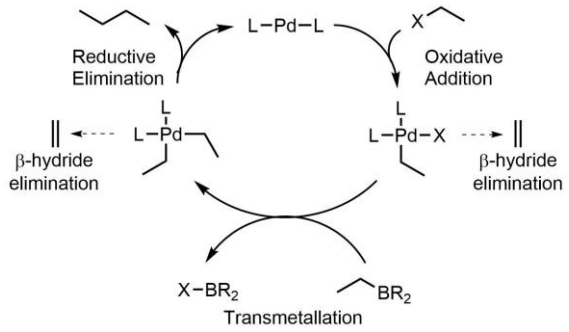
MARM 231

Progress toward the utilization of *in-situ* generated alkyl hypervalent iodine species for the cross-coupling of sp^3 carbons

***Ivan D. Hyatt**, dempseyhyatt@hotmail.com. Adelphi University, Garden City, New York, United States*

Due to β-hydride elimination, the oxidative addition and reductive elimination processes of most palladium cross-coupling reactions fail to afford products resulting from a C_{sp3}-C_{sp3} bond forming reaction. The proposed method presented uses a novel approach by which the metal-like properties and the hypernucleofugality of hypervalent iodine compounds are exploited. The methodology uses metallated alkyl groups, such as trifluorborates, to transmetallate with hypervalent iodine compounds thereby producing an unstable alkyl-hypervalent iodine intermediate. The alkyl-hypervalent iodine intermediate can then be treated with hard metal alkyl groups, such as Grignard reagents, to create the carbon-carbon bond.



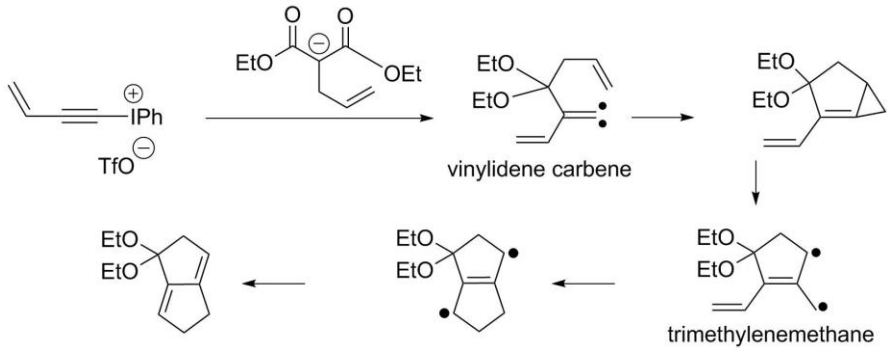


MARM 232

Reactions of hypervalent iodonium alkynyl triflates with unsaturated nucleophiles: Fused ring structures through trimethylenemethane intermediates

***Tian Li**, tianli@mail.adelphi.edu, Kiet Pham, Dempsey Hyatt. Adelphi University, Garden City, New York, United States*

Hypervalent iodonium alkynyl triflates (HIAT) are electrophilic reagents that behave with umpolung reactivity when compared to the typical nucleophilicity of alkynes. The unique reactivity of HIAT make them suited to efficiently generate trimethylenemethane (TMM) intermediates when interacting with strategically placed alkenes in an alkyl chain. Once the TMM is formed, it is theorized that a series of intramolecular radical reactions will lead to cyclization. The purpose of this research is to develop a robust methodology that will allow chemists to synthesize fused ring systems with low cost and ease of access. Once the methodology has been developed, it can be used in areas such as material science and pharmaceutical drug design.



MARM 233

Displacement of trichloroacetimidates with trimethylaluminum for the synthesis of substituted diarylethanes and related systems

***Nivedita Mahajani**, nsmahaja@syr.edu. Chemistry, Syracuse University, Syracuse, New York, United States*

Trichloroacetimidates are readily displaced by trimethylaluminum under Lewis acid promoted conditions to provide the corresponding methyl substitution product. This method is a convenient way to access diarylethanes and related systems. Diarylethanes play a significant role in medicinal chemistry, with a number of systems owing their biological activity to the presence of this functionality.

MARM 234

Catalytic hydroamination of propargyl imidates

***Michael W. Fennie**, michael.fennie@scranton.edu. Department of Chemistry, The University of Scranton, Scranton, Pennsylvania, United States*

Intramolecular hydroamination is an effective synthetic method for formation of nitrogen-containing heterocycles whose utility is often limited by the use of expensive precious metal catalysts. It has been found that propargyl imidates derived from aryl and alkyl nitriles readily cyclize at room temperature in high yields when treated with catalytic amounts of inexpensive Cu(I) salts. This *5-exo-dig* process affords dihydrooxazoles which do not aromatize under the reaction conditions and which are readily isolated. Further investigations regarding the reaction scope, rates, subsequent functionalization of the reaction products, and the development of a one-pot imidate formation / cyclization will be presented.

MARM 235

Modeling nitric oxide signaling chemistry at copper sites

***Timothy H. Warren**, thw@georgetown.edu, Subrata Kundu, Shiyu Zhang, Zeinab Sakhaei. Department of Chemistry, Georgetown University, Washington, District of Columbia, United States*

Nitric oxide (NO) plays numerous, disparate biological roles which range from signaling in the respiratory system to vasodilation in the cardiovascular system to host defense against microbial pathogens. Nonetheless, the discrete molecular mechanisms involved in NO processing are not well understood: its molecular relatives *S*-nitrosothiols (RSNOs) and nitrite (NO_2^-) can also serve as reservoirs of NO-like behavior. Thus, an understanding of the discrete mechanistic pathways by which NO, RSNOs, and NO_2^- form, interconvert, and react with molecular targets of biological relevance is crucial in understanding the molecular basis for physiological effects ascribed to NO and its molecular relatives.

Employing a family of biologically relevant copper model complexes, we examine the reactivity and interconversion of NO, RSNOs, and NO_2^-. These studies offer mechanistic insight into the copper-catalyzed release (and uptake) of NO via RSNOs at models for type 1 Cu electron-transfer sites as well as conversion of NO_2^- to RSNOs and NO. Additionally, we will describe the reductive coupling of NO at copper(I) centers which may proceed via novel *cis*-hyponitrite complexes [Cu](κ^2-ONNO) that leads to the oxidation of C-H bonds with formation of N_2O. These studies with copper models offer new insights into the biological reactivity and interconversion of key molecules involved in nitric oxide signaling.

MARM 236

Different products of hydride attack on five- and six-coordinated ferric heme nitrosyls: A DFT investigation of reaction mechanisms

*Rahul Khade, **Yong Zhang**, zhanguiucedu@gmail.com. Chemistry, Chemical BiologyBiomedical Eng., Stevens Institute of Technology, Hoboken, New Jersey, United States*

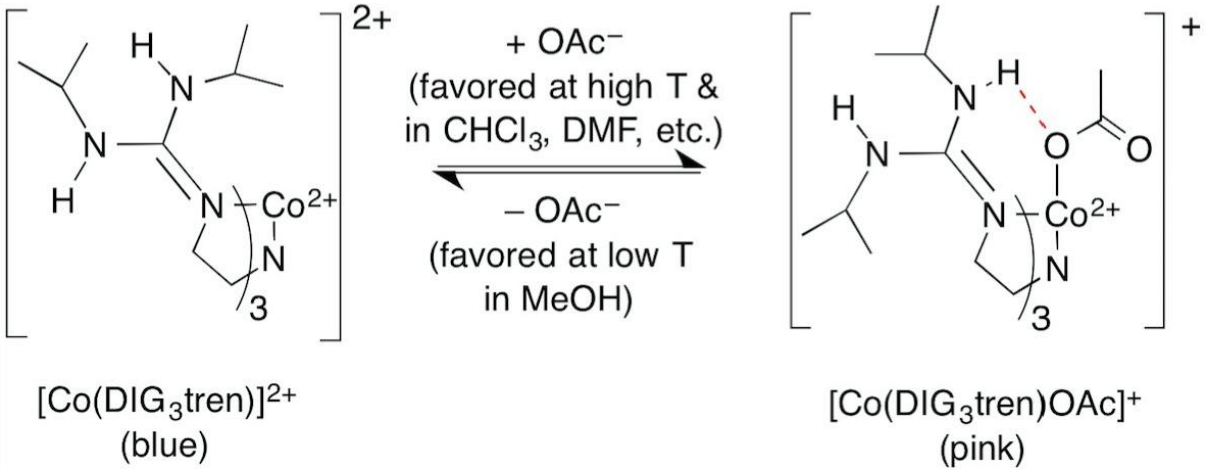
HNO has broad biological effects and pharmacological activities and heme-HNO species are crucial intermediates in several biological processes. Although nucleophilic attack by hydride (H-) at a ferric-NO moiety is a key step in NO detoxification by fungal P450 NO reductase, there are no well-defined examples in Fe heme models until recently our collaborator George B. Richter-Addo group has successfully demonstrated the first experimental generation of a heme model-HNO complex from hydride attack at a ferric nitrosyl moiety, with careful IR and NMR characterizations. In contrast with this and similar six-coordinate ferric heme nutrosyls, the five-coordinate system was found to have the hydride attack the metal center. Our DFT calculations clearly show that in the case of the six-coordinate system, the hydride attack on the N atom of the coordinated ferric nitrosyl is both kinetically and thermodynamically much more favorable than the attack on the O atom, which supports the formation of Fe-HNO complex. The computed IR and ^{1}H NMR data are also in good agreement with experimental results. For the five-coordinate system, however, calculations show that the Fe-hydride formation is kinetically more favorable than Fe-HNO, with the predicted hydride NMR shift also in excellent agreement with experiment. In addition, calculations helped discover the true boron-containing product from the use of borohydride, which was later confirmed by NMR experiments.

MARM 237

Auxiliary ligand binding to divalent metal complexes of DIG$_3$tren, a tripodal, triguanidine ligand with H-bond donors

***Robert C. Scarrow**, rscarrow@haverford.edu, Karina Gomez, Nathaniel Rolfe. Haverford Colg, Haverford, Pennsylvania, United States*

The tripodal, triguanidine ligand DIG$_3$tren coordinates divalent late-first row transition metals in the presence of non-coordinating anions (such as BPh_4^- or OTf^-) to form four-coordinate trigonal monopyramidal complexes. These complexes can bind auxiliary ligands (small molecules or anions) to form five-coordinate trigonal bipyramidal complexes in which the auxiliary ligand is bound not only by a coordination bond, but also by between one and three hydrogen bonds donated from the diisopropylguanidine arms of the DIG$_3$tren ligand. Thus the DIG$_3$tren is a general model of both first and second coordination sphere effects in metalloenzymes. One example of the concurrent changes in first and second coordination sphere is the binding of acetate to the cobalt compound (see figure); another example is the binding of nitric oxide to the iron compound. The strength of auxiliary ligand binding in various solvents will be discussed.



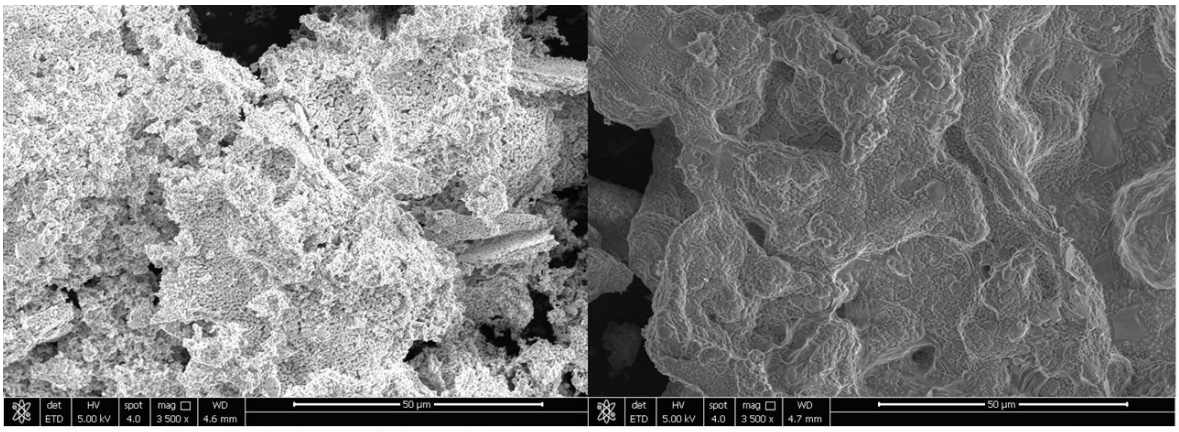
MARM 238

Benefits of biological batteries: A study on the effects of biological templates as a means to enhance lithium-ion batteries

***Scott J. Riley**[1], sriley6@umbc.edu, Mark A. Allen[2]. (1) Chemistry, UMBC, Brooklyn, Maryland, United States (2) Chemistry and Biochemistry, University of Maryland Baltimore County, Baltimore, Maryland, United States*

In the modern world there exists an ever increasing demand for more efficient forms of energy storage. Electrochemical cells are the most widely used form of portable energy storage and are possible candidates for applications on larger scales. From mobile devices to cars, batteries are integrated into many facets of daily life, yet little improvement in their performance is being recognized. While batteries have been improving over the years, the growth is slow and staggered. A new avenue involving biology's exceptional control over synthesis and binding materials together could lead to the significant improvement that is needed. My work is centered on maximizing battery performance by interfacing biology and batteries.

My research is focused on using an approach involving an array of interdisciplinary techniques to address performance issues commonly found in batteries. I use the technique of phage display to isolate Solid Binding Peptides (SBP) that bind to lithium cathode materials, specifically Lithium Cobalt Phosphate (LCP). This technique has yielded several peptides that bind to LCP. These peptides are utilized in several ways both to synthesize LCP and also bio-tether it to conducting Carbon Nanotubes (CNT). Preliminary and exciting evidence will be presented in support of this method of synthesizing materials and constructing electrodes as well as the enhancement of multiple aspects of battery performance including capacity, cyclability, and power.



Citric Acid Templated Lithium Cobalt Phosphate

Phage Templated Lithium Cobalt Phosphate

MARM 239

Electrochemical studies of cysteine/zinc interactions

Graham T. Cheek[1]*, cheek@usna.edu, Michelle Y. Doan*[2]*. (1) Chemistry Dept Stop 9b, US Naval Academy, Annapolis, Maryland, United States (2) Chemistry, United States Naval Academy, Annapolis, Maryland, United States*

The electrochemical behavior of L-cysteine in the presence of zinc(II) ion has been investigated in various aqueous media at glassy carbon, gold, and platinum electrodes. The results are intended to provide a better understanding of “zinc finger” protein structures, in which zinc(II) ions determine the local protein structure by complexation with cysteine residues. L-Cysteine in pH 7.4 phosphate buffer was found to undergo a broad oxidation process at +0.5 V vs Ag/AgCl, followed by formation of cystine as a coupling product. This behavior is relatively uncomplicated at glassy carbon; however, the formation of an oxide layer on gold at similar potentials restricts access of the L-cysteine to the electrode surface. Upon addition of $ZnSO_4$ to the pH 7.4 phosphate buffer, the L-cysteine oxidation peak at glassy carbon underwent a positive 0.2 V shift, presumably due to the formation of a L-cysteine/Zn^{2+} complex. At gold, similar behavior was observed, although lower current for the oxidation process was observed due to the oxidation occurring in the gold oxide region. The stoichiometry of the complex was briefly investigated by initial addition of $ZnSO_4$ to pH 7.4 phosphate buffer, resulting in the formation of a precipitate (zinc phosphate). Additions of L-cysteine at the 2:1 L-cysteine : Zn^{2+} point gave a clear solution, apparently due to the stronger interaction of Zn^{2+} with L-cysteine than with phosphate. These results imply that a $Zn(Cys)_2$ complex was formed, in agreement with previous spectroscopic studies in the literature.

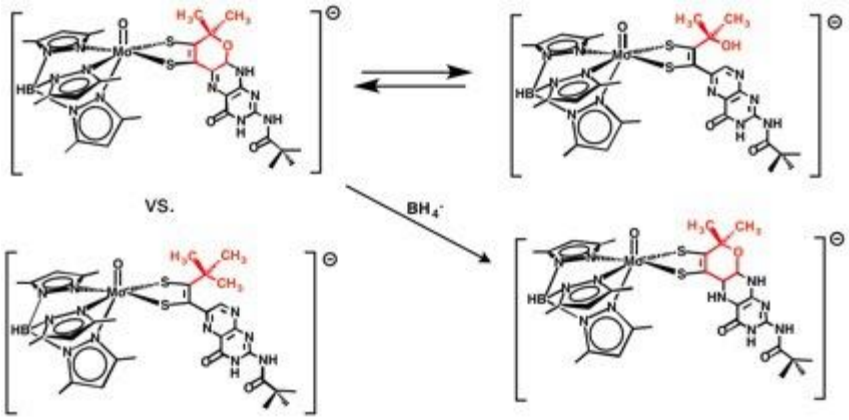
MARM 240

Modeling the molybdenum cofactor: Exploring molybdenum pterin-dithiolene reaction chemistry

Sharon J. Nieter Burgmayer[1]*, sburgmay@brynmawr.edu, Douglas R. Gisewhite*[2]*, Benjamin Willilams*[2]*, Alexandra Nagelski*[3]*, Nam Khanh Nhat Nguyen*[4]*. (1) Bryn Mawr College, Bryn Mawr, Pennsylvania, United States (2) Chemistry, Bryn Mawr College, Wayne, Pennsylvania, United States (3) Chemistry, Bryn Mawr College, Bryn Mawr, Pennsylvania, United States*

The pterin-dithiolene ligand found uniquely in molybdenum and tungsten enzymes continues to fascinate us. The complexity of this exceptional ligand has been postulated as key to the diversity of Mo and W enzyme function. The pterin dithiolene ligand has been increasingly appreciated as contributing a highly flexible electronic structure, not only because of the redox capability of both pterin and dithiolene, but also because of the role that pterin and pyranopterin conformation may play in adjusting the Mo reactivity.

Our approach to the conundrum of the pterin dithiolene function has been to develop a model system that can be adjusted to explore a variety of questions pertinent to the enzymes. Here we present recent results from several areas of exploration. First, the documented reversible equilibrium between pyranopterin and uncyclized forms will be further elaborated. Second, data from a new model complex that is unable to cyclize to a pyranopterin is compared to address the electronic consequence of pyranopterin formation. Third, the outcome of pterin reduction within the model will be described. Together these results provide experimental evidence that the pyranopterin dithiolene ligand in molybdenum and tungsten enzymes could participate in many ways in catalysis through processes modulated by the protein.



MARM 241

Careers in cosmetic sciences

***Danielle Wheeler**, danielle.wheeler@imcdus.com. Society of Cosmetic Chemists, Jacksonville, Florida, United States*

This presentation will be an informative session for soon to be graduates with degrees in Chemistry about the amazing world of art and science that is Cosmetic Chemistry. Subjects addressed in the presentation will be:

-What is cosmetic chemistry?
-What is a cosmetic vs. a drug?
-What is a cosmetic chemist?
-Why become a cosmetic chemist?
-What does a cosmetic chemist do?
-5 Steps to a career in cosmetic chemistry
-Q&A session on ways to get connected to the cosmetic industry

About the Presenter
Danielle Wheeler received her B.S. in Chemistry from the University of Florida and has been in the personal care cosmetics industry for over 15 year. She has held numerous roles in the industry including Quality, Regulatory, R&D, Technical Marketing and Sales. She has worked for companies such as Johnson &Johnson, Key West Aloe, Hawaiian Tropic and DSM Nutritional Products.
She has also been very actively involved in the Society of Cosmetic Chemists, and has held the positions of Chair-elect (2010-2011) and Chair (2012-2013) for the Florida Chapter and recently served as the Area IV Board Director and NextGen University Outreach Chair for the National Society of Cosmetic Chemists.

MARM 242

University of Cincinnati cosmetic science degree and certificate programs

***Harshita Kumari**, kumariha@ucmail.uc.edu, Gerald Kasting, Gary Kelm, Kavssery Ananthapadmanabhan, Neil MacKinnon, Randall R. Wickett. College of Pharmacy, University of Cincinnati, Cincinnati, Ohio, United States*

James L. Winkle College of Pharmacy at University of Cincinnati is one of the pioneering institutes, which provide graduate education in Cosmetic Science. Dr. Leon Lichten, Ph.D., in 1973 initiated this effort with a MS degree in Pharmaceutical Science with emphasis in Cosmetic Science at CoP. This program was further expanded in the early 1990s under supervision of Drs. Randy Wickett and Gerald L. Kasting to include a PhD degree with emphasis in Cosmetic Science. The students graduating from this program have become well-known scientists and industry leaders in the global cosmetic and personal care field. Given the rich history, the program has continued to grow over the years. Recognizing the needs of the industry, CoP introduced a distance learning MS degree track with emphasis in Cosmetic science in 2008 and launched a Graduate Certificate program in Cosmetic Science 2011. The current enrollment in our GC-MS program is over 100 graduate students. Our outstanding faculty includes experts in the cosmetic and personal care area with significant academic and industrial experience in areas such as skin care science, hair care science, colloid and interfacial chemistry, oral care, microbiology, nanoscience and quality assurance. The CoP is starting a new BS with MS degree program with the UC Chemistry department (2018) and we envision having our graduates representing UC across the globe.

MARM 243

Anti-aging cream that expands sun care to help protect against infrared damage: The next generation of skincare

***Mindy S. Goldstein**, mindy@drmindyg.com. Mindy S. Goldstein, Ph.D. Consulting Co., West Orange, New Jersey, United States*

In the 1980's, research lead to the finding that Infrared radiation (IR) may contribute to premature skin aging due to damage that it caused in the skin. Initially it was believed that IR would not penetrate the skin but it has since been shown that IRA, wavelengths 760-1440 nm, penetrates the skin as deeply as UVA. Continuing research has shown that the skin damage that IRA causes is similar to both UVA and UVB skin damage and it may actually increase the damage done by UVA and UVB radiation. There is some belief that IRA plays an important role in dermal inflammation, photoaging and cancer formation. Thus considering the mounting evidence on IR skin damage, suncare products that filter the UVA and UVB rays may be insufficient since they do not block all the damaging rays emitted from the sun. It would be in the consumer's best interest to consider a new perspective on IR radiation and that protection from IR should be incorporated into modern suncare products. A number of *In vitro*, *Ex vivo* and *In vivo* methods have been used to look at the protection from the damaging effects of IR radiation. This presentation will look at the testing of an anti-aging formula that extends sun protection to include protection against infrared radiation using a new *In vivo* assay. The results of the testing will show that it is possible to measure the erythema caused by infrared radiation and the statistically significant reduction in erythema by bio-active ingredients targeting the underlying damage caused by IR.

MARM 244

Cosmetic ingredient names: The story behind the label

***Joanne Nikitakis**, nikitakisj@personcarecouncil.org. Science, Personal Care Products Council, Washington, District of Columbia, United States*

INCI stands for International Nomenclature Cosmetic Ingredients and is a globally recognized nomenclature system for ingredients used in cosmetic products around the world. In many regions, INCI names are required for the ingredient labeling of cosmetics and personal care products. This presentation will explain the system of standardized names for cosmetic ingredients, called INCI, and provide an understanding for its importance to the industry, consumer, regulatory authorities, and medical professionals. An historical perspective will be provided, along with examples for some of the science-based conventions that have emerged to facilitate the creation of this unique and informative naming system.

MARM 245

Cosmetic and personal care product safety and efficacy claims testing

***Craig Weiss**, crweiss@cptclabs.com. Consumer Product Testing Company, Inc., Fairfield, New Jersey, United States*

Safety testing of cosmetics and personal care products in today's market will be discussed in this presentation, as well as possible upcoming changes, and the claims that can be made based on safety testing. Product efficacy claims most popular today will also be discussed, as well as how to substantiate the claims. The presentation will take a deeper dive into instrumentation, methodology, testing environment, study design and study implementation.

MARM 246

In memoriam: Wayne Wamer

***Andrija Kornhauser**, akornhause@gmail.com, Stanley Milstein. OCAC, CFSAN, FDA, College Park, Maryland, United States*

Wayne obtained a B.S. in chemistry from The Ohio State University, his Masters Degree in Science from Miami and also worked toward his doctorate at Cornell University. Wayne joined my branch at Food and Drug Administration in Spring 1979. The main task of the unit was to study the phototoxicology of mammalian skin, including the human skin. Wayne, already well educated in physical chemistry, became a member of the phototoxicity team, studying the effects of sunlight, or light generated from artificial sources, to both in vitro and in vivo systems. At that time, the medical-scientific community was already well aware of the role of sunlight in inducing various types of skin cancers in humans. Wayne conducted many experiments and studies, on both molecular and cellular levels, to elucidate the mechanisms of light-induced carcinogenesis. His work contributed significantly to the knowledge of specific cellular alterations, such as thymine dimers and psoralen photo adducts formed after exposure to UV. In addition, he also performed investigations of how some natural products, such as

carotenes, present in many green vegetables and fruits, can protect against carcinogenesis. During the later years in his carrier, he designed and performed studies on the effect of various pigments, found in tattoos on the homeostasis of human skin. In addition he he also studied and published data on the antioxidant-mimicking nanomaterials, which could have preventive or therapeutic potential against oxidative stress related disorders. His work was reported in many publications in scientific journals, as well as in his presentations and posters in a number of national and international meetings. He was well known in the scientific community, both at home and abroad. Wayne was an active member in various professional societies.

Wayne was a very private person. He was soft-spoken, but also very strong. He was always ready to help anybody who needed it, regardless of the time and energy he had to sacrifice. He always kept a high ethical standard at work, as well as in his private life. He was liked by members of the FDA community, whoever interacted with him. A short summary of his scientific contributions will be presented.

MARM 247

Analysis of natural rubber latex proteins in cosmetic products

*Stanley R. Milstein[1], **Anna-Marie Brown**[1], annamarie.brown@fda.hhs.gov, Michelle Herrmann[1], Anne D. Lucas[2], Enio Miranda-Bermudez[1], Jonathan Hicks[1], Brian Watson[3], Andrew Tebsherani[4], Robeena Aziz[1]. (1) Office of Cosmetics and Colors, U.S. Food and Drug Administration - CFSAN, Olney, Maryland, United States (2) US FDA, Rockville, Maryland, United States (3) Chief Technical Officer, Vanadis Laboratories, Carlsbad, California, United States (4) Chief Operating Officer, Vanadis Laboratories, Carlsbad, California, United States*

Many cosmetic products contain natural rubber latex (NRL) from the rubber tree, *Hevea brasiliensis.* The prevalence of Type 1 allergic responses to NRL in the general population is as high as 6.5%. The severity of allergic responses ranges from a mild local reaction (Type I) to severe anaphylactic shock (Type IV). Fourteen (14) allergenic proteins of *H. brasiliensis* have been identified in lgE-mediated latex allergy by the World Health Organization and International Union of Immunological Societies Allergen Nomenclature Sub-committee. Presently, there are no known threshold levels for latex allergenic proteins. FDA believes that there is a need for a sensitive assay that is capable of accurately measuring latex levels in cosmetic matrices and products. Methodology targeting total latex protein and antigenic latex protein in cosmetic products holds great potential to this end.

In this study, fifty seven (57) cosmetic samples broken down in the product categories of hair adhesives, eye lash adhesives, eye liners, body paints, and stage cosmetics were tested for both total latex protein and total latex antigenic protein. . Estimation of total protein was determined using ASTM 5712-10 (Modified Lowry Method), coupled with the “Method of Standard Additions (MSA)”. Antigenic latex protein was determined using ASTM 6499-12 (Modified ELISA Method), with modifications to reduce matrix interference.

Test results demonstrated that latex protein and latex antigenic protein can be extracted and quantified from cosmetic products, with good repeatability in both the Lowry and ELISA Assays.. Overall, the repeatability was good (≤22%) for both the Lowry and the ELISA assays

Latex proteins were detected and quantitated in all of the 57 samples (100%) using the Lowry assay. The ELISA assay yielded somewhat similar results, detecting and quantifying latex antigenic protein in 96% of the samples labeled to contain latex. The Lowry assay will yield an assay signal for most proteins, including those not associated with NRL, due to its non -specific nature. Conversely, latex antigenic proteins represent the total protein fraction with potential to be allergenic.

FDA plans to continue this initial study and expand its review of emerging data on NRL ingredients in cosmetic products.

MARM 248

Environmental risk assessment of plastic personal care and cosmetic ingredients

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Microbeads, a type of particulate plastic ingredient used in personal care and cosmetic products, have received substantial scientific, legislative and media attention in recent years. This has been driven by concern over environmental exposure and potential ecological hazards of microbeads. Of initial concern was the belief that microbeads could not be “filtered” by wastewater treatment plants (WWTPs) and that they could subsequently be released into the aquatic and marine environment. Once in the environment, it was argued, microbeads posed a potential hazard to animals, such as fish and invertebrates. On top of this, it was hypothesized that microbeads could act as a vector for transport of POPs (persistent organic pollutants) to aquatic organisms, increasing their exposure to toxic hydrophobic pollutants, such as PCBs and PBDEs.

As more scientific data have become available, however, it has become apparent that cosmetic products represent a very minor source of plastic litter in the environment. Moreover, studies now show that WWTPs efficiently

remove plastic particles, substantially reducing environmental exposure of these ingredients. In addition, despite a huge number of ecotoxicological studies having investigated the effects of plastic particles on wildlife, ecological impacts have not been shown to occur at environmentally relevant concentrations. An ever-increasing body of literature has also conclusively demonstrated that particulate plastic cosmetic ingredients do not increase exposure of aquatic and marine life to POPs.

The weight of evidence therefore suggests that particulate plastic cosmetic ingredients are minimally discharged to the aquatic and marine environment and do not pose a demonstrable hazard to aquatic and marine organisms. However, the issue of particulate plastic pollution continues to be of concern to scientists, regulators and legislators globally. With this in mind, we present a novel environmental modeling tool to assess environmental exposure of plastic particles that may potentially be discharged to the environment *via* WWTPs. We also present an environmental risk-based approach to assessing particulate plastic cosmetic ingredients. Finally, we examine how applying accurate terminology characterizes those polymeric cosmetic ingredients that could potentially contribute to aquatic and marine plastic litter. This allows particulate plastic cosmetic ingredients to be prioritized for environmental assessment.

MARM 249

New solutions to an old problem: Modernizing quaternary ammonium antiseptics

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Quaternary ammonium compounds (QACs) have been a first line of antiseptic defenses for about a century. By virtue of targeting a fundamental bacterial target – cell membranes – these molecules were thought to be safe from bacterial resistance. However, decades of overuse coupled with modest innovation have left the door open to the development of bacterial resistance, leading to the urgent need for novel QACs. Our group has prepared over 400 novel QAC compounds for antimicrobial evaluation, and has learned lessons about resistance, the importance of amphiphilic structure, and the role of a PUI in addressing a medical shortcoming.

MARM 250

Bioactive polycationic amphiphiles as novel antiseptics

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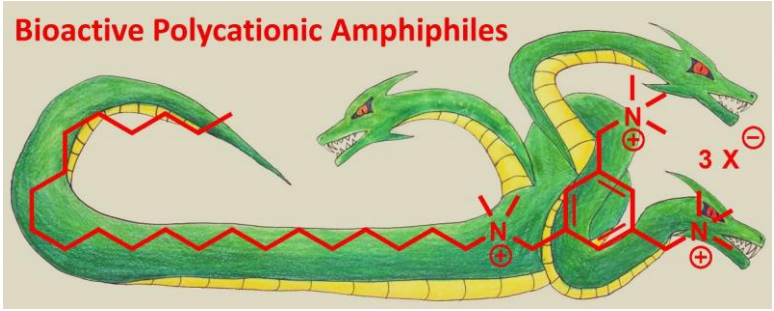
We have prepared a number of novel surfactants with a variety of non-conventional structures as part of our efforts to better understand colloidal and antibacterial activity. These include compounds with two to six cationic head groups and one to three non-polar tails. Structural variation includes modification of tail length, core structure, cationic groups and counterions. This work has allowed us to begin to develop an understanding of the relationship between amphiphile structure and colloidal activity, as measured by critical aggregation concentration (CAC) in aqueous solution. Collaborations with JMU Biology and JMU Physics have also led to an understanding of the relationship between structure and antibacterial and foam-forming ability, respectively. This has led to the development of several compounds with notable antibacterial activity. Ongoing work aims to optimize our search for potent and fast-acting antiseptics.



MARM 251

Carbon dioxide measure with reference to oxygen use in respiration of *Bryophyllum sanctulum*

***Cyril E. Broderick**, cbroderick@desu.edu. Agriculture and Natural Resources, Delaware State University, Dover, Delaware, United States*

Since Priestley and Lavoisier discovered oxygen (ca. 1773-1775), and with the recognition of the roles of carbon dioxide and oxygen in photosynthesis and respiration, functional roles of these gases (carbon dioxide and oxygen) in plants have focused mostly on photosynthesis; nevertheless, the respiratory processes in plants also deserve attention. Exercises reported here are addressed to that question, and our objectives are to compare the net evolution of carbon dioxide from plants under (a) diurnal conditions of light and darkness and (b) during continuous darkness. Bryophyllum plants were selected because the plant is resilient and does not die easily. It is a Crassulacean Acid Metabolism (CAM) species that closes it stomata during the day but opens them up during the night, minimizing water loss but picking up CO_2 at night. Carbon dioxide uptake is catalyzed by the activity of the enzyme phosphoenol (PEP) carboxylase. We found very little data on oxygen uptake and carbon dioxide emission from plant leaves. Measures found were mainly for aerenchyma cells in plant roots. We measured carbon dioxide emission from these plant leaves by the neutralization of the base by emitted cartbon dioxide in four replications each. Ten-milliliter aliquots of 1 N NaOH in small jars were set in larger jars which contained five whole leaves from Bryophyllum plants. Jars were in complete darkness or in a diurnal environment of approximately 11 hours of daylight and 13 hours of night. After 8 days, five milliliters from the 10 ml aliquots were removed from each jar and titrated with 1 N H_2SO_4. NaOH aliquots from the diurnal exposed leaves averaged 4.83 ml upon titration whereas leaves from the dark averaged 4.5 ml.The results showed some variability, and confidence limit was not the highest. Moreover, leaves in the dark developed new roots in their leaf margins. These results encourage our introduction of new equipment and measures to secure more complete data. The measure of tissue plant respiration has enormous implications, because plants do not have hermoglobin or other molecules to transport gases in their vascular systems, but oxygen uptake and carbon dioxide emission deserve further evaluation.

MARM 252

Pharma: Friend or foe? Development, implementation, and assessment of a cross-disciplinary non-majors course about the pharmaceutical industry

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Despite the significant positive impact that medicines have had on our society, the public little understands the process of drug discovery and development, which tends to trigger health conspiracy theories and other criticisms, especially pertaining to cost, efficacy, and side effects. College courses in this field often target science majors, but at Muhlenberg College, we developed (Spring 2017) a cross-disciplinary non-majors course about the pharmaceutical industry titled “Pharma: Friend or Foe?” Taught by two professors as a “cluster”—two courses from separate disciplines linked by common themes and assignments—it fulfills part of the college’s integrative learning requirement. On the science side, taught by Professor Sherri Young, students learn about molecular structure, pharmacokinetics, and small molecule and biologic drugs, as well as marketing, development time, pricing, manufacturing, and FDA regulation. On the ethics side, taught by Professor Gilles Colin, students debate the role of lobbyists and politics in the industry and the ethical issues surrounding animal testing. A course overview and schedule, sample assignments, preliminary assessment data, and reflections by the instructors will be presented.

MARM 253

Chemistry on the backs of frogs: Bioactive small molecules from an amphibian-bacterial-fungal ecosystem

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A rich chemistry surrounds the emerging fungal disease chytridiomycosis, which has been linked to worldwide amphibian population declines. The causative agent, *Batrachochytrium dendrobatidis* (Bd), produces immunomodulatory compounds that may be involved in infection and disease progression. Bacteria present on the amphibian’s skin produce antifungal compounds, providing a level of detection against Bd. In some instances, interspecies microbial interactions influence the production of such metabolites. These bioactive compounds produced by the amphibian cutaneous microbiome can be detected, characterized, and studied using HPLC, HRMS, and NMR in order to better understand chytridiomycosis and the chemical interactions between host, pathogen, and bacterial symbionts.

MARM 254

Evolving landscape of drug discovery and drug development: Advances in pediatrics

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Mandated by FDA and EU regulations to assess new medicinal innovations in appropriate pediatric populations, companies are required to develop age appropriate drug delivery in means that are acceptable to patients and their caregivers. Pediatric drug development encompasses approaches to address the challenges embedded in the complexity of these regulatory requirements. The challenges faced in pediatric drug development relate directly to the diversity of the pediatric population--spanning newborns (even those born preterm!) to patients 18 years of age and the fact is that a one size fits all approach is neither realistic nor practical. Utilizing examples of pediatric products on the market, products modified once on the market and new technologies in development, this talk will provide a discussion on pediatric centric drug development current state and vision for the future. The evolution of technologies to address the varying patient needs across pediatric populations is a subject worthy of discussion as it may provide insights and tools to lead the industry into the patient centric pharmacy of the future.

MARM 255

Developability: Bridging the gap between drug discovery and development

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Developability plays a vital role for the success of new chemical entities transitioning from preclinical to clinical development through commercialization. The majority of new chemical entities being discovered in many disease areas have a poor aqueous and biorelevant solubility. These are often available in the amorphous and chemically impure form for in-vitro enzyme assays, pharmacokinetic, pharmacological and toxicological studies in animal models. These molecules are often dosed as a suspension/solution orally/parenterally respectively and candidate selection is based on results obtained from these studies. Therefore, it is very important to select a physical form as early as possible so that the same form can be used for preclinical and clinical studies, as changes in physical form or formulation principle could significantly affect the pharmacokinetic performance and formulation characteristics (i.e. stability/solubility/compatibility) and toxicity. The selected candidate must exhibit adequate physical and chemical stablility during the formulation development process with desirable pharmacokinetic parameters. If pharmacokinetics parameters of these molecules are different due to different physical form or formulation selection, a significant delay may occur during development. It's important to explore enabling technologies with existing molecules depending on the clinical/market need. This presentation will cover early formulation strategies for preclinical and clinical studies ensure the successful development of new chemical entities by bridging the gap between discovery and development.

MARM 256

Evolution from a failed reaction to spawning a start-up company: Development of a novel pro-drug technology

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Ever wonder what to do with a failed chemical reaction? The instinct we train into ourselves is to put it in the waste can, push forward and successfully find the reaction conditions needed to solve the original problem. However, there are times when you should step back, look at the data with fresh eyes, and consider whether you have made a discovery worth investigating further.

This is the story of such a situation that could only be born from years of experience of success and failure in a research lab. While searching for an approach to developing a traditional pro-drug for a known cardiac drug, we encountered a FAILED reaction. Upon further investigation, we uncovered a potentially novel way to make pro-drugs, with the capability of improving the solubility of nearly any drug in a pH independent way with a release mechanism that can be tailored to maintain the PK (pharmacokinetic) profile of the drug or alter it in a predictable way.

The ability to take any drug or drug candidate and make it more soluble with a tunable PK profile is highly desirable in drug discovery. This approach has been applied to many drugs; several examples will be provided which include repurposing a cardiac drug for chronic kidney disease and development of an improved version of a classic oncology drug, paclitaxel.

Looking at the problem differently permitted us to develop a novel pro-drug technology, spawn several collaborations and spin-off a company.

MARM 257

Investigation of sample preparation and acquisition method effects on non-targeted screening using LC/HR-MS

***Ann Knolhoff**, aknolhoff@gmail.com, Caitlin Kneapler, Timothy R. Croley. FDA/CFSAN, College Park, Maryland, United States*

The majority of chemical methods for food safety applications are for specified contaminants and adulterants, but analyses become more challenging if unknown, potentially hazardous compounds are present. There are multiple advantages for using ultra-performance liquid chromatography and high-resolution mass spectrometry (UPLC/HR-MS) such as improved separation in both the chromatographic and mass-to-charge regimes and mass accuracies less than 5 ppm, which result in reduced chemical complexity and the generation of molecular formulae to aid in the identification of unknown compounds. The aim of this work is to determine optimal conditions for the detection of compounds for non-targeted screening. To this end, infant rice cereal, orange juice, and yogurt were chosen to investigate sample preparation methods, chromatographic gradient length, and MS acquisition methods. Extraction methods included QuEChERS, the Universal method, and an acetonitrile shake-out; these samples were analyzed with a Nexera UPLC (Shimadzu) with a Kinetex C18 column hyphenated to a Q-Exactive mass spectrometer (Thermo). Data processing was performed using Compound Discoverer (Thermo). In general, the Universal method appeared to be the best choice for all three sample matrices analyzed in both positive and negative ion modes; this method extracted many of the same compounds as the other methods, but also had a large percentage of unique compounds associated with it. Multiple MS methods were examined to determine the number of features that can be extracted from the data, including acquiring with different resolving powers, MS and MS-MS scans, and positive and negative ion modes. The combined result of these analyses will be discussed with an emphasis on improving the detected chemical coverage for different sample types.

MARM 258

Mass spectrometric analysis of the effects of a proline endopeptidase on gluten in a wheat gluten incurred model sorghum beer

***Katherine L. Fiedler**, katherine.l.fiedler@fda.hhs.gov, Rakhi Panda, Timothy R. Croley. U.S. FDA/CFSAN, College Park, Maryland, United States*

Proline endopeptidase (PEP) is an enzyme used by some brewers to degrade immunogenic gluten sequences in an attempt to produce beer that is safe for consumption by individuals with celiac disease. The goal of this study is to determine the effects of proline endopeptidase on gluten by using mass spectrometry to characterize the hydrolyzed gluten present in beers brewed with and without PEP. Sorghum beer incurred with 200 ppm wheat gluten was brewed with and without the addition of PEP at the start of fermentation. The beer samples were fractionated into the hydrolyzed peptides, which were analyzed directly by LC-MS/MS and database matching, and the intact proteins, which were analyzed using a traditional bottom-up proteomics approach via digestion with chymotrypsin. A number of gluten peptides were identified in both of the hydrolyzed peptide and intact protein fractions of the untreated and PEP treated samples, indicating that some gluten proteins remain, at least partially, intact after fermentation and enzymatic treatment. This observation confirms Western Blot results from these samples, which showed the presence of intact proteins after fermentation and enzymatic treatment. More hydrolyzed gluten peptides were identified in the PEP treated samples compared to the untreated samples, whereas more chymotryptic gluten peptides were identified in the untreated samples compared to the PEP treated samples. This suggests that PEP treatment does lead to increased degradation of intact gluten proteins; however the gluten was not degraded completely and gluten protein fragments and gluten peptides remained. The identified hydrolyzed and chymotryptic gluten peptides were compared to a database of known celiac disease relevant T-cell epitopes, using a custom python script, to determine how PEP treatment changed the profile of immunogenic gluten sequences in beer. A few known T-cell relevant epitopes were observed in the PEP treated samples, including an immunodominant peptide from the 33-mer.

MARM 259

Detection and characterization of nanomaterials used in food

***Sadia A. Khan**, sadia.afrin.khan@gmail.com, Timothy R. Croley. U.S. Food and Drug Administration, College Park, Maryland, United States*

As nanotechnology has advanced, the uses of nanomaterials in the food sector have also increased. Nanomaterials have been used to improve the taste, color, flavor and texture in food, supplements, and other consumer products. While nanomaterials may offer many unique benefits in the food materials, there are disputed opinions about their safety. Some of these materials are used in the bulk form as FDA approved food additives; however, concern is rising over the nano-sized materials of the same additives, which necessitates detection and

characterization of these nanomaterials. Despite a number of studies in this area, there remains a gap to address the problems associated with sample preparation for nanomaterial analysis in food and food related matrices. In this presentation, we will give an overview of the current use of nanomaterials in food as well as different analytical methods that are being used for the detection and characterization of nanomaterials. In addition, we will show a comparison of different characterization techniques with specific case studies.

MARM 260

Vanilla authentication using SPME-GC-MS

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Vanilla is one of the most popular flavoring ingredients used in foods and beverages with vanillin being the major sensory compound. Vanillin can be extracted directly from the vanilla bean using water, alcohol or other organic solvents. Alternatively, vanillin can be produced synthetically, most commonly from guaiacol, but the flavor profile differs significantly to that of natural vanillin. Natural vanilla extracts contain over 200 components, 26 of which are present at concentrations in excess of 1 part per million. The combination of all these compounds are what give natural vanilla its distinctive flavor.

Natural vanilla production is limited, prices are high, and demand for the flavor cannot be met with vanilla beans alone. It is important to have a method that can distinguish between authentic vanilla extracts and artificial vanilla flavoring. Building on a previously published SPME GC-MS method, modifications were made to expand the number of analytes detected. The resulting method was used to analyze commercially available vanilla products and to determine if appropriate labeling is being used.

MARM 261

Identification of potential neurotoxicants using in vitro enzyme inhibition assays

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A number of contaminants and naturally occurring chemicals in foods, cosmetics, and dietary supplements have unknown effects on the nervous system. Consequently, rapid in vitro screening methods serve as important initial steps in identifying potential chemical hazards and prioritizing subsequent toxicological testing. Compounds that inhibit activities of two enzymes in the nervous system, monoamine oxidase (MAO) and acetylcholinesterase (AChE), are associated with adverse effects including serotonin toxicity, gastrointestinal distress, emesis, and salivation. Therefore, MAO and AChE inhibition assays were developed as an inexpensive and rapid means to identify potential neurotoxicants.

First, a MAO inhibition assay was developed using human recombinant enzyme and fluorescence detection. Inhibition of MAO activity by an amine stimulant in dietary supplements and four analogs were measured, and the mode of inhibition identified. Methyl and ethyl substitutions on the amines yielded differences in potency over a wide range (Ki, 5–250 μM), but were much weaker than estimated blood concentrations (0.5 μM), an important aspect in understanding the relevance of in vitro results to human health. A second method was developed to measure inhibition of AChE activity in a human neuroblastoma cell line using absorbance and fluorescence detection. The assays accurately quantified potency of several known inhibitors, and the assays were adopted into a high-throughput screening platform where 19 inhibitors were detected (IC_{50} < 10 μM) among 1368 compounds screened. These examples illustrate the value of in vitro neurotoxicity studies, which provide a comprehensive assessment of potential neurotoxicity through structure-activity relationships, and the importance of considering bioactive metabolites and estimated blood concentrations in vivo.

MARM 262

Collecting, preserving, and sharing the history of science and engineering at the Chemical Heritage Foundation

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In the thirty-five years of its existence, the Chemical Heritage Foundation (CHF) in Philadelphia, Pennsylvania, has evolved into an organization that has expanded well beyond its original form. Today it is a research library, a museum, and a center for scholars in the history of chemistry, chemical engineering, and the life sciences with a mission to foster dialogue on science and technology in society. We fulfill that mission in a variety of ways: by

supporting a professional library, archive, and museum to collect, preserve, and exhibit our historical materials, by engaging communities of scientists and engineers to see the value of their legacy and support our continuing efforts to embrace it, and by sharing the stories of the people behind the scientific breakthroughs, innovations, and regular ongoing work that has had a tremendous impact on society. Because of our relatively brief period of existence so far and our rather rapid evolution over that time, we are challenged with properly communicating to our supporters just who we are and what we do. This paper will discuss, in brief, how CHF got to where it is today, and then go into more detail about the work that we do, including our extensive library, museum, and oral history collections, our history fellowship program, our research activities, our growing online presence, and our magazine, podcast, and other public programs and exhibitions.

MARM 263

19th Century undergraduate chemical education in Pennsylvania's Lehigh Valley

***Roger A. Egolf**, rae4@psu.edu. Chemistry, Pennsylvania State University, Allentown, Pennsylvania, United States*

During the 19th century, three institutions in Pennsylvania's Lehigh Valley offered degrees in chemistry. Those institutions were Lafayette College, Lehigh University, and Muhlenberg College. This paper will cover the early histories of undergraduate chemical instruction at these schools and biographical information about the faculty and a few of the more prominent students who graduated from these programs.

MARM 264

19th Century graduate chemical education in Pennsylvania's Lehigh Valley

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Graduate education in chemistry started very early in Pennsylvania's Lehigh Valley. All three institutions in the area that offered undergraduate chemical education, Lafayette College, Lehigh University, and Muhlenberg College, also offered graduate degrees, including the PhD at some point in the late 19th century. Lehigh University was the last of these three schools to start a graduate program, but is the only one that still grants graduate degrees. This paper will present information about the schools, their 19th century graduate programs in chemistry, and biographical information about about a few of the faculty and doctoral graduates of these programs.

MARM 265

Miles Pickering (1943-1991): A mentor, a friend: Primarily a chemical educator

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Though Miles Pickering's life of 48 years was cut short by a heart attack, from 1972 to 1991 he published 79 papers that covered many topics in general and organic chemistry such as teaching and learning in lab and lecture, and attacking "sacred cows" in chemistry education. He also participated in interesting hands-on research involving fission products. In only one short year he became a mentor and friend whose impact became long-lasting.

MARM 266

Hubert Alyea: Life-long learner

***James L. Ealy**, jle15@psu.edu. Science, Penn State University, LV campus, Nesquehoning, Pennsylvania, United States*

Hubert Alyea (1903 – 1996) was a gifted lecturer at Princeton University and developed a multitude of chemical demonstrations for his students. Many of the demos that Dr. Alyea performed for his students, were smelly, choking, noisy, and most importantly imaginative. The success behind Alyea's demonstrations were that they were simple. If you read the recipe once, you could easily remember it; there was no real need to look over pages of notes. However, four decades later, more time is now spent cleaning up and following all safety protocols, than preparing and presenting demos. Two of the many aspects of Hubert Alyea's career : "Lucky Accidents and the Prepare Mind" and "Tested Demonstrations" will be the focus of this presentation.

MARM 267

Legacy of tetraethyl lead

***Jessica L. Epstein**, jepstein1@saintpeters.edu. Saint Peters College, Jersey City, New Jersey, United States*

Accounts of lead exposure are sprinkled through out human history. Lead poisoning remained a rare disorder, confined mostly to mine workers, until the early 20th century when lead found it's way into the consumer market in the form of lead solder on food cans, paints, pesticides, toothpaste packaging and water stored in lead lined tanks. However, it was the introduction of tetraethyl lead, a gasoline additive that prevents common engine knocking, that dramatically introduced lead into the Earth's biosphere. Tetraethyl lead increased lead levels in every inhabitant of earth, and years after the protracted battle to ban lead from gasoline, remains a legacy that is with us today and in our bodies.

MARM 268

Amino acid interaction networks in enzyme catalysis

*Kathleen F. O'Rourke, Jennifer Axe, Eric M. Yezdimer, Nicole E. Kerstetter, Rebecca N. D'Amico, **David D. Boehr**, ddb12@psu.edu. Chemistry, The Pennsylvania State University, Port Matilda, Pennsylvania, United States*

Our previous studies have demonstrated that enzymes fluctuate into lowly populated conformations that correspond to their next structural state in the catalytic cycle. These fluctuations appear to prepare the enzyme for the next structural transition, and may be rate-limiting bottlenecks in enzyme catalysis. However, it is poorly understood how these different motions and structural transitions are effectively coordinated. One proposal is that there are interaction networks of amino acids operating throughout the protein that help to synchronize these structural transitions.

Here, we have used NMR chemical shift covariance analyses (CHESCA) and R_2 relaxation dispersion experiments to identify long-range amino acid interaction networks in the alpha subunit of tryptophan synthase both for the resting state (in the absence of substrate and product) and for the working state (during catalytic turnover). The amino acid networks observed stretch from the surface of the protein into the active site and are different between the resting and working states. Amino acid interaction networks in enzymes are thus *dynamic*, and change to regulate the various stages of catalysis, from substrate binding and product release to chemical catalysis itself. Modification of surface residues on the network alters both catalytic function and interactions with the beta subunit.

Altogether, these findings demonstrate that amino acid interaction networks, similar to those studied here, are likely important for coordinating structural changes necessary for enzyme function and regulation. The ability to re-wire such networks would provide new opportunities for engineering stimulus-responsive materials that may find applications in nanotechnology and synthetic biology.

MARM 269

Lack of folding and yet a function: Structural insights into intrinsically disordered proteins and transcription

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Intrinsically Disordered Proteins (IDPs) partially or completely lack a co-operatively folded structure under native conditions, making their equilibrium state very different from that typically described through high-resolution structural biology. Our view is that IDPs do possess native structure that is responsible for imparting their specific functions; describing these structures simply requires a broadening of the traditionally narrow structure-function paradigm. To better understand the function of IDPs, our laboratory focuses on transcription factors and the enzymes that carry out transcription in eukaryotes. In this presentation, we will focus on the Carboxy-Terminal Domain (CTD) of the RNA polymerase II (Pol II) large subunit in order to illustrate our approach. CTD cycles through multiple phosphorylation states that correlate with progression through the transcription cycle and regulate nascent mRNA processing. Structural analyses of yeast and mammalian CTD have been hampered by their repetitive sequences. Here we identify a region of the *Drosophila melanogaster* CTD that is essential for Pol II function *in vivo* and capitalize on natural sequence variations within it to facilitate structural analysis. Mass spectrometry and NMR spectroscopy reveal that hyper-Ser5 phosphorylation transforms the local structure of this essential region via proline isomerization. The sequence context of this switch tunes the apparent activity of the CTD phosphatase Ssu72, suggesting a mechanism for the selective recruitment of *cis*-proline specific regulatory factors that may synergize with CTD phosphorylation to augment gene regulation in developmentally complex organisms.

MARM 270

Investigating the effect of alpha-synuclein tyrosine-39 phosphorylation on synaptic vesicle trafficking

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Post-translational modifications (PTMs) are covalent modifications made to proteins that give rise to the complexity and diversity of proteomes. New functional groups -- such as methyl, acetyl, phosphate groups -- sugars, lipids, and even small proteins such as ubiquitin can be attached to target proteins, generally through enzymatic processes. PTMs can regulate protein activity, folding, stability, and localization, playing a key role in biological processes including signaling and pathogenesis. Phosphorylation is the most common PTM on proteins, and indeed many phosphorylation sites have been identified and studied in alpha-synuclein (α-syn), an intrinsically disordered protein believed to mediate synaptic vesicle trafficking. Abnormalities in this protein's interactions with lipid vesicles and membranes lead to the formation of non-functional, misfolded fibrils, which are implicated in Parkinson's disease. Recently, phosphorylation of Tyr-39 on α-syn has been identified and found to switch the protein conformation from an extended-helix to a broken-helix state when bound to lipid vesicles. We combine protein semi-synthesis and single molecule fluorescence spectroscopy techniques to determine the effect of this PTM on the ability of α-syn to mediate vesicle fusion. Using peptide synthesis, recombinant production of proteins with unnatural amino acids, and native chemical ligation (NCL), we produce modified, fluorescently labeled α-syn. We then determine changes in its binding affinity for lipid vesicles through Fluorescence Correlation Spectroscopy (FCS) and validate the structural changes induced by Tyr-39 phosphorylation via single molecule Forster resonance energy transfer (smFRET) in the presence of lipid vesicles. We examine the effects of these structural and interactional changes on protein function by assaying the fusion of fluorescently labeled vesicles mediated by phosphorylated α-syn. Our study provides insight into the impact of post-translational modifications on protein structure, ability to carry out physiological function, and potential contribution to disease.

MARM 271

DNA-crowded enzyme complex with enhanced activity and stability

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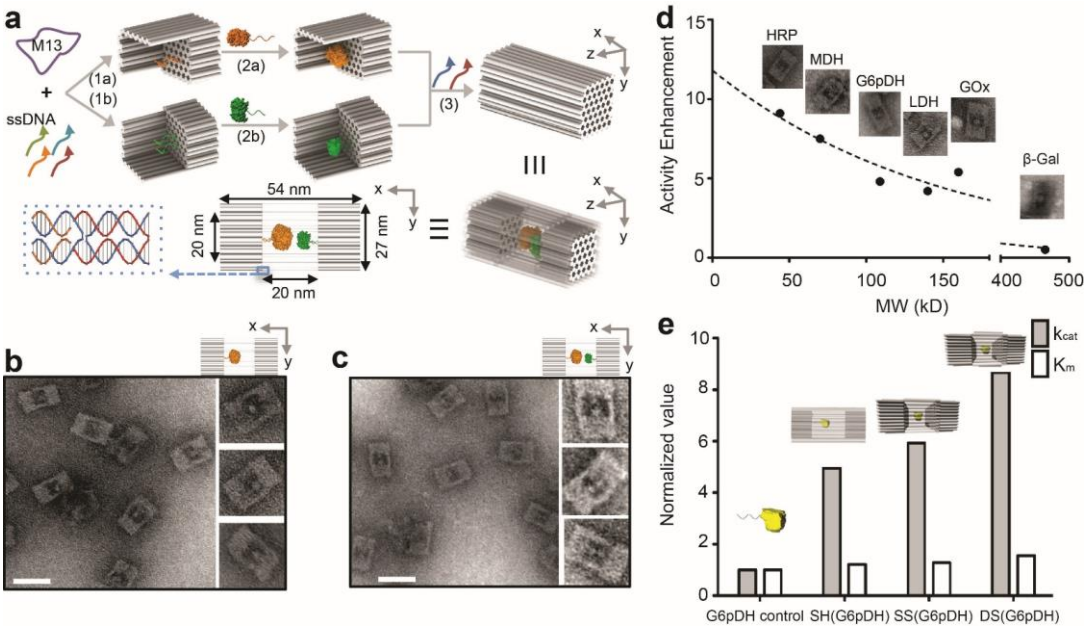
Cells routinely compartmentalize enzymes for enhanced efficiency of their metabolic pathways. Here, we report a general approach to construct DNA nano-caged enzymes for enhancing catalytic activity and stability. Nano-caged enzymes are realized by self-assembly into DNA nanocages with well-controlled stoichiometry and architecture that enabled a systematic study of the impact of both encapsulation and proximal polyanionic surfaces on a set of common metabolic enzymes. Activity assays at both the bulk and single-molecule levels demonstrate increased substrate turnover numbers for DNA nanocage-encapsulated enzymes. Unexpectedly, we observe a significant inverse correlation between the size of a protein and its activity enhancement. This effect is consistent with a model wherein distal polyanionic surfaces of the nanocage enhance the stability of active enzyme conformations through the action of a strongly bound hydration layer. We further show that DNA nanocages protect encapsulated enzymes against proteases, demonstrating their practical utility in functional biomaterials and biotechnology.
As shown in **Fig. 1a**, our approach for enzyme encapsulation within DNA nanocages involves two steps: 1) the attachment of an individual enzyme into an open half-cage and 2) the assembly of two half-cages into a full (closed) nanocage.The encapsulation of enzymes within DNA nanocages are characterized using transmission electron microscopy (TEM) (**Fig. 1b and c**). For most of encapsulated enzymes, their activities were boosted for from several folds up to 10-fold depending on their protein sizes (**Fig. 1d**). The smaller enzymes were observed for more enhancements, as compared with larger enzymes. Further, we investigated the effect of DNA helix density on the encapsulated enzyme activity. As shown in Fig. **1e**, encapsulated enzymes exhibit higher activity within densely packed DNA cages, consistent with our hypothesis that the highly ordered, hydrogen-bonded water environment near closely spaced phosphate groups are responsible for this effect.



MARM 272

Structural and functional analysis of POT1-TPP1 disease mutations in cancer

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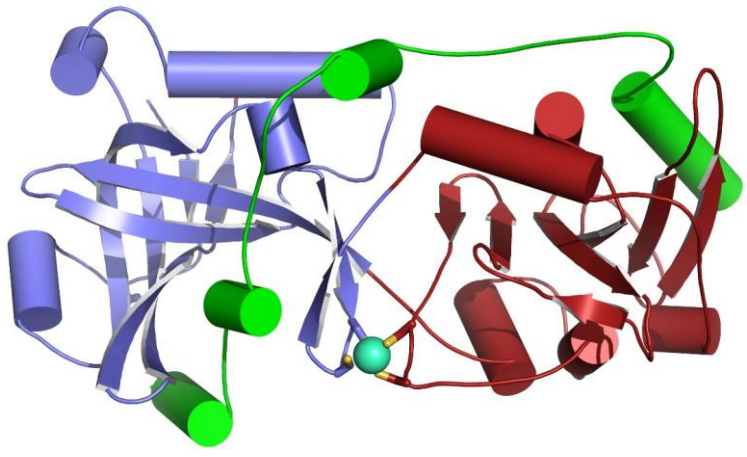
The telomeric, nucleoprotein complex shelterin binds telomeres and maintains the integrity of the ends of our chromosomes. The POT1-TPP1 shelterin, subcomplex binds specifically the single stranded, telomeric overhang; it assists in telomere length regulation; and suppresses the ATR-dependent DNA damage response at telomeres. Naturally occurring mutations of POT1 have been implicated in glioma, melanoma and chronic lymphocytic leukemia. Here we report the atomic structure of the POT1-TPP1 complex. The POT1 C-terminus (POT1C) consists of an OB-fold and a holiday junction resolvase domain (HJ). The HJ makes extensive contacts with the OB fold and together they form an extensive surface for TPP1 binding. The TPP1 polypetide consists of several loops and helices, which span the entire length of the POT1C surface and make extensive interactions with the OB-fold and HJ. Biochemical data shows that several of the disease associated mutations partially disrupt POT1-TPP1 binding, which affects its ability to bind telomeric DNA efficiently. Inefficient telomeric DNA binding by POT1-TPP1 leads to persistent telomerase-dependent telomere replication, which in turn promotes telomere length deregulation, genomic instability and cancer.



Structure of the human POT1-TPP1 telomeric complex

MARM 273

Molecular mechanisms in heme protein function: A thermodynamic perspective from fluoride-binding studies

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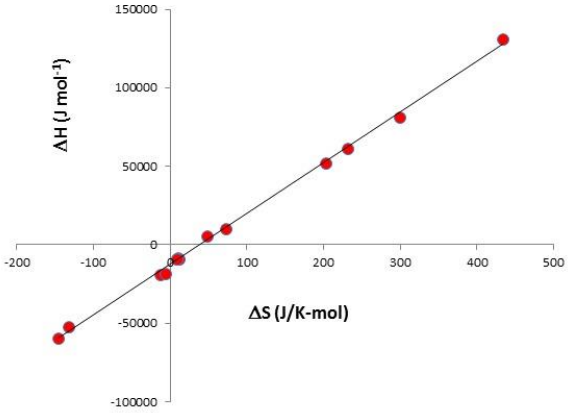
Heme proteins carry out a wide range of biological functions such as oxygen storage and transport, electron transfer, peroxidase, and gas sensing. Our research focuses on understanding how heme-protein interactions can specifically define the biological role of a heme protein. In our studies, we use fluoride binding as a heme pocket probe for Hb, Mb, horseradish peroxidase (HRP), and clam hemoglobins. Using this approach, we have performed pH-dependence studies of fluoride binding in these systems. Fluoride binding affinity in heme proteins that have a distal histidine, as in Mb and Hb, is affected by the protonation state of the histidine with a measured pK_a of 5.7. HRP and hemoglobins II and III from the clam *Lucina pectinata* which have instead distal arginine and tyrosine, respectively, bind fluoride ion with an affinity that is 10 times stronger than that of Mb and Hb. These results indicate how the pH profile of fluoride binding is affected by the identity of the distal amino acid. Additionally, to achieve a greater scope in understanding the role of the protein structure, we have performed temperature-controlled experiments to study the thermodynamic properties of fluoride binding. We measured the enthalpies and entropies of fluoride binding in Hb, Mb, and HRP. We have observed that all three proteins show a strong correlation between the entropy and enthalpy of fluoride binding (see Figure). We have also noticed that despite their similarities in the heme pocket structure, Mb and Hb show differences in their thermodynamics of fluoride binding. Unlike Mb, Hb is able to utilize entropy for favorable fluoride binding. These thermodynamic differences between Mb and Hb could be a reflection of the difference in the protein structures, mainly the quaternary structure of Hb which is lacking in Mb.



Enthalpy *vs* Entropy of Fluoride Binding in Mb, Hb, and HRP

MARM 274

Defining the limits of the solvent dependence of protein dynamics

Nathaniel V. Nucci[1]*, nucci@rowan.edu, Veronica R. Moorman*[3]*, Kathleen Valentine*[2]*, Andrew J. Wand*[2]*. (1) Physics & Astronomy, Biomedical Sciences, Rowan University, Philadelphia, Pennsylvania, United States (2) Biochem Biophysics, University of Pennsylvania, Philadelphia, Pennsylvania, United States (3) Kettering University, Flint, Michigan, United States*

Proteins exhibit the majority of their conformational entropy in the motions of individual bond vectors on the pico- to nanosecond timescale. These motions can be examined experimentally through determination of the Lipari-Szabo generalized squared order parameter (O^2) using high-resolution nuclear magnetic resonance spin relaxation measurements. It is frequently argued that the majority of protein motions are intimately dependent on the nature of the solvating environment. Here the solvent dependence of the fast local motions of proteins is directly assessed. Using the 76-residue model protein ubiquitin, the fast dynamics of the backbone and methyl-bearing side chains of this protein are shown to be generally unaffected by up to a six-fold increase in bulk solvent viscosity. These motions are also insensitive to encapsulation of the protein in the nanoscale interior of a reverse micelle. In addition, the reverse micelle condition permits direct comparison of protein dynamics to the mobility of

the protein hydration layer; no correlation is observed. The dynamic behavior of aromatic side chains are also assessed and provide an experimental estimate of the length- and timescale of protein motions where clear solvent dependence is seen. These findings demonstrate that the majority of the conformational entropy of proteins is independent of the solvation environment, clarifying a long-held misconception in the fundamental behavior of biological macromolecules.

MARM 275

Water at the ionic liquid-vapor interface probed by ambient pressure x-ray photoelectron spectroscopy

***Alicia Broderick**, johnstoa@udel.edu, Yehia Khalifa, John T. Newberg. University of Delaware, Newark, Delaware, United States*

Ionic liquids (ILs) are molten salts with a melting point below 100°C. With tunable properties, ILs are sparking interest in a variety of applications including their use as electrolytes, catalysts, an alternative to traditional organic solvents, and as a CO_2 absorbent from atmospheric flue gas. The ability of ILs to absorb water has been heavily studied, with even the most hydrophobic ILs absorbing small amounts of water over time. For this reason, water is viewed as an impurity. Understanding water uptake within the surface layers is important since water has been shown to affect their physical properties including density, viscosity, and conductivity. Water uptake appears to play a role in the bulk absorption of other gases, particularly CO_2. Bulk gas absorption requires gases to pass the IL-gas interface, and more studies are needed to assess the concentration profile of water in the interfacial region. We will present a quantitative assessment of water uptake at the IL-gas interface of 1-butyl-3-methylimidazolium acetate, [BMIM][OAc]. This was accomplished using ambient pressure X-ray photoelectron spectroscopy (APXPS), performing experiments at room temperature up to a maximum water vapor pressure of 5 Torr. The kinetics of interfacial water uptake probed by APXPS is rapid compared to bulk water absorption probed by gravimetric analysis. Increasing water uptake also leads to a relative binding energy shift in O 1s, C 1s, and N 1s regions due to electronic environment changes for each moiety.

MARM 276

Molecular and electronic structures of ionic liquids in bulk and interfacial regions

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Current research in our group combines an array of structural and dynamical experiments with classical force field and electronic structure calculations of ionic liquids (ILs). While prior work has focused on the properties bulk ILs, recently we have expanded our experimental and theoretical repertoire to include interfacial studies of ILs. Specific examples include studies of how the IL molecular anions and cations arrange themselves differently at the vacuum-liquid interface relative to the bulk, using molecular dynamics simulations compared with interfacial depth profiling by angle-resolved X-ray photoelectron spectroscopy. In other experiments, the electronic structure of ultrathin films of ILs is measured on atomically flat substrates, such as Au(111) and Cu(100). Electron spectroscopies are used to probe monolayer through multi-layer film thicknesses, and are compared with electronic structure predictions.

MARM 277

Ionic liquid ordered structures near and far from solid surfaces

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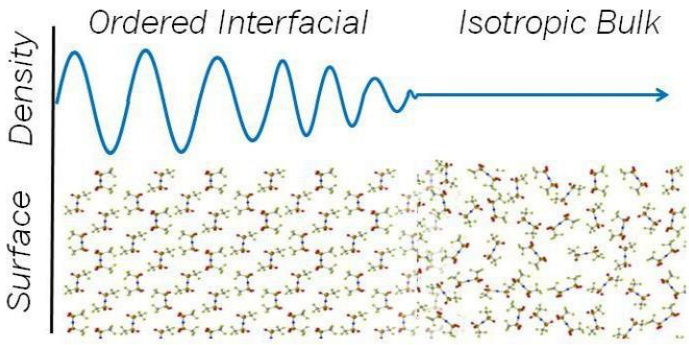
The rich variety of intermolecular interactions present in ionic liquids (ILs) often results in unique molecular architectures near surfaces and in bulk phases. These structures have dimensions from nano- to micrometer scales and result in electrochemical and self-assembly behaviors that diverge significantly from molecular fluids' behaviors. This talk presents spectroscopic, thermal, and electrochemical data to characterize IL ordering and interactions with surfaces. We present 1) spectroscopic measurements that characterize extended IL interfaces that form slowly to micron length scales, 2) electrochemical measurements of the IL electrical double layer (EDL) capacitance that show IL behaviors at electrodes are drastically different than classical dilute electrolytes, and 3) hysteresis effects seen across IL systems and how they might be explained by strong intermolecular interactions that lead to slow or frustrated molecular dynamics. Our measurements show that most IL structures are insensitive to substrate surface chemistry or small amounts of absorbed water. This indicates that the liquid-liquid interactions are central to understanding IL system behaviors. Results advance a working picture of the IL interface and EDL.



MARM 278

Uncovering the molecular arrangement of ionic liquids confined to solid surfaces

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Many important applications of ionic liquids (IL), e.g., lubrication, energy storage and catalysis, involve ILs confined to solid surfaces. In order to optimize the performance, it is critical to understand the molecular arrangement of ILs and the governing mechanisms at the IL-solid interface. Here we present our recent works at IL-Mica and IL-graphite interfaces. Previously, extended layering of ILs on the mica surface has been reported and it is generally accepted that the electrostatic interaction at the IL/mica interface is critical to the observed extended layering. We found that, indeed, water adsorption on the mica surface is the key to the extended layering of ILs. The atomic force microscopy (AFM), attenuated total reflectance-fourier transform infrared spectroscopy (ATR-FTIR) and contact angle (CA) results showed that ILs form extended layering on a mica surface under ambient conditions when water is adsorbed on the mica surface under such conditions. However, when airborne hydrocarbon contaminants replace the water on the mica surface at elevated temperatures, instead of layering, ILs exhibit droplet structure, i.e., dewetting. Based on the experimental results, we propose that water enables ion exchange between K+ and the cations of ILs on the mica surface and thus triggers the ordered packing of cations/anions in ILs, resulting in extended layering. The finding here provides a potential approach to manipulate the macro- and nano-scale wetting of ILs on solid surfaces. Different from mica, there is no electrical charge on the graphite surface. Interestingly, some previous report showed that ILs exhibit more extended layering on graphite than on mica. To uncovering the underlying mechanism, we conducted AFM topography study on nanometer-thick ILs confined to an amorphous carbon (AC) surface. The results indicated that the existence of the delocalized ring in the cation is critical to the layering of ILs. Extended layering was observed only when there is imidazolium ring in the cation. When the imidazolium ring is replaced by an aliphatic moiety, “drop-on-layer” (dewetting) structure was observed. Based on the experimental results, we proposed that pi-pi+ stacking between sp^2 carbon and the imidazolium cation in the ILs is the key to the extended layering of ILs at the IL/carbon interface.

MARM 279

Anomalous nanofriction in ionic liquids: The devil is not in the tails

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When compared to molecular solvents, ionic liquids (ILs) are seen to have a much richer liquid structure. Indeed, most ILs exhibit a nanoscale landscape dominated by antagonistic interactions between their nonpolar (tail) and polar (head) constituents. The complexity and strength of the intermolecular interactions also leads to a dynamical behavior which is heterogeneous. In most cases, dynamical anomalies in ILs have been related to heterogeneities arising from the nanostructured tail-head landscape. In the cases presented in this contribution, anomalous dynamics is seen to arise from energetic heterogeneities instead. These anomalies, although loosely related to the tail-head structure, emerge mostly from slowly-relaxing fluctuations of charge density (head-head) across the liquid landscape. In our approach, localized and temporal nanoenvironments exhibiting charge enhancement or depletion are identified by their coupling with heterogeneities in translational/rotational regimes of small molecular probes. Thus, anomalous nanofrictional environments, giving rise to some forms of heterogeneous dynamics in ILs, appear to originate mostly from (polar) heads than from (apolar) tails.

MARM 280

Insights into the mechanism for CO_2 reduction bismuth-film cathodes in the presence of room temperature ionic liquids

***Joel Rosenthal**, joelr@udel.edu. Dept of Chemistry Biochemistry, University of Delaware, Newark, Delaware, United States*

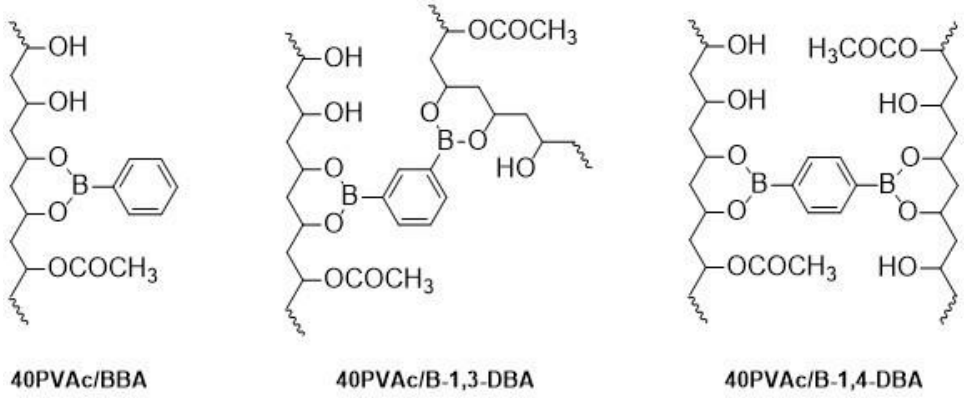
Heterogeneous electrochemical reduction of CO_2 to CO, which can be coupled to liquid fuel production, provides a pathway to address current issues in solar energy storage. We have recently developed a class of electrodeposited bismuth based materials that can readily drive conversion of CO_2 to CO with fast kinetics and high efficiencies in the presence of imidazolium based RTILs. The metrics with which the Bi/RTIL systems drives electroreduction of CO_2 is comparable to that observed using expensive precious metals, with Faradaic efficiencies and current densities for CO production of FE_{CO} ~ 90 % and j_{CO} ~ 5–25 mA/cm^2, respectively at applied overpotentials of ~ 300 mV. We have undertaken a multipronged study to elucidate the mechanistic pathways and molecular design principles that drive CO_2 activation at the Bi/RTIL interface. A combination of spectroscopic, electroanalytical and computational methods has been used to interrogate the dynamics between electrocatalyst, RTIL and CO_2 at the cathode/electrolyte interface. These experiments have provided insight into the pathway by which these catalyst systems activate CO_2 and have revealed the primary factors that drive fuel generation at the cathode/electrolyte interface. Implications for the future development of systems and electrolytes that can efficiently promote CO_2 reduction with high selectivity and efficiency will be discussed.

MARM 281

Investigation of crosslinker structure in organogels from partially hydrolyzed poly(vinyl acetate)

***Teresa Duncan**[3], ttd5@georgetown.edu, Barbara H. Berrie[2], Richard G. Weiss[1]. (2) National Gallery of Art, Washington, District of Columbia, United States (3) Department of Chemistry, Georgetown University, Washington, District of Columbia, United States*

Stable organogels can be formed from 40% hydrolyzed poly(vinyl acetate) (40PVAc) and benzene-1,4-diboronic acid (B-1,4-DBA) in a range of organic liquids, including dimethyl sulfoxide, dimethylformamide, tetrahydrofuran, 2-ethoxyethanol, and methanol. Here, we compare those 40PVAc organogels formed with B-1,4-DBA to those formed with benzene-1,3-diboronic acid (B-1,3-DBA) to investigate how the structure of the crosslinks effects the gelation and physical properties of the materials. Rheology shows the formation of soft gels with both B-1,3-DBA and B-1,4-DBA. These organogels are also compared to solutions formed with 40PVAc and phenylboronic acid (BBA). BBA, with only one boronic acid group, is incapable of forming crosslinks between polymer chains. Insights into gel formation and crosslinker structure are obtained with fluorescence and ^{1}H NMR spectroscopies.



Boronate ester formation upon aromatic boronic acid reactions with hydroxyl groups on 40PVAc.

MARM 282

Factors affecting catalytic activity for nitrophenol hydrogenation on colloidal nanocatalysts

***Anderson L. Marsh**, marsh@lvc.edu. Chemistry, Lebanon Valley College, Annville, Pennsylvania, United States*

Hydrogenation reactions are typically considered to be structure insensitive, but in certain instances changing particle size may influence catalytic activity. One such reaction has been proposed to be the hydrogenation of p-nitrophenol to p-aminophenol using sodium borohydride. Still, no direct evidence has been published regarding this hypothesis. In our work, we are utilizing polyvinylpyroolidone (PVP) capped Pt and Pd nanocatalysts

synthesized in the 1-10 nm size range to catalyze this reaction under pseudo-first-order conditions. UV/Vis absorbance spectroscopy is being employed to monitor product disappearance and calculate apparent rate constants for the selected particle sizes. Data from reactions carried out at selected temperatures over the 293 to 333 K temperature range are being used to calculate apparent activation energies for the reaction catalyzed by platinum nanocatalysts of selected particle sizes. These results will be used in further clarifying the molecular level steps involved in the mechanism of this reaction.

MARM 283

Aqueous ionic liquid solutions and their effects on protein structures and lipid bilayers

***Timothy D. Vaden**, vadent@rowan.edu. Chemistry and Biochemistry, Rowan University, Glassboro, New Jersey, United States*

Ionic liquids (ILs) as additives in aqueous solution have numerous applications in biomedical technology, including protein solubilization, enzyme activity modulation, drug delivery, and antibiotic enhancement. There is a great deal of fundamental interest in how ILs as solutes affect biomolecules. This talk will present recent studies investigating the effects of ILs on protein structures and lipid bilayers. The alpha-helical myoglobin and beta-sheet mCherry proteins have been studied in solutions with different ILs including conventional species as well as novel amino acid-based ILs. Biophysical characterization combined with molecular dynamics simulations helps elucidate how dilute ILs can destabilize protein structures without direct interaction. Interest has also been focused on how ILs interact with cell membranes due to their ability to enhance antibiotic activities, and therefore this talk will also present recent work assessing effects of ILs on lipid bilayer vesicles. Dynamic light scattering measurements combined with a novel fluorophore “leakage” assay show how ILs can permeabilize cell membranes and enhance the transport of the antibiotic polymyxin.

MARM 284

Toward structural design rules for unconventional solar energy conversion in organic conjugated materials

***Ryan D. Pensack**, rpensack@princeton.edu, Gregory D. Scholes. Department of Chemistry, Princeton University, Princeton, New Jersey, United States*

Sunlight is a renewable energy source with vast abundance. Because of the prohibitive cost of solar cells, however, harvesting this energy has remained at a limited scale. Unconventional solar energy conversion, i.e., that which circumvents conventional thermodynamic limits, has garnered substantial interest recently because of its fundamental and practice importance, especially as a strategy to improve solar cell efficiencies and reduce cost. Singlet fission is an unconventional form of solar energy conversion unique to organic conjugated materials where one spin-zero singlet excitation is split into two spin-one triplet excitations. While the basic description of singlet fission is generally understood, additional details, especially those relevant to detrimental losses, are only just beginning to emerge. In this talk, I will describe our efforts combining materials chemistry with ultrafast spectroscopy to elucidate the mechanism of singlet fission and develop structural design rules for high-efficiency singlet fission. We have developed nanoparticles of pentacene derivatives as a convenient materials platform to study singlet fission, and showed using ultrafast spectroscopy how to probe two key intermediates that interconvert through a critical triplet transfer process whose significance has been grossly underappreciated. Our most recent work has led us to a set of structural design rules positioned to inspire expansion of the exceedingly limited set of highly efficient singlet fission materials.

MARM 285

Analysis of undergraduate student survey on guided-inquiry laboratory activities implemented in a general chemistry laboratory course

***Susette E. Ingram**[1], singram126@gmail.com, Stephanee Synnott[2], Lindley Winchester[2], Y Y Tong[1], Milena Shahu[1]. (1) Chem Dept, Georgetown Univ, Washington, District of Columbia, United States (2) Georgetown University, Washington, District of Columbia, United States*

The benefits of inquiry-based learning have been widely reported in the literature. In particular, guided-inquiry experiments have been shown to help students build their critical thinking and problem solving skills. However, many of the existing studies only survey students’ opinions towards guided-inquiry labs following one semester of implementation. At Georgetown University, we have conducted multi-year (2013-2016) surveys of a total of 103 students enrolled in the General Chemistry Laboratory for Majors course. Our survey focuses on students’ experiences with and opinions towards the guided-inquiry laboratory activities implemented throughout both semesters of the course, in addition to how guided-inquiry experiments prepare students for an open-inquiry freelance project. Statistical analysis of students’ responses will be presented and the benefits of guided-inquiry

labs on students' learning will be discussed. Overall, the majority of students surveyed recommend the guided-inquiry lab format for the General Chemistry Laboratory for Majors.

MARM 286

Using guided inquiry to study the stoichiometry of carbonate neutralization reactions

***Gail Salter**, salterg58@gmail.com. Chemistry and Biochemistry, Lafayette College, Bethlehem, Pennsylvania, United States*

This presentation describes an experiment in which a Vernier gas pressure sensor is used to study the stoichiometry of carbonate and bicarbonate neutralization reactions. This experiment was developed at Lafayette College, a liberal arts college, as a guided inquiry experiment for the General Chemistry lab. Typical student data will be presented.

MARM 287

Taking molecular modeling beyond the ball and stick

***Denise Beautreau**, deb313@lehigh.edu. Chemistry, Lehigh University, Bethlehem, Pennsylvania, United States*

Teaching molecular geometry and the Valence Shell Electron Pair Repulsion (VSEPR) theory presents a challenge in the General Chemistry classroom and extends into the laboratory and attempting to bring the concept full circle with the students is perplexing. Traditionally, the laboratory presentation involves the use of lecture modules and modeling kits that do not fully engage the students in learning and stops short of thoroughly explaining the concepts.
Innovative approach to molecular modeling laboratory experiment was introduced in the general chemistry first semester course with a student population of 360 students. A technology and iPad in the classroom program, which was instituted based on information and ideas learned at *The National Science Foundation sponsored* Chemistry Collaborations, Workshops and Community of Scholars (cCWCS) program was used to develop the molecular modeling and VSEPR theory experiment currently being used in the course. The experiment involved students using the Wavefunction Inc. ODYSSEY VSEPR Theory app installed on iPads along with modeling kits to do 2-D and 3-D molecular modeling, as wells as bond angle calculations and molecular geometry determination. The application provides a variety of options to model chemical compounds, investigate resonance and understand the effect of valence electrons on bond angles. The experiment is made interactive between students and instructor with the use of Mersive Inc. Solstice app that facilitates mirroring and sharing of iPad screens with the entire classroom audience.
The peak in student learning and understanding as a result of introduction of this new experiment was evident based on their responses to the laboratory inquiry report questions and overall increased engagement during the lab. The use of technology will always be a vital tool in developing new, innovative and informative laboratory experiments in General Chemistry, particularly when attempting to enhance learning of topics such as VSPER and molecular modeling.

MARM 288

What is in my shampoo? From active ingredient to active learning

***Alan M. Rosan**, arosan@drew.edu. Drew Univ, Madison, New Jersey, United States*

Early in the first semester of the sophomore organic chemistry sequence at Drew University students investigate the names, structures and properties of selected organic compounds present in their favorite personal care product (PCP). This laboratory exercise is designed to build skills in accessing and retrieving library and database resources, analyzing and assessing the primary and secondary literature and assembling accumulated information into a final instructive written project. By encouraging active engagement with the chemical components of a common, daily used commercial substance, the assignment provides a platform which informs and empowers students to connect organic chemistry with their daily lives. This laboratory also includes an introduction to toxicology and the fate of personal care products in the larger environment. The full assignment will be described and discussed.

MARM 289

Developing two inquiry-based experiments for sophomore organic chemistry teaching laboratory at Drew University

***Sandra K. Keyser**, skeyser@drew.edu, Alan M. Rosan. Chemistry, Drew University, Florham Park, New Jersey, United States*

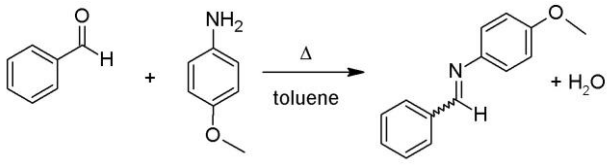
To increase the number and scope of guided inquiry-based experiments at Drew University, two new laboratories have been introduced during the year-long sophomore organic chemistry sequence. The first laboratory highlights the competition between substitution and elimination pathways, using two substrates with identical reaction conditions. The second experiment emphasizes the pH effects of alpha-halogenation of ketones. In both operationally-simple modules, students synthesize, isolate, and characterize the products using NMR and IR. Elucidation of structures using spectroscopic analysis is followed by inference of the reaction mechanisms. The implementation of the two discovery laboratories will be discussed.

MARM 290

Azeotropic preparation of a C-phenyl N-aryl imine: An introductory undergraduate organic chemistry laboratory experiment

***Lee J. Silverberg**[4], ljsilverberg@verizon.net, David Coyle[4], Kevin C. Cannon[3], Robert T. Mathers[2], Jeffrey A. Richards[2], John Tierney[1]. (1) Penn State Brandywine, Media, Pennsylvania, United States (2) Penn State New Kensington, New Kensington, Pennsylvania, United States (3) Penn State Abington, Abington, Pennsylvania, United States (4) Pennsylvania State University, Schuylkill, Schuylkill Haven, Pennsylvania, United States*

Imines are important in biological chemistry and as intermediates in organic synthesis. An experiment for introductory undergraduate organic chemistry is presented in which benzaldehyde was condensed with *p*-methoxyaniline in toluene to give 4-methoxy-*N*-(phenylmethylene)-benzenamine. Water was removed by azeotropic distillation using a Dean-Stark trap. The reaction was readily performed in one three-hour laboratory period, gave a crystalline product, and was easily followed visually by the amount of water collected. It demonstrated important concepts from second-year undergraduate organic chemistry, including equilibrium processes, condensation reactions, and imine formation. The experiment also gave students exposure to important laboratory techniques including azeotropic distillation, use of a water trap, and mixed-solvent recrystallization.



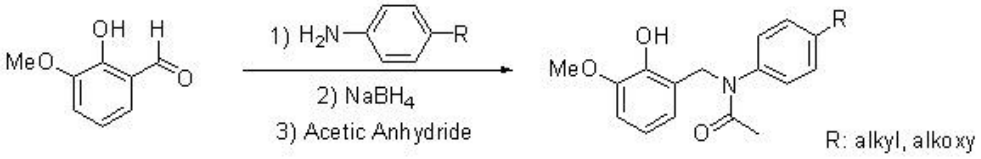
MARM 291

Further explorations of efficient one-pot, three-step reductive amination sequence; and iron (III) chloride catalyzed Friedel-Crafts acylation reaction for the organic laboratory experiments

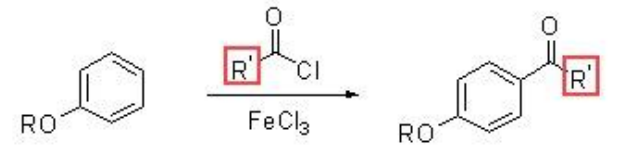
***Xiaodong Fan**[1], xfan00@gmail.com, Hsuan-Yu Chen[2], Elenore Wiggin[3], Chenyu Zhang[4]. (1) Chemistry, Lafayette College, Center Valley, Pennsylvania, United States (2) Lafayette College, Easton, Pennsylvania, United States*

Both reductive amination and Friedel-Crafts acylation reactions have been widely covered and practiced in undergraduate organic laboratory experiments. Herein we describe our efforts of further explorations on the following two experiments: 1) The reductive amination of *ortho*-vanillin with a series of *para* substituted aniline derivatives followed by acylation with acetic anhydride to explore the scope of the reaction (Scheme 1); 2) The Friedel-Crafts acylation reaction using iron (III) chloride as a Lewis acid catalyst. In this reaction, a wide variety of acid chlorides are allowed to react with a series of alkoxy benzenes (Scheme 2). Both experiments allow the students to work and characterize of their own unknown products with IR and ^{1}H NMR.

Scheme 1. An efficient one-pot three-step reductive amination sequence .



Scheme 2. Friedel-Crafts Acylation.



MARM 292

Implementation of an olefin metathesis experiment into the undergraduate organic laboratory course

*Thanuka Udumulla[1], Amran Hussain[1], Daniel Richiuso[1], Matthew McCloskey[1], Mayra Romero[1], Kevin C. Cannon[2], **Sarah L. Carberry**[1], sbolton@ramapo.edu. (1) Chemistry Department, Ramapo College of New Jersey, Mahwah, New Jersey, United States (2) Penn State Abington, Abington, Pennsylvania, United States*

A solventless olefin metathesis reaction of styrene to produce E-stilbene, using the Hoveyda-Grubbs catalyst, was incorporated into organic chemistry laboratory courses over the past year. Over 150 students (working in pairs) completed this lab procedure. E-Stilbene yields of 60% or greater were realized by nearly all students, and yields of 85% or greater were not uncommon. Student surveys showed that all students finished the procedure within the scheduled lab period of 3 hours, and students found the experiment to be instructive. Procedures are currently being tested to extend this exercise by using the E-stilbene produced as the starting material in a two-step synthetic sequence of bromination followed by elimination to provide diphenylacetylene. The conversion of styrene to diphenylacetylene would extend over three lab periods.

MARM 293

Role of charge transfer excitons in high-mobility polymers

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Polymers with high hole mobilities often have rigid backbones and ordered macroscopic structures. The two polymers, PBTTT and IDTBT, have hole mobilities of $1 cm^2V^{-1}S^{-1}$ and $2 cm^2V^{-1}s^{-1}$, respectively. PBTTT is semi-crystalline, while the stable thermodynamic phase of IDTBT is amorphous. To understand why an amorphous polymer exhibits a higher mobility than a semi-crystalline polymer, we turn to the microscopic properties of the polymer. From the view of the donor-acceptor pairs that underlie electronic transport, backbone rigidity and macroscopic order facilitate strong donor-acceptor coupling and in-crease the rate of adiabatic transfer. Expanding the view of electronic transport to a manifold of Born-Oppenheimer electronic states, low energy excitons couple to ground state and affect the rate of nonadiabatic transfer. The presence of low energy charge transfer (CT) excitons

can only increase the overall transfer rate, by way of nonadiabatic coupling. Using linear-response TDDFT, we identified the sub-band-gap excitons of the two polymers. The charge transfer character of these excitons was determined from a density-based analysis, forgoing the need for a simplified orbital picture. The analysis shows that the lowest energy excitation of PBTTT does not involve charge transfer, while the lowest energy excitation of IDTBT transfer charge over an average distance of 4.55 Å. Similar trends are found for higher energy excitons. The nonadiabatic coupling between ground and excited states are expected to be significant but must be assessed, in order to unequivocally demonstrate the relationship between low lying CT excitons, thermal transfer rates, and transport properties. With this work, we recognize that molecular-level properties are responsible for high-mobilities in polymers and demonstrate a correlation between charge transfer excitons and ideal transport characteristics.

MARM 294

From molecular electronics to energy storage: Striving for a unified approach to electron transfer in open systems

***Ryan Jorn**, ryan.jorn@villanova.edu. Chemistry, Villanova University, Villanova, Pennsylvania, United States*

Nano-scale devices provide a unique environment to probe the effects of decoherence on quantum systems. In particular, the roles of molecular vibrations and disorder on charge transport between two conductive contacts have been studied for several decades. However, these effects are usually discussed in terms of models which assume either entirely coherent or entirely decoherent charge transfer between the electrodes. There have been comparatively fewer examples of methods that have effectively spanned both extremes from first principles with regard to interaction between scattering charges and their vibrational thermal environment. In this work, the development of a new treatment based on scattering theory in the Liouville space formalism is discussed to unify the electron tunneling and electron hopping regimes of transport. Expressions for the evolution of vibronic populations and coherences as a function of time are derived as well as the current transmission through the junction starting from a simple Newns-Anderson Hamiltonian and the Liouville equation. Several instructive limits will be discussed spanning the assumption of isolated molecular resonances in the elastic limit to the effect of coupling to molecular vibrations without any restrictions placed on the location of charge states. In addition to describing nano-junctions, attention will also be given to a single charge state model in order to demonstrate the transition from a neutral to a charged molecule with increased bias voltage. The latter scenario corresponds to charge transfer at an electrode surface as found in energy storage devices and provides a first glimpse of connecting the worlds of molecular electronics with charge transfer in energy storage devices.

MARM 295

Spectroscopy of liquids and molecules at metal surfaces: Markovian and non-Markovian electron dynamics

***Michele Pavanello**, m.pavanello@rutgers.edu. Department of Chemistry, Rutgers, the State University of New Jersey, Newark, New Jersey, United States*

Over the past four years the Pavanello research group has developed an array of Density Functional Theory (DFT) embedding methods for the description of periodic and molecular systems alike, including their electronic and nuclear dynamics. The overarching goal of this effort has been to allow first principle simulations to approach realistic time- and length-scales, and to shed light on the dynamical behavior of complex systems. Our theory development has resulted in a new open-source DFT embedding software called *embedded Quantum-ESPRESSO* – eqe.rutgers.edu.

When inspecting the electron dynamics of condensed phase systems in real time, we observe all the relevant regimes proper of non-Markovian open quantum system dynamics, such as electronic energy transfer, and screening. In addition, the ab-initio modeling of system-bath interactions brought us to observe and justify the holographic time-dependent electron density theorem.

Real-time TDDFT embedding simulations show that non-Markovian effects in the electron dynamics of molecular bulk systems are typically small due to their low polarizability and low coupling. Conversely, for molecules at metal surfaces, the non-Markovian effects are dramatic. Metals have large polarizabilities, and even in a regime of low coupling their effect on impinging molecular species is significant –line broadening, peak shift, and intensity borrowing are observed, characterized, and explained in terms of inter-subsystem dynamical interactions.

MARM 296

Development of effective stochastic potential method using random matrix theory for describing electronic excitations in noisy quantum systems

*Jeremy Scher, **Arindam Chakraborty**, archakra@syr.edu. Chemistry, Syracuse University, Syracuse, New York, United States*

Spectroscopic properties of semiconductor nanoparticles (NPs) exhibit a strong dependence on the shape and size of the NPs. At finite temperatures, the NPs exists in an ensemble of structures and inclusion of these structures is essential for accurate theoretical investigation of the optical properties of these materials. However, performing ensemble-averaged calculations using conventional electronic structure theories is prohibitive because of steep computational cost. This problem is exacerbated in solution-phase, where NP-solvent interactions also contribute in the modification of the optical and electronic properties of the NP. In this work, we present a random matrix based method for ensemble-averaged calculations of optical properties of semiconductor NPs. This approach is based on treating the NPs as quantum subsystems embedded in a noisy classical environment and deriving an effective stochastic potential (ESP) for incorporating the thermal fluctuations in the system. The method was applied to a series of CdSe quantum dots (Cd20Se20-Cd515Se515) and was used for calculation of ensemble-averaged excitonic properties including quasiparticle gap, optical gap, exciton binding energies, and electron-hole recombination probabilities. Statistical analysis of the results reveals that some excitonic properties are more sensitive to structural deformation than others. The ESP method was also used to study the effect of temperature and solvents on the NP properties, and a discussion of these results will be presented. The results from these calculations highlight the importance of ensemble averaging and demonstrate the limitations of using a single optimized NP structure for computational prediction of optical properties of NPs.

MARM 297

On-the-fly heuristic reordering approach to deterministic optimization for qualitative chemical property prediction

*Jennifer M. Elward, **Christopher B. Rinderspacher**, crinders@gmail.com. Army Research Laboratory, Baltimore, Maryland, United States*

Chemical optimization and design affords current and future researchers the ability to harness the potential of chemical space towards the fast and efficient discovery of novel materials. In the present work, a multi-constraint deterministic optimization technique based on the on-the-fly heuristic reordering of chemical subspace has been developed and used towards materials discovery in several systems of interest. The competitive advantage of the deterministic optimization method results from the combination of fast computational techniques and innovative design algorithms which allow for intelligent screening of a large number of chemical compounds within a reasonable computational time. A family of search algorithms has been used to approach the problem of navigating chemical subspace, including general base line search and general base gradient local search techniques. Because ideal ordering of the chemical subspace is not known, measures must be taken to ensure that the space is being sampled properly. There are several strategies utilized in this work to ensure this requirement is being satisfied. First, optimization algorithms based on heuristic reordering of the chemical subspace are developed to assist and direct the optimization procedure. The heuristic reordering algorithms play an essential role in optimization efficiency and each heuristic scheme has been uniquely developed as an effort to further enhance the subspace sampling. Each of these algorithms have been benchmarked and tested for their performance with respect to candidate structure discovery. In addition, to further combat the potential subspace sampling partiality, a binary entropic, enhanced sampling approach has been employed. This technique allows for generation and searching of structures which are chemically maximally different from the local best candidate structure. This is advantageous because a larger breadth of space is able to be sampled in an equally efficient manner. This method has been applied to several systems of interest including high-hyperpolarizability materials, energetic materials and optically switchable materials. Detailed analysis was performed for each of these systems and qualitative structure property relationships were determined.

MARM 298

Toward accurate classical molecular dynamics simulations of molecules on metallic surfaces

*Zhi Li[1], Alexandre Tkatchenko[2], **Ignacio Franco**[1], ignacio.franco@rochester.edu. (1) Department of Chemistry, University of Rochester, Rochester, New York, United States (2) Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany*

We propose an accurate and computationally efficient strategy to capture non-reactive metal-molecule interactions that adapts the Tkatchenko-Scheffler scheme for van der Waals interactions into a simple and transferable classical force field. The resulting force field requires just two adjustable parameters per atom type-metal pair that

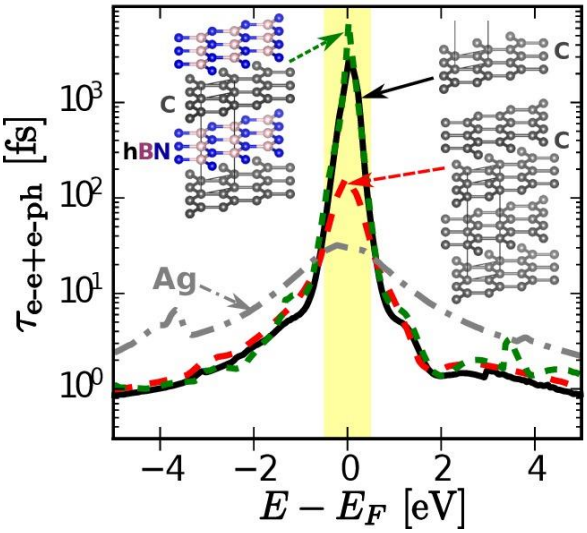
are needed to capture short range interactions. The strategy allows for classical molecular dynamics simulation of molecules on surfaces with the accuracy of high-level electronic structure methods but for system sizes (10^4 − 10^7 atoms) and timescales (~μs) that go well beyond what can be achieved with first principle methods. Parameters for H, and sp2 C and O on Au(111) are developed and employed to atomistically model experiments that measure the conductance of a single polyfluorene on Au(111) as a continuous function of its length. The simulations capture the experimentally observed decay of the conductance during junction elongation, the conductance plateaus due to the sliding motion of the polymer on the metal surface, and even fine features such as conductance spikes caused by abrupt molecular lateral movement. The proposed strategy can be employed to investigate non-reactive long-time dynamics of large molecules on surfaces with minimal parametrization effort.

MARM 299

Plasmonic hot carriers: Towards material design

Ravishankar Sundararaman, *sundar@rpi.edu. Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, New York, United States*

Plasmon-enhanced absorption could enable efficient energy conversion and photodetection in metallic nanostructures, provided that the generated hot carriers are extracted prior to thermalization. We present first-principles calculations of hot carrier generation, transport and thermalization, which fully account for electronic structure and phonon effects, critical for understanding the differences between materials. We find that electronic structure characteristics that enable light absorption at small length scales also facilitate rapid thermalization of energetic carriers. We investigate whether this undesirable link can be severed in new classes of plasmonic materials such as alloys and low-dimensional heterostructures, in order to retain efficient light absorption while minimizing carrier thermalization.

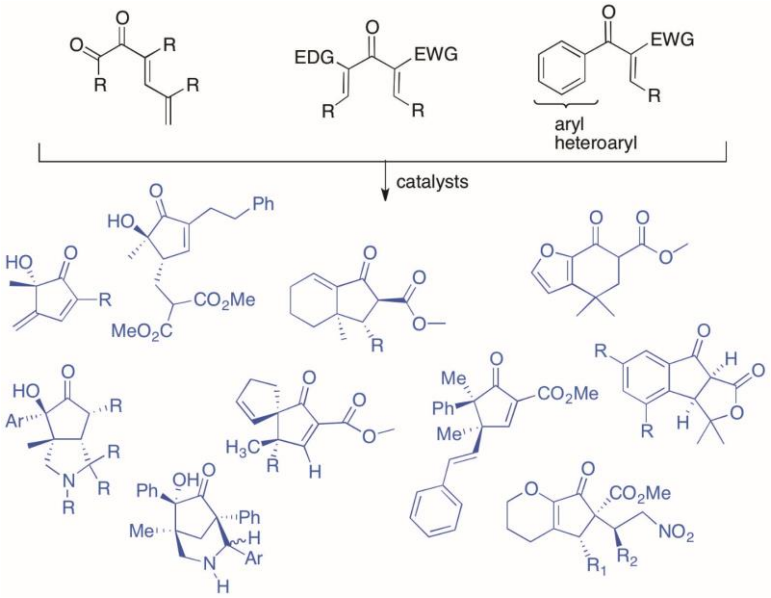


MARM 300

New stereocontrolled reaction cascades for organic synthesis

Alison J. Frontier, *frontier@chem.rochester.edu. Chemistry Dept, University of Rochester, Rochester, New York, United States*

Bioactive polycyclic compounds are derived from both natural sources and from purely synthetic approaches. Non-natural polycyclic small molecules with novel scaffolds are sought after as potential leads in the drug discovery process. The development of reaction cascades for rapid assembly of complex small molecules will be described. Many of the cascades center on variations of the Nazarov electrocyclization, coupled with cationic rearrangements and other multistep cascades that occur with high levels of stereochemical control.

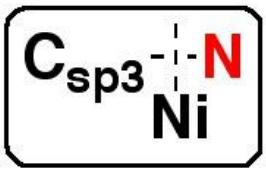


MARM 301

Harnessing alkyl amines in nickel-catalyzed cross couplings via C–N bond activation

***Mary P. Watson**, mpwatson@udel.edu. Chemistry & Biochemistry, University of Delaware, Newark, Delaware, United States*

Transition metal-catalyzed cross-coupling reactions have revolutionized organic synthesis, particularly the construction of bonds to sp^2-hybridized carbons. However, the discovery of analogous reactions of C_{sp3} electrophiles have lagged behind, despite their potential to deliver a range of important targets, including chiral molecules in high enantiopurity. Towards solving this challenge in organic synthesis, we have developed nickel-catalyzed cross-couplings of alkyl amine derivatives. In particular, we have developed stereospecific, nickel-catalyzed cross couplings of benzylic amine derivatives. These reactions utilize starting materials that are readily available in high optical purity; proceed with high levels of stereochemical fidelity; employ air-stable, functional group tolerance coupling partners, such as aryl boronic acids; and display excellent functional group tolerance. We have also developed nickel-catalyzed cross-couplings of alkyl amine derivatives with non-activated alkyl groups (non-benzylic, non-allylic). This exciting new chemistry is particularly useful for late-stage functionalization of alkyl amines. The optimization, scope, and mechanistic studies of these reactions will be presented.



MARM 302

Catching the frequency: New photochemical and microwave mediated methods for heterocycle synthesis

***Emily C. McLaughlin**, emily.mclaughlin.79@gmail.com. Chemistry Program, Bard College, Germantown, New York, United States*

As the diversity of strategies found within the proverbial “synthetic tool-kit” are expanded, the challenges often associated with the construction of target compounds, even those of great molecular complexity, become more manageable. In our laboratory, we strive to continue to develop an assortment of these “tools” and to understand the mechanistic underpinnings of each transformation. More precisely, the design and development of novel protocols to prepare heterocycles, including and small, strained ring systems will be presented here. These methods are enhanced by or rely on the power of photochemical or microwave irradiation, which is a central theme to our work.

MARM 303

Oxygen driven fragment coupling by activation of C-H, N-H, and O-H bonds

***Marisa Kozlowski**, marisa@sas.upenn.edu. Univ of Penn, Philadelphia, Pennsylvania, United States*

Inspired by Nature's use of oxidative couplings to construct carbon-carbon, carbon-oxygen, and carbon-nitrogen bonds in many natural products, we have undertaken studies of these important transformations. The development of selective catalytic processes for naphthol coupling, phenol coupling, N-arylation, and alkyl C–H activation that utilize oxygen as the terminal oxidant will be discussed. Applications to the synthesis of natural products including cercosporin, bisoranjidiol, and honokiol as well as to the synthesis of novel optically active materials will be presented.

MARM 304

Power and perils of high throughput experimentation in process chemistry

***Iulia Strambeanu**, iulia.i.strambeanu@gsk.com. GlaxoSmithKline, Philadelphia, Pennsylvania, United States*

This talk will discuss the power and efficiency of High Throughput Experimentation (HTE) in reaction optimization by going over several examples. One case study will be presented in more detail in order to show how HTE and process development combined can rapidly lead to a successful process.

MARM 305

Keynote address: Madeleine Joullie

***Madeleine M. Joullie**, mjoullie@sas.upenn.edu. Univ of Penn, Philadelphia, Pennsylvania, United States*

Prof. Madeleine Joullie has served as a mentor and inspiration to hundreds of women (and men) in organic chemistry over her long and illustrious career. Madeleine received both her M.S. and Ph.D. from the University of Pennsylvania, working with Prof. Allan R. Day, where she was the only full-time female chemistry graduate student at the time. In 1953 Madeleine was appointed as a tenure track faculty member at the University of Pennsylvania, becoming the first female organic chemist to hold such a position at a major american university. Her scientific accomplishments stand as some of the most significant of her generation, regardless of gender. Her research has focused primarily on the synthesis of heterocyclic compounds and bioactive molecules, making significant impacts in medicinal chemistry and natural products synthesis. She is particularly well known for her work with cyclopeptide alkaloids, providing seminal syntheses and probing mechanisms of action of this challenging class of therapeutic molecules. She has over 300 peer-reviewed publications and has received numerous awards and accolades for her achievements. Having just celebrated her 90th birthday, Madeleine is still going strong with an active research group at Penn and she is truly an inspiration and a trailblazer for women in chemistry. It is our true honor to have her join us.

MARM 306

Logic-gated catalytic circuits for sensing bio-targets

***Sung Won Oh**[1], sungwon.oh@rutgers.edu, **Adriana Pereira**[2], arp179@scarletmail.rutgers.edu, Ting Zhang[2], Ariel Lane[2], Jinglin Fu[2,1]. (1) CCIB, Rutgers University - Camden, Cherry Hill, New Jersey, United States (2) Chemistry, Rutgers University - Camden, Camden, New Jersey, United States*

In biochemical pathways, swinging arms play an important role in multi-step, catalytic transformations in multi-enzyme complexes. In this project, artificial swinging arms are designed to channel the transfer of cofactors in multi-enzyme reactions. DNA logic-AND-gated (LG) circuits are implemented into swinging arms to control the release and activation of cofactor arms to modulate enzyme reactions. Logic-gate circuits are composed of single-stranded DNA molecules carrying a NAD cofactor. An 'AND' logic-gated swinging arm is designed (Figure 1), then native polyacrylamide gel electrophoresis (PAGE) is used to characterize the opening and closing of logic-gate circuits for release of swinging arm. The input of two single-stranded DNA (Fuel 1 and 2) releases the swinging arm, causing the NAD arm and G6pDH conjugated to the second input strand to come in close proximity to produce the enzymatic signal. Applications to LG are developed to detect small molecules, such as adenosine and cocaine, using an aptamer and are currently under progress. Small molecules (adenosine and cocaine) and single-stranded DNA (Fuel 2) are required to release the NAD arm and produce a signal. Eventually, logic-gated NAD-swinging arm will be applied to detecting bio-targets with signal amplification in a small test tube and visible color change such as paper-based detection.

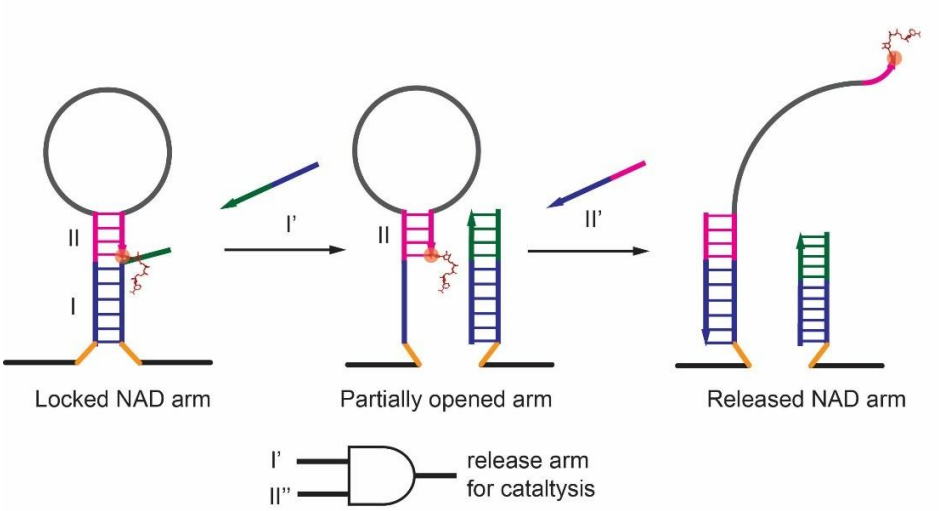


Figure 1. Overall schematic outline of Logic-AND-Gate (LG) DNA circuits.

MARM 307

Study of the potential antioxidant properties of the reduced form of Nicotinic Acid Adenine Dincleotide (NADPH) using luminometry

***Charles Saladino**, csaladin@misericordia.edu. Chemistry/Biochemistry, Misericordia University, Dallas, Pennsylvania, United States*

Our previous research has clearly demonstrated that luminometry can be utilized to quantify the chemiluminescence generated by likely free radical intermediates of a H_2O_2-initiated luminol reaction at pH 7.2. We have also shown that glutathione (GSH) in its reduced state inhibits this chemiluminescence in a dose response manner. There is an accumulating interest in the coenzyme NADPH as an antioxidant, whereas such action is acting as a coenzyme of the enzyme glutathione reductase. Thus, we have chosen to explore the potential antioxidant properties of NADPH using luminometry and UV/Vis spectrophotometry. A direct dose-response curve for the inhibition of chemiluminescence produced by a luminol reaction was achieved with NADPH concentrations of 0, 0.23, 0.48, 0.95, and 2.0 nM, respectively. This was repeated with NADP+ using the same concentrations as the dose response curve with NADPH. Except for the highest concentration of $NADP^+$ (where there was an unexplained enhancement of chemiluminescence), there was no significant inhibition observed. After determining the spectra for $NADP^+$ and NADPH, the luminol reaction was reproduced in the spectrophotometer in the presence of 2.0 nM $NADP^+$ and 2.0 nM NADPH, respectively. With $NADP^+$ in the reaction, there are no spectral changes. However, with NADPH present, there is a significant increase in the spectra defining $NADP^+$ and a concomitant decrease in the spectra for NADPH. This demonstrates a probable donation of the hydrogen of NADPH, as would be expected for an antioxidant, while the resulting $NADP^+$ is increased, as would also be expected.

MARM 308

Study of the potential antioxidant properties of Ascorbic Acid (AA) using luminometry and UV/Vis spectrophotometery

***Charles Saladino**, csaladin@misericordia.edu. Chemistry/Biochemistry, Misericordia University, Dallas, Pennsylvania, United States*

Previous research by us has clearly demonstrated that luminometry can be utilized to quantify the chemiluminescence generated by likely free radical intermediates of a H_2O_2-initiated luminol reaction at pH 7.2. We have also shown that ascorbic acid (AA) in its reduced state inhibits this chemiluminescence in a dose response manner, using 0, 21, 42.5, and 85 µM, respectively. These kinetic reactions are now carried out in the presence of K3[Fe(CN)6] as a catalyst. The results exhibit a similar dose response, except that all corresponding chemiluminescent values are approximately 470-fold greater than that without the catalyst. To insure that the increase in chemiluminescence in the presence of the catalyst were not due to a Fenton-type reaction, the $K_3[Fe(CN)_6]$ was reacted with H_2O_2without luminol. The chemiluminesence under these conditions was only 0.06 % of that seen in the catalyzed reaction, thus ruling out a Fenton-like enhancement of chemiluminescence. In order

to demonstrate that the reduced form of AA was donating a hydrogen, so as to act as an antioxidant, as opposed to just interfering with the luminol reaction in general, the spectrum of AA was observed in a UV/Vis spectrophotometer at its approximate pKa values, 2.4, 7.2, and 12.0. This provided baseline spectra for AA in its reduced and oxidized forms. The luminol reaction was then reproduced without the Fe catalyst in the spectrophotometer at pH 7.2. The results showed a spectral shift indicative of AA in its oxidized state, which thus demonstrates hydrogen donation, as expected of an antioxidant. This shift is being investigated further using infrared analysis.

MARM 309

Thioamides: Improved incorporation methods and effects on protein stability

D. Miklos Szantai-Kis[1]*, szd@mail.med.upenn.edu, Christopher R. Walters*[1]*, Yanxin J. Wang*[1]*, Taylor Barrett*[1]*, Eileen M. Hoang*[2]*, E. James Petersson*[1]*. (1) University of Pennsylvania, Philadelphia, Pennsylvania, United States (2) Swarthmore College, Swarthmore, Pennsylvania, United States*

In recent years, our laboratory has developed the thioamide, a single O to S substitution in canonical amide bonds, as a versatile probe for fluorescence and protease studies. Thus far, thioamides have been incorporated into the backbone of proteins via native chemical ligation (NCL) with a Cys or homocysteine (Hcs) at the ligation site. We utilized two different strategies to facilitate the site-specific incorporation of thioamides into proteins. First, we investigated selective thiol-desulfurization in the presence of thioamides. This allows us to perform traceless ligation reactions in the presence of thioamides and circumvent the dependence on Cys at the ligation site in NCL reactions. In another approach, showed that using alternative deprotection reagents in solid phase peptide synthesis, reduced epimerization and improved yield of thioamide containing peptides. With these strategies in hand, we synthesized different thioamide containing proteins and assessed their effect on protein stability using Circular Dichroism and thermal denaturation. We were able to rationalize the effects of thioamides on protein stability and have now a better understanding of which sites in proteins are suitable for substitution.

MARM 310

Thioamides suppress dipeptidyl peptidase 4 proteolysis of therapeutic peptide hormones while maintaining bioactivity

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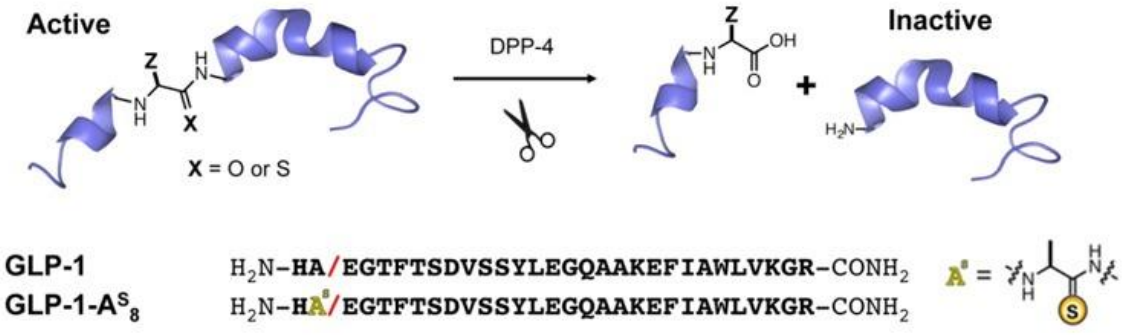
We describe a simple strategy to stabilize peptides toward proteolysis while preserving bioactivity, using three substrates of dipeptidyl peptidase 4 (DPP-4) as examples. Thioamide substitution at positions near the scissile bond in glucagon-like peptide-1 (GLP-1), gastric inhibitory polypeptide (GIP), and neuropeptide Y (NPY) renders these peptides 200-1000-fold more stable toward DPP-4 cleavage than the corresponding oxopeptides. GLP-1, GIP, and NPY thiopeptide analogs substituted at the amino acid preceding the scissile bond (P2 position) are proteolytically stable and nearly equipotent with the parent peptide in cell-based assays. Finally, proof-of-concept tests show that a thioamide GLP-1 analog is active in rats, with an *in vivo* potency surpassing that of GLP-1. Taken together, these experiments demonstrate the potential for thioamides to be used in stabilizing peptides for use in *in vivo* activity probes, diagnostic imaging agents, or even pharmacotherapies.



MARM 311

Positional effects of thioamides on cleavage rates of proteases

***Xing Chen**, cxing@sas.upenn.edu, Taylor Barrett, Elisha K. Keenan, **Jieliang Wang**, wji@sas.upenn.edu, **Chunxiao Liu**, chunxl@sas.upenn.edu, E. James Petersson. Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania, United States*

Thioamide substitution in the peptide backbone can be applied in two ways to protease studies. As a fluorescence quencher, thioamides can be paired with compact fluorophores to design “turn-on” fluorescent protease substrates. As a hydrogen bond disrupter, thioamide modification can be a very simple and general method to inhibit proteolysis without significantly altering the structure of the peptide. To guide fluorescence sensor applications as well as peptide stabilization applications, we have examined several model peptides with a thioamide scanned from the P3 positon to the P3' postion, and identified thioamide perturbing and non-perturbing positions. Further mechanistic investigation showed that the primary effect of the thioamide is often to prevent binding to the protease. Findings from these models will be used to predict which positions are best for thioamides and to exclude positions up front when analyzing a novel peptide with a known protease, and the stabilization patterns observed in these model substrates will be translatable to real signaling peptides.

MARM 312

Enhancing fractional ^{13}C incorporation in biosynthetically prepared proteins

***Xiaoyuan Wang**, xw002@bucknell.edu, Reilly E. Sonstrom, David S. Rovnyak. Bucknell Univ, Lewisburg, Pennsylvania, United States*

Nuclear magnetic resonance (NMR) is widely used in determining the three-dimensional structures of macromolecules including proteins in the solution phase. However, only certain nuclei such as ^{1}H, ^{13}C, and ^{15}N that possess the property of nuclear spin can be used in NMR. It is particularly important to minimize the cost of the more expensive enriched nutrient, uniformly 13C enriched glucose, used in bacterial host expression of recombinant proteins. We first summarize recent work in the laboratory to enhance the fractional incorporation of ^{13}C nuclei in to expressed proteins. We devised a method to add fractional amounts of u-^{13}C-glucose solely at the time of induction (Prot. Expr. Pur. 115, 2015, 1-10). Typical results utilize just 10% $^{w/w}$ ^{13}C-glucose in the media to provide almost 20% ^{13}C incorporation in to the expressed protein. Proteins expressed in this fashion are amenable to all common protein backbone 3D-NMR experiments but their ca. 20% overall ^{13}C incorporation does mean they show reduced sensitivity compared to uniformly enriched proteins. We report here recent work that achieves greater fractional ^{13}C incorporation in order to address this sensitivity challenge. Specifically, we devised an approach that combines our prior methodology with centrifugal methods that have been tried by others only for uniform enrichment. The combination of these approaches, which include careful management of starvation of *E*. coli cultures has resulted in major progress. Using just 18$^{\%\ w/w}$ ^{13}C-glucose, incorporation now significantly exceeds 40% in expressed proteins. Details of the implementation of this protocol will be described.

MARM 313

Purification of hypoxia-inducible factor prolyl-hydroxylases for studies of structure and function

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Prolyl-hydroxylase domain (PHD)-containing proteins are the primary regulators of the hypoxia inducible factors (HIFs). HIFs are responsible for controlling the low-oxygen response within a cell. PHDs have been identified as an important potential protein target for treatment of ischemic events including heart attack and stroke. There are three known PHD isoforms that differ significantly in size and activity. To investigate the structure and function of these proteins, we will use solution nuclear magnetic resonance (NMR). Initial efforts for this project focused on PHD-3 (27.3 kDa) and the catalytic domain of PHD-2 (27.5 kDa). These are the smallest of the HIF-prolyl hydroxylases, and size is an important factor to consider when studying the protein using nuclear magnetic resonance (NMR). It is difficult to analyze NMR data when using molecules larger than ~25 kDa, so reverse micelles will be used to facilitate study of these proteins. Prior to NMR studies, however, the proteins must be purified in large amounts. Histidine-tagged versions of both proteins were recombinantly expressed in inclusion bodies in *E. coli*. The unfolded protein was extracted from the inclusion bodies and refolded. The native protein was then purified by affinity chromatography, tag cleavage, and size exclusion chromatography. Optimization and characterization of the purification procedure is presented and the catalytic activity is being measured by fluorescence assay.

MARM 314

Novel fluorescently labeled anthraniloyl-m^{7}G capped RNA as a biomarker for biophysical studies

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Fluorescent mRNA molecules offer a wide range of applications for studying capping/decapping reactions, translation, and other biophysical studies. Furthermore, fluorescent tags prove invaluable for tracking RNA molecules in cells. Here, we present an efficient synthesis of a fluorescent cap analog, anthranioyl-GTP, its purification, and in vitro cap labeling of transcribed mRNA catalyzed by the recombinant Vaccinia capping enzyme to produce anthranioyl-m^{7}GpppG-capped RNA. Efficient capping was observed with 60–100% of the RNA transcripts capped with this fluorescent molecule. The Ant-m^{7}G derivative, previously shown to interact with the eukaryotic cap binding proteins (e.g., pokeweed antiviral protein (PAP) and eIF4E), serves as a substrate for the Vaccinia capping enzyme and the DCP2 decapping enzyme from Arabidopsis. Further, the Ant-m^{7}GTP-capped RNA is readily translated. This Ant-m^{7}GTP-capped RNA provides an important tool as a biomarker for biophysical studies.

MARM 315

Fluorescent labeling of α-synuclein for studying aggregation, propagation, and strain emergence

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Synucleinopathies are a family of related neurodegenerative disorders including Parkinson's Disease (PD), Dementia with Lewy Bodies (DLB) and Multiple System Atropy (MSA). Despite different symptomatic presentation and progression, each of these disorders is characterized by the presence of proteinaceous aggregates comprised primarily of the amyloidogenic protein α-Synuclein (αS) in the affected brain tissues. Recent observations on the cell-to-cell transmissibility of protein aggregates, as well as the existence of fibril isoforms, or "strains," of many amyloidogenic proteins has suggested that etiologically related neurodegenerative disorders may arise from fibril isoforms of the same protein. Understanding the process of αS aggregation, structural differences differences between fibril isoforms, and the cell-to-cell transmission of αS fibrils will significantly enhance our knowledge of synucleinopathies, informing strategies for therapeutic intervention for PD, DLB, and MSA. We have addressed these goals by utilizing fluorescent labeling of αS, which allows us to track aggregation in real time in a site-specific manner, gain insight into the structural remodeling of fibrils by small molecules, and understand the mechanisms by which pathological aggregates of αS are internalized by neurons. By installing complementary fluorophores for Förster Resonance Energy Transfer (FRET) studies of αS, we address how αS fibril formation occurs and elucidate conformational differences between fibril strains. Understanding the molecular level differences between strains will illuminate how fibril isoforms exhibit differential propagation and seeding capacities.

MARM 316

Characterization studies and activity assay development for sfnaC of the staphyloferrin A biosynthetic pathway

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Staphylococcus aureus is a Gram-positive bacterium responsible for numerous types of infections including those of the eye, skin, and heart. The methicillin-resistant strain of *S. aureus*, or MRSA, has gained additional resistance in recent years and is considered a serious health threat. The purpose of this research is to inhibit iron uptake into MRSA, thereby reducing its virulence and inhibiting its growth. SfnaC is the putative first enzyme in the biosynthetic pathway of staphyloferrin A, one of two iron-binding siderophores produced by S*taphylococcus aureus*. Inhibition of this enzyme could prevent staphyloferrin A production thus reducing iron uptake. This research presents recent characterization studies of SfnaC along with activity assay development results. Progress towards the synthesis of a mechanistic-based fluorinated inhibitor is also presented.

MARM 317

Thermodynamics of pHLIP binding and folding is dependent on titration of key acidic residues

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pH (Low) Insertion Peptide (pHLIP) is a peptide with the intrinsic ability to penetrate cell membranes under acidic conditions. As a result of this inherent trait, pHLIP is a potential candidate in delivering therapeutics and diagnostic imaging agents to tissues characterized by acidosis such as cancer, arthritis, and heart disease. In spite of this, our understanding of the energetic contributions of the molecular interactions and the structural features controlling biological function in pHLIP is limited. Through computational modeling, these molecular interactions can be studied at an atomistic level of detail inaccessible to most conventional experimental techniques. The process of pHLIP function has been separated into individual components of binding, and helix formation, and insertion: 1) pHLIP in solution; 2) pHLIP at the membrane surface, and 3) pHLIP inserted into the membrane. This project focuses on the formation of helical structure in pHLIP while bound to the membrane surface, a key precursor in the pHLIP penetration of the cell membrane. By modeling the helical formation of pHLIP, we aim to gain an understanding of the energetic contributions of pHLIP-membrane interactions. Our long-term goal is to build a complete thermodynamic picture of pHLIP folding and insertion. These insights will be crucial in our fundamental understanding of how pHLIP can be developed for applications in diagnostic imaging and drug delivery.

MARM 318

Effects of a neutral cosolute on the B to Z transition for DNA duplexes incorporating both CG and CA steps

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In the cell, nearly 40% of the volume is occupied by macromolecular crowding agents and smaller osmolytes that accumulate in response to environmental stresses. Of particular interest is the influence of osmolytes on the transition of the right-handed B-DNA to the left-handed Z-DNA. Due to the correlation between Z-DNA formation potential and regions of active transcription, Z-DNA is believed to serve a vital role in the transcription process, and changes in osmolyte concentration may influence transcription as a part of the cellular stress response. We utilized circular dichroism spectroscopy to monitor changes in conformation of DNA duplexes containing a full-turn of Z-DNA in the presence and absence of PEG 200, which we used as a model neutral cosolute. Sodium ion titrations revealed that PEG 200 influenced the formation of Z-DNA compared to dilute solution conditions, by lowering the *in vitro* [Na^+] and number of ions required for the transition. Also, the presence of PEG 200 decreased the free energy required to adopt the Z-form and increased the cooperativity of the transition for all DNA duplexes tested, even those that included CA steps instead of the classic CG repeat sequence. Moreover, the presence of 40% PEG 200 induced the Z-form conformation in sequences that would not fully adopt the Z-form structure even in 5M NaCl. These results suggest that osmolytes may play a significant role in supporting the transient formation of Z-DNA *in vivo*, and that sequences containing significant amounts of CA steps may more favorably adopt the Z-conformation as a part of binding and regulatory processes than had been previously considered.

MARM 319

Engineering green fluorescence protein derivatives with cytochrome *c* heme binding sites

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Cytochrome *c* is an ubiquitous electron carrier protein essential for various cellular processes such as energy transduction and programmed cell death (apoptosis). As a functional form, cytochrome *c* contains at least one heme (iron protoporphyrin IX) cofactor that is covalently and stereospecifically attached to the cysteine sulfhydryl groups of a conserved CXXCH motif within the polypeptide substrate. Multiple evolutionarily distinct biogenesis (Ccm) systems that accomplish the production of functional cytochrome *c* have been defined. One of these systems (Ccm system III) is confined to mitochondria of fungi, metazoans and some protozoa. In natural cellular environments, it includes one or two components with heme lyase activities towards cytochrome *c* protein substrates, and a heme reductase as an accessory factor. However, in a heterologous bacterial (*Escherichia coli*) expression host, it has been shown that the Ccm system III component cytochrome *c* heme lyase (CCHL) alone is sufficient to form functional cytochrome *c* upon coexpression. Furthermore, it has been found that an 18 amino acid residues long consensus sequence (including the CXXCH motif) within the cytochrome *c* polypeptide (CCCS) is required for protein substrate recognition and heme ligation by CCHL. In this work, we inserted this CCCS into a

green fluorescent protein (GFP) model at different positions (amino-terminus, carboxy-terminus, and three internal loops). We present data on the questions i) whether these insertions effect the fluorescent properties of the constructed protein fusion derivatives and ii) whether these protein fusion derivatives can be covalently and stereospecifically attached with heme molecules upon coproduction CCHL.

MARM 320

Efficacy of truncated synthetic analogues of the human antimicrobial peptide salvic against *Escherichia coli* persister cells

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Since their widespread adoption in the 1940s, antibiotics have been used to treat infections and save the lives of millions of people throughout the world. Unfortunately, the prolific use of antibiotics has gradually led to an increase in antibiotic-resistant bacteria. Beyond antibiotic-resistance, one of the many challenges facing researchers and healthcare providers is the role of bacterial persistence to this epidemic. Bacterial persisters are a phenotypic variant that comprise 1:1,000,000 of the cells in a bacterial colony. While not able to grow in the presence of antibiotic like antibiotic-resistant bacteria, these persister cells are antibiotic-tolerant and able to survive antibiotic treatment. These cells can evade the damaging effects of antibiotics by slowing their metabolic processes. Following antibiotic treatment, persister cells are able to repopulate the colony, leading to chronic infection and serious health complications for the infected individual. To combat the presence of these cells, we have turned to a class of antimicrobials called antimicrobial peptides. A common mode of action for these antimicrobial peptides is membrane disruption, which we hypothesize will be effective against the slow/non-growing persister cells. The human salivary peptide salvic has been shown to exhibit some antimicrobial activity. After analyzing the sequence, we determined a small truncated region that we predict can exist as a cationic, amphipathic α-helix, all traits that would be indicative of a membrane disrupting mode of action. We synthesized, purified, and characterized this truncated peptide as well as a series of analogues and then tested the efficacy of our peptides against planktonic *Escherichia coli* persister cells.

MARM 321

Synthesis and effectiveness of antimicrobial peptide temporin F analogues against *Escherichia coli* persister cells

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The growing problem of bacterial resistance is an increasingly prevalent issue around the world today. As antibiotics become less effective and bacteria become more and more resistant to these once powerful medications, scientists have been researching potential alternatives to combat these deadly bacteria. A further factor complicating this research is the role of bacterial persisters. Persisters are a highly antibiotic-tolerant dormant bacterial phenotype and are unique from normal antibiotic-resistant bacteria in that they are genetically identical to those bacteria that are susceptible to antibiotics. However, these persister cells are able to survive antibiotic treatment. Once the antibiotic is no longer present, the persister cells revert back to their normal phenotypic expression and repopulate the bacterial colonies. Their ability to enter a dormant state is what renders standard antibiotic treatment ineffective, leading to recurrent infections. We hypothesize that, even though the persister cells are tolerant of conventional antibiotics, an antimicrobial substance that affects membrane integrity will be successful in killing these persister cells. Antimicrobial peptides are naturally occurring host defense peptides produced across many different species. One common mode of action for these antimicrobial peptides is membrane disruption. In particular, small, cationic amphipathic α-helical structures exhibit this mode of action against bacterial cells. In this work, we synthesized, purified, and characterized temporin F peptide as well as a series of analogues, and tested the efficacy of these peptides against *Escherichia coli* persisters.

MARM 322

Application of fluorescence spectra in the analysis of cocaine samples

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Cocaine is a schedule II drug that is commonly abused. Street versions of cocaine are often cut with other agents that have pharmacological activity. Common cutting agents include benzocaine, lidocaine, procaine, tetracaine and levamisole. In the current study, cocaine and the cutting agents listed above were analyzed via ultraviolet-visible and fluorescence spectroscopy in buffers at various pHs with the purpose of identifying a unique spectral difference that might be useful in quantitating cocaine in the presence of these cutting agents. Solutions of cocaine

and cutting agents at a concentration of 0.01 mg/mL were first analyzed by UV-visible spectroscopy to determine starting wavelengths for fluorescence spectroscopy. Solutions were then diluted to 0.001 mg/mL for fluorescence analyses. Examination of fluorescence spectra revealed that cocaine solutions of neutral and acidic pH exhibited a strong fluorescence peak compared to cutting agents. A pH 7 buffer was chosen for further analyses of cocaine mixtures as the cocaine peak was strong and distinct under those conditions using an excitation wavelength of 230 nm and emission wavelengths ranging from 240 to 440 nm. Cocaine was quantitated under these conditions using fluorescence maxima of 1135. The linear range for quantitation was established. Binary mixtures containing cocaine and select cutting agents were prepared at 3:1, 1:1, and 1:3 ratios and were cocaine was quantitated using fluorescence spectroscopy. Cocaine was successfully quantitated in the presence of the cutting agents using fluorescence spectroscopy.

MARM 323

Purification of mycobacteriophage terminase and portal proteins in *Escherichia coli*

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A bacteriophage is a virus that is able to infect and replicate inside a bacterium host. Catdawg is a *mycobacteriophage* belonging to Cluster O and the siphoviridae family. Catdawg GP30, the large terminase protein and GP 32, the portal protein were isolated and purified to 95% purity in *E. Coli* in route to structure determination. The structure of GP 30 and 32 are important because the amount of structural information on phages is limited. Homology modeling of GP30 and GP32 were generated and compared to known crystal structures.

MARM 324

Study co-aggregations of nucleic acid nanostructures with tetracycline molecules and their potential applications in smart drug delivery

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Recently, DNA has been broadly used on research area, including drug delivery. It can bind to small molecules because it has highly programmable structure and high efficient. Several published studies have demonstrated that DNA binding with small molecules to enhance their release. In this project, we are exploring DNA nanoscaffolds for binding to a neuroprotective minocycline (MO) for its releasing to a diseased area. It seems challenge to study their reaction with depending on specific concentration of divalent metal, which is Magnesium (Mg^{2+}), where Magnesium plays as bridge between DNA and minocycline through electrostatic charge and it is critical for the MO-DNA particle formation. We have demonstrated that, the encapsulation yield of Minocycline with DNA changed depending on length and shape of DNA. Moreover, pH level of buffer play important role on the aggregations of DNA with MO, where the pH=7 or 6 are compatible with body physiological conditions.The study will have important impact on drug delivery for spinal cord therapy.

MARM 325

Probing environments in *Thermoanaerobacter tencongensis* H-NOX

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Heme Nitric Oxide and/or Oxygen (H-NOX) binding proteins are sensor domains with a heme co-factor that binds gaseous ligands such nitric oxide, carbon monoxide, and/or oxygen. These H-NOX domains interact with an effector domain, controlling a cascade of signals required for cellular functions. In this study, distinct local environments in *Thermoanaerobacter tengcongensis* H-NOX (*Tt* H-NOX) protein were probed using a genetically encoded vibrational reporter unnatural amino acid (UAA). Specifically the spectroscopic reporter UAA 4-cyano-L-phenylalanine (pCNF) was incorporated at a variety of locations in the protein including surface sites and sites near the heme co-factor. The solvation status of the local environments was elucidated by the position of the nitrile symmetric stretching frequency of pCNF and these spectroscopic results will be presented.

MARM 326

Synthesis and evaluation of copper binding properties and BACE 1 inhibition activity of multi-target compounds

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Alzheimer's disease (AD) is the most common form of dementia affecting more than 28 million people in the world. Only symptomatic treatments are currently available. Anticipated tri-fold increase of AD incidence in the next 50 years has established the need to explore new possible treatments. The accumulation of extracellular amyloid-b (Ab) plaques, intracellular tangles in the brain, and formation of reactive oxygen species (ROS) are the major hallmarks of the disease that lead to an uncontrolled neuronal death. Because of the key role that two secretases (b- and g-) play in the production of Ab peptides and the mounting evidence supporting the implication of some metal ions like Cu^{2+} and Zn^{2+} in the progression of AD, inhibition of secretases, specially b -secretase BACE 1, and metal chelation have attracted enormous interest and have become leading strategies. Due to the complex pathophysiology of AD and the identification of numerous potential targets, the multi-target directed ligand design (MTDL) approach is currently preferred in the search for improved drugs. In this work, a series of 4 disease-modifying and multi-target compounds (**1-4**) have been synthesized and characterized. All compounds bind Cu^{2+} selectively over other biologically relevant metal ions. They form 2:1 (compound:Cu^{2+}) complexes with association constants logK_a 12-14 depending on the molecular design. Our results indicate that compounds **1-4** possess excellent antioxidant properties: they inhibit the Cu^{2+}-catalyzed reactive oxygen species production between 60% and 100%, and they scavenge AAPH-induced free radicals better than ascorbic acid and comparably to resveratrol. Importantly, compounds **1-4** display a moderate inhibition of BACE 1 enzyme with IC_{50}'s up to 6 mM. Therefore, this family of compounds represents a promising alternative as potential treatment for AD.

MARM 327

Conformation of Influenza M2 protein is sensitive to the curvature propensity of membrane lipids

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Viral budding requires localized regions of high negative Gaussian curvature (NGC). Synchrotron small-angle X-ray scattering (SAXS) studies have demonstrated that the addition of Influenza M2 to certain lipid mixes induces regions rich in NGC. M2 protein is a 97-residue homotetrameric membrane-bound protein critical to viral infection. M2 variants that have impaired viral budding show significantly reduced ability to generate regions rich in NGC. Using site-directed spin label electron paramagnetic spectroscopy (SDSL-EPR) we have shown that the conformation, dynamics and membrane topology of the M2 protein differs depending on the curvature propensity of the membrane lipid bilayer in which the M2 protein is reconstituted.

MARM 328

Characterization of the region of the influenza membrane bound M2 protein critical to cholesterol dependent viral budding

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The M2 protein plays a critical role in the influenza A virus life cycle. The 97-residue homotetramer consists of an N-terminal ectodomain, a transmembrane (TM) helix domain spanning residues 22-46, a juxtamembrane amphipathic helix (AH) comprising residues 46-61 and a C-terminal cytoplasmic tail spanning residues 61-97. Previously published biophysical studies have focused on the TM and AH domains. Much less is understood about the cytoplasmic tail. Using site-directed spin label electron paramagnetic spectroscopy (SDSL-EPR) we have studied the conformation, dynamics and membrane topology of the cytoplasmic tail in membrane bilayers both with and without the presence of cholesterol. We have also compared the properties of WT M2 protein with a mutant of the protein that has impaired viral budding properties.

MARM 329

Determining chaperone protein requirements for the propagation of heterologous poly-glutamine aggregates in *S. cerevisiae*

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Amyloid-based yeast prions are heritable aggregates of misfolded protein that can be passed on to daughter cells following a process called fragmentation. This fragmentation is carried out by chaperone proteins including Hsp70, Hsp104, and the Hsp40 Sis1. Yeast prions usually exhibit an amyloid structure, forming cross-beta sheets of sections known as the prion-forming domain, or PrD. *In vivo*, long tracts of glutamine have been shown to form amyloid structures. Alexandrov et al. have created a system of polyQ sequences with a single heterologous amino acid interspersed every fifth residue (QQQXQ), fused to the MC regions of yeast Sup35, the protein which forms the prion [*PSI*$^{+}$]. When expressed in a strain of *Saccharomyces cerevisiae* lacking Sup*35,* these polyQX sequences form aggregates *in vivo* which are stably propagated to daughter cells via chaperone-based fragmentation. Using this system, we are testing the primary and secondary chaperone requirements of these aggregates using yeast plasmid-shuffling and chemical repression of gene expression which will provide information that can be compared with the previously determined chaperone requirements of other known yeast prions. Comparison of the results for different polyQX aggregates is expected to provide insight into the interactions of chaperones and prions, and how specific amino acid composition may affect these interactions.

MARM 330

Investigating the role of J-proteins in Hsp104-mediated curing of prion [PSI^{+}]

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The amyloid-based prions of *Saccharomyces cerevisiae* are heritable aggregates of misfolded protein, passed to daughter cells following fragmentation by a set of molecular chaperones which includes the J-protein Sis1, Hsp70, and Hsp104. Overexpression of Hsp104 efficiently cures the prion [*PSI*$^{+}$], a phenomenon which has promoted the exploration of Hsp104 as a potential therapeutic agent for neurodegenerative diseases. However, the mechanism of [*PSI*$^{+}$] elimination by Hsp104 overexpression has been the subject of significant debate for the past two decades and has garnered significant interest in the recent literature as multiple conflicting models have been proposed. Yeast prion propagation is inexorably reliant on the function of molecular chaperones of the Hsp100, Hsp70, and Hsp40 classes. Specifically, four Hsp40s (also called J-proteins) have been implicated in various aspects of yeast prion biology: Sis1, Ydj1, Apj1, and Swa2. We found that overexpression of Sis1 or Apj1 accelerates strong [*PSI*$^{+}$] elimination by Hsp104 overexpression, yet Ydj1 overexpression has a profound and opposing effect, completely blocking Hsp104-mediated curing, indicating that Apj1 and Sis1 likely have similar and partially overlapping roles in this process. Interestingly results for weak variants of [*PSI*$^{+}$] indicated potentially no role for J-proteins in curing as no J-protein alteration whatsoever affected the ability of Hsp104 to cure these variants. Additional experiments to determine the specific J-protein domains responsible for various effects are underway. Overall our data support the hypothesis that Hsp104-mediated curing may occur by biochemically distinct, variant-specific mechanisms, only some of which involve J-proteins.

MARM 331

Spectrophotometric determination of the binding affinity and computationally determined estimated binding energy of neutral red, riboflavin, and flavin derivatives with riboflavin binding protein

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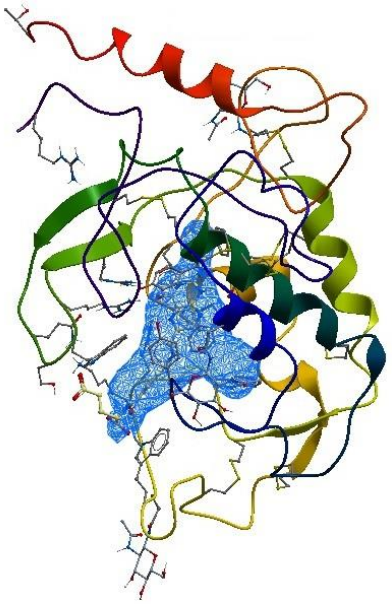
The role of riboflavin binding protein (RBP) is to bind to and transfer the coenzyme, riboflavin or vitamin B2, to the tissues where it is required for normal physiological functions such as cellular respiration. One type of RBP, specific to pregnancy, is responsible for transporting riboflavin to the fetus to sustain its development. The protein is also important in the chicken egg where it is stimulated by estrogen and is critical for survival of the fetus. Riboflavin binding protein was purified from egg whites and the binding affinity was determined using absorption spectrophotometry with neutral red that is similar in structure to riboflavin. Additionally**,** the binding affinity of riboflavin and several flavin derivatives was also determined using absorption spectrophotometry. The estimated binding energy of the same molecules was computationally determined using ICM-Pro (Molsoft, LLC) with the protein, human folate receptor (4LRH.pdb), based on its sequence similarity and evolutionary relationship to riboflavin binding protein from egg whites.



Human folate receptor (4LRH.pdb) with sequence similarity and an evolutionary relationship to riboflavin binding protein from egg whites.

MARM 332

Functional and high-affinity binding of dopamine D4 receptor-selective partial agonists as pharmacological tools to study substance use disorders

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The dopamine D4 receptor (D4R) is enriched in the prefontal cortex where it is believed to modulate cognition, attention, and executive function. In previous studies using D4R ligands, it has been determined that D4R agonism may improve cognition while D4R antagonism may reduce drug-taking behavior. Developing novel D4R-selective ligands will give insight to the biological roles of D4R signaling and may lead to new pharmacotherapies for neuropsychiatric disorders. We describe a rational drug design strategy leading to the design, synthesis, *in silico* and *in vitro* analyses of novel D4R partial agonists. A library of ligands structurally related to the prototypical D4R partial agonist A-412997 was synthesized and evaluated for binding affinity, as well as *in vitro* efficacy, in D4R-expressing HEK293 cells. All novel compounds were partial agonists or antagonists and several of them featured improved D4R affinity and subtype selectivity over the parent compound. A D4R homology model was created using the high-resolution X-ray structure of D3R in complex with a ligand (3PBL). Using experimental affinity values, the best docking score function was selected and subsequently used to predict the binding affinities of the novel library. After model validation, an *in silico* screen was used to design a second generation library that is now being evaluated.

MARM 333 Withdrawn

Ubiquitin receptor Rpn13's role in proteasomal processivity

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Proteins within eukaryotic cells are targeted to the proteasome for degradation by polyubiquitination. Ubiquitin chains linked to substrates activate the proteasome’s ability to unfold substrates. However, it is not fully understood how ubiquitin plays a role in substrate unfolding and degradation, since ubiquitin chains are thought to be removed before the unfolding process begins. There are three known ubiquitin receptors on the proteasome, Rpn10, Rpn1, and Rpn13. A ubiquitin receptor of particular interest is Rpn13, which has been suggested as a target for cancer therapeutics. We studied the ability of Rpn13 proteasome mutants to unfold and degrade ubiquitinated substrates. Deletion of the entire Rpn13 gene (ΔRpn13) or mutation of Rpn13 to prevent ubiquitin binding led to global defects in unfolding ability.

MARM 334

Engineering of a protein probe for alpha synuclein detection

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The aggregation of the amyloid, alpha-synuclein (αS), has been implicated in the pathology of the neurodegenerative disorder, Parkinson's Disease. Natively unstructured monomers of αS mis-fold and self-assemble to form prefibrillar oligomers, which are the most neurotoxic conformers. A system for the rapid and specific detection of these oligomeric intermediates would be beneficial towards uncovering the mechanism behind αS oligomerization, developing therapeutic treatments, and the discovery of early diagnostic tools. Our group has developed a biomolecular probe, which retains the natural self-assembly of αS and incorporates a conformational fluorescence sensitivity to the biarsenical dye, FlAsH, in the presence of oligomers. A directed evolution approach was applied to optimize the probe and identify the best recombinant variants.

MARM 335

Optimization of a permissive aminoacyl tRNA synthetase for a target unnatural amino acid

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The amino acid acridon-2-ylalanine (Acd) can be a valuable fluorescence probe of protein dynamics either alone or as part of a Förster resonance energy transfer (FRET) or photo-induced electron transfer (eT) probe pair. The first generation of aminoacyl tRNA synthetase (aaRS), developed from a library of permissive RSs for Acd incorporation, also incorporated *N*-phenyl-amino-phenylalanine (Npf), a trace byproduct of one Acd synthetic route. We have performed negative selections in the presence of Npf to prevent its incorporation and analyzed the selectivity of the resulting AcdRSs in terms of both *in vivo* protein expression and detailed kinetic analyses of the purified RSs. We find that selection conferred a ~50-fold increase in selectivity for Acd over Npf, eliminating incorporation of even 10% Npf contaminants, and allowing one to use a high yielding and efficient Acd synthetic route for improved overall expression of Acd-containing proteins.

MARM 336

Creating peptide hydrazides *via* intein splicing for expressed protein ligation

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Peptide hydrazides are powerful thioester surrogates for chemical ligation. Hydrazides can also serve as an effective tool in introducing site-selective modifications. Currently, peptide hydrazides are generated via solid phase peptide synthesis (SPPS). The generation of peptide hydrazides using SPPS has proven difficult due to limitations in peptide length and solubility. Here we have introduced a recombinant approach for creating hydrazides on the C-terminal of a model protein using intein *trans* splicing technology. PhoRadA split inteins were used to introduce a hydrazide at the C-terminal of Maltose Binding Protein. The versatility of this recombinant hydrazide has been shown by its ability to undergo an aldehyde coupling reaction to produce hydrazone. The use of recombinant peptide hydrazides can be extended to making difficult protein targets through expressed protein ligation.

MARM 337

Protective function of *Azadirachta indica* (neem) in WI38 lung fibroblast cells subjected to oxidative stress

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Physiological barriers such as senescence and apoptosis play vital roles in restricting cells that have been subjected to irreparable DNA damage. While cancer therapy rely on their tumor suppressive mechanisms, current treatments also pose the risk of targeting the healthy cells. Novel bioactive compounds that counteract oxidative stress-induced DNA damage have emerged as alternative approaches to treat cancer patients, without the deleterious secondary effects generated by traditional chemotherapy and radiotherapy approaches. Polyphenols which has antioxidant properties can be found in high concentration in Azadirachta indica (neem).Our research will analyze the effect of neem extract on proof of fibroblast, subjected to oxidative stress. Our goal is to elucidate the physiological mechanism of neem in protecting human cells from oxidative damage.

MARM 338

Matrix effects on equilibria in atmospheric aerosol

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The chemical composition of atmospheric aerosol is complex and poorly understood. Further, many chemical reactions occurring within the aerosol are at equilibrium. The surrounding matrix affects the equilibrium constants of these equilibria and the dominant species in solution can shift based on changes in water availability, pH, ionic strength, and the presence of other organic compounds. As the dominant form in solution varies, so do properties such as pK_a, light absorption, and reactivity. In order to accurately model the chemical and physical properties of aerosol, it is important that we understand the actual chemical composition under conditions found in the atmosphere. This work indicates that the acidity of a solution has direct impacts on the tautomeric equilibrium between the aldehyde and diol form of imidazole-2-carboxaldehyde, a compound recently identified as a possible photosensitizer found in atmospheric aerosol. Depending on which tautomeric species is dominant, the light absorption properties significantly differ. This has a direct effect on the ability of the imidazole-2-carboxaldehyde to absorb sunlight. We also present data highlighting the importance of considering matrix effects when predicting the degree of oligomerization of small oxidized organic molecules such as glyoxal and glycolaldehyde.

MARM 339

Chemical analysis of water near hydraulic fracturing sites

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The processes of Hydraulic Fracturing (fracking) and its effects on water quality are of increasing concern. Fracking has profuse economic benefits, but the environmental and health effects are becoming well represented within the literature. The fracking of shale formations consists of injecting an average of 20 million L of water with sand and thousands of chemicals, most being toxic and carcinogenic, at high pressure to drill fissures at each well. The wastewater acquired after fracking can lead to surface water contamination which may result in major effects to the food chain. During this study, water and sediment was obtained from six public sites along the Meshoppen Creek in Susquehanna and Wyoming counties in Pennsylvania. Fractrack was used to count fracking sites in 1, 3, and 5-mile radius around each collection site. Water and Sediment was analyzed for Pb, Mn, Fe, and Na using Atomic Absorption Spectroscopy. HPLC was used to analyze 7, 12, dimethyl benzo(a) anthracene, an organic compound found in fracking wastewater. Ion conductivity, pH, and temperature was also qualified at each site. Analysis of water and sediment produced from collections in large fracking areas will better help identify the impact of fracking on the environment.

MARM 340

***In vitro* assays for assessment of estrogenic activity of the novel Bisphenol-A alternative, four Bisguaiacol-F compounds**

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Bisphenol-A (BPA), largely used in polycarbonate plastics and polystyrene resins, is considered to be an endocrine disruptor due to its estrogenic activity. Recent extensive kinds of literature have reported the evidence on the relationship between BPA exposure and chronic human disease, including diabetes, obesity, reproductive disorders, breast cancer, birth defects, chronic respiratory and cardiovascular diseases. Therefore, a sustainably sourced, and less toxic BPA alternative is desirable for the manufacture of containers for edible products. Bisguaiacol-F (BGF) is structurally similar to BPA, with two hydroxyphenyl groups. BGF can be synthesized by reacting two derivatives of lignin and is considered as a green alternative to BPA. In this study, estrogenic activity (EA) of four isomers BGF were evaluated at six concentrations (from 10^{-13} to 10^{-8} M) by cell proliferation assay. Chemicals with EA activate the ERs and ER-dependent transcription of estrogen-responsive genes, which leads to proliferate of breast cancer cells (MCF-7 cells).The MTT assays revealed that BPA at 100pM, 1nM, and 10nM significantly promoted the *in vitro* proliferation of MCF-7 cells after exposure for 96 h (p<0.05). The EA of BPA is dose dependent. There is no EA effect of BGF6 and BGF8 at the wide concentration range from 10^{-13} to 10^{-8} M, or of BGF1 and BGF4 at 100pM and 1 pM when compared to the no treatment group (p<0.05). Even BGF1 and BGF4 at 10 nM, 1 nM, and 10 pM significantly increased the cell proliferation compared to the no treatment group,

the cell proliferation was still lower than that determined at the same concentration of BPA (p<0.05). All the results indicate that both BGF6 and BGF8 are the potential less toxic and sustainable alternatives to BPA.

MARM 341

Comparison of 1,4-dioxane cometabolism with the amendment of different alkane gases

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1,4-Dioxane (dioxane) groundwater contamination represents a remedial challenge for environmental engineers due to its carcinogenicity, mobility, and recalcitrance for degradation. Gases alkane degrading microorganisms (e.g., methanotrophs, propanotrophs, and butanotrophs) are known for their relaxed substrate range, which enables cometabolism of a large variety of organic pollutants with the presence of their primary substrates. In this study, we compared the biostimulatory performance of methane and propane for decontamination of dioxane using microcosm assays and investigate the putative biotransformation pathways by the enriched consortium. In microcosms stimulated with methane, a lag time of approximately three weeks was observed for methane degradation. Proliferation of methanotrophs was evident by the enhanced methane consumption with no lag time after the second amendment of methane to the microcosms. However, no significant dioxane removal was indicated after 2 amendment cycles of methane. As for propane, it was found to be able to stimulate dioxane cometabolism by the indigenous bacteria, though the lag time was relatively long (i.e., greater than 5 months). No degradation of dioxane was observed until approximately half of the initial propane has been consumed. The consumption rate on propane was approximately three-times slower than methane, suggesting a relatively low abundance of propanotrophs in the field samples. These results showed different treatment performance by adding different gaseous alkane as the stimulants, which underscores the need for a better understanding of the mechanisms of dioxane cometabolisms. It is also notable that using traditional microcosm assays to discover the effectiveness of biostimulation can be quite time-consuming and unproductive given the long incubation time and high variety of biostimulants. To tackle this problem, molecular tools that allow for quick determination of the prevalence of genes encoding the catabolic enzymes that are proficient in cometablizing dioxane need to be developed.

MARM 342

Exploring the fate of sulfur in regions of abandoned mine drainage

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Abandoned mine drainage (AMD) is an important environmental issue in central Pennsylvania. AMD occurs when mining activities expose sulfur-containing minerals (especially pyrite) to air and water, creating acidic sulfur-rich wastewaters. In most cases, aqueous sulfate ions are eventually reduced to H_2S by sulfate-reducing bacteria, giving AMD sites their characteristic “rotten egg” odor. Accurately quantifying the H_2S is important for understanding the overall chemistry, yet it has not been directly measured over AMD sites. Because the H_2S concentrations are very low (sometimes in the ppb range), *in situ* detection by chemical sensors or other methods is challenging. Transporting samples from field sites to the laboratory for measurement comes with its own set of challenges. In this presentation we will outline the history of this project and discuss lessons we’ve learned and limitations we’ve discovered so far.

MARM 343

Liquid-phase hydrogenation of furfural and furfuryl alcohol assisted by metal chlorides

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Furfural, an intermediate for biomass conversion, and furfuryl alcohol, a hydrogenation product of furfural, were reacted in the liquid phase with a supported Pd catalysts. The effects of several metal chloride additives to act as Lewis acids were observed. The catalyst used for reactions at atmospheric pressure and high temperature and pressure reactions was carbon-supported palladium; however, commercial alumina-supported palladium was also studied under atmospheric pressure in isopropyl alcohol with a hydrogen balloon present. Products were principally identified through gas chromatography-mass spectrometry (GC/MS) with some use of gas chromatography-infrared spectroscopy (GC/IR). Depending on the metal chlorides used in the reaction, the observed reaction pathways were hydrogenation, etherification, and oligomerization. Under atmospheric pressure, iron (III) chloride yielded virtually 100% conversion of furfural to products with little to no detected oligomerization products, while tin and copper were selective toward oligomerization. This selectivity may aid in identifying the pathway of humins formation during biomass conversion processes. High pressure and high temperature

conditions show promise for catalytic transfer hydrogenation (CTH). Other alcohol solvents and a nitrogen atmosphere were examined under atmospheric pressure to examine the role the solvent has in the reaction process, and specifically the etherification pathway. Proposed reaction schemes will be presented and compared to current literature in the field of biomass conversion.

MARM 344

Impact of cationic forms of organic matter in natural waters on the nitrogen assimilation processes

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Ammonia, originated from the decomposition of organic matter, being the richest natural substance in nitrogen, with the exception of that molecule, is non-toxic for a wide range of bacteria at the level of a few mol/L, unlike animal and plant cells. In this paper, the difference in the impact of amines of natural origin (diethylamine, DEA) and synthetic origin (1-naphtylamine, 1-NA and diphenylamine, DFA) on the processes of ammonia oxidation has been investigated. 1-NA significantly inhibited nitrification by a mixed population of Nitrobacter and Nitrosomonas species isolated from activated sludge; a concentration of 15 mg/L gave a 50% inhibition. Maximum admissible concentrations (MAC) for 1-NA and DEA differs by two orderd. The laboratory simulations have been carried out in water of the Nistru River (in the section of the Vadul-lui-Voda town). To river water samples of water, the NH4Cl solution has been added, in order to achiieve concentrations of ~ 3.2 mg/L and ~ 6.4 mg/L of ammonium, which are characteristic for rain water and a series of contaminated objects. Both DEA and 1-NA influence in the redox processes generated by bacterial enzyme activity even within the MAC values. In the case of 1-NA the braking effect is related to the toxic effect, while for DEA this effect is doubled (due to the toxic effect and also that related to the aminic carbon). It has been shown that the aminic nitrogen exhibits more pronounced toxic effects in comparison with ammonia. Typically, the amines, originated from the decomposition of organic materials of natural origin, have less toxicity and lower MACs by about ten times higher than those of synthetic origin. Here, it is important to mention that laboratory models are sensitive even at concentrations below MAC.

MARM 345 Withdrawn

Recycling of waste printed circuit boards by delamination using different organic solvents and study of its mechanism

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Comparative evaluation of solvent dimethylformamide (DMF) and dimethylacetamide (DMA) to delaminate waste printed circuit boards (WPCBs) has been investigated. The study revealed that dissolution of brominated epoxy resin (BER) results in the delamination of WPCBs layers. Dissolution of BER is governed by the factors like-reaction temperature, WPCBs size, WPCB:DMF, time etc. Investigation showed that DMA is relatively better solvent and result in 217% more resin dissolution than DMF. The delamination of layers ensures liberation of metal layer cladded on the WPCBs surface and thus separation of metal – nonmetal is possible. It is also found that the solvent after usage may be regenerated with negligible volume loss and drop in its dissolution efficiency. Investigation of the mechanism of dissolution has also been carried out. The proton, carbon nuclear magnetic resonance spectroscopy and Fourier transform infrared spectroscopy of solvent containing BER revealed that the hydroxyl moiety of the polymeric chain of BER is involved in hydrogen bonding with the carbonyl (C=O) moiety of DMA molecule. Separation of different components and regeneration of solvent are the inherited features of this process that makes the process quite cost effective and very less effluent generating.

MARM 346

Detection and cell sorting of cyclic ether degrading *Pseudonocardia* species by fluorescence *in situ* hybridization and flow cytometry using 16S rRNA-targeted oligonucleotide probes

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Recent studies with molecular tools and isotopic analysis have unveiled the occurrences of indigenous microorganisms that are capable of degrading cyclic ethers (e.g., 1,4-dioxane and tetrahydrofuran) might be more widespread than previously assumed at the contaminated field. Isolating and characterizing bacteria with unique biodegradation capacities is helpful to understand their metabolic and physiological idiosyncrasies and advance

the development on novel bioremediation techniques. However, this is not an easy task if one relies on traditional isolation techniques (e.g., enrichment and serial dilution for separating colonies on plates) due to the fastidious nature of many indigenous organisms. In general, less than 5% of known bacteria can grow on plates. In this study, we aimed to develop sensitive and specific fluorescent probes to identify and sort indigenous cyclic ether degraders in enriched environmental samples using advanced flow cytometry and cell sorting technique. Specifically, oligonucleotide probes targeting the genus of *Pseudonocardia* was developed and assessed for its coverage and specificity. These probes suggest great potential to rapidly detect cyclic ether degraders, economically identify them, and stably predict bioremediation. This study advanced our understanding of the phylogenetic and metabolic diversity of indigenous microbial degraders and availed us with innovative molecular technique for *in situ* enumeration and detection.

MARM 347

Paper-based mercury detection implementing gold nanoparticles and mercury-specific oligonucleotide

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Mercury, as a toxic element, has always been a concern of health to us. Thus detecting mercury content in samples is essential for the safety of human body, especially in water samples. A paper-based mercury detection method that implements the mercury-induced aggregation of gold nanoparticles and mercury-specific oligonucleotide (MSO) was developed. The MSO binds to mercury ions and forms a hairpin structure that is no longer able to protect gold nanoparticles; with addition of salt, the gold nanoparticles would aggregate, and different degrees of color changes respect to mercury content in the water sample can be read by naked eyes. Nanomolar of mercury is determined with paper easily and accurately by using this method, which would be promising in practical use to test the quality of our drinking water.

MARM 348

Tetramethylguanidinidum amino acid-based ionic liquids and their effects on beta sheet proteins

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Synthesis and research of biocompatible aqueous ionic liquids have been under greater scientific investigation recently due to their potential biochemical and biomedical applications. We prepared two novel amino acid-based aqueous ILs specifically for biochemical applications and evaluated their effects on the beta sheet protein mCherry. The protein was expressed in *Escherichia coli* cells and subsequently isolated and purified. We measured the thermal stability in different aqueous ionic liquid solutions and characterized how they affect the stability of the overall tertiary and quaternary structure. We also modeled the protein in aqueous ionic liquid solution using molecular dynamics simulations. By combining the biophysical chemistry characterization of the protein with the detailed simulations we can obtain a detailed picture as to the nature of the ionic liquid interactions with the beta sheet protein structure and the effects of these novel species on the protein conformational stability.

MARM 349 Withdrawn

Fluorescence studies of putative inhibitor binding interactions with liver glutaminase (LGA) for specific metabolic control of cancer proliferation

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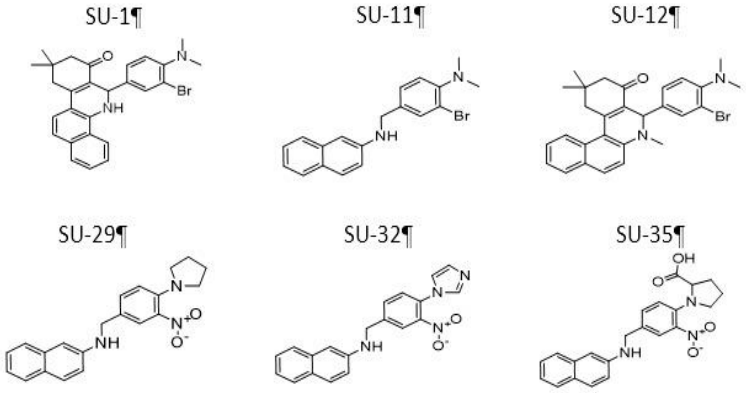
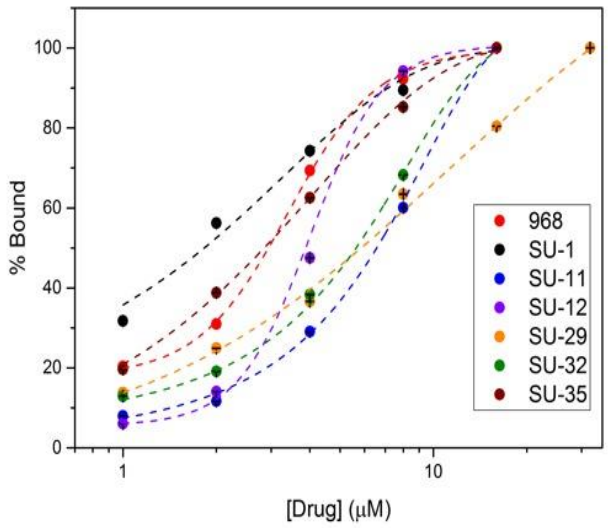
Cancer is the second leading cause of death in the US. In an effort to combat cancer, studies have shown promise for inhibiting the unique metabolic needs of rapidly growing cancer cells. This is accomplished through the targeting of an energy source that cancer cells become reliant on, the amino acid glutamine. This specifically starves the cancer cells but, not normal cells less reliant on glutamine. Drugs that have been previously shown to be effective inhibitors of glutamine metabolism within the kidney, were investigated for their efficacy towards a glutamine hydrolyzing enzyme specific to liver cells found upregulated in some cancers.





MARM 350

Investigation of drug delivery options for putative glutaminase inhibitors implicated as cancer therapeutics

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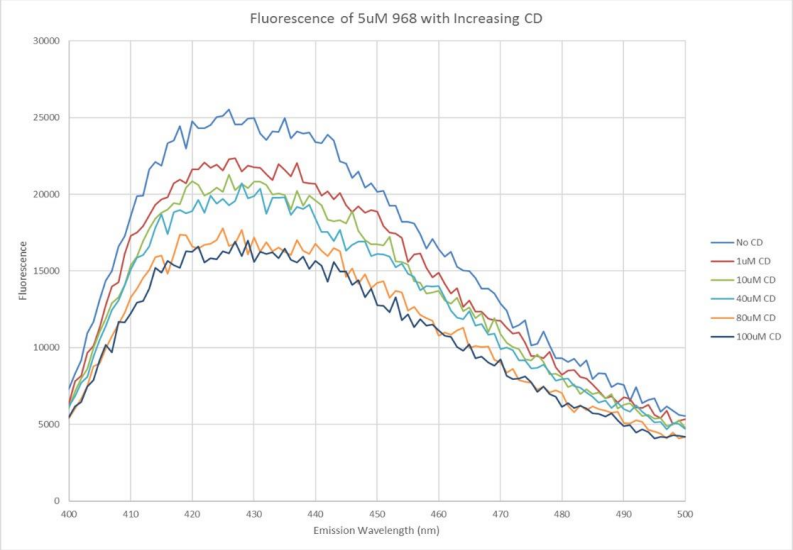
Drug delivery is a significant challenge for the development of a new drug. Many therapeutics are small molecules that inhibit enzymes and are very hydrophobic in nature. The solubility of a molecule can pose challenges for the delivery of the drug in vivo, an aqueous environment. One group of molecules that have been studied for their ability to encapsulate hydrophobic drugs to increase solubility in aqueous environments are cyclodextrins (CDs). CDs are naturally occurring polymers that link to form a cyclic molecule. This molecule orients its hydroxyl groups towards the exterior making it hydrophilic and water soluble, whereas the interior harbors a hydrophobic environment. CDs are useful drug delivery systems, as drugs readily bind within the interior cavity, leaving the exterior to solubilize the drug in what is termed an inclusion complex. The drug in use, 968, is an inhibitor of the enzyme glutaminase, which catalyzes the breakdown of glutamine to glutamate and ammonia. It has been shown that glutamine is a fuel source for highly proliferative cells, which is vtial in metabolism for cancer cells. The drug binds to the target glutaminase enzyme, altering its active site allosterically. By changing this active site, it renders the glutaminase useless to the cell.

The drug 968 was tested for complex formation when introduced to either hydroxypropyl-β-CD or dimethyl-β-CD. One benefit of using 968 is the highly conjugated structure, which makes this molecule fluoresce. Fluorescence is important for this experiment as it is indicative of the polarity of the immediate environment of the molecule. Through fluorescence readings, the interaction of 968 with the CDs was analyzed, monitoring the change in fluorescence respective to concentration of CD. The inclusion complex formation of 968 with the CD leads to a decreased value for fluorescence due to its environment (Figure 1). In compliance to fluorescence changes, ^{1}H-

NMR of the inclusion complex was collected to aid in determining the proton interactions of the inclusion complex formation.



MARM 351

Physical stability of fixed-dose combination tablets: A systematic investigation into the cause of SLS and amorphous API crystallization under conditions of high moisture activity

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Amorphous solid dispersions (ASDs) have become the primary means of increasing solubility and exposure of hydrophobic active pharmaceutical ingredients (API). Without having to overcome the high lattice energy barrier of crystalline API, the amorphous phase of a drug has a higher apparent solubility and improved dissolution rates. The amorphous state, being at a higher chemical potential, has a thermodynamic tendency to crystallize and reside in a lower energy state. In ASDs the API is dispersed in a polymer matrix which reduces the mobility of the API molecules and prevents the formation of crystallization nuclei. The success of an ASD is dependent on types of polymers, % drug loading and the addition of surfactants.

In this case study, a fixed-dose combination (FDC) tablet is examined; the FDC is an example of an oral dosage form which contains two different ASDs formulated into one monolithic tablet. Compound 1 single entity tablets, the ASD is physically stable with the API remaining amorphous during 12 months of storage under conditions of high moisture activity. By contrast, the FDC tablets demonstrate a different physical stability profile. When formulated with Compound 2 ASD, Compound 1 ASD shows evidence of API crystallization after 12 months of storage under conditions of high moisture activity.

In this work we evaluate the FDC formulation by systematically removing a single excipient that is present only in the combination tablets. This series of formulations were stressed under conditions of high water activity and evaluated by XRPD. A hypothesis into the origin of crystallization is presented and tested. The outcome of this study will improve the sensitivity of amorphous-to-crystalline conversion and inform formulation scientists of physical stability changes earlier in development. Product characterization studies of this type are used to determine final packaging configurations. Additionally, this study highlights undesired inter-ASD effects in enabled combination products.

MARM 352

Small-molecule approach to the inhibition of botulinum neurotoxin A

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The *Clostridium botulinum* bacterium is commonly found in soil and produces a neurotoxin which paralyzes muscles. Due to the availability and potency of this neurotoxin, its potential use as a bioweapon poses a threat to the human population. Botulinum neurotoxin A is also the main component of Botox. In recent years Botox has expanded from being used cosmetically to being used medicinally to treat many disorders including overactive bladder, migraines and spasticity. As Botox's potential continues to be investigated, one major concern is the lack of effective medical intervention (except supportive care), should someone be exposed to elevated concentrations of the toxin. For this reason, our team identified a small-molecule inhibitor and then synthesized structural analogs to explore the effect that the changes would have on the compound's inhibitory ability. From our biological assay data, we generated a structure-activity relationship (SAR) for this class of compounds. We are continuing to explore the chemical space of these compounds and will present the results of our latest syntheses and HPLC bioassays.

MARM 353

Metal initiated aggregation induced emission of asymmetric cycloheptatrienylidene substituted fluorophores

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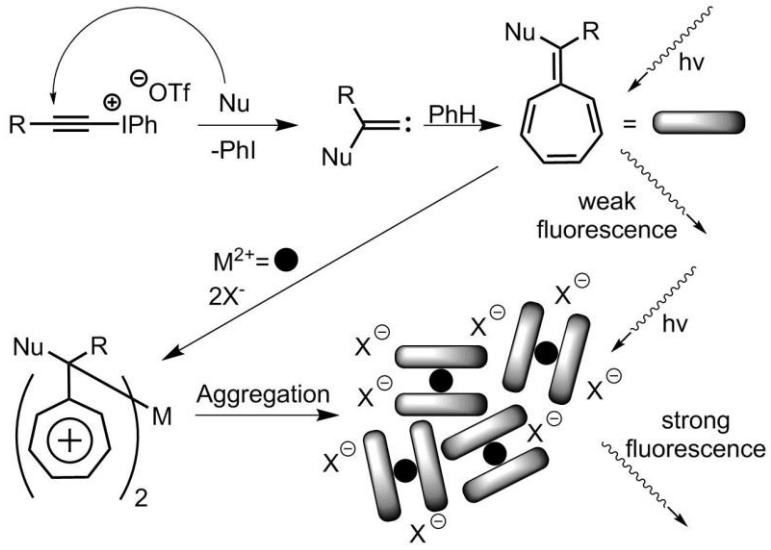
Typically, luminescence is inversely proportional to concentration due to aggregation induced quenching. Quenching is the reduction of luminesce due to molecular pi-stacking, any emission emitted by one molecule is absorbed by another. Molecules that have no emission in dilute solutions but fluoresce when concentrated are deemed Aggregate Induced Emission (AIE) materials. The work presented will show progress towards the development of new AIE materials through a novel methodology that utilizes hypervalent iodonium alkynyl triflates (HIAT).
The focus of the methodology reacts the HIAT with a nucleophile called Tos-MIC. Various crystallized reaction products were analyzed by X-ray diffraction after structure determination by NMR proved to be inconclusive. A long term goal of the project is to use non-toxic fluorophores to light-up upon aggregation and effectively "turn-on" when encountering specific stimuli inside biological systems.



MARM 354

Stereoselective synthesis of the allo bile acids

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Allo bile acids comprise the C(5) diastereomers of common bile acids that result in a trans AB ring fusion. Recent studies have found that select members of these rare secondary metabolites can potentiate varied immune responses. Our lab has developed a general synthetic approach to the allo bile acids beginning from inexpensive commercial sources of bile acids. The successful protocol harnesses a highly stereoselective alkene reduction as the key step in the synthesis of allolithocholic acid. Efforts to optimize our findings, prepare related analogs, and understand the stereochemical outcome of the reduction will be presented.

Allolithocholic Acid

MARM 355

Studies directed towards the synthesis of a sparteine surrogate

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(-)-Sparteine, a tetracyclic lupin alkaloid, has long been used as a chiral ligand in enantioselective deprotonations and additions. (-)-Sparteine, which is obtained from natural resources, is expensive and its antipode is even more difficult to acquire. This project aims to develop a synthesis of a surrogate for (-)-sparteine and its antipode from readily accessible starting materials. We propose to exploit the bicyclo[3.3.1]nonane intermediate in our synthetic route to create a new library of ligands, including chiral phosphines, phosphoric acids, and cyclams.

MARM 356

Ter-pyridine derived catalyst system for the cyanation of aldehydes and imines using Et_2AlCN

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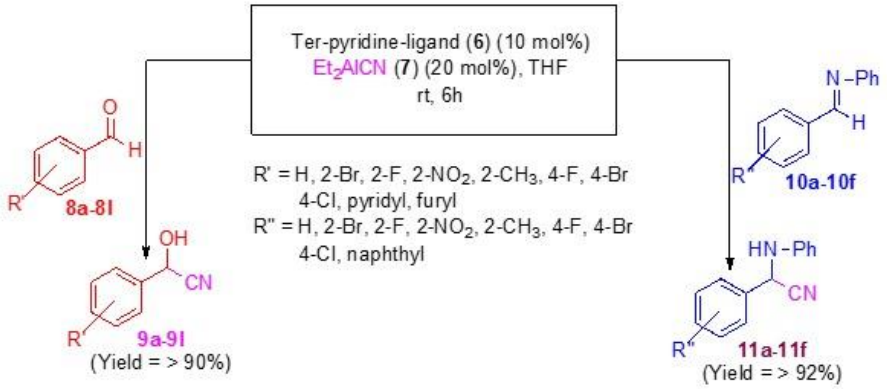
A variety of aromatic and heterocyclic aldehydes were subjected to cyanide addition reaction using diethyl aluminium cyanide solution (Et_2AlCN). The reaction was catalyzed using a ter-pyridine derived catalyst system. The catalyst system used was simpler than a variety of other systems reported in literature. Moreover, a less toxic and easier to handle cyanide reagent, Et_2AlCN, was used to carry out the reaction successfully. Seventeen examples were studied to give excellent yields (>90%). A series of different solvents and other reagents for cyanide addition were also screened for comparison.

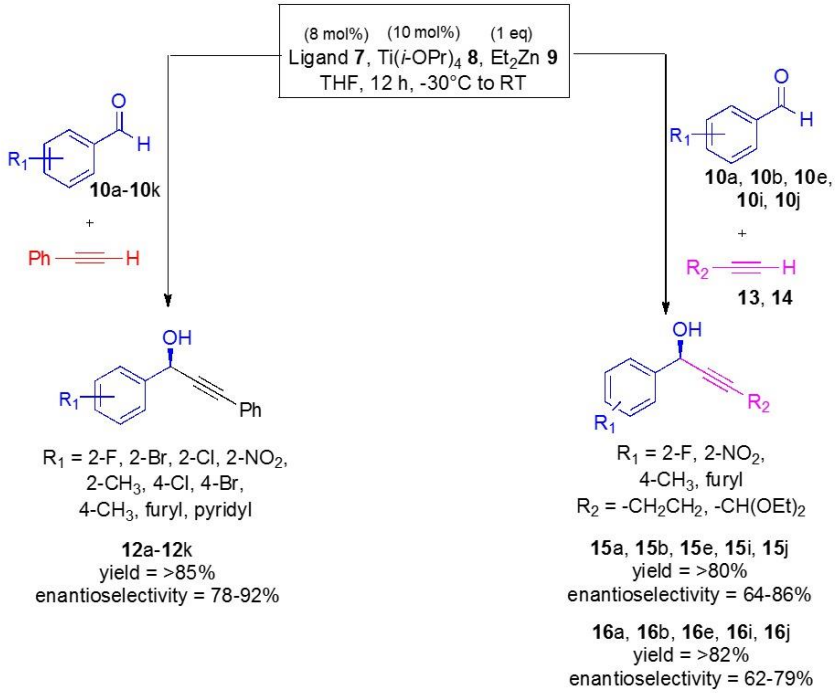


MARM 357

Titanium-proline derived system for the asymmetric synthesis of propargyl alcohols

***Chelsea Sweet**, sweetc1@student.wpunj.edu, Parminder Kaur. Chemistry, William Paterson University, Wayne, New Jersey, United States*

A novel titanium/proline-derived catalyst system is reported for the enantioselective synthesis of *propargyl alcohols*. The reaction proceeded smoothly under mild conditions with efficient reaction times. Initially, lithium acetylide was employed to carry out the nucleophilic addition reaction, however poor reaction profile was achieved with poor enantioselectivities. When diethylzinc was used instead, high product yields (>85%) and moderate to high enanitoselectivities were achieved (68-92%). Three different alkynes were used to carry out the reaction with a series of different aromatic and heterocyclic aldehydes. Better reaction profiles were achieved with aromatic alkynes than with aliphatic ones.



MARM 358

Tropone iron tricarbonyl complex as a platform for the synthesis of bridged nitrogen heterocycles

***Daniel Griffith**, dan.griffith@gmail.com, Zhiyuan Huang, Daniel Sweitzer, Rachel Tritt, Shelby Valent. Chemistry, Lafayette College, Easton, Pennsylvania, United States*

Efforts to develop a strategy for the synthesis of bridged nitrogen heterocycles containing a seven-membered ring are described. This strategy utilizes the known η^4-tropone iron tricarbonyl complex as an electrophile in an aza-Michael reaction. Our studies in developing this aza-Michael reaction are reported. Further efforts have been made at decomplexing the products of the reactions from the metal center revealing functional handles that are are instrumental in construction of the diverse bicyclic heterocycles.

MARM 359

Exploring the utility of peptidomimetics as blood-brain barrier shuttles

***Sherri C. Young**, sherriyoung@muhlenberg.edu, Andrew Rice, Yeonji Kim, Alyssa Wiest, William Bowman. Chemistry, Muhlenberg College, Allentown, Pennsylvania, United States*

The prevalence of Alzheimer's disease (AD) is predicted to increase dramatically as the population ages. An AD cure has not yet been discovered, in part, due to an incomplete understanding of the disease pathology and the challenges associated with CNS drug delivery. Peptidomimetics such as N-substituted glycine oligomers (i.e., peptoids) have properties amenable to blood-brain barrier (BBB) penetration and could serve as delivery agents, or shuttles, for AD drugs, including anti-inflammatory drugs. The solid-phase synthesis and BBB penetrabilities,

measured via a parallel artificial membrane permeability assay, of a series of peptoids and peptoid-drug conjugates will be presented. In addition, the relationship between flexibility, assessed experimentally and computationally, and BBB permeability will be described; this information could lead to more rational CNS drug design.

MARM 360

Studying the transmission of substituent effects on comparable ^{1}H and ^{13}C sites in monosubstituted benzenes and pyridines

***Madeline Malfara**, mfm5553@psu.edu, John Tierney. Penn State University, Media, Pennsylvania, United States*

Studies were carried out in the 1960's by Maciel on the chemical shift variations at ^{1}H and ^{13}C sites within monosubsituted benzenes (Figure 1A). Similar studies were conducted on monosubstituted pyridines (Figure 1B) by Retcofsky. Subsequent to these initial studies, databases of readily available NMR spectra are now available. This presentation revisits these studies utilizing an increased number of substituents on both the benzene and pyridine ring systems. In addition, the relationship between ^{1}H and ^{13}C substituent chemical shifts with Hammett σ constants, as well as Swain Lupton Dual substituent correlations, are discussed.

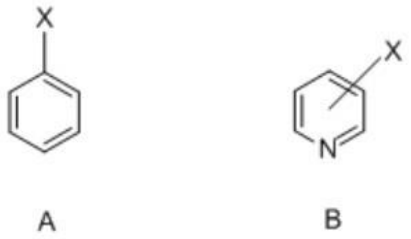


Figure 1: X = NO_2, F, Cl, Br, I, H, Me, MeO, CH_3CO, CO_2H, CN, OH and these are in both the *meta* and *para* positions in 1B

MARM 361

Synthesis of N-methylarylamines by reduction of isocyanates

***George D. Mendenhall**, norsource2004@yahoo.com. Eastern Sources, Inc., Pomona, New York, United States*

Reduction of aryl isocyanates is a convenient strategy for the synthesis of N-methylarylamines, which otherwise are accessible by a number of indirect methods. We have found that reaction of isocyanates with lithium aluminum hydride in ether-toluene at -20C accomplishes this goal in good yields. At room temperature or in toluene alone the reaction gives multiple products, prominently demethylation to the corresponding aniline. Since isocyanates may be prepared from carboxylic acids via the aroyl azide, this route is a way to introduce an isotopically labelled carbon not involving alkylating agents.

MARM 362

Photocycloaddition to aromatic ring: A potential synthetic methodology for ring systems

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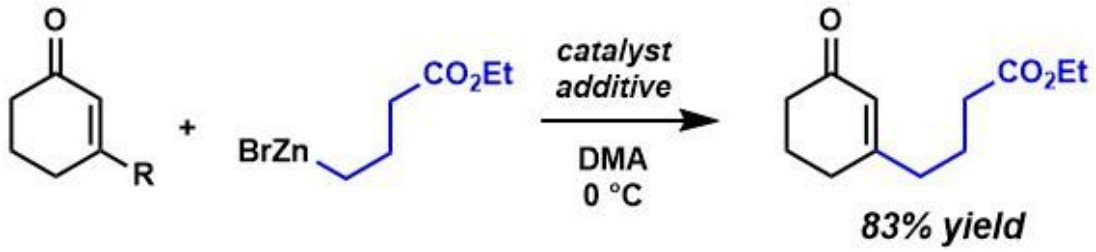
The genesis of a carbon ring larger than 6-membered ring in a conventional way is kinetically unfavorable. Common difficulties with the synthesis include angle strain, probability (entropy), and poor interactions involving the molecular orbitals. Our study of the ring formation using a different synthetic pathway via photochemistry, allows for favorable conditions through [2+2] cycloaddition. Although ring synthesis is successful, we analyze how the many products are formed with regioselectivity, and how different substituents with various Hammett constants that dictate the formation. Using Gaussian, a quantum computational tool, theoretical data is presented to explain the reactions correlations. Based on the computational data, along with matching with experimental results, we were able to conclude that the regioselctivity is controlled by both the steric and electron effects of substituents. This information can facilitate those interested in forming large rings with specific configuration, which is often seen in pharmaceutical industries as top cancer treatment contain such rings.

MARM 363

Metal-catalyzed cross-coupling reactions of functionalized organozinc reagents for the synthesis of β,β-disubstituted enones

***Heather R. Rensch**, hrensch30@gmail.com, Michael R. Krout. Bucknell University, Lewisburg, Pennsylvania, United States*

β,β-disubstituted α,β-unsaturated ketones (enones) are an important class of organic compounds commonly used in various types of reactions such as cycloadditions, conjugate additions, and direct nucleophilic additions for the synthesis of more complex molecules like natural products and pharmaceuticals. A versatile method to prepare derivatives is therefore desirable. Current methods employ highly reactive Grignard reagents which introduce chemoselectivity limitations. Our method involves cross-coupling reactions with vinylogous ester and vinylogous halide substrates utilizing mild functionalized organozinc reagents in which electrophilic functional groups can be incorporated to increase the structural diversity. Reaction screening was performed by varying the vinylogous substrate, catalyst identity and quantity, additives (e.g., Lewis acids), and organozinc reagent. Reaction optimization has led to high yields of β,β-disubstituted enone products utilizing a simple copper catalyst with easily synthesized functionalized organozinc reagents. The observation of a second, undesired organozinc addition was leveraged to use two non-equivalent organozinc reagents in the one-pot synthesis of ketones with β-quaternary stereocenters.



MARM 364

Synthesis and characterization of 3-cyclohexyl-2-aryl-1,3-thiazolidin-4-one triphenyltinchloride complexes

***Kevin C. Cannon**[1], kcc10@psu.edu, Miguel Costa[1], Albina Ongari[1], John Tierney[2]. (1) Penn State Abington, Abington, Pennsylvania, United States (2) Penn State University, Media, Pennsylvania, United States*

A series of substituted 3-cyclohexyl-2-aryl-1,3-thiazolidin-4-one triphenyltinchloride complexes were synthesized. The x-ray structure of the 3-cyclohexyl-2-phenyl-1,3-thiazolidin-4-one substituted complex shows a trigonal bipyramid structure with the thiazolidinone and chloride occuppying axial positions; the thiazolidinone ring is coordinated to the ring via the carbonyl oxygen at C4. Substituent chemical shift correlations utilizing ^{13}C NMR for both the complexed and uncomplexed thiazolidinones were less robust than observed for uncomplexed diphenylthiazolidin-4-ones. ^{13}C NMR data for a series of sulfoxide- and sulfone-thiazolidinone complexes is also presented.

MARM 365

There is an absolute zero on the NMR chemical shift scale

***Donald D. Clarke**, clarke@fordham.edu. Fordham Univ, Bronx, New York, United States*

Chemical shifts are caused by differences in the bonding patterns of electrons in a molecule on the nucleus in question. This was discovered for organic compounds for the protons of ethanol in 1951. While carbon-bound hydrogens have characteristic shifts, the OH signal is quite variable, affected by intermolecular and intramolecular bonding. Neighboring groups e.g., C=O and S=O. raise them to higher values. Tetramethylsilane [TMS] is now the standard reference substance for ^{1}H and ^{13}C NMR spectra. The chemical shift of a naked proton (no electrons shielding it) is by definition zero on the chemical shift scale. H^{+} doesn't exist in solution. It is produced in cyclotrons under high vacuum. Direct measurements of this would require molecular beam experiments; scarcely appropriate for an undergraduate lab. However, our undergraduate research students using quantum chemical programs [Gaussian or Spartan] can calculate the chemical shift of TMS on the absolute scale [31.8 ppm], the maximum chemical shift for a proton. Modern NMR instruments are calibrated with this value so we don't need to teach it in the way we do for gas laws where ^{o}C must be converted to ^{o}K. We should stress to students that they should not be surprised when calculated values for OH chemical shifts using quantum chemical programs do not match closely their observed values. That is due often to the effects of impurities in the sample or solvent.

MARM 366

Surface analysis of fibronectin-coated QCM-D sensors by atomic force microscopy

***Tucker J. Collins**, tc636@drexel.edu, Jennifer Y. Chen, Jun Xi. Drexel University, Philadelphia, Pennsylvania, United States*

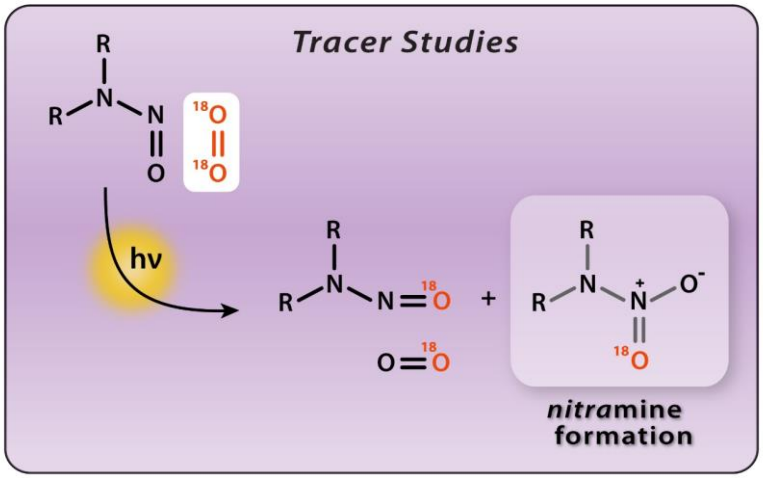
Fibronectin is an important regulator of cellular adhesion as the point of contact between the membrane anchored integrins and other extracellular matrix proteins (collagen, fibrin, etc.). The regulation of integrin-fibronectin interactions is critical to the processes of cellular growth, differentiation, and migration, as well as tissue development. In this study, the effects of concentration and deposition time on the morphology of fibronectin-coatings were characterized using Atomic Force Microscopy. Time-dependent factors have thus far been identified as impacting surface roughness nonlinearly. The results of this study will advance our understanding of the impact of the fibronectin morphology on cell adhesion, which has broader applications in the research of embryonic development, and in cancer metastasis, such as that mediated by epithelial growth factor. It may also further our understanding of the mechanism by which fibronectin forms the coat layers analyzed in this study, and thereby expanding our understanding of the structural arrangement of the extracellular matrix.

MARM 367

Experimental and DFT computational evidence for new nitrosamine peroxide intermediates generated by photooxidation

*Ashwini Ghogare[2,3], Ciro Debaz[2], Marilene Silva[2,4], Inna Abramova[2], Prabhu P. Mohapatra[2], Kitae Kwon[5], Edyta Greer[1], Fernanda Manso Prado[4], Hellen Paula Valerio[4], Paolo Di Mascio[4], **Alexander Greer**[2,3], agreer@brooklyn.Cuny.edu. (1) Baruch College, New York, New York, United States (2) Brooklyn College, Brooklyn, New York, United States (3) Ph.D. Program in Chemistry, Graduate Center, New York, New York, United States (4) Biochemistry, University of São Paulo, SP, São Paulo, Brazil (5) Natural Sciences, Baruch College, New York, New York, United States*

A nitrosamine photooxidation reaction is shown to generate a peroxy intermediate by physical-organic methods. In this study, the irradiation of phenyl and methyl-substituted nitrosamines in the presence of isotopically labeled 18-oxygen revealed two oxygenation reactions. First, a dioxygen molecule covalently attached to the N=O bond of nitrosamine, presumably as a ring-closed 1,2,3,4-trioxazetidine or dimer, after which dioxygen was released back. Second, an O atom was transferred from the peroxy intermediate to a trimethylphosphite or triphenylphosphine trap, or to the nitrosamine itself, forming two moles of nitramine. The unstable peroxy intermediate showed chemiluminescence upon thermal decomposition, which is reminiscent of the behavior of 1,2-dioxetanes, indicating the formation of a cyclic nitrogen peroxide species. A DFT study is also consistent with the formation of a cyclic nitrogen peroxide species on the reaction surface.

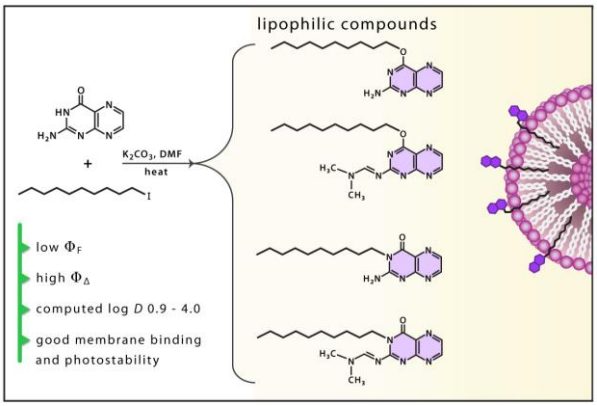


MARM 368

Long chain-pterin conjugates with interesting lipophilic and sensitizer properties

*Mariana Vignoni[1,3], Niluksha Walalawela[1,2], Sergio M. Bonesi[4], **Alexander Greer**[1,2], agreer@brooklyn.Cuny.edu, Andrés H. Thomas[3]. (1) Brooklyn College, Brooklyn, New York, United States (2) Ph.D. Program in Chemistry, Graduate Center, New York, New York, United States (3) INIFTA, Departamento de Química, Facultad de Ciencias Exactas, Universidad Nacional de La Plata (UNLP), La Plata, Argentina, Argentina (4) CONICET, Química Orgánica, Universidad de Buenos Aires, Buenos Aires, Argentina, Argentina*

A new series of decyl chain [**–**$(CH_2)_9CH_3$] pterin conjugates have been investigated by photochemical and photophysical methods, and with theoretical solubility calculations. To prepare the pterin products, a nucleophilic substitution (S_N2) reaction was developed for the regioselective coupling of the alkyl chain to the *O* site over the N^3 site. However, the *O*-alkylated pterin converts to N^3-alkylated pterin under basic conditions, pointing to a kinetic product in the former and a thermodynamic product in the latter. Two additional adducts were also obtained from an *N*-amine condensation of DMF solvent molecule as by products. Comparison to natural pterins shows further utility of the new pterins, they had reduced fluorescence quantum yields due to deactivation of the singlet-excited state, and increased singlet oxygen quantum yields. It is shown that the DMF condensed pterins were more photostable compared to the N^3- and *O*-alkylated pterins bearing amine groups. The new pterins efficiently intercalate in large unilamellar vesicles, which is a good indicator of their potential use in biomembranes. Our study serves as a starting point where the synthesis can be expanded to produce novel lipophilic, photooxidatively active pterins.



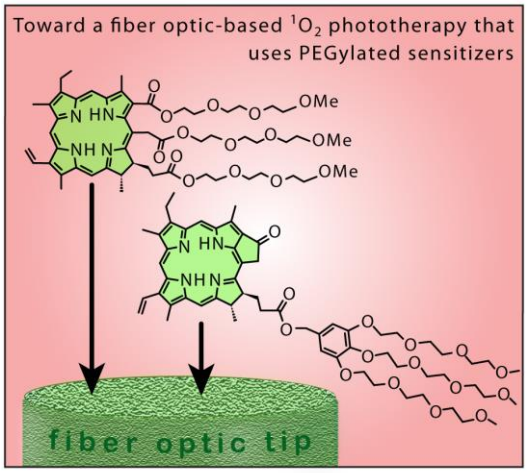
MARM 369

Synthesis, photophysics and evaluation of mono-, di-, tri- and hexa-PEG sensitizers for pointsource photodynamic therapy

*Tobias Bornhütter[3], Ashwini Ghogare[1,2], Annegret Preuß[3], **Alexander Greer**[1,2], agreer@brooklyn.Cuny.edu, Beate Röder[3]. (1) Brooklyn College, Brooklyn, New York, United States (2) Ph.D. Program in Chemistry, Graduate Center, New York, New York, United States (3) Physics, Humboldt-Universität zu Berlin, Berlin, Germany, Germany*

Pointsource photodynamic therapy (PSPDT) is a newly developed fiber optic method aimed at the delivery of photosensitizer, light and oxygen to a diseased site. Because of a need for developing photosensitizers with desirable properties for PSPDT, we have carried out a synthetic, photophysical and phototoxicity study on a series of PEGylated sensitizers. Chlorin and pheophorbide sensitizers were readily amenable to our synthetic PEGylation strategy to reach triPEG and hexaPEG galloyl pheophorbides and mono-, di-, triPEG chlorins. On screening these PEG sensitizers, we found that increasing the number of PEG groups, except for hexaPEGylation, increases phototoxicity. We find that three PEG groups but not less or more was optimal. Of the series tested, a triPEG gallyol pheophorbide and a triPEG chlorin were the most efficient at generating singlet oxygen, and produced the highest phototoxicity and lowest dark toxicity to Jurkat cells. A detailed kinetic analysis of the PEGylated sensitizers in solution and cell culture and media is also presented. The data provide us with steps in the

development of PSPDT to add to the PDT tools we have in general.



MARM 370

Synthesis of α, α, -dibromoketone catalyzed by organosilanes from alkynes

***Carlos Chong**, chongc@student.wpunj.edu. Chemistry, William Paterson University, Paterson, New Jersey, United States*

Bis (3- (trimethoxysilyl)propyl) amine is an organosilane and is typically used as an silsesquioxane precursor to synthesize organosilica materials. Organosilanes have a history of employment in a variety of chemical entities, most commonly used as protecting groups in organic synthesis. The unique feature of silanes are the ability to act as a moisture scavenger, alkoxy groups on silanes will hydrolyze and cross link in water. In our laboratory, we are interested in alkyne difunctionalization using environmentally friendly reagents. Our previous work included Au^{III} catalyzed synthesis of a-halomethyl ketones and $FeCl_3$ catalyzed synthesis of α,α,-dibromoketone from alkynes. This organosilane was found to be a catalyst for halo-functionalization of terminal and internal alkynes into α, α, -dibromoketone in high yields. This synthesis features desirable functional group compatibility and high regioselectivity in a one pot reaction. Further investigation of the substrate scope of the organosilane, Bis (3-(trimethoxysilyl)propyl) amine is in process in our laboratory.

MARM 371

Design and synthesis of novel lithocholic acid carboxamides with antiproliferative and pro-apoptotic effects on human cancer cells

***Srinivasa Ramisetti**, srr197@psu.edu, Deepkamal Karelia, Shantu Amin, Arun K. Sharma. Pharmacology, Hershey College of Medicine, Hershey, Pennsylvania, United States*

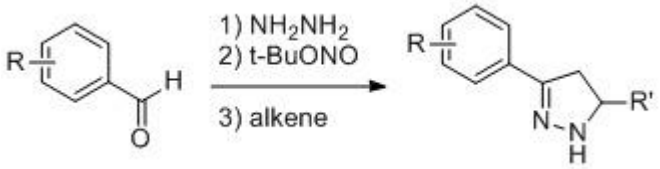
Bile acids, the products of cholesterol catabolism, are synthesized in liver and subsequently excreted into bile canaliculus and digestive tract as *N*-acyl conjugates of glycine or taurine. Among all bile acids, Lithocholic acid (LCA) and Ursodeoxycholic acid (UDCA) conjugates have been reported to inhibit the growth of various human cancer cells both in vitro and in vivo. Most importantly LCA has been shown to inhibit growth of different cancer cell lines including prostate and neuroblastoma cells, while sparing normal cells. In addition, a report has shown LCA-amphiphiles to be effective anti-tumor agents in a colon cancer xenograft model. In contrast, there are reports indicating that LCA may promote dimethyl hydrazine (DMH) induced colon carcinogenesis and may also act as a carcinogen itself. This indicates that despite having anti-cancer properties, LCA may pose a risk of developing colon cancer. We hypothesized that LCA structure can be optimized to eliminate the carcinogenesis promoting properties, while enhancing its potency to create effective therapeutics against colon, prostate, and other cancers. Therefore, we designed and synthesized a series of novel cyclic and acyclic LCA-carboxamides by blocking acid functionality of LCA. The cytotoxicity of novel analogs was evaluated against colon (HT29) and prostate (DU145) cancer cells. Three analogs ASR-320, ASR-322 and ASR-339 inhibited the viability of these cells with an EC_{50} value of 5-10 mM, while LCA had no effect on cell viability at highest dose used (50 mM). The results suggest that new analogs are 10 times more potent than parent compound, LCA. One of the compounds, induced apoptosis in both prostate (DU145) and colon (HT29) cancer cells, as indicated by Caspase 3 activation and PARP degradation. Currently, we are further optimizing structure based on initial leads. Detailed results of these investigations will be presented.

MARM 372 Withdrawn

Synthesis of 3-aryl-4,5-dihydro-1H-pyrazoles

***Thomas Arena**, ta814498@wcupa.edu, James R. Pruitt. Chemistry, West Chester University, West Chester, Pennsylvania, United States*

Our research has focused on the preparation of 5-alkyl-3-aryl-4,5-dihydro-1H-pyrazoles. We have tried a variety of approaches with limited success. Most of the literature approaches prepare N-substituted pyrazoles which were undesirable, given our biological target, macrophage migration inhibitory factor (MIF) a pro-inflammatory protein. We have optimized a method starting with substituted benzaldehydes and in a 1-pot, 2-step reaction prepared the desired pyrazoles in moderate yield.

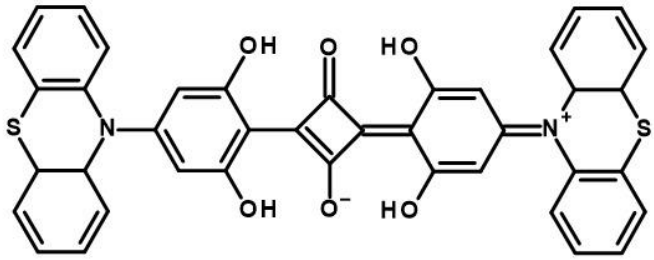


MARM 373 Withdrawn

Synthesis of a novel, highly conjugated squaraine dye for use in organic photovoltaic devices

***Daniel M. Saviola**[1], dms3185@rit.edu, Chris J. Collison[2], Jeremy A. Cody[1]. (1) School of Chemistry and Materials Science, Rochester Inst of Technology, Rochester, New York, United States (2) Rochester Institute of Tech, Rochester, New York, United States*

Squaraines (SQ) have shown great promise as materials for organic photovoltaics (OPV) due to their high absorbance in the near infra-red, the ability to manipulate their aggregation in thin films, and their relatively easy synthesis. It is hypothesized that by further red shifting the absorbance as well as creating more planar structures that the efficiencies of SQ OPV devices can be improved further.
In this work, we synthesize a novel SQ using phenothiazine as the donor group. Using phenothiazine (i) significantly increases the effective conjugation length of the molecule which further red shifts its absorbance, (ii) creates a completely planar molecule to allow for more efficient aggregation in thin films and improves charge transfer efficiency, and (iii) incorporates a third period atom, sulfur, which increases the donating quality of the group, and has been shown to improve excited state lifetimes in many cases. This molecule has additional advantages over many of the alternating donor-acceptor type oligomers that are so common in the literature nowadays as the synthesis is cheaper, and only contains 3 steps each with fairly good yields and with minimal purification needed. In theory, this phenothiazine SQ should be among the highest performing SQ available.



MARM 374 Withdrawn

Development of iron-binding spiroligomer catalysts for potential C–H activation

***Melody A. Pham**[1], melody.pham@temple.edu, Taylor M. Keller[1], Michael Zdilla[1], Ted J. Amundsen[2], Christian E. Schafmeister[1]. (1) Chemistry, Temple University, Philadelphia, Pennsylvania, United States (2) Mainstream Engineering Corporation, Rockledge, Florida, United States*

The regio– and stereoselective activation of aliphatic C–H bonds is a significant but challenging area in synthetic organic chemistry. Most of the current direct C–H functionalization strategies require precious transition metals such as rhodium and iridium. Our lab is developing macrocycles to bind iron within a chiral environment to investigate C–H activation catalysis. Our macrocycles are comprised of two spiroligomers, which are functionalized with 2,2-bipyridine and linked by click chemistry to create a chiral iron-binding pocket in the center of the

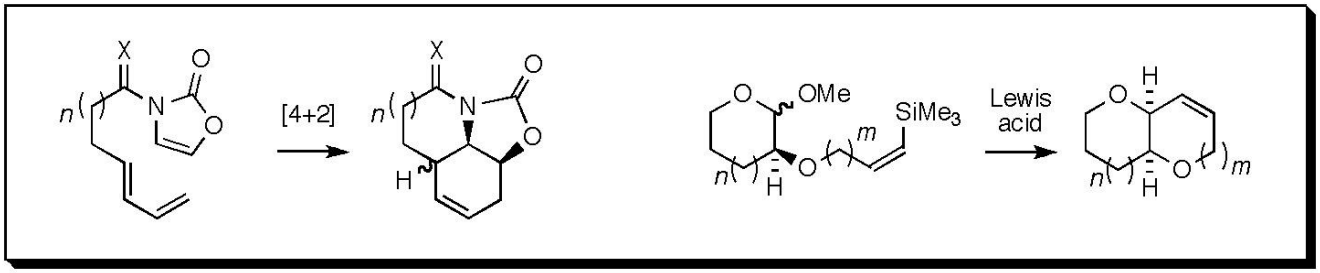
macrocycle. We will present the syntheses and characterization of these potential enantioselective C–H activation catalysts.

MARM 375

Heterocyclic motifs for natural products synthesis

Stephen P. Fearnley[1,2]*, fearnley@york.Cuny.edu, Charnsak Thongsornkleeb*[1]*, Maciej E. Domaradzki*[2]*, Robert C. Lapo*[2]*, Pedro M. Lory*[1]*. (1) Dept of Chemistry, York College, the City University of New York, Jamaica, New York, United States (2) Ph.D. Program in Chemistry, The Graduate Center of the City University of New York, New York, New York, United States*

Our group's research focuses on the development of new heterocyclic methodology for the synthesis of bioactive natural products. Specific efforts include:
- Investigation and use of oxazolone as a useful heterocyclic scaffold for alkaloid synthesis – chiefly, intramolecular Diels-Alder reactions with oxazolone as the dienophilic species. Application in the synthesis of several alkaloid targets is currently underway.
- Novel organosilane chemistry for approaches to bioactive ether targets – a rapid synthesis of cis-fused bicyclic ether arrays in which oxocarbeniums undergo nucleophilic attack by vinylsilanes via a novel intramolecular annulation process. A wide variety of ether natural product motifs are thus accessible.



MARM 376

Soxhlet extraction and analysis of capsaicin from various pepper flesh and seeds

Jennie Cawley[1]*, jc6516@desales.edu, Francis C. Mayville*[2]*. (1) Chemistry, DeSales University, Bethlehem, Pennsylvania, United States (2) Natural Science, Desales University, Center Valley, Pennsylvania, United States*

The objective of this study is to extract, isolate, and quantify the active ingredient, capsaicin, from various types of pepper flesh and seeds. Soxhlet techniques were used to extract the capsaicin from the flesh and seeds of each type of pepper using 95% ethanol. Ultraviolet/ Visible (UV/Vis) spectroscopy and High Pressure Liquid Chromatography (HPLC) were used to evaluate and quantify the total amount of capsaicin extracted from the flesh and seeds of each type of pepper. Most recently, capsaicin was identified to have antioxidant properties. In this study, the amount of capsaicin isolated from each pepper as a whole has some correlation to the amount of heat the pepper contains based on the Scoville scale for the hotness of peppers. Therefore, the hotter the pepper, the more capsaicin it contains and the more antioxidant potential.

MARM 377

Evolution of a manufacturing route to omarigliptin (MK-3102), a long-acting DPP-4 inhibitor for the treatment of type 2 diabetes

Amude Kassim*, amude_kassim@merck.com. Process Research, Merck & Co, Inc., Rahway, New Jersey, United States*

Development of a convergent synthesis of omarigliptin (MK-3102) suitable for commercial manufacturing is described. The target molecule is assembled through a diastereoselective reductive amination of a highly functionalized Boc protected pyranone with a mesylated pyrazole followed by deprotection of the Boc group. The synthesis of the pyranone depends on three Ru-catalyzed reactions: (1) a DKR reduction of racemic α-amino ketone to set the two contiguous stereogenic centers, (2) a cycloisomerization of the bis-homopropargylic alcohol to the dihydropuran, and finally, (3) a Ru-catalyzed oxidation to the desired pyranone. The regioselective synthesis of the N-Boc-1-mesyl pyrazole fragment was achieved *via* base-promoted mesyl group isomerization to provide 30:1 selectivity. A highlight of the endgame process development is telescoping a Boc deprotection and reductive amination followed by direct crystallization of the penultimate from the reaction mixture. This avoids handling of

any unstable, mutagenic 1-mesyl pyrazole BSA salt used in the earlier multikilligram deliveries and improves the overall diastereoselectivity and efficiency of the process.

MARM 378

Determination of important catalytic species in heterogeneous layered manganese dioxide materials for water oxidation application

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Cheap and efficient water-oxidation catalysts remain one of the major hurdles in the implementation of a hydrogen economy. A promising solution to this hurdle is the use of inexpensive oxide minerals, particularly layered 2D manganese oxides and metal dichalcogenides due to their low cost, large abundance, and ability to easily tune it physical and chemical properties. Through combined experimental and theoretical approaches, we have explored the roles of oxidation states, lattice dopants, and interlayer ions on the material's properties and water oxidation capabilities. Our finding suggest increasing manganese(III) and cobalt(IV) content in the lattice of the layered manganese oxide system as well as introduction of harder, redox active species such as nickel in the interlayer greatly enhance water oxidation activity through charge delocalization and increase of high energy, frustrated water activity that rivals that of ruthenium and iridium oxide OER catalysts can be achieved. These interlayer species act as the active site of these layered manganese oxides providing ordering of the water increased ordering of the water molecules and electron transfer rates through the system.

MARM 379

Electrocatalytic plasticity: Switching the outcome of CO_2 reduction at post-transition metal cathodes in the presence of room-temperature ionic liquids

Abderrahman Atifi*, aatifi@udel.edu, Joel Rosenthal. Dept of Chemistry Biochemistry, University of Delaware, Newark, Delaware, United States*

Ionic liquids (ILs) have been established as effective promoters for the electrocatalytic conversion of CO_2 to various commodity chemicals. Using a catholyte based on the IL 1,3-dialkylimidazolium ($[IM]^+$), we have shown that bismuth and tin catalysts can efficiently reduce CO_2 to CO with very high selectivities (FE_{CO} > 80%) and rapid kinetics. To further understand how IL structure influences the ability of post-transition metal electrodes to activate carbon dioxide, the activation of CO_2 by bismuth and tin electrocatalysts in the presence of non $[IM]^+$ ILs has also been evaluated. Specific attention was devoted to studying ILs with structural and chemical similarities to $[IM]^+$. These studies have revealed that by modifying the IL structure, a significantly different catalysis can be observed with CO_2. Electrolysis of CO_2 in the presence of these new generation ILs using both bismuth and tin cathodes promotes the reduction of CO_2 to yield predominantly $HCOO^-$, with selectivities as high as FE_{FA} ~ 80% at j_{tot} ~ 20–70 mA/cm^2. Notably, the selectivity for production of CO is significantly suppressed in the presence of these new ILs (FE_{CO} ~ 20%). We will discuss the catalytic plasticity that is displayed by these [electrode]/[IL] systems, and reveal factors that dictate how the selectivity displayed by post-transition metal cathodes for CO_2 reduction can be manipulated via the choice of IL.

MARM 380

Small-molecule activation with metal-organic polyhedra

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Reactive oxygen species, including both terminal and bridging oxo, superoxo, and peroxo moieties, are among the most widely studied units in transition metal chemistry and are featured prominently in biology and the solid state. The work presented in this seminar will highlight the use of both bimetallic catalysts and metal-organic polyhedra containing coordinatively-unsaturated transition metal cations to stabilize these reactive species. In the case of the former, novel binucleating ligands featuring acac, amide, and carboxylate groups will be presented. The synthesis, metallation, and preliminary reactivity of these products toward oxygen containing species will be discussed. The metal-organic polyhedra presented here, in addition to their utility in stabilizing reactive species, serve as soluble metal-organic framework analogs. Spectroscopic and crystallographic characterization of the metal-adsorbate interactions responsible for the high adsorption selectivities and reactivity displayed by these materials will be highlighted.

MARM 381

Well-defined chromium catalysts for selective ethylene trimerization

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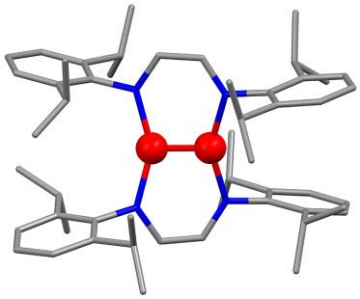
The selective catalytic oligomerization of ethylene is an attractive process for the production of commercially valuable α-olefins, such as 1-hexene and 1-octene. Primarily catalyzed by chromium compounds, the selectivity of the reaction is thought to reflect the differential reactivities of metallacycles of different ring sizes. Detailed mechanistic understanding is to be gained from an investigation of well-defined chromacycles and homogeneous catalysts operating in the absence of cocatalysts.

The dinitrogen complex [(^{i}Pr$_2$-Ph)$_2$nacnacCr]$_2$(μ-η^2:η^2-N$_2$) catalyzes the trimerization of ethylene to 1-hexene at very mild conditions (i. e., RT and 1 bar), yielding the unusual dinuclear ethylene complex [(^{i}Pr$_2$-Ph)$_2$nacnacCr]$_2$(μ-η^2:η^2-C$_2$H$_4$) as the final organometallic product. The synthesis and structural characterization of both mononuclear and binuclear metallacycles such as (Me$_2$-Ph)$_2$nacnacCr(py)(C$_4$H$_8$) and [(^{i}Pr$_2$-Ph)$_2$nacnacCr]$_2$(μ-C$_4$H$_8$) has allowed us to address the question whether the catalysis involves mononuclear or binuclear species.

Another catalyst for the same reaction is the quintuply bonded dimer [(^{i}Pr$_2$-Ph)$_2$DadCr]$_2$. There is spectroscopic evidence for the formation of an ethylene complex and we have isolated a binuclear metallacycle resulting from addition of two ethylene molecules. Nevertheless, further mechanistic investigation implicates mononuclear intermediates as the catalytically active species.

The synthesis and structure of various chromacycles will be described, and their kinetic competence for catalysis will be discussed. Based on our observations, we suggest that the catalysis involves an interplay between mononuclear chromium complexes in the formal oxidation states +I and +III.



The quintuply bonded chromium complex [(^{i}Pr$_2$-Ph)$_2$DadCr]$_2$

MARM 382

Iron polypyridyl complexes for hydrogen generation in aqueous solutions

***William McNamara**, wrmcnamara@wm.edu. Chemistry, College of William and mary, Williamsburg, Virginia, United States*

We recently reported a series of Fe(III) complexes that are stable and active electrocatalysts for reducing protons into hydrogen gas. This presentation will focus on the incorporation of these electrocatalysts into a photocatalytic system for hydrogen production. Hydrogen evolution is observed when these catalysts are paired with fluorescein (chromophore) and triethylamine (sacrificial electron source) in a 1:1 ethanol:water mixture. The photocatalytic system is highly active and stable, achieving TONs > 2100 (with respect to catalyst) after 24 hours. The catalysts are robust and hydrogen evolution is also observed when using local lake water. Catalysis proceeds through a reductive quenching pathway with a quantum yield of over 3%.

MARM 383

Electrocatalytic ammonia oxidation with molecular copper catalysts

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Due to its high energy density and massive worldwide production, ammonia is an attractive chemical fuel. Since conversion of NH$_3$ to N$_2$ and H$_2$ is nearly thermoneutral, ammonia possesses essentially the same energy content as molecular hydrogen on a per H atom basis. Employing copper-based molecular electrocatalysts, we describe

our approach to convert NH_3 to N_2, protons, and electrons for ultimate use in ammonia fuel cells. Our strategy is based on mechanistic findings from our laboratory that indicate that some β-diketiminato copper(II) amides [Cu^{II}]-NHR are unstable towards reductive coupling to [Cu^{I}] and hydrazines RNH-NHR which are easily oxidized to diazenes RN=NR.

Cyclic voltammetry studies outline the electrocatalytic oxidation of ammonia by copper(I) β-diketiminates [Cu^{I}]. While such copper(I) complexes exhibit reversible oxidation behavior in MeCN, in the presence of excess ammonia, oxidation of [Cu^{I}] is no longer reversible. Detailed electrocatalytic studies outline the rate of ammonia oxidation as well as the kinetic order of [Cu^{I}] and NH_3. Mechanistic studies reveal that [Cu^{I}]-NH_3 intermediates are isolable, but addition of NH_3 to cationic copper(II) species {[Cu^{II}](NCMe)$_2$}$^+$results in immediate reduction to [Cu^{I}] with formation of NH_4^+ and N_2H_4. We will share catalyst design strategies that connect the overpotential to the electronic and steric properties of the [Cu^{I}] catalyst.

MARM 384

Nontraditional porphyrinoid scaffolds as efficient electrocatalysts for the oxygen reduction reaction

***Joel Rosenthal**, joelr@udel.edu. Dept of Chemistry Biochemistry, University of Delaware, Newark, Delaware, United States*

The selective $4e^-/4H^+$ reduction of dioxygen to water is an important reaction that takes place at the cathode of fuel cells. The partial reduction ($2e^-/2H^+$) of dioxygen generates hydrogen peroxide via a process that is significantly less exothermic. Despite the fact that the $4e^-/4H^+$ reduction of O_2 to generate two equivalents of H_2O is more downhill than the analogous $2e^-/2H^+$ process to generate H_2O_2 most transition metal complexes show a preference for the incomplete reduction reaction. Tetrapyrrole complexes of cobalt and iron have been heavily studied as platforms for the oxygen reduction reaction (ORR). In general, monotopic cobalt and iron macrocycles, including porphyrins and corroles are not capable of promoting the $4e^-/4H^+$ ORR to generate H_2O with high selectivities. It is against this backdrop that we have developed efficient synthetic strategies for preparation of a variety of novel *nonaromatic* tetrapyrrole macrocycles that contain one or two sp^3 hybridized carbons on the tetrapyrrole periphery. These unconventional structural motifs attenuate the structures and electronic properties of these architectures, and significantly improve the ability of these ligands to donate multiple electrons, as compared to more traditional porphyrinic complexes. In addition to reporting the synthesis, photophysics and redox properties of a variety of new nonaromatic tetrapyrrole metal complexes, we will demonstrate that the cobalt complexes of some of these platforms can selectively promote the ORR via the $4e^-/4H^+$ pathway to generate water. Detailed voltametric and rotating ring disk electrode experiments will be described to demonstrate how these new systems are superior O_2 reduction catalysts when compared to most previously studied monomeric cobalt macrocycles. The potential application of these new architectures for incorporation into fuel cell cathodes will also be discussed.

MARM 385

Development of imino and amino pyridine iron(II) catalysts for Atom Transfer Radical Polymerization (ATRP)

***Deanna L. Zubris**, deanna.zubris@villanova.edu. Villanova University, Villanova, Pennsylvania, United States*

Our group has prepared a family of iron(II) complexes with electron-rich nitrogenous ligands to be used for Atom Transfer Radical Polymerization (ATRP) of styrenic and acrylic monomers. We have isolated and characterized examples of monomeric, dimeric, and bis-ligated cationic iron(II) complexes, and have demonstrated their success as polymerization catalysts for styrene. Under our reaction conditions, we find evidence for ATRP along with competitive Catalytic Chain Transfer (CCT). Current efforts are focused on identifying catalyst features and reaction parameters that may help favor ATRP versus CCT for future catalysis.

MARM 386

Leveraging P(III)-P(V) oxide ligands: Enabling polar alkene polymerization by group 10 metals

*Wei Zhang[2], Margaret Tiedemann[1], Christian Padilla[1], Jiajun Mei[1], **Brad P. Carrow**[1], trapskeetman@gmail.com. (1) Chemistry, Princeton University, Princeton, New Jersey, United States (2) Princeton University, Princeton, New Jersey, United States*

A new class of group 10 catalysts for insertion polymerization will be presented. The enabling feature of these catalysts is a new hard/soft chelating ligand motif containing a phosphine and a phosphonic diamide group. Structural and spectroscopic data suggest the donor strength of the formally L-type oxygen atom in the phosphine-phosphonic diamide (PPDA) actually occupies a range characteristic of oxygen anions. Single component precatalysts possessing a PPDA exhibit rates that are among the highest observed for this metal. PPDA-Pd complexes also catalyze the copolymerization of ethylene with a number of polar alkene monomers to generate

linear, high molecular weight materials. The strong coordination of the phosphonic diamide also engenders stability; steady polymerization rates occur over prolonged periods at temperatures relevant to industrial processes. Most importantly, translation of the ability of the PPDA to engender high reactivity and thermal stability to a base metal (Ni) will also be described.

MARM 387

Bis(guanidinyl)pyridines as ligands for late first-row transition metals

*James E. Allen[2], Lawson Wilkinson[1], William S. Kassel[1], **Nicholas A. Piro**[2], napiro@gmail.com. (1) Department of Chemistry, Villanova University, Villanova, Pennsylvania, United States (2) Department of Chemistry & Biochemistry, Albright College, Reading, Pennsylvania, United States*

Guanidine ligands make versatile building blocks for the synthesis of a variety of coordination complexes. Here we will discuss complexes of chelating guanidinyl ligands made from the bicyclic guanidine 1,4,6-triaza-bicyclo[3.3.0]oct-4-ene (Htbo), and related molecules. In particular, focus will be on complexes of the bisguanidinyl ligand 2,6-bis(tbo)pyridine with iron(II), cobalt(II), and copper(I), including the redox chemistry of the copper(I) complex. Discussion will also include recent attempts at synthesizing 2,6-bis(imidazole-2-imine)pyridine molecules.

MARM 388

Sterically reduced design considerations toward the completion of dinitrogen fixation cycles by group 6 Pentamethylcyclopentadienyl, Amidinate (CPAM) complexes

***Leila M. Duman**, leiladuman@gmail.com, Lawrence R. Sita. Chemistry, University of Maryland, Silver Spring, Maryland, United States*

We have recently reported a group 6 metal-mediated and thermally-driven dinitrogen fixation cycle that can produce value-added, silylated organic nitrogen products, such as Me_3SiNCO, from readily-available and inexpensive chemicals – including N_2, CO_2, and Me_3SiCl. These breakthroughs were achieved by careful steric pruning of the supporting cyclopendienyl, amidinate (CPAM) ligand environment of second- and third-row group 6 metal dinuclear dinitrogen complexes of the general formula, $\{(\eta^5\text{-}C_5Me_5)[N(R')C(R'')\text{-}N(R')]M\}_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-}N_2)$ (R' = Et or iPr, R" = Me or Ph, and M = Mo or W). Reduced sterics about the metal center decrease energy barriers associated with cleavage of the N≡N bond, N-atom functionalization reactions, and subsequent liberation of products from dinitrogen fixation that also leaves a metal complex in a form to reengage in the next N_2 fixation cycle. This contribution will present new results related to the ultimate objective of successfully developing an energy-efficient and atom-economical fixation cycle via group 6 CPAM dinitrogen complexes.

MARM 389

Synthesis of moderately coordinating anions: Towards the design of organometallic ion pairs

***Graham Dobereiner**, dob@temple.edu. Chemistry, Temple University, Philadelphia, Pennsylvania, United States*

Ion pairing effects in organometallic chemistry can dictate the course of a catalytic reaction, yet most common anions in organometallics, such as BF4, PF6, or BArF are assumed to offer "weak coordination" in solution. To further explore how ion pairing can facilitate reactivity of organometallic complexes, a library of "moderately coordinating" anions are prepared, and their solution behavior compared to conventional anions. With the ultimate goal of promoting cooperative reactivity between two oppositely charged organotransitional metal complexes, the lessons from this study are extended to the preparation of heterobimetallic ion pairs.

MARM 390

Designing ligands for the cluster-surface analogy

*Peng Cui, Qiuran Wang, Laura M. Thierer, Shaoguang Zhang, Brian C. Manor, Patrick J. Carroll, **Neil C. Tomson**, tomson@upenn.edu. Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania, United States*

Decades of research have sought to model the chemistry of heterogeneous metallic catalysts with soluble, low-valent cluster complexes bound by strong-field ligands. This research has led to catalysts that perform interesting transformations in their own right but provide only limited data on the mechanisms by which heterogeneous metallic catalysts function. We are interested in re-evaluating the cluster-surface analogy using ligand frameworks built to more accurately model the electronic structure of a metal surface. This contribution describes our initial work on the synthesis of dinuclear complexes of mid- to late-first row transition metal clusters housed within macrocycles constructed of *N*-alkyl linkers between 2,6-diiminopyridine moieties. The redox-flexibility of the ligand is shown to work in concert with the geometric flexibility of the alkyl linkers to allow weak M–M bonding capable of further reactivity with substrates. Of particular interest is a $Fe^{III}_2\text{-}\mu^2$-nitride, which converts into a $Fe^{II}_2\text{-}\mu^2$-amide on

heating in acetonitrile, as well as a unique example of a Fe^{II}_2-μ^2-methylidene. These structures and their reactivity profiles will be discussed in the context of both the Mittasch catalyst (Haber-Bosch) and Fischer-Tropsch catalysts.

MARM 391

Strategies for transition-metal catalyzed, non-directed C-H functionalization

***Marion Emmert**, mhemmert@wpi.edu. Gateway Park, Worcester Polytechnic Institute, Worcester, Massachusetts, United States*

Directly functionalizing C-H bonds of complex molecules at specific positions has the potential to revolutionize late-stage transformations of biologically active molecules. The majority of the reactions available in this area currently employ catalyst directing groups to achieve site selectivity.
This talk will detail the development of alternative strategies: The design and mechanistic understanding of catalysts that allow C-H bond functionalization in a site-selective manner without the use of catalyst directing groups. Approaches for functionalizations of both weak and strong C-H bonds will be discussed.

MARM 392

Combined, high-throughput, mechanistic approach to the development of catalytic reactions for the synthesis of active pharmaceutical ingredients

***David Leitch**, david.c.leitch@gsk.com. API Chemistry, GlaxoSmithKline, King of Prussia, Pennsylvania, United States*

There are two fundamental challenges with development and optimization of catalytic transformations in organic synthesis. First, the chemical space to be explored is considerably larger than for non-catalytic processes due to myriad additional reaction variables at play. Secondly, because the reaction mechanism necessarily involves minute concentrations of highly reactive species, subtle changes to reaction conditions can have large effects on the reaction outcome. In order to address both of these challenges in the pursuit of optimal catalytic reactions in API synthesis, the Chemical Catalysis group at GlaxoSmithKline is taking a combined approach involving the use of high-throughput experimentation to rapidly explore the reaction space, as well as kinetic and mechanistic understanding of the underlying processes. Successful examples of this combined approach involving a variety of homogeneous organometallic catalytic reactions will be presented.

MARM 393

New advances in polydifluoromethylenation reactions

***David A. Vicic**, dvicic@hotmail.com. Department of Chemistry, Lehigh University, Bethlehem, Pennsylvania, United States*

Until World War II, there was no commercial production of elemental fluorine, and thus studies on fluorinated molecules and materials were limited. Once it was discovered that UF_6 exhibits a high vapor pressure and could be used to purify isotopically enriched uranium, production of, followed by reserves of, fluorine grew. Scientists were able to tap into these reserves and develop the field of organofluorine chemistry. Organofluorine chemists have been able to parse out the properties and reactivities of various fluorine-containing functional groups, and the development of new methods to incorporate such groups into organic substrates has received considerable attention. The fluoroalkyl family represents one class of fluorinated functional groups that has grown in significance in recent years. Metal catalyzed methods to incorporate fluoroalkyl groups into organic substrates can represent an atom economical synthetic approach, but the stabilizing properties of fluoroalkyl groups makes fluoroalkylations difficult because fluoroalkyl ligands can also render a metal catalyst more stable and less reactive. Here we describe our efforts to develop new catalysts for transferring the CF_3, CF_2H, and $(CF_2)_n$ groups into organic halides. We will focus on the use of cheap, readily available, and environmentally benign metals in efforts to overcome certain obstacles and to make the new methods as universal as possible.

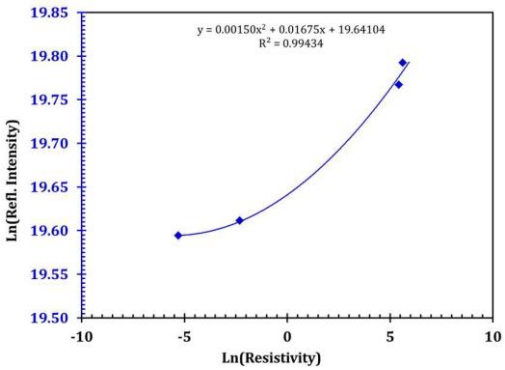
MARM 394

Measurement of resistivity of semiconducting materials via terahertz reflectance route

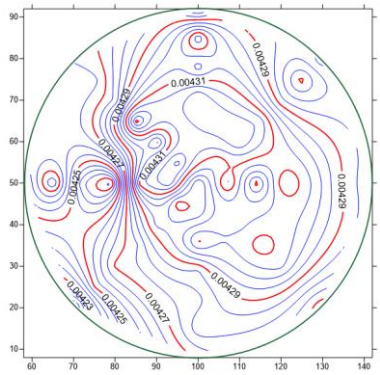
***Anis Rahman**, a.rahman@arphotonics.net, **Aunik Rahman**, aunik@arphotonics.net. Applied Research and Photonics, Harrisburg, Pennsylvania, United States*

Electrical properties such as the resistivity may be computed from optical measurements. Terahertz falls between the IR and microwave frequencies on the electromagnetic spectrum; as such the concept is extendable in the terahertz regime. An algorithm for the impedance related calculations was attempted from the measured reflectance of terahertz beam from various semiconducting substrates. Fig. 1 shows the proposed model and Fig. 2 shows multipoint contour plot of resistivity of an n-type silicon wafer that were computed from the reflectance

measurement. It was surmised that a layer by layer measurement of resistivity is possible by the terahertz technique. Details of the technique will be discussed with exemplary data.



Proposed resistivity vs. reflectance model.



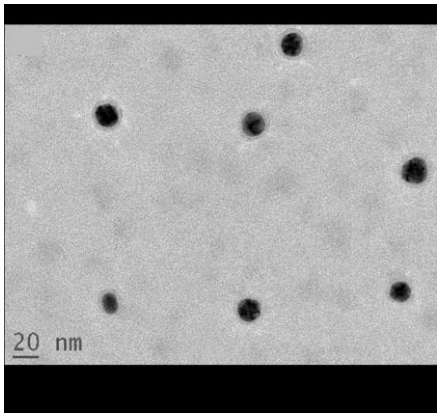
Contour plot of resisitivity of a Si <100> wafer.

MARM 395

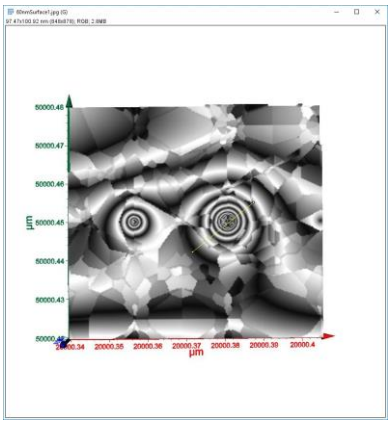
Terahertz multispectral imaging and other analyses of gold nanoparticles

***William Ghann**, wghann@coppin.edu. Center for Nanotechnology, Coppin State University, Baltimore, Maryland, United States*

In this paper, we report the use of Terahertz reconstructive multispectral imaging to visualize and measure the size of individual gold nanoparticles and accordingly the number of unit cells per gold nanoparticle. The gold nanoparticles were synthesized by the Frens-Turkevich citrate method and characterized by several techniques such as UV-vis absorption spectroscopy, Dynamic light scattering (DLS), and Transmission Electron Microscopy. The size of a single gold nanoparticle as determined by the Terahertz reconstructive imaging was 18.5 nm which was comparable to the size obtained by aforementioned other techniques. The DLS technique, however, produced a much bigger size of ~26 nm. This is because the fact the DLS actually measures the hydrodynamic diameter, rather than the nanoparticle in solid state. We have also calculated the number of unit cells per gold nanoparticle using the size of the gold nanoparticles as determined by terahertz reconstructive imaging technique. It was found that the number of unit cells in a single gold nanoparticle was ~ 48,825. The results demonstrate that Terahertz imaging is a powerful nondestructive, non-contact technique for the size analysis of gold nanoparticles. The technique may be used for other nanoparticle system.



TEM Image of Gold Nanoparticles



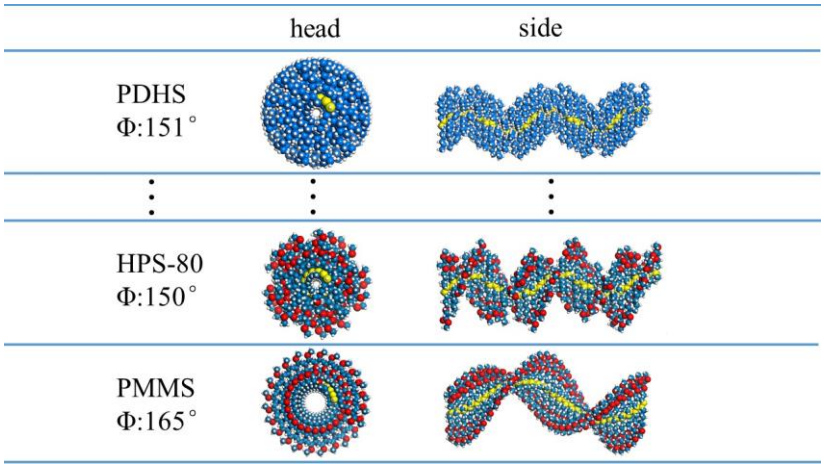
Surface area of Gold Nanoparticles using THz multispectral Imaging

MARM 396

Helical polysilane: Conformational study with molecular dynamics simulation

***zhang muyang**, 704564702@qq.com, Yuming Zhou. chemistry and chemical engineering of seu, southeast university, Atlanta, Georgia, United States*

Optical active helical polysilanes: poly(methoxycarbonyl ethyl propyl ether)methylsilane (PMMS), poly[di-n-hexylsilane-co-(methoxycarbonyl ethyl propyl ether)methylsilane] (HPS) and poly(di-n-hexylsilane) (PDHS) were prepared by Wurtz-type coupling reaction. The chiral monomer dichloro (methoxycarbonyl ethyl propyl ether)methylsilane (DCMMS) was obtained by hydrosilylating methyl (S)-2-(allyloxy)propanoate with dichloromethylsilane. Characterizations like ultraviolet-visible spectroscopy (UV-Vis) and circular dichroism (CD) were utilized to study the conformation of polysilane. To clarify the interaction pattern of the sidechain and the helicity of mainchain, computational simulations were also applied. All of the polysilanes have been tested by Infrared Emissometer to obtain the infrared emissivity property.



MARM 397

Characterization of cigarette paper by terahertz spectroscopy and multispectral imaging

*John H. Lauterbach[2], **Aunik Rahman**[3], aunik@arphotonics.net, **Anis Rahman**[1], a.rahman@arphotonics.net. (1) Applied Research and Photonics, Harrisburg, Pennsylvania, United States (2) Lauterbach Associates, LLC, Macon, Georgia, United States (3) Applied Research & Photonics, Harrisburg, Pennsylvania, United States*

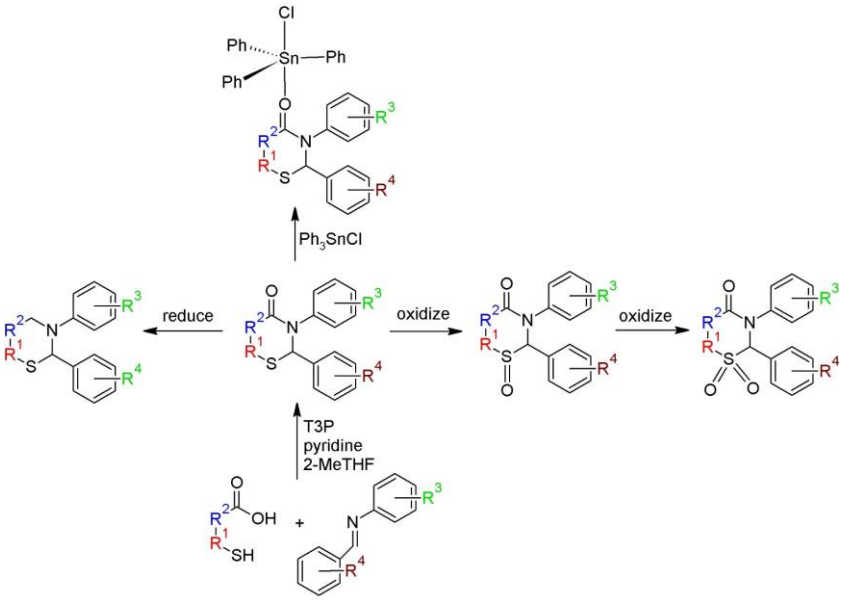
Cigarettes manufactured for sales in the United States, the European Union, and some other countries must be made with Fire Safe Compliant (FSC) cigarette paper. FSC cigarette paper is manufactured by coating bands of polysaccharides and other additives at defined intervals on the cigarette paper. Generally bands are 5 -7 mm wide and are spaced about every 20 mm. Bands are reportedly applied to the cigarette paper by gravure printing or similar techniques and the composition of a band may vary across its thickness as different “inks” are printed at the same location using multi-station gravure presses. The materials used in the banding formulations are very similar to those used to manufacture cigarette paper. Cigarette paper is manufactured from cellulose, calcium carbonate, burn control additives (acetate, citrate, or phosphate sales of potassium and/or sodium), and other polysaccharides such as modified celluloses, guars, and starches that are used in many paper making operations. The main banding polysaccharides reportedly cellulose, modified cellulose, modified starch or alkali alginate salts. However, these complicated systems are only defined in practice by rather crude tests that may not accurately predict the performance of the papers in ignition propensity tests and machine smoking tests required by regulators. Consequently, we have investigated the banded and band-free areas of FSC cigarette papers using terahertz absorbance spectroscopy with a goal for characterizing banding agents. The primary banding agent was known to be cellulose, alginate, or modified starch. Five different FSCs from different brands of cigarettes were investigated. The terahertz spectra show distinguishable absorbance peaks for different samples. A common peak was also observed for all samples. Details will be discussed in terms of data and their interpretation.

MARM 398

More studies on cyclic six- and seven-membered 2,3-diaryl-1,3-thiaza-4-ones

Lee J. Silverberg[2]*, ljsilverberg@verizon.net, Hemant Yennawar*[4]*, Carlos Pacheco*[4]*, Anthony F. Lagalante*[3]*, Hany F. Sobhi*[1]*, Kaitlin Alemany*[2]*, Joshua Bachert*[2]*, Lucas Baker*[2]*, Kaitlyn Bandholz*[2]*, Austin Bayliff*[2]*, Ryan Bendinsky*[2]*, Heather Bradley*[2]*, Michaela Buchwalter*[2]*, Aaron Cali*[2]*, Omar Cardenas*[2]*, Liuxi Chen*[2]*, Baylee Colburn*[2]*, Avril Cooper*[2]*, David Coyle*[2]*, Jonathon Dahl*[2]*, Megan Felty*[2]*, Ryan Fox*[2]*, Jasra Islam*[2]*, Emily Kimmel*[2]*, Stacy Koperna*[2]*, Madeline Lawler*[2]*, Quentin Moyer*[2]*, Caitlin Mroz*[2]*, Duncan Noble*[2]*, Kristen Perhonitch*[2]*, Haley Reppert*[2]*, Harnoor Singh*[2]*, Connor Verhagen*[2]*, Ryan Vidal*[2]*, Alexander Weisbeck*[2]*, Yiwen Xie*[2]*, Ziwei Yang*[2]*. (1) Chemistry, Coppin State University, Ellicott City, Maryland, United States (2) Chemistry, Pennsylvania State University, Schuylkill, Schuylkill Haven, Pennsylvania, United States (3) Villanova Univ, Villanova, Pennsylvania, United States (4) Chemistry, Pennsylvania State University, University Park, State College, Pennsylvania, United States*

Six-and seven-membered 1,3-thiaza-4-ones have shown various modes of biological activity. However, the *N*-aryl compounds have not been widely explored because of the difficulty of coaxing an *N*-aryl imine into reacting with a thioacid. T3P-promoted condensation of *N*-aryl-*C*-aryl imines with thioacids has allowed entry into a wide variety of 2,3-diaryl-1,3-thiaza-4-one heterocycles, and the results to date will be discussed. Synthetic elaboration of these compounds is under investigation and will also be reported on. Testing for anti-microbial activity is also underway and will be disclosed.



MARM 399

Challenges in the management of pancreatic cancer: How a chemist can help?

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Pancreatic adenocarcinoma is generally associated with a dismal prognosis. It is expected to be the second cause of cancer death by 2020. Surgery is the only curative intent for cure. Risk factors for pancreatic cancer are well recognized, however, there is no efficient screening program or reliable tumor markers for early diagnosis of pancreatic cancer. Surgical resection is complex and only benefits patients at early stage of their disease. Neoadjuvant chemoradiation and new ablative techniques can potentially convert some locally advanced cancer patients to resectability. On the other hand, once metastatic, pancreatic cancer patients receive only palliative chemotherapy with dismal prognosis (0% 5-year survival). Recently, multiple biomarkers did show potential role in pancreatic adenocarcinoma but with limited clinical validation. Future direction should focus on clinical applications of biomarkers allowing early diagnosis of pancreatic adenocarcinoma in high-risk patient groups as well as overcoming barriers for efficient chemotherapy.
This communication will highlight the clinical particularity of pancreatic cancer, summarize current management strategies and discuss current role and future potential of biomarkers in pancreatic adenocarcinoma.

MARM 400

Therapeutic relevance of the endocannabinoid system and enzyme-mediated synthesis of 2-arachidonoylglycerol (2-AG)

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The endocannabinoid system (ECS) includes signaling molecules for cannabinoid receptors (CB1 and CB2), as well as the enzymes that are responsible for their biosynthesis and degradation. 2-arachidonoylglycerol (2-AG) is the predominant signaling molecule able to interact with the CB receptors in a fashion similar to Δ^9-tetrahydrocannabinol (THC), a classical cannabinoid isolated from the *Cannabis sativa* plant. There is significant interest in the therapeutic utility of the ECS as an important target of drug design and development. Specifically, the role of 2-AG in neurodegenerative diseases, namely Parkinson's Disease, has been investigated. Recent studies show that elevated levels of 2-AG limit the presence of pro-inflammatory mediators. Furthermore, reports indicate that inhibition of 2-AG's enzymatic degradation leads to increased neuroprotection, and attenuation of pro-inflammatory responses. These findings make 2-AG a potentially promising therapeutic target.

The synthesis of 2-AG has been critical to understanding its therapeutic relevance. Although 2-AG syntheses have been previously reported, many of these approaches suffer from lengthy reaction times carried out at high temperatures, acidic conditions required for the removal of protecting groups, as well as extensive work-up and purification steps. Furthermore, these syntheses require the use of hazardous and environmentally damaging reagents and solvents. Herein, we highlight a novel enzyme-mediated synthesis, producing 2-AG in three steps. In the synthesis, glycerol is treated with vinyl butyrate in the presence of *Candida antarctica* lipase B to regioselectively yield 1,3-dibutyrylglycerol. Esterification of this diglyceride using arachidonic acid and coupling agents yields 2-arachidonoyl-1,3-dibutyrylglycerol. Finally, to synthesize the desired product, 2-AG, the butyryl groups are regioselectively removed in the presence of ethanol and *Candida antarctica* lipase B. To the benefit of this synthesis, biocatalytic transformations are performed under mild reaction conditions, which reduce the occurrence of unwanted byproducts, and thus, extensive purification. This synthesis was subsequently adapted for use in the undergraduate organic chemistry laboratory. As coverage of the endocannabinoid field is lacking in undergraduate curricula, this multi-step synthesis provides a means to expose students to this valuable area of study.

MARM 401

Synthesis and characterization of lipophilic acyl: Coenzyme A thioesters for clinical diagnosis of mitochondrial fatty acid oxidation disorder

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Medium-chain acyl-CoenzymeAs (CoA) are key intermediates in lipid metabolism. The determination of the acyl-CoA dehydrogenase activities is very important for the investigation of patients with suspected fatty acid oxidation disorder. The study of these activities required to prepare a series of substrates of medium chain CoA thioester derivatives. Multiple methods have been used to prepare these compounds by modifying Coenzyme A. These involve selective acylation of the CoA-thiol group with activated acid derivatives, which include acid anhydrides, acid chlorides, mixed anhydride, and N-hydroxysuccinimide esters of the fatty acids. Therefore, there is no uniform method to synthesis these acyl-CoAs. The synthesis of medium-chain and non-standard, i.e. unsaturated, branched acyl-CoAs was reported with low yield. Additionally, the only reported characterization of acyl-CoA focuses on the CoA moiety not the acyl group. In contrast, in our recent studies to identify and characterize acyl CoAs we used high performance liquid chromatography (HPLC), mass spectrometry, and NMR spectroscopy. Herein, we establish a procedure for the synthesis of medium-chain and non-standard acyl-CoA derivatives using an anhydrous organic solvent system. We optimized this synthetic procedure to obtain the highest yields. We synthesized 2,6- dimethylheptanoyl-CoA, as well as Cis 4- decenoyl-CoA. The synthesized COAs were purified by ion exchange solid-phase extraction using functionalized silica gel, followed by high-performance liquid chromatography with ultraviolet detection (HPLC–UV). The purified acyl-CoAs were characterized by analytical HPLC–UV followed by mass spectrometry (MS/MS) analysis. The yields of the purified acyl-CoAs were between 50 % and 60 % based on CoenzymeA (CoASH). Acyl-CoA dehydrogenase activities were measured in rat skeletal muscle mitochondria using these new synthesized CoA substrates. These results were compared with the results using known substrates such as Hexanoyl-CoA, octanoyl-CoA, and palmitoyl-CoA. We also prepared, purified, and characterized other branched CoAs, such as 2-[6-(2,4-dinitrophenoxy) hexyl]oxirane CoA, and 2-[6-(4-chlorophenoxy) hexyl]oxirane CoA using a similar approach with yields ranged between 38 % and 45 % based on CoA and was used as inhibitors for CPT I activity.

MARM 402 Withdrawn

Cell wall piracy by synthetic analogs reveals metabolic adaptation in vancomycin-resistant enterococci

***Marcos M. Pires**, map311@lehigh.edu. Lehigh University, Bethlehem, Pennsylvania, United States*

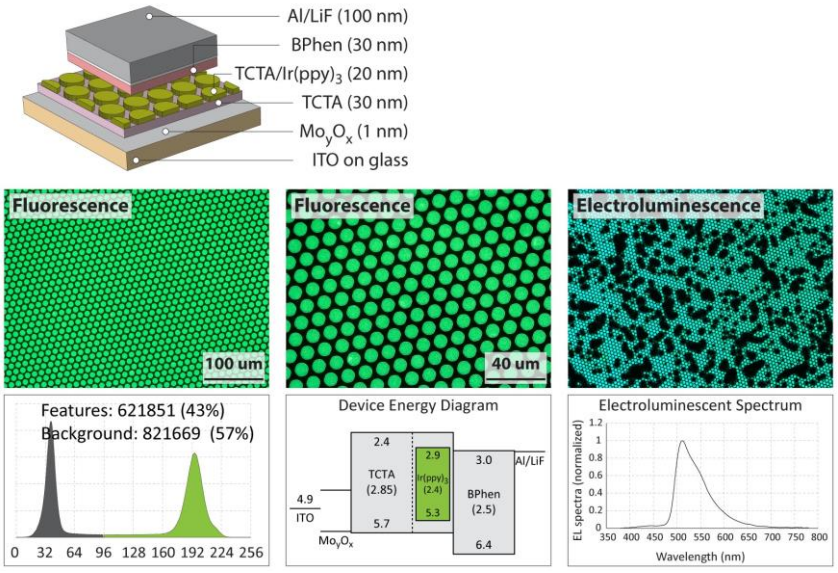
Drug-resistant bacterial infections threaten to overburden the healthcare system and disrupt modern medicine. A large class of potent antibiotics, including vancomycin, operate by interfering with bacterial cell wall biosynthesis. Vancomycin-resistant Enterococci (VRE) evade the blockage of cell wall biosynthesis by altering cell wall precursors, rendering them drug insensitive. Herein, we reveal, for the first time, the phenotypic plasticity and cell wall remodeling of VRE in response to vancomycin in live bacterial cells. Synthetic cell wall analogs were designed and constructed to monitor cell wall structural alterations. Our results demonstrate that the biosynthetic pathway for vancomycin-resistant precursors can be hijacked by synthetic analogs. Finally, we describe a rapid proof-of-principle diagnostic tool based on our synthetic cell wall reporter strategy for the visual classification of VRE. Together, the direct monitoring of VRE cell wall remodeling by our probes establishes the contribution of individual metabolic processes to the evolution of drug resistant phenotypes.

MARM 403

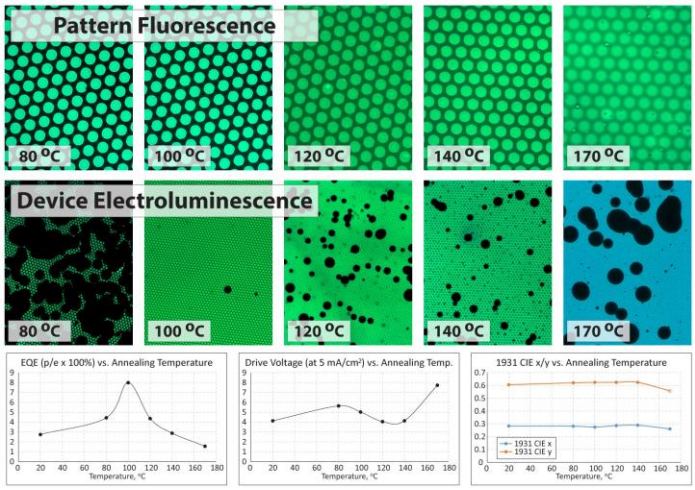
Fabrication of high-resolution OLEDs via contact printing

***Jinhai Li**[2], jinhai.li@globalfoundries.com, Lisong Xu[2], Ching W. Tang[2], Alexander Shestopalov[1]. (1) Chem Eng, 248 Gavett Hall, University of Rochester, Rochester, New York, United States (2) Chemical Engineering, University of Rochester, Rochester, New York, United States*

In this study, we report the fabrication of high-resolution organic light emitting diodes (OLEDs) via contact printing method. Polyurethane acrylate (PUA) is employed as the printing stamp to pattern the emitting layer of OLEDs. A uniform patterning of the emitting material is achieved over a large scale. It is demonstrated that the post-printing thermal annealing can significantly improve the device performance – the external quantum efficiency of the printed device is comparable to the traditional vacuum-deposited devices. Further using of this contact printing technique allows the patterning of light emitting material with sub-micrometer features, which is then fabricated into functional OLEDs. This contact printing technique, which uses PUA as stamp, provides an alternative way to the traditional shadow mask deposition for the manufacturing of OLED displays with sub-micrometer resolution.



Device structure, fluorescent image of the patterned emitting layer and the electroluminescent image of the working OLEDs.



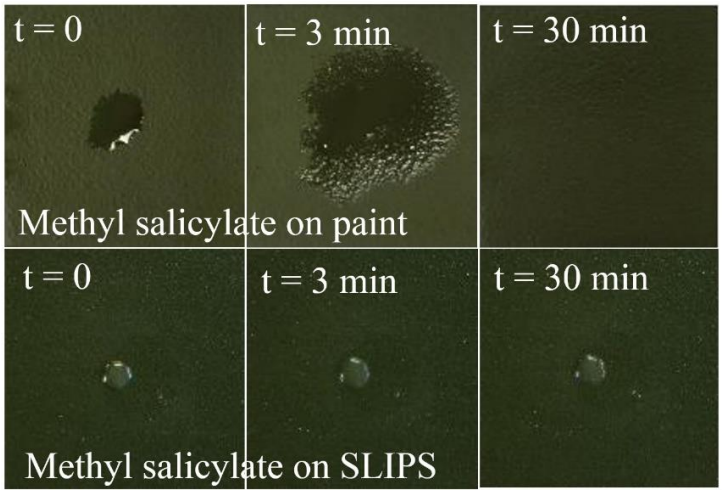
Post-printing annealing at various temperatures and the corresponding device performance

MARM 404

Topcoats for improved decontamination of painted surfaces

Brandy J. Johnson, *brandy.white@nrl.navy.mil, Brian J. Melde, Brett D. Martin. CBMSE - Code 6900, Naval Research Laboratory, Washington, District of Columbia, United States*

Our ongoing efforts are focused on development of coatings intended to provide protection of the warfighter against primary or secondary chemical agent exposure. To this end, we have been evaluating coatings that may provide improved decontamination of painted surfaces following an exposure event. Penetration of chemical threats into traditional porous surfaces and coatings presents a significant threat as the target can be retained through the decontamination process. Retained target then presents additional, often unexpected, exposure hazards. A number of recently reported approaches offer the potential for decreasing target penetration into a surface with a resulting improvement in decontamination performance. We have evaluated the benefits of several variations of Slippery Liquid-Infused Porous Surface (SLIPS) topcoats, including an approach based on a textured poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) layer. This coating and a polyurethane variation of the coating provide reduced retention of simulant compounds following decontamination, but present some challenges related to durability. The wetting and target retention characteristics of a coating combining texture provided by two sizes of beads (100 and 500 nm) with fluorinated block copolymers has also been evaluated. The performance characteristics of this material can be significantly impacted through varying the ratios of the beads and the total loading of the material. Beyond identification of potential coatings technologies and their evaluation, this effort has accessed the relevance of traditional screening approaches and performance evaluations. The work highlights the relationships between wetting behavior and target retention.



MARM 405

Coatings with improved performance through the use of polymer pigment composites

***Stan Brownell**, as_brownell@yahoo.com. Dow Coating Materials, Lansdale, Pennsylvania, United States*

In the United States, approximately 700 million gallons of house paint are produced each year. Practical adsorbing latex polymer technology is a new innovation in the coatings industry which offers the ability to improve the hiding, sustainability, and other key performance metrics of the coating, and all while lowering the cost of the formulated paint. This is accomplished by reducing dependence on TiO_2, a key raw material present in many architectural coatings. This novel technology replaces the conventional paint binder with a smarter material which does everything the conventional binder does while additionally improving pigment efficiency. These polymeric pre-composite binder particles have been designed to interact with coatings grade TiO_2 particles. By employing pre-composite binders during the standard paint making process, pigment / polymer composites self assemble which result in a more ordered distribution of TiO_2 in the paint film. Besides the improvement in hiding, this technology allows for a more uniform paint film, and that directly impacts key paint performance properties, including stain resistance, scrub resistance, and overall durability.

MARM 406

Development of modified conducting substrates using on-surface cross-coupling methods with carbon-based electrodes

*Joel Rosenthal[3], **Rachel Pupillo**[1], rcp@udel.edu, Amber A. Gietter-Burch[1], Donald A. Watson[2]. (1) Chemistry and Biochemistry, University of Delaware, New Castle, Delaware, United States (2) Chemistry/Biochemsitry, University of Delaware, Newark, Delaware, United States (3) Dept of Chemistry Biochemistry, University of Delaware, Newark, Delaware, United States*

Electrode modification chemistries allow for the construction of conducting substrates with properties tailored for an array of applications. While there is an assortment of well-known surface functionalization chemistries such as diazonium-based electrochemical grafting, generation of self-assembled monolayers of alkyl thiols on gold and phosphonate conjugation to metal oxides, the development of post-secondary surface reactions have not been as thoroughly studied. Recent development of electrochemical deposition of diazonium include a triisoprpyl (TIPS) protected alkyne-phenyl-diazonium. These derivatives can be electrodeposited as a thin-film on an electrode surface, and upon deprotection of the TIPS group, the surface is comprised of a monolayer of terminal alkynes. Alkyne functional groups are known to participate in several types of cross coupling chemistries, one of which is the Songashira cross coupling reaction that joins an aryl halide with alkynes. We will show how this cross coupling chemistry can be translated to four different alkyne modified carbon surfaces. The four electrodes with varying oxide content, can all be successfully coupled with iodophenylferrocene to afford ferrocene appended molecular wires on the distinct carbon surfaces. The degree to which the surface coverage, surface fouling, electrode dynamics and resistivity of the electrode is effected by the homogeneity of the underlying carbon electrode will be discussed. We also probed the conductivity of these ferrocene modified electrodes and have found that the electron transport rate constant of each modified electrode assembly is strongly dependent on the conductivity of the parent electrode. These results suggest that the topology of the synthesized films does not out compete the underlying electron transport ability of the electrode materials we have surveyed. Extension of the above concepts toward the construction of bioelectrodes arrays for sensing applications will also be discussed.

MARM 407

Roundtable panelist with undergraduate education experience

***Birgit Albrecht**, balbrecht@loyola.edu. Loyola College, Baltimore, Maryland, United States*

Birgit Albrecht was born in Dingolfing, Germany. She earned a MChem from the University of Surrey and a DPhil from the University of Oxford under the directions of Drs. W. Graham Richards and Guy H. Grant. After a postdoctoral position with Prof. William L. Jorgensen at Yale University, she joined the chemistry faculty at Loyola University Maryland in Baltimore. Birgit is currently an Associate Professor of Chemistry and Dean of the Class of 2021. Her research interest include chemical education, Molecular Dynamics and Monte Carlo Simulations, Quantum Chemistry and Protein Structure.

MARM 408

Roundtable panelist with a background in undergraduate education

***Henry J. Castejon**, henry.castejon@wilkes.edu. Wilkes Univ, Wilkes Barre, Pennsylvania, United States*

Henry J. Castejon was born in Coro, Venezuela. He earned undergraduate degrees in Chemistry and in Materials Science Engineering from Simon Bolivar University and a Ph.D. from Yale University under the guidance of

Kenneth B. Wiberg. After completing postdoctoral work at Yale University, he joined the College of Science at Notre Dame as a Professional Specialist. Dr. Castejon is currently a Professor of Materials Science and Chemistry at Wilkes University. His research interests include Non-equilibrium Statistical Mechanics, Transport Phenomena and Phase Behavior.

MARM 409

Roundtable panelist with experience in pharmaceutical and information technology industries

***Wendy D. Cornell**, cornell@us.ibm.com. Healthcare and Life Science Research, IBM, Yorktown Heights, New York, United States*

Wendy Cornell was born in Greensburg, PA. She earned a B.S. from Case Western Reserve University and a Ph.D. from the University of California at San Francisco (UCSF) under the direction of the late Peter Kollman. After a postdoctoral stint at European Molecular Biology Laboratory (EMBL), she joined Parke-Davis followed by positions at Novartis and Merck where she led Chemistry Modeling & Informatics groups and also a Text Mining & Knolwedge Management group. Wendy is currently a Principal Research Staff Member in Healthcare and Life Science Research at IBM in Yorktown Heights, NY and an MBA candidate at Case Western Reserve University Weatherhead School of Management (May 2017). She is an ACS Fellow, past Program Chair and Division Chair of Computers in Chemistry (COMP), and current Chair of the Committee on Chemical Abstracts Service (CCAS). Her research interests include developing and applying modeling and informatics tools to support drug discovery and the intersection between business and information technology.

MARM 410

Roundtable panelist with experience in research, education, diversity and policy sectors

***Rigoberto Hernandez**, r.hernandez@jhu.edu. Chemistry, Johns Hopkins University, Baltimore, Maryland, United States*

Rigoberto Hernandez was born in Havana, Cuba. He holds a B.S.E. in **Chemical Engineering and Mathematics** from Princeton University (1989), and earned a Ph.D. in **Chemistry** from the University of California, Berkeley (1993) under the direction of William H. Miller. After postdoctoral positions with Eli Pollak at the Weizmann Institute and Greg Voh at the University of Pennsylvania, he joined the faculty at Georgia Tech. As of July 2016, he is the Gompf Family Professor in the Department of Chemistry at the Johns Hopkins University, and remains as the Director of the Open Chemistry Collaborative in Diversity Equity (OXIDE) since 2011. Hernandez serves on numerous advisory boards, including the Board of Directors of the American Chemical Society, where he represents District IV. Dr. Hernandez's research area can be broadly classified as the theoretical and computational chemistry of systems far from equilibrium. This includes a focus on microscopic reaction dynamics and their effects on macroscopic chemical reaction rates in arbitrary solvent environments. His current projects involve questions pertaining to the diffusion of mesogens in colloidal suspensions and liquid crystals, the structure and dynamics of assemblies of Janus and other patchy particles, fundamental advances in transition state theory, design principles for sustainable nanotechnologies and the dynamics of protein folding and rearrangement.

MARM 411

Roundtable panelist: Experienced in undergraduate education

***Michelle M. Ivey**, mivey@stevenson.edu. Dept of Chemistry, Stevenson University, Owings Mills, Maryland, United States*

Michelle M. Ivey was born in Los Angeles, CA. She earned a B.S. in Chemistry from Harvey Mudd College and a Ph.D. from University of California, Irvine under the direction of Prof. John C. Hemminger. After a postdoctoral position with Prof. Krishna L. Foster at California State University, Los Angeles she joined the faculty at the Wilkes Honors College at Florida Atlantic University. Michelle is currently an Associate Professor of Chemistry at Stevenson University in Maryland. Her research interests include ion chromatography detection of anions in samples of environmental interest and incorporating computational chemistry into the undergraduate chemistry curriculum.

MARM 412

Roundtable panelist with experience in undergraduate education, research, and software development

***William F. Polik**, polik@hope.edu. Department of Chemistry, Hope College, Holland, Michigan, United States*

Dr. William F. Polik double-majored in chemistry and mathematics at Dartmouth College and graduated as class valedictorian in 1982. He received a NSF graduate Research fellowship to study physical chemistry at UC Berkeley and received his PhD under the mentorship of Dr. C. Bradley Moore. In 1988 he joined the faculty of Hope College and started a research program to experimentally characterize potentially energy surfaces of

polyatomic molecules through dispersed fluorescence spectroscopy in free jet expansions. His experimental studies included the development of Pure Vibrational Spectroscopy (PVS), a technique that revealed the largest number of excited vibrational levels in the polyatomic molecule H_2CO. After sabbatical leaves with Prof. Robert W. Field at MIT and Dr. Peter R. Taylor at UCSD, he initiated a computational chemistry research program using cluster computers. He published the first correct formulation of the VPT2+K formulas for computing vibrational energy levels including resonance effects. Dr. Polik is the co-developer of the WebMO program, the most widely-used interface for computational chemistry programs. Dr. Polik currently teaches physical chemistry, runs an active research group in molecular spectroscopy and computational chemistry, and serves as the Associate Dean for Research and Scholarship at Hope College.

MARM 413

Roundtable panelist with experience in undergraduate education

***Kevin Range**, krange@lhup.edu. Chemistry, Lock Haven University, Lock Haven, Pennsylvania, United States*

Kevin Range earned a B.S. in Chemistry from Moravian College and a Ph.D. in Physical Chemistry from University of Minnesota under the direction of Darrin York. Kevin is currently a Professor of Chemistry at Lock Haven University in Lock Haven, PA.

MARM 414

Roundtable panelist with experience in undergraduate education in physical chemistry

***Carl Salter**, salterc@moravian.edu. Chemistry, Moravian College, Bethlehem, Pennsylvania, United States*

Carl Salter was born in Swindon England and grew up in Mobile, AL. He attended Spring Hill College and earned a Ph. D. from Vanderbilt University under the direction of Prof. Joel Tellinghuisen. Carl is currently a professor at Moravian College in Bethlehem, PA. His research interests include molecular orbital calculations, laser spectroscopy, and applications of least squares fitting to chemistry.

MARM 415

Roundtable panelist with experience in industry

***Veerabahu Shanmugasundaram**, veerabahu.shanmugasundaram@pfizer.com. Worldwide Research & Development, Pfizer, Groton, Connecticut, United States*

Veer Shanmugasundaram was born in Madras, India. He received a B.E. (Electrical & Electronics Engineering) & M.Sc. (Chemistry) from Birla Institute of Technology & Science, Pilani, India. Following that he conducted his doctoral studies at the State University of New York at Buffalo and received his Ph.D. (Medicinal Chemistry) under the tutelage of Prof. David Hangauer. He then conducted post-doctoral studies at Pharmacia & Upjohn in Kalamazoo, Michigan with Dr. Gerald M. Maggiora and Michael S. Lajiness. Subsequently he joined the Computer-Aided Drug Design Group at Pharmacia in Kalamazoo and later moved to Ann Arbor, Michigan. Veer is currently the Head and Director of the Computational Analysis & Design Group at Pfizer Worldwide Research & Development in Groton, Connecticut. His current research interests at Pfizer are in expanding target space through novel modalities and mechanisms. He is also building next generation computational capabilities in allosteric modulation, enzyme activators, protein degradation, biased GPCR signaling and computational chemical biology.

MARM 416

Roundtable panelist with experience in small bio-tech and large pharmaceutical industries

***Edward C. Sherer**, edward_sherer@merck.com. Modeling and Informatics, Merck Co. Inc., Rahway, New Jersey, United States*

Edward Sherer was born in Champaign, Illinois. He earned a PhD in Chemistry from the University of Minnesota under the direction of Chris Cramer. Prior to his doctoral work, he obtained an MPhil in Pharmaceutical Sciences as a Fulbright Fellow to the University of Nottingham in the United Kingdom with Charlie Laughton. He performed undergraduate computational work with George Shields at Lake Forest College. Ed is currently a Principal Scientist at Merck Research Laboratories in Rahway, NJ. In 2017 he chaired the Division of Computers in Chemistry. He directs a group of computational chemists who apply predictive methods to process chemistry, analytical chemistry, and biocatalysis.

MARM 417

Roundtable panelist with experience in undergraduate research and formation of the Molecular Education and Research Consortium in Undergraduate computational chemistRY (MERCURY)

***George C. Shields**, george.shields@furman.edu. Deans Office, 113 Marts Hall, Bucknell University, Lewisburg, Pennsylvania, United States*

George C. Shields was born in Marcellus, NY. He earned a B.S, M.S, and Ph.D. from the Georgia Institute of Technology under the direction of Prof. Thomas F. Moran. After a postdoctoral position with Prof.Thomas A. Steitz at Yale University, he joined the chemistry faculty at Lake Forest College in Illinois. He was Chairperson at Lake Forest College before moving to Hamilton College, NY, as Chair, follwed by a stint as the founding dean of the college of science and technology at Armstrong State University, follwed by a six-year term as dean of the college of arts and sciences at Bucknell University. He is currently Vice President for Academic Affairs, Provost, and Professor of Chemistry at Furman University. He founded the **M**olecular **E**ducation and **R**esearch **C**onsortium in **U**ndergraduate computational chemist**RY** (**MERCURY**) in 2000, a consortium that has dramatically increased the diversity of students majoring in chemistry. He was awarded the ACS Award for Research at an Undergraduate Institution in 2015.

MARM 418

Tweaking our chemical biology platforms to increase the translational potential of the data

***Craig J. Thomas**, craigt@mail.nih.gov. NIH Chemical Genomics Center, Rockville, Maryland, United States*

Targeted drug therapies hold great promise for the treatment of human cancers. Our team has established a high-throughput platform for the examination of drugs as single agents and in combination to hasten translational efforts. Further, the successful identification of the most promising therapies hinges upon our ability to establish cell culture models that recreate the altered signaling and metabolic states that are present, functional and contributing to the unchecked viability and proliferative advantage of cancer cells in the in vivo setting. Traditional, monolayer culture models are giving way to three-dimensional models which often display a key oncogene associated cellular signatures. We have recently completed an integrated-omics evaluation of selected cancer cell lines cultured in monolayer and three-dimensional formats incorporating genomic (RNA-seq), metabolomic and phosphoproteomic assessments to better characterize the fundamental changes associated with these divergent culture conditions. An examination of cells in both culture formats within our drug screening platform identified several pharmacological classes with specific activity in only one model. Several of the lessons learned from these studies suggest new opportunities in cancer therapy.

MARM 419

Overview of US prescription pharmaceutical market and future viability of products approved by 505(b)2 new drug application regulatory pathway

***Kevin Ostrander**, kevin.ostrander@glenmarkpharma.com. Glenmark Pharmaceuticals Inc., Mahwah, New Jersey, United States*

For calendar year 2015, US sales of prescription pharmaceutical products reached a record high of $425 billion dollars. This was an approximately 12% increase from the prior year. When viewed as a function of product dispensed, the figure for 2015 is estimated at 4.3 billion prescriptions, an increase of only 1% relative to the previous year. At a macro level, this does bring into question the rate for drug price increases.
Within these figures, however, one needs to consider the segmentation across 505(b)1 New Drug Applications (NDA), Biologics License Applications (BLA), 505(b)2 NDA and Abbreviated New Drug Applications (ANDA). Generic product substitution occurs in about 80% of all prescriptions issued by physicians; therefore accounting for an estimated 80% of the volume or 3.4 billion prescriptions, but only 16% of market sales. This general trend is expected to continue with further pricing pressure to manage escalating pharmacy benefits within healthcare plans. That being said, brands still account for the majority of drug sales revenues and fill an important clinical need to patients as well as garnering profits that fuel the research and development apparatus of most innovator companies.
A 505(b)2 NDA is primary used in the case where the drug is already the subject of a previous approval, however, the applicant is seeking a new formulation, altering the route of administration, a new combination therapy using the drug or possibly defining a new clinical indication. The number of approved 505(b)2 NDAs in 2015 was estimated at 44, which is tied for the second highest level over the past ten years. This is in stark contrast to the 22 novel NDAs approved by FDA in 2014. The overall development costs, time and clinical risks are certainly factors in this variance and supportive of the 505(b)2 pathway from a business standpoint. This presentation will explain the differences in filing requirements, define market exclusivities for the applicant and highlight several in-market

product examples that have been commercialized under this filing approach, thus supporting the case for continuation in the future.

MARM 420

Assessing metal contamination and contaminant sources in urban streams

*Gianna Makler, **Erica R. McKenzie**, ermckenzie@temple.edu. Civil & Environmental Eng., Temple University, Philadelphia, Pennsylvania, United States*

Philadelphia has a long-standing history and industrial activity, which extends into the present day. This research was undertaken to assess the metal concentrations in the urban streams of the greater Philadelphia area. More specifically, the goal was to assess if elevated metals concentrations were present in more industrial areas, or if seasonal changes in water quality resulted in metals mobilization; As, Cd, Cr, Cu, Ni, Pb, and Zn are assessed. Four sampling sites were monitored during summer 2016 (four sampling efforts); winter 2017 sampling efforts are currently underway. Overall, the abudance of metals is as follows (highest to lowest concentration): Zn<Cu~Pb<Ni<Cr~As<Cd. As, Cu, and Ni were all found to generally be mostly dissolved (i.e., not removed by 0.45 um filter). Enrichment factor analysis revealed that Pb was substantially enriched in a site-specific manner, suggesting that legacy emissions from smelters may still be contributing to urban stream concentrations.

MARM 421

Identifying redox transition zones in the subsurface

***Xin Yin**[1], xy239@njit.edu, Han Hua[1], Lisa Axe[2]. (1) Civil and Environmental Engineering, New Jersey Institute of Tech, Newark, New Jersey, United States (2) Otto H. York Department of Chemical, Biological and Pharmaceutical Engineering, New Jersey institute of Tech, Newark, New Jersey, United States*

Reactive mineral coatings play an important role in contaminant transformation. This research focuses on identifying and studying redox transition zones where reactive mineral coatings are expected to be significant. To accomplish this study, a 60-foot core was collected from an area of concern at the Chambers Works Site in NJ. With stainless steel liners, 2-foot sub-sections of the core were obtained, protected with argon-purged PVC tubes, and stored at 4^{o}C. The cores were jacked in a glove box into a total of 225 2-inch subsamples preserved with triple-layer protection to prevent oxygen permeation and organic interactions with the container. A suite of analytical tools was used on each sample including X-ray fluorescence (XRF) for composition, soil pH, redox potential (ORP), and volatile organic carbon (VOC) concentration in the headspace. From XRF results, iron and sulfur were among the dominant elements present with gradients observed throughout the core. Iron concentrations peaked at multiple depths with the most significant gradients observed from 32’ to 38’ and 49’ to 50’. Sulfur concentrations peak as well at depths consistent with Fe trends and gradients spanning five orders of magnitude; the increases in the S and Fe concentrations are consistent with sulfide precipitation. Over the 60 feet, soil pH ranged from 3.74 to 8.03. Steep gradients in the oxidation-reduction potential included -141.4 – 651.0 mV. VOCs were detected using the photo-ionization detection and reported as chlorobenzene; readings ranged from below detection limit to 6.4 ppm. As a result of this screening process, a number of redox transition zones were identified and include depths 21.0’-22.8’, 31.0’-34.3’ and 39.0’-43.0’. Other analyses that have corroborated the importance of the zones being studied involve evaluating bacteria abundance and contaminants of concern found in groundwater. A more detailed study is being conducted in four of the transition zones.

MARM 422

Distinct effects and molecular basis of inducing and non-inducing auxiliary substrates on 1,4-dioxane biostimulation

***Mengyan Li**, mengyan.li@njit.edu. New Jersey Institute of Technology, Newark, New Jersey, United States*

Recent research has demonstrated that indigenous bacteria that can degrade 1,4-dioxane (dioxane) might be more widespread than previously assumed and acclimated near the source zone area due to the selective pressure. However, the intrinsic biodegradation of dioxane is typically hindered by the limited availability of carbon and energy sources and the presence of toxic co-occurring contaminants. To date, the potential to stimulate dioxane biodegradation by adding auxiliary carbon sources has received limited attention. Such auxiliary substrates might be beneficial when dioxane is present at trace concentrations that are insufficient to induce or sustain specific degraders. In this substrate interactions study, we compare the merits and limitations of biostimulation of dioxane degradation with a non-inducing growth substrate (1-butatnol [1-BuOH]) versus an inducing substrate (tetrahydrofuran [THF]). A microcosm study was conducted to assess two biostimulation strategies (relative to natural attenuation) to bioremediate 1,4-dioxane contamination at a site in west Texas. Amendment of 1-BuOH (100 mg/L) to microcosms that were not oxygen-limited temporarily enhanced dioxane biodegradation by the indigenous microorganisms. However, this stimulatory effect was not sustained by repeated

amendments, which was attributed to i) the inability of 1-BuOH to induce dioxane-degrading enzymes, ii) curing of catabolic plasmids, iii) metabolic flux dilution and catabolite repression, and iv) increased competition by commensal bacteria that do not degrade dioxane. Experiments with the archetype dioxane degrader *Pseudonocardia dioxanivorans* CB1190 repeatedly amended with 1-BuOH (500 mg/L added weekly for 4 weeks) corroborated the partial curing of catabolic plasmids (9.5 ± 7.4% was the plasmid retention ratio) and proliferation of derivative segregants that lost their ability to degrade dioxane. Addition of THF (300 µg/L) also had limited benefit due to competitive inhibition; significant dioxane degradation occurred only when the THF concentration decreased below approximately 160 µg/L. Overall, these results illustrate the importance of considering the possibility of unintentional hindrance of catabolism associated with the addition of auxiliary carbon sources to bioremediate aquifers impacted with trace concentrations of dioxane.

MARM 423

Self-decontaminating polymer additives for CWA protection

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Self-decontaminating materials have potential to significantly mitigate exposure risk resulting from surfaces contaminated with persistent CWAs. Specifically, self-decontaminating polymeric coatings and fibers would reduce the need for decontamination of painted surfaces, as well as afford promising filtration applications. Here, the development and analysis of several promising additives to impart self-decontamination into polymers and coatings are discussed. Reactive additives include C_{60} fullerene, nickel and zirconium containing polyoxometalates (POMs), and zirconium hydroxide ($Zr(OH)_4$). C_{60} and POMs were chemically modified with amphiphilic ligands to facilitate their automatic segregation to the polymer-air interface. *In operando* analysis of $Zr(OH)_4$ was performed to better understand the effects of ambient conditions (CO_2, H_2O, SO_2) on the performance of the catalyst. Surface characterization included SEM, XPS, contact angle, laser confocal microscopy, ATR-IR, and XRD. Decontamination challenges against simulants were performed in simulated daylight conditions and analyzed via GC-MS. Preliminary results on the compatibility of reactive additives into polymer coatings are presented.

MARM 424

Characterizing reactive iron mineral coatings in redox transition zones

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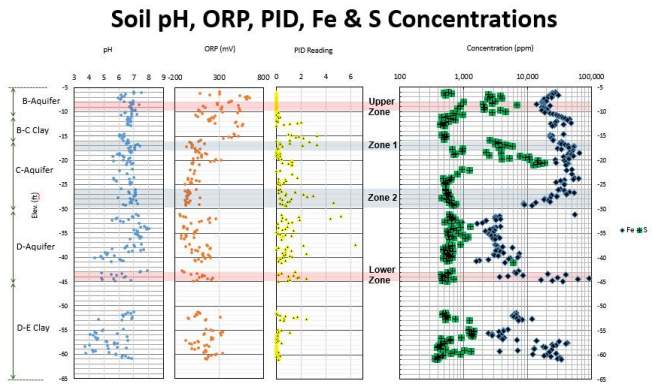
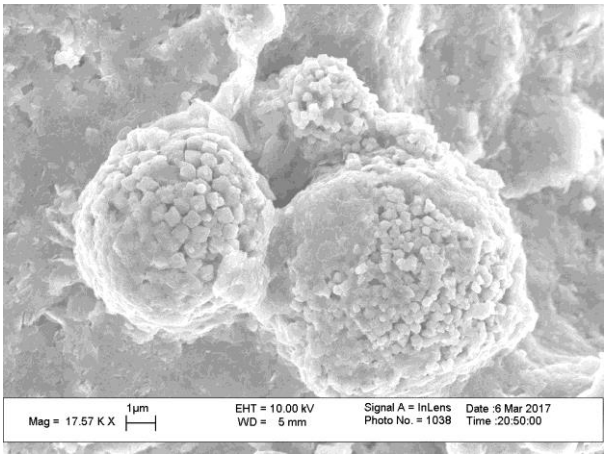
The purpose of this research is to characterize reactive Fe mineral coatings in redox transition zones of a contaminated site. An anaerobic 60 foot core was collected from the Chambers Works Site in Deepwater, NJ. Two inch subsamples were used to evaluate redox transition zones using bulk composition, redox potential, pH, volatile organic carbon in the headspace, as well as microbial community. A suite of complementary analyses is being applied to characterize the surface chemistry in the four transition zones. The analyses include sequential extraction (phases and speciation), x-ray diffraction (mineralogy), x-ray fluorescence (composition), field-emission scanning electron microscopy (surface morphology down to the nm scale) with energy dispersive analysis (surface composition), and bench-scale experiments. Evidence from multiple lines suggest a clear trend in reactive iron (II)/(III) mineral coatings throughout transition zones. Bulk minerals observed included quartz, muscovite, clinochlore, and zeolite. Other zones have also included albite and anorthite. Using the suite of tools, reactive iron mineral coatings involve the iron (II) minerals pyrite, mackinawite, pyrrhotite, and siderite in the transition zone between depths from 21’ to 22.8’. Ferrihydrite, goethite, and lepidocrocite were the dominant iron (III) minerals in zone 31’ to 34.3’, while pyrite, greigite and gypsum were the most abundant mineral coating in zone 13’ to 15’. The presence of reactive mineral coatings through the redox transition zones is a strong indicator of Fe^{2+}/Fe^{3+} cycling. Therefore, further studies on abiotic degradation of the halogenated solvents present will be investigated.





MARM 425

Adapting and extending general chemistry experiments for the analytical chemistry laboratory curriculum

***Donald Mencer**, mencer@wilkes.edu. Department of Chemistry and Biochemistry, Wilkes University, Wilkes-Barre, Pennsylvania, United States*

At times, college students do not grasp the connections between courses and also have anxiety related to the perceived level of difficulty of upper division chemistry courses. A strategy that can be used to combat both of these mindsets involves the adoption, with modification, of general chemistry laboratory experiments for use in the analytical chemistry curriculum. Students are provided with the primary literature source of the experiment along with a description of any procedural and / or data analysis modifications. Students are therefore aware that (a) general chemistry students can complete the experimental work and (b) the material relates directly to pre-requisite general chemistry concepts. Three examples of this approach will be presented. The first is the classic experiment demonstrating the affect of ionic strength on the solubility of potassium hydrogen phthalate. Instead of simply demonstrating the affect of ionic strength, the students compare experimentally determined and calculated activity coefficients. A second experiment involves the construction of a simple photometer along with a verification of the Beer-Lambert law. The students are required to determine limit of detection (LOD), limit of quantitation (LOQ), and explore the limit of linearity (LOL) of the stand curves. The final example is a multi-week investigation of seawater samples for total dissolved solids, pH, conductivity, Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, Br^-, and SO_4^{2-}. In all cases, the students learn the fundamental physical operating principles of methods of analysis, assess the precision and accuracy of their work, and complete more advanced treatments of the data than typically required in the freshmen year.

MARM 426

Instrumental analysis at Lafayette College

***Melissa M. Galloway**, gallowam@lafayette.edu. Chemistry, Lafayette College, Easton, Pennsylvania, United States*

Instrumental analysis at Lafayette College is a writing intensive course generally taught to senior level students. My approach to teaching this course is to give students as much practice as possible with real-world examples and hands-on experiences. This course meets for three hours of lecture and six hours of lab per week, and carries a writing intensive designation. Lecture time focuses on how the instruments work and strengthening the students' scientific writing skills, while laboratory time focuses on individualized hands-on time with the instruments. Throughout the first seven weeks of the semester, instrumental analysis labs are divided into two days per week; students make standards and prepare samples for analysis on the first day and then use departmental instrumentation to analyze their samples the second day. Afterwards, they write up their results in the format of an Analytical Chemistry journal article. During the last seven weeks of the semester, students design and implement an independent research project. This involves writing an NSF style research proposal, acting as reviewers on the research proposals of two other students, designing and carrying out a research plan, and writing up their work in the Analytical Chemistry journal format.

MARM 427

Incorporation of Laser Induced Breakdown Spectroscopy (LIBS) into analytical chemistry/instrumental analysis and an innovative lab experience for students

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Most undergraduate curriculums introduce students to atomic spectroscopy using atomic absorption spectroscopy (AAS); this lab experiment has been designed to introduce students to a different type of atomic spectroscopy, namely laser induced breakdown spectroscopy (LIBS). In LIBS, a high powered laser is focused onto a surface. The focused laser pulse heats, ablates, atomizes, and ionizes the sample and results in the formation of a plasma. The light from the plasma is spectrally resolved and detected; elements can be identified by their unique spectral features. For this lab experiment, the students use a standard set of synthetic silicate samples that contain elements at various concentrations. Calibration curves are created to aid in determining detection limits and sensitivities.

Another project was created for Instrumental Analysis. During Instrumental Analysis lab, a variety of instruments are used; labs were developed which allow students to gain experience using the available instrumentation. During the last few weeks of the semester, the students are assigned a project in which they design their own lab experiment. This provides them the opportunity to gain more experience using a specific instrument for their purpose.

Both of these laboratory experiments have been successfully added to Alvernia's undergraduate curriculum. Both lab experiments/projects provide students with valuable experiences in using a different atomic technique and in creating a laboratory experiment on their own.

MARM 428

Quantitative determination of artemisinin in extracts and supplements using TLC and ImageJ software

***David Rusak**, david.rusak@scranton.edu. Chemistry, University of Scranton, Scranton, Pennsylvania, United States*

Artemisinin combination therapies (ACT) have proven to effective treatments for some types of malaria. However, the quality of commercially available drugs varies widely, and there is a significant counterfeit market for substandard drugs. In this experiment developed for Instrumental Analysis Laboratory, students extract artemisinin from over-the-counter supplements and determine concentration by using thin-layer chromatography (TLC) and comparing to prepared standards. The quantification requires an "on-plate" derivatization and image analysis using the ImageJ software made available at no charge by the National Institute of Health. The image analysis can be done a cell phone, and is the only part of the experiment that involves electricity. Good estimates of concentration can be done by visual comparison of standards to the extracts. The experiment is an example of effective analytical chemistry that can be accomplished with minimal equipment and potentially used in underserved areas of the world.

MARM 429

Balancing breadth and depth in the design of an analytical course for environmental science majors

***Julie A. Palkendo**, palkendo@kutztown.edu. Physical Sciences, Kutztown University, Kutztown, Pennsylvania, United States*

This interactive session will focus on the challenges of integrating the content of a traditional analytical course with the needs of an environmental science major and how to package it into a one-semester three credit course. Specific lecture and lab topics will be discussed that showcase the delicate balance of breadth (a multitude of techniques and variations thereof), and the right kind of depth (focus on theory, applications, and/or technical skills). Strategies and resources will be shared as well as how to use student feedback to build and mold a robust, environmentally relevant course founded on the basic principles of analytical chemistry.

MARM 430

Joseph Priestley House Museum

***Dee A. Casteel**[1,2], casteel@bucknell.edu. (1) Bucknell Univ, Lewisburg, Pennsylvania, United States (2) Joseph Priestley House, Northumberland, Pennsylvania, United States*

When Joseph Priestley (1733-1804) is remembered today, it's usually for his 1774 discovery, in England, of oxygen. Fewer know he spent the last 10 years of his life in rural Pennsylvania. Priestley moved to Northumberland, Pennsylvania, where he continued his work in science, religion, and education. Joseph Priestley House and laboratory is an historic site that preserves and interprets the contributions and significance to American history of Joseph Priestley. As a National Historic Landmark and National Historic Chemical Landmark, the site features Priestley's manor house with its laboratory. The Joseph Priestley House welcomes visitors 9 months of the year staffed by volunteers. The Jospeh Priestley House is a Partner Property with the Pennsylvania Historic and Museum Commission.

MARM 431

Priestley residences

***Tom Bresenhan**, tompat01@ptd.ent. Joseph Priestley House, Northumberland, Pennsylvania, United States*

Famed scientist Jospeh Priestley lived in a number of locations throughout his life, in England and in the US. Several of these sites are preserved as as historic places. This paper will review his residences and the important works, particularly his chemical discoveries, at each site. Archealogical reports and structural studies are available for some of the locations and they provide a glimpse of Priestley life.

MARM 432

On being Joseph Priestley

***Ronald C. Blatchley**, rblatch@dejazzd.com. Joseph Priestley House, Northumberland, Pennsylvania, United States*

Having been an re-enactor of Joseph Priestley for 34 years, I have gained much insight into Priestley as a person and as a chemist. My role as Priestley has induced me to explore his writings, his experiments, and his history. I have also traveled to England to research the places and traces of Priestley's days there. I will share some of my findings and impressions and give some insight into the rewards of bringing chemistry to the general public.

MARM 433

Joseph Priestley House: A National Historic Chemical Landmark

***Sophie Rovner**, S_Rovner@acs.org. National Historic Chemical Landmarks program, American Chemical Society, Washington, District of Columbia, United States*

The American Chemical Society's National Historic Chemical Landmarks program grants Landmark status to seminal achievements in the history of the chemical sciences and provides a record of their contributions to chemistry and society in the U.S. In 1993, the Joseph Priestley House was among the earliest sites afforded this status. This presentation will provide background on the NHCL program in its 25th anniversary year and highlight the 12 NCHL sites in the state of Pennsylvania as well as the specific importance of the Joseph Priestley House for the development of the ACS itself.

MARM 434

Intellectual property protection for small chemical businesses

Andrew H. Berks[1,2]*, andrew@berksiplaw.com. (1) Cittone & Chinta LLP, New York, New York, United States (2) Counsel 4 Creatives, New York, New York, United States*

An overview of patent and trademark protection for small businesses and startups will be presented. Topics covered will include a brief primer on why IP protection is important, filing provisional patent applications, US and international patent applications, patent prosecution strategies in the United States and other countries, trademarks for small businesses and startups, and financial considerations.

MARM 435

Expanding the perspective of drug development: Understanding real world medicine and real world patients

Michael N. Liebman[1,2]*, m.liebman@strategicmedicine.com. (1) IPQ Analytics, Kennett Square, Pennsylvania, United States (2) Pharmacology and Physiology, Drexel College of Medicine, Philadelphia, Pennsylvania, United States*

Drug development has evolved over time from the examination of natural products and their potential ability to manage disease symptoms to the highly technological-based approaches of today. Independently, the healthcare system in developed countries, has evolved to incorporate a diverse and complex environment, the healthcare ecosystem, which includes the patient, physician, pharma company, payer, regulatory agency and underlying science. The interaction of these elements yields systems-based behavior that impacts the potential for a molecule to become a drug and, more critically, a commercial product. The complexities include differences in clinical practice, clinical guidelines, formularies, co-morbid conditions and government regulations. The ability to model, analyze and evaluate such factors early in the drug development process can be used critically to optimize the probability for success in drug development. A basis for such an approach and its application to specific drugs will be presented as has been studied with our colleagues at the National Research Council of Italy (CNR-Pisa).

MARM 436

American Horror Story, small business edition: A company possessed by high legal fee demons

Randy Micheletti*, rmicheletti@perkinscoie.com. Perkins Coie LLP, Glen Ellyn, Illinois, United States*

Do you cringe when your lawyer's bill arrives? Do your legal expenditures routinely exceed budgeted amounts? Do you often wonder what value your attorneys bring to the party? Offering true tales from the crypt, we will highlight (para)normal experiences small business owners encounter and discuss how to reduce your company’s legal fees without being haunted by risk.

MARM 437

Reverse pharmacology and systems approaches for chemical biology, drug discovery and development: Inspiration from Mother Nature and the wisdom of the Rishis

Mukund Chorghade*, chorghade@verizon.net. Chorghade Enterprises, Natick, Massachusetts, United States*

While biotechnological advances, genomics and high throughput screenings or combinatorial and asymmetric syntheses have long promised new vistas in drug discovery, the pharmaceutical industry is facing a serious innovation deficit. Critics suggest that “we have become high throughput in technology, yet have remained low throughput in thinking”. Post marketing failures of blockbuster drugs have become major concerns of industries, leading to a significant shift in favor of single to multi targeted drugs and affording greater respect to traditional knowledge. Scientifically validated and technologically standardized botanical products may be explored on a fast track using innovative approaches like reverse pharmacology and systems biology, which are based on traditional medicine knowledge. . We begin the search based on Ayurvedic medicine research, clinical experiences,

observations or available data on actual use in patients as a starting point. Since safety of the materials is already established from traditional use track record, we undertake pharmaceutical development, safety validation and pharmacodynamic studies in parallel to controlled clinical studies. Thus, drug discovery based on Ayurveda follows a 'Reverse Pharmacology' path from Clinics to Laboratories. Herein we describe such approaches with selected examples based on previous studies.

"THINQ Discovery" desires to derive inspiration and intellectual value from the wisdom of the Rishis to discover and develop New Chemical Entities for a variety of pharmaceutical, agrochemical and cosmoceutical applications. Traditional Medicine (Complimentary Alternate Medicine to the Western World) has historically involved clinic THINQ's natural product discovery programs utilize biologically active natural products as an advanced starting point for discovery. NPs can be considered "pre-validated by nature", having been optimized for interaction with biological macromolecules through evolutionary selection processes. Embedded in these bioactive natural products are a number of diverse, chiral functional groups which are potential sites for protein binding. This diverse source of novel, active agents serve as leads/scaffolds for elaboration into desperately needed efficacious drugs for a multitude of disease indications. We aim to reconfigure products into chemical hybrid "Molecular Legos" and to screen the deck of diverse compounds against targets.

. We present herein selected examples of our research efforts.

MARM 438

Optical control of protein function through unnatural amino acid mutagenesis

***Alexander Deiters**, alexdeiters@gmail.com. Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania, United States*

Nature regulates biological processes, for example signal transduction, protein function, and gene expression, with high spatial and temporal precision. In order to study and understand these processes, equally precise external control is required. Light is an excellent tool for this purpose, as it can be easily regulated in timing, location, wavelength, and amplitude, thereby enabling high-resolution optical control of biological processes. We are developing optochemical tools to control protein function through genetic code expansion with unnatural amino acids that can be activated with light. We have applied this approach to the conditional control of DNA recombination, gene editing, RNA polymerization, cell signaling, and other essential biological processes.

MARM 439

Exploring protein environments with unnatural amino acids

***Scott H. Brewer**, scott.brewer@fandm.edu. Chemistry, Franklin & Marshall College, Lancaster, Pennsylvania, United States*

The ability to study local protein structure and dynamics has been significantly increased by the use of unnatural amino acids containing vibrational reporters that can be genetically incorporated into proteins with site-specificity. The nitrile and azide groups are both effective vibrational reporters due in part to the position of the nitrile and azide stretching frequencies, the sensitivity and relatively high extinction coefficients of these vibrations, and the small size of these reporters. Recently, we have expanded the utility of a nitrile-modified phenylalanine unnatural amino acid (UAA) to probe local protein environments through the synthesis of three isotopomers (^{15}N, ^{13}C, ^{13}C^{15}N) of this UAA. The isotopomers permit the unambiguous assignment of the nitrile symmetric stretch vibration in addition to permitting multiple local protein environments to be probed simultaneously. Additionally, we have recently developed a photo-stable azido-modified phenylalanine UAA to effectively probe local protein environments. The synthesis of these UAAs, the genetic incorporation of these UAAs into proteins, and the spectral characterization of the resulting protein constructs will be discussed.

MARM 440

Studying Parkinson's disease using semi-synthetic proteins

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Our laboratory develops methods to study the misfolding of proteins, including alpha-synuclein, which has been implicated in the pathogenesis of Parkinson's Disease. We utilize unnatural amino acid mutagenesis, bioorthogonal labeling techniques, and protein ligation to produce homogenous alpha-synuclein labeled with fluorescent probes. Fluorescence measurements are used to generate models of alpha-synuclein conformations in monomers or in fibrils. Labeled alpha-synuclein constructs are also used to understand the mechanisms by which small molecules proposed as Parkinson's Disease therapeutics or diagnostics interact with fibrils. Taken together,

our studies should provide insight into the role of alpha-synuclein aggregation in Parkinson's Disease, and provide strategies for diagnosis and treatment.

MARM 441

Exploring the solvation state at various sites in proteins

***Christine M. Piro**, tine.piro@gmail.com. Chemistry, Franklin Marshall College, Lancaster, Pennsylvania, United States*

Unnatural amino acids can be site specifically incorporated into proteins to examine local protein environments. The vibrational reporter unnatural amino acid *p*-cyano-L-phenylalanine (pCNF) is sensitive to the solvation environment (11 cm^{-1} shift between a DMSO or water solvent) and the nitrile stretching frequency of the CN group (~2220 cm^{-1}) appears outside the range of functional groups natively found in proteins. As such, pCNF has been used to report on local solvation environments in proteins. We have incorporated pCNF at two unique solvation positions in superfolder GFP and subsequently examined these structures using FTIR and X-ray crystallography. X-ray crystallographic studies indicate that the thoughtful incorporation of pCNF into a protein does not perturb the structure at either a solvent accessible or partially buried site, supporting the use of pCNF to study near-native solvation environments in proteins. We then incorporated pCNF into the heme nitric oxide and/or oxygen binding (H-NOX) protein from *Thermoanaerobacter tencongensis* at sites both in the gas binding heme pocket and sites elsewhere on the protein. These spectroscopic studies have illustrated that the heme pocket is buried and inaccessible to solvent when O_2 is bound to the protein.

MARM 442

Designing fluorinated proteins for stability and imaging

***Jin K. Montclare**, montclare@nyu.edu. Chemical and Biomolecular Engineering, Polytechnic Institute of New York University, Brooklyn, New York, United States*

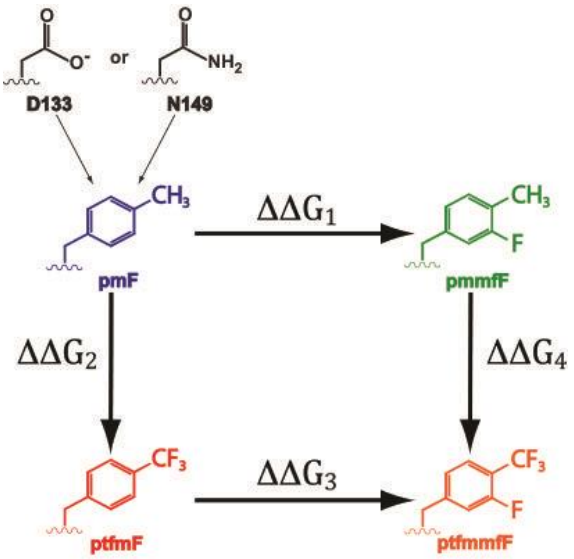
Through centuries of evolution, nature has developed biopolymers capable of folding and assembling into discrete structures with a functional consequence. By exploiting nature's biosynthetic machinery we are able to integrate non-canonical amino acid into proteins to improve stability as well as endow new function. In particular, we investigate the impact of residue–specific incorporation of fluorinated amino acids on enzymes and biomaterials. For the enzyme work, we explore whether we can improve the stability of phosphotriesterase in conjunction with computational methods. In the case of biomaterials, we design novel self-assembling protein micelles bearing fluorinated amino acids for imaging. These studies demonstrate the power of fluorinated amino acids in protein design.

MARM 443

Examining the fluoro-stabilization effect using *in vivo* unnatural amino acid incorporation

***Christopher Henkels**, christopher.henkels@wilkes.edu. Dept of Chemistry, Wilkes University, Wilkes Barre, Pennsylvania, United States*

In vivo unnatural amino acid (UAA) incorporation has greatly enhanced the ability to introduce novel chemical functionalities through the expansion of the genetic code. In *E. coli* the amber codon (TAG) is reprogrammed to encode for a 21st amino acid, the desired UAA. This genetic code alteration is facilitated by an orthogonal suppressor tRNA ($tRNA_{CUA}$) and a directly-evolved $tRNA^{Tyr}$ synthetase (UAA-RS), which specifically charges the suppressor $tRNA_{CUA}$ with the designated UAA. Some of the selected UAA-RS's have the added beneficial ability to incorporate multiple structurally-similar UAAs, a property termed "permissivity", which affords the investigator the ability to rapidly produce UAA-containing protein variants. Here, we use a permissive UAA-RS to incorporate a family of structurally related (predominantly) fluorinated UAAs (F-UAAs) to generate a series of single-site superfolder green fluorescent protein (sfGFP) variants with varying degrees of fluorination. F-UAA substitution into proteins may be a useful strategy in protein design given fluorine's unique chemistry, minimal structural perturbation and enhanced stability upon incorporation. A systematic study to examine the magnitude and molecular basis of the "fluoro-stabilization effect" using our single-site-F-UAA-containing sfGFP variants is presented. Interestingly, preliminary thermodynamic experiments suggest that fluorocarbon bond substitution stabilizes sfGFP in a position-dependent manner. Further elucidation of the thermodynamic and kinetic mechanisms of F-UAA protein stabilization may uncover the general utility of this protein design strategy.



MARM 444

Electrografting application toward surface plasmon resonance biosensor

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Point-of-Care Testing (POCT) is a clinical analysis performed near the patient, rather than in a remote, dedicated laboratory. **POCT** is typically performed by non-laboratory personnel and the results are used for clinical decision-making. Acute Coronary syndrome (ACS) is a group of conditions that considerably decreases or stops blood flow to the heart muscle, causing the heart to be damaged or stressed. Such events cause the release of biomarkers into the blood stream. **Myocardial Infarction (MI),** commonly called “heart attack”, is a well-known ACS that is diagnosed by measuring the change in the level of cardiac biomarkers (preferably troponin) in the blood. Here 4-aminophenylalanine is electrografted on the gold sensing surface as the linker to allow receptors immobilization. Electrokinetics is then to be combined with surface plasmon resonance, to enhance the sensitivity and selectivity of a cardiac protein biosensor.Surface Plasmon Resonance (SPR) is a real time, label free optical method that measures the refractive index change when the analyte binds receptors immobilized at the surface of a metal, here gold. In this report we will show how electrografting of 4-aminophenylalanine allows the fabrication of an in channel reference pad to enhance the reliability of SPR sensors application as troponin biosensors.

MARM 445

Influence of brain gangliosides on vesicle adsorption, rupture, and supported bilayer formation determined by quartz crystal microbalance sensing

Luke Jordan*, luj216@lehigh.edu, Nathan Wittenberg. Chemistry, Lehigh University, Bethlehem, Pennsylvania, United States*

Gangliosides are glycosylated sphingolipids that reside primarily in the extracellular leaflet of plasma membranes. In most tissues gangliosides are present at low levels (~1% of lipids), but in the nervous system gangliosides are present at levels approaching 10% of total lipids. The major gangliosides found in the brain and CNS are GM1, GD1a, GD1b, and GT1b. These molecules share the same general head group structure, but are differentiated by the number and position of pendent sialic acid groups. At physiological pH, sialic acid carries a negative charge, which imparts a charge on gangliosides that varies from (-1, GM1) to (-3, GT1b). Gangliosides function as receptors for toxins and viruses, as well as a number of endogenous biomolecules. As such, supported lipid bilayer (SLB)-based biosensors have been used to detect molecular interactions with gangliosides. However, the influence gangliosides have on the adsorption and rupture of phospholipid vesicles to form SLBs has not been characterized in detail. In this work we used quartz crystal microbalance with dissipation monitoring (QCM-D) to measure the kinetics of SLB formation from vesicles containing varying levels of GM1, GD1a, GD1b, and GT1b. We found that all the gangliosides tend to slow SLB formation kinetics in a concentration and charge dependent manner, and the critical surface vesicle concentration increases with increasing ganglioside concentration and charge. Additionally, calcium can accelerate the formation of SLBs with gangliosides, and the nature of the SLB hydration layer may be altered by the presence of gangliosides.

MARM 446

Sensing and investigating the interactions between small molecule drugs and lipid membranes

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A biosensor based on interfacial potential changes on the lipid membrane surface has been developed. By incorporating pH sensitive fluorescent dyes into supported lipid bilayers, we can monitor the interactions between lipid membranes and small molecule drugs without labeling them. The biosensor is assembled in microfluidic device and signals are given by surface potential induced fluorescence changes, which allows for high throughput, interfacial specificity and excellent sensitivity to molecules with low molecular weight that would be difficult to sense by QCM-D or SPR measurements. To investigate the interaction mechanisms of these molecules, we have applied complementary interfacial characterizing techniques including vibrational sum frequency spectroscopy and Langmuir monolayer compression experiments. Furthermore, by varying the membrane lipid composition, we demonstrate that both the chemistry of the headgroups and the packing of lipid acyl chains can modify the interactions between drug molecules and the membranes. Our studies should help elucidate the importance of drug-membrane interactions and provide insights into new drug development and drug screening.

MARM 447

Analysis and comparison of N-linked glycans in *Naja kaouthia* and *Naja mossambica* snake venoms via mass spectrometry

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Previous biochemical research has heavily focused on proteomics, but there is a growing emphasis on the area of glycomics. The new focus is due to many studies emphasizing that post-translational N-glycan attachment introduces great structural variability, which then allows a broader range of protein function. This research analyzes cobra venom toxin glycosylation. N-glycan peptides of *Naja Kaouthia* and *Naja mossambica* venom were enzymatically released from their proteins, separated from their peptides via solid phase extraction, and desalted using porous graphitized carbon. Reduction and permethylation were performed to serve as directional markers when analyzing structural data. The glycans were analyzed through MALDI-TOF mass spectrometry. A number of peaks correlate with previously discovered N-glycans, and in addition new putative structures were determined.

MARM 448

N-glycome profile of bird serum using mass spectrometry

John Ebeid*, john.ebeid@scranton.edu, Kate A. Stumpo. Chemistry, University of Scranton, Scranton, Pennsylvania, United States*

Glycome analysis of avian immunoglobulin Y (IgY) has proved important for biologic therapeutic development. N-glycans on IgY affect the protein folding, structure, transport, and half-life. Depending on the physiological state of the organism, different glycan moieties are produced. In this experiment, IgY glycan moieties of *Dumetella carolinensis* (gray catbird) are determined using mass spectrometry. Moieties from serum samples with *Heamoproteus beckeri* infection are compared with non-infected samples to determine specific immune responses to infection.

MARM 449

Gold nanoparticles for laser-desorption ionization mass spectrometry of biomolecules

Cody Sacks*, cody.sacks@scranton.edu, Benjamin Kelly, Kate A. Stumpo. Chemistry, University of Scranton, Scranton, Pennsylvania, United States*

Nanoparticles (NPs) exhibit intriguing optical and chemical characteristics that enable them for use in various applications. These properties are dependent on NP size, shape, and degree of aggregation, and they can be affected significantly by their surrounding solute concentration and composition, and “capping” reagents. When used as a matrix for LDI-MS, AuNPs have been shown to enhance the ionization of a “target” chemical in that same solution, when compared to traditional organic acid matrices. Here, a library of compounds has been evaluated and specific classes that ionize well with AuNPs have been identified. Notably, interesting fragmentation is observed, and is compare to other MS methods. By applying these findings to *in vivo* conditions, it could be determined whether higher-quality spectra can generated for biological samples.

MARM 450

Gel permeation chromatography: An analytical tool

***Carol Stein**, cmstein03@yahoo.com. Organic Division, Intertek, Allentown, Pennsylvania, United States*

Knowing the molecular weight, polydispersity and degree of long chain branching of the polymer can help provide valuable information on a polymer. Gel permutation chromatography (GPC) or size exclusion chromatography (SEC) is a great analytical tool for determining this valuable information. What is GPC? What is the difference between conventional GPC and absolute GPC? What information can be obtained from different detectors? I will provide the information obtained from this analytical technic but it will be your job to know how to apply the results to your samples.

MARM 451

Investigating the structural and thermodynamics aspect of bile salt enantio-selectivity in MEKC

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Cholate, deoxycholate and taurodeoxycholate are facial amphiphiles that form micellar aggregates in aqueous solution. When employed in micellar electrokinetic capillary chromatography (MEKC), these aggregates are capable of resolving chiral compounds that have planar sub-structures. Here, the structural, mechanistic, and energetic aspects of the interactions that give rise to enantio-selectivity are investigated. Mobility and resolution data from MEKC separations, thermodynamic data from isothermal titration calorimetry (ITC) experiments, and chemical shift data from nuclear magnetic resonance spectroscopy (NMR) experiments are used to study this natural bile salt micellar system. In general, chiral resolution in MEKC is maximal at intermediate concentrations of bile salt, and is usually improved with increased temperature. 1D and 2D NMR data suggest an antiparallel bile dimer is the fundamental unit that binds binaphthyl compounds, and that this dimeric unit is preserved throughout a progressive micellization process. Further, the R- and S-binaphthyl isomers prefer to bind from opposite sides of this dimer. Curiously, chiral resolution decreases with increasing temperature at bile concentrations just above the cmc. Systematic investigation of the bile salt micelle formation/deformation with ITC reveals that the enthalpy of micelle formation crosses from endo- to exothermic just above room temperature, and that the difference in enthalpy of binding for the two chiral isomers of binaphthyl compounds is about 1 kJ/mole. These structural and thermodynamic data support an entropically-driven micellization process and suggest a MEKC chiral separation mechanism that may rely on a kinetic effect. In all, a more complete picture of the chiral recognition process with bile salt micelles is emerging, making the larger goal of rational design of bile salt chiral separation systems approachable.

MARM 452

Monitoring folding and interactions of polyproline peptides using capillary electrophoresis

***Alison Holliday**, hollidaya@moravian.edu, Amanda M. Miller, John D. Barr. Department of Chemistry, Moravian College, Bethlehem, Pennsylvania, United States*

Protein folding is key to protein function; however, for most systems, it is extremely difficult to directly observe the steps involved in folding, as they occur on a very rapid timescale. An exception is the folding of polyproline peptides induced by changing solvent conditions. With increasing solvent polarity, the dominant conformation of polyproline shifts from a tightly packed right-handed helix to a more loosely-packed left-handed helix. As this process involves *cis-trans* isomerization of peptide bonds, it occurs over the course of minutes or hours. As a result, we have been able to observe intermediate conformations using capillary electrophoresis, corroborating the gas-phase results of parallel experiments using ion mobility spectrometry.

This presentation will focus on recent experiments examining the effect of polyproline length on the observation of intermediates in peptide folding. It will also explore how interactions of polyproline with a proline-binding cell signaling peptide change as the polyproline folds.

MARM 453

Efficient synthetic route to a highly modular turn-on fluorescence probe through regio-selective cross coupling

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Small-molecule fluorescent probes have become an essential tool for examining biological phenomena. However, despite the number of probes available, there is only few number of fluorescent scaffolds with synthetic flexibility and easiness to pursue combinatorial studies. Here, we introduce a highly modular fluorogenic azide probe containing four strategic domains that can be easily engineered and optimized for various applications. Such domains are allotted for 1) compound polarization 2) activation upon ligation 3) optimization of photophysical properties and 4) potentially detection of ions. We successfully synthesized our probe in three steps from commercially available starting materials in overall yields of up to >80% in large scale. Facile synthesis of our probe was permitted by regioselective palladium-catalyzed cross coupling, which paves the way for combinatorial probe development. A library of probes has shown a significant turn-on fluorescence response upon click ligation to a target molecule and exhibited tunable absorption and emission, spanning the visible spectrum. We have further applied our probe to study the folding of α-synuclein (αS), aggregates of which are hallmarks of Parkinson's disease. Most importantly, our turn-on probes allow live-cell imaging without wash out of excess dye providing the least perturbed system to understand the dynamics of biomolecules. Rational design and facile synthesis of chemical probes can provide tools for convenient, continuous assays for studying amyloidgenic proteins including αS in cellular environments.

MARM 454

Surface functionalized metal-oxo magnetic nanobeads as potential T_1 contrast agents for magnetic resonance imaging

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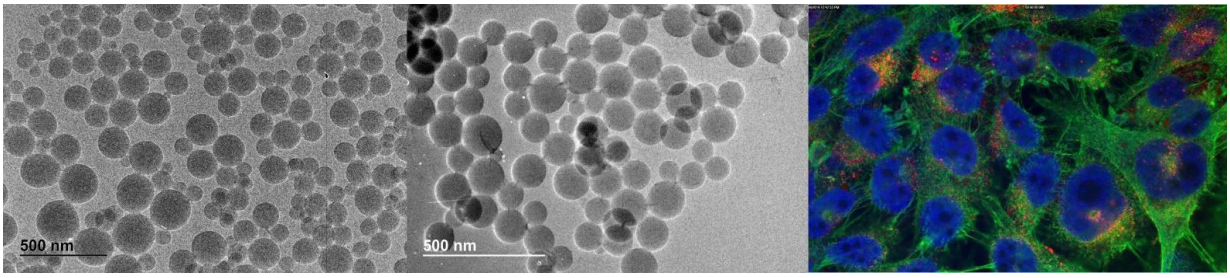
At least half of clinical magnetic resonance imaging (MRI) scans utilize paramagnetic substances known as contrast agents (CAs) to enhance the signal. For this purpose, Gadolinium chelates and super paramagnetic Iron oxide particles are currently being used. However the need to use gram level doses, toxic effects, under performance at high field strengths and lack of T_1 contrast have started to make these CAs obsolete.

Our work has identified a biologically benign poly nuclear metal-oxo cluster,$[Mn_8Fe_4O_{12}(O_2CCH_3)_{16}(H_2O)_4]$ or Mn_8Fe_4, as a potential CA. Exploiting its proneness for ligand exchange, the acetate groups were replaced for the polymerizable ligand, 4-vinylbenzoate.The substituted cluster was then subsequently incorporated into polystyrene latex beads by way of the miniemulsion polymerization process resulting in monodispersed nanobeads (70.9 ± 9.4 nm in diameter) with positive T_1 contrast. $[Mn_3O(O_2CCH_3)_6(bpy)_2]$ or Mn_3bpy is another cluster that we have incorporated into nanobeads (130.9 ± 4.2 nm) of polyacrylamide using the inverse miniemulsion polymerization process (Fig.1L). Initial screening of these hydrophilic beads showed high T_1 contrast.

Carboxyl and amino functionalized co-monomers were used to yield covalently bound surface charges on the aforementioned polystyrene nanobeads. Well-formed beads with homogenous metal content was identified via TEM (Fig.1M). These were found to be non-toxic by hemolytic and MTT cytotoxicity assays. Furthermore, these surface modified beads were marked for fluorescence with a perylene based dye. Cell uptake experiments were encouraging showing retention around the nuclei as seen by confocal laser scanning microscopy (Fig.1R).Preliminary *in vivo* mouse studies also showed promising T_1 contrast via MRI.

Magnetic beads conjugated to folic acid at the surface are also under investigation in order to target folate receptors which are over expressed in certain tumor cells. We have also identified Iron only clusters that have the potential to be incorporated into nanobeads for even higher T_1 contrast.



Left; TEM of Mn_3bpy polyacrylamide beads. ***Middle;*** TEM of COO^- surface functionalized Mn_8Fe_4-VBA-co-polystyrene nanobeads. ***Right;*** cLSM Image of PC-3 prostate cancer cells treated with fluorescent polystyrene nanobeads, λ_{em}=613nm(Red), DAPI(Blue,Nucleus) and Phalloidin(Green,F-Actin).

MARM 455

Synthetically accessible tetrapyrrole metal complexes as efficient photochemotherapeutic agents with remarkably high phototoxicity index

Andrea M. Potocny, *apotocny@udel.edu, Maxwell Martin, Joel Rosenthal. Dept of Chemistry Biochemistry, University of Delaware, Newark, Delaware, United States*

Photodynamic therapy (PDT), which involves the photoinduced sensitization of singlet oxygen is an attractive treatment for certain types of cancer. The development of photochemotherapeutic agents remains an active area of research because PDT is less invasive than surgical options, lacks the side effects associated with conventional chemotherapy or radiation treatments, and allows cancerous tissues to be selectively targeted via directed irradiation of the affected area. Macrocyclic tetrapyrrole compounds such as derivatives of porphyrins, phthalocyanines, chlorins, and bacteriochlorins have been pursued as sensitizers of singlet oxygen for PDT applications but historically are different to prepare/purify and can also suffer from high dark toxicity, poor solubility in biological media and/or slow clearance from biological tissues. Given these shortcomings, the widespread success of PDT treatment strategies awaits the development of new photochemotherapeutic agents. Toward this end, we have developed a series of novel tetrapyrrole architectures as potential PDT agents. More specifically, we have established a facile synthetic approach for the synthesis of linear tetrapyrrole complexes of late transition metals. We find that these dimethylbiladiene (**DMBil1**) tetrapyrrole complexes efficiently sensitize generation of singlet oxygen upon irradiation with light of wavelengths longer than 550 nm with quantum yields that are close to unity. Derivatization of the periphery of the tetrapyrrole scaffold allowed for installation of polyethylene glycol (PEG) functionalities, making these systems water soluble and biocompatible. Photophysical studies demonstrate that the **DMBil1–PEG** conjugates maintain their ability to sensitize singlet oxygen production and are highly stable under aqueous conditions. Preliminary cell studies with the **DMBil1–PEG** derivatives indicate that this new class of tetrapyrrole is an extremely promising candidate for photochemotherapeutics; millimolar concentrations of the DMBil1 complexes are well tolerated by cells in the dark, while incubation with nanomolar concentrations of these complexes are highly toxic upon illumination with red light. As such, the **DMBil1** conjugates show a remarkably high phototoxicity index, approaching 10,000, which is significantly larger than that observed for traditional tetrapyrrole PDT agents. Additional efforts to elaborate the **DMBil1** construct for development of photochemotherapeutics will also be discussed.

MARM 456

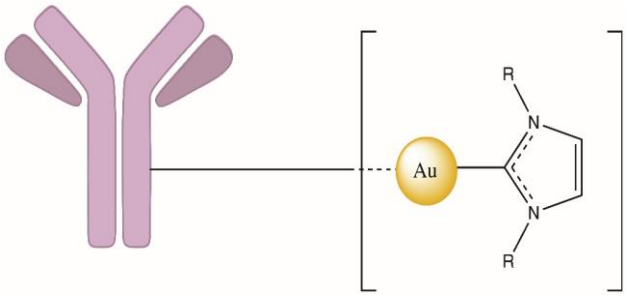
Synthetic approaches to novel antibody-gold-based drug conjugates for targeted delivery in cancer chemotherapy

Natalia Curado Dianez[1], *natalia.curado@brooklyn.Cuny.edu, Guillaume Dewaele Le Roi*[1,2], *Benelita T. Elie*[1,3], *Mike Cornejo*[1], *Maria Contel*[1,4]*. (1) Chemistry, Brooklyn College, The City University of New York, New York, New York, United States (2) Chemistry, Brooklyn College, Chemistry PhD Program, The City University of New York, New York, New York, United States (3) Chemistry, Brooklyn College, Biology PhD Program, The City University of New York, New York, New York, United States (4) Chemistry, Brooklyn College, Chemistry and Biology PhD Program, The City University of New York, New York, New York, United States*

Antibody-drug conjugates (ADCs) represent an emerging new paradigm in cancer chemotherapy. This novel and promising approach consists of three main parts: antibody, linker and payload. Accordingly, the success of these entities relies on the different functionalities of their components, including the high specificity of the antibody and therefore their non-negligible role as delivery agent for high potent cytotoxic agents. Only two ADCs have been

approved by the FDA so far: brentuximab vedotin (Adcetris®) and ado-trastuzumab emtansine (Kadcycla®), not including the Mylotarg (gemtuzumab ozogamicin) withdrawn from the market. Despite of this fact, an increasing number of ADCs have entered clinical trials in the last years, which highlights the potential of these targeted therapies.

Our research group at Brooklyn College has envisioned novel ADCs based on cytotoxic payloads consisting on gold (I)-based complexes and N-heterocyclic carbene ligands, which have shown potent cytotoxicity on several cancer cell lines (low nanomolar range). The gold(I)-L compounds are further modified with azide or alkinyl groups amenable to react with the corresponding terminal counterpart in the linker, according to a cooper-free click spontaneous reaction developed by Gray to generate gold(I)-triazolates. Preliminary results with [AuN_3(NHC)] and [$AuN_3(PR_3)$] have shown successful cycloaddition reactions, as well as an increase of cytotoxicity of the corresponding triazolate complexes compared to the [AuClL] (L = NHC, PR_3) precursors. These results pave the way for further studies with different NHC ligands, as well as suitable linkers for subsequent bio-conjugation with the antibody.



MARM 457

Synthesis, DNA binding study, and anticancer activity of organorhenium sulfonato compounds on hormone-dependent MCF-7 and hormone-independent triple-negative MDA-MB-231 breast cancer cells

Tijesunimi J. Odebode*, tiode1@morgan.edu, Santosh K. Mandal, Angela J. Winstead. Chemistry, Morgan State University, Baltimore, Maryland, United States*

Breast cancer is a worldwide concern. The most effective treatments for breast cancer are associated with significant side effects and tumor resistance after extended use. Previous studies have described organometallic rhenium complexes as highly promising anticancer compounds since low IC_{50} values can be obtained and they exhibit low toxicity on normal cells. Other studies have demonstrated strong anticancer activity of tricarbonylrhenium(I)(α-diimine) complexes against U-937 leukamia cancer cell lines. In this study, we are exploring the synthesis and anticancer properties of novel rhenium complexes of the type $XRe(CO)_3Z$ [X = α-diimines and Z = tosylate, 1-naphthalenesulfonate and 2-naphthalenesulfonate] against hormone-dependent MCF-7 and hormone-independent triple-negative MDA-MB-231 breast cancer cells. Several derivatives were synthesized by treating a pentylcarbonato complex with a corresponding sulfonic acid. These compounds were characterized using IR, ^{1}H NMR, and ^{13}C NMR. UV-Vis DNA interaction and cytotoxicity studies were carried out. The p-toluenesulfonato (TOS), 1-naphthalenesulfonato (1NS) and 2-naphthalenesulfonato (2NS) complexes were synthesized with excellent yields. The UV-vis DNA binding studies suggest groove binding, but more studies would be needed to conclude. The TOS, 1NS and 2NS complexes were found to be more potent (IC_{50} < 2.0 μM) than current treatments for breast cancer.

MARM 458

Mechanism of solar water oxidation in Photosystem II

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The solar water-splitting protein complex, photosystem II (PSII), catalyzes one of the most energetically demanding reactions in Nature by using light energy to drive water oxidation. The four-electron water oxidation reaction occurs at the tetranuclear manganese-calcium-oxo (Mn_4Ca-oxo) cluster that is present in the oxygen-evolving complex of PSII. The electronic and geometric structure of the Mn_4Ca-oxo cluster, which is exquisitely tuned by smart protein matrix effects, is central to the water-oxidation chemistry of PSII. However, the mechanism of water oxidation at the Mn_4Ca-oxo cluster is not well understood because of the inability of conventional methods to directly probe the reaction intermediates. We are developing high-resolution two-dimensional (2D) hyperfine

sublevel correlation spectroscopy methods that provide direct ‘snapshots’ of the photochemical water oxidation intermediates of the Mn_4Ca-oxo cluster of PSII. I will describe ongoing efforts in our laboratory to understand the mechanism of water oxidation in PSII.

MARM 459

Characterization and regulation of weak and strong siderophores by soil nitrogen-fixing *Azotobacter sp.*

Oliver Baars[1]*, obaars@princeton.edu, Sebastian H. Kopf*[2]*, Xinning Zhang*[1]*, Francois Morel*[1]*, Mohammad R. Seyedsayamdost*[3]*. (1) Geosciences, Princeton University, Princeton, New Jersey, United States (2) University of Colorado Boulder, Boulder, Colorado, United States (3) Chemistry, Princeton University, Princeton, New Jersey, United States*

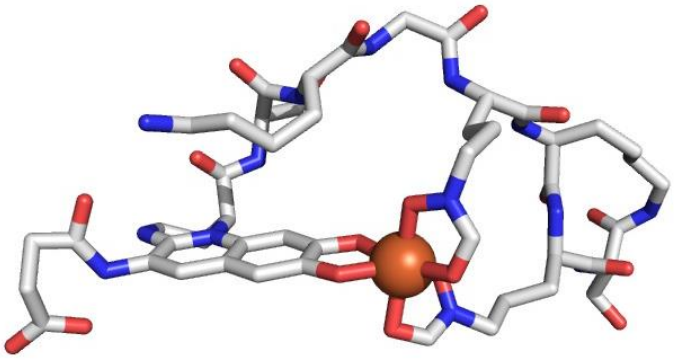
A. vinelandii and *A. chroococcum* are ubiquitous nitrogen-fixing soil bacteria with agricultural relevance. *Azotobacters* use various extracellular iron chelators called siderophores to acquire this trace metal under conditions of Fe limitation. While the siderophore structures of *A. vinelandii* have been studied in detail, the siderophores from *A. chroococcum* remain still unknown. Using a new bioinformatics and high-resolution LC-MS driven workflow, we performed a comprehensive siderophore profiling study with *A. chroococcum*. The identified iron chelators fell into three structural families. *A. vinelandii* and *A. chroococcum* share a common weak siderophore called vibrioferrin. In contrast, stronger siderophores differ between both species. Among these high-affinity Fe chelators, we discovered chrochelins, a new class of siderophores with a novel iron binding motif produced only by *A. chroococcum*. We then studied the regulation of siderophore production by both species using chemostat and batch incubations with controlled metal availabilities. The results revealed a downregulation of the weak siderophore in a severe starvation response that was common to both species and gives conceptual insight into the role of bacterial weak siderophores.

MARM 460

Interactions of titanium with the siderophore pyoverdine: Ti(IV) complexation, TiO_2 dissolution, and bacterial interactions

Ann Valentine*, ann.valentine@temple.edu, Kayleigh Jones. Temple University, Wynnewood, Pennsylvania, United States*

Siderophores, produced by organisms to render Fe(III) bioavailable, can also bind Ti(IV) avidly in aqueous solution and preclude its hydrolytic precipitation over a wide range of conditions. Some siderophores can solubilize large amounts of Ti(IV) from otherwise-insoluble TiO_2. Siderophores are sometimes implicated in triggering biofilm growth, and biofilm growth is also associated with TiO_2 coatings on titanium alloy materials. Pyoverdines are the major siderophores of important biofilm-forming bacteria. We report on the pH-dependent binding in solution of Ti(IV) and pyoverdine from *Pseudomonas fluorescens* 13525 investigated by using spectropotentiometric titrations from pH 2-10, fluorescence spectroscopy and mass spectrometry. The binding constants of Ti(IV)-PVD were determined using spectrophotometric titrations with various competitor ligands and by isothermal titration calorimetry (ITC). The ability of PVD to dissolve Ti from TiO_2 was also investigated by using inductively coupled plasma-optical emission spectrometry (ICP-OES). The surface of TiO_2 exposed to pyoverdine was characterized by using scanning electron microscopy (SEM). *Pseudomonas fluorescens* was grown in the presence of TiO_2, Ti-citrate, and Ti-desferrioxaime B, and the interactions and implications for cell growth and biofilm formation will be discussed.



Pyoverdine from *Pseudomonas fluorescens* 13525 bound to Fe(III). Figure prepared with Pymol with coordinates from PDB ID 2W78.

MARM 461

Influences of inorganic additives in organotransition metal catalysis

***Graham Dobereiner**, dob@temple.edu. Chemistry, Temple University, Philadelphia, Pennsylvania, United States*

Additives can change the rate and selectivity of an organometallic catalytic reaction, and gaining an understanding of these influences can help unlock new and useful synthetic protocols. Two recent examples will be described. In the first, a zwitterionic gold complex, itself competent for the selective hydration of internal alkynes, is found to be accelerated by silver salts, but with a concomitant loss in selectivity for internal vs. terminal alkynes. The second case is a palladium-catalyzed *N*-arylation of amides that undergoes significant acceleration upon the addition of metal triflate salts, allowing for good to excellent yields for a variety of aryl bromide and amide substrates.

MARM 462

C-H insertion mechanism for heme carbenes

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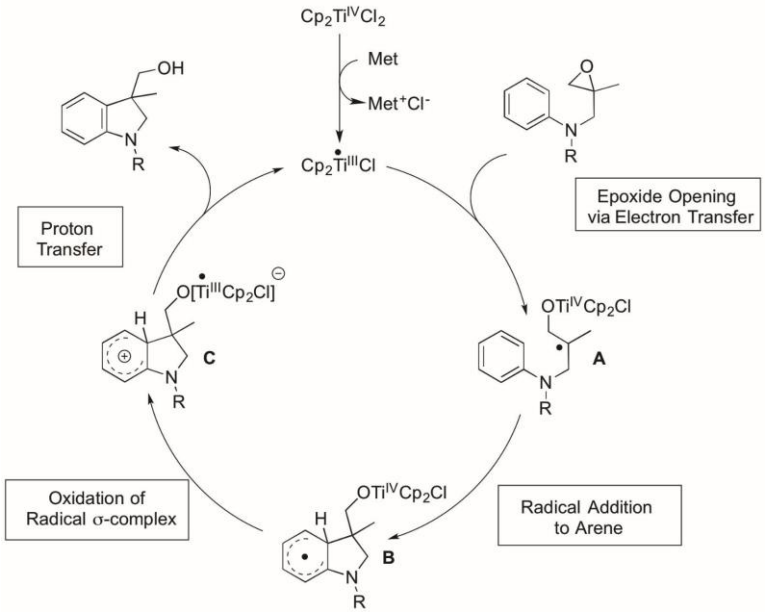
Recent experimental reports of heme carbene C-H insertions show promising results toward sustainable chemistry due to good yield and selectivity, low cost of iron, and low/no toxicity of hemes. But mechanistic details are largely unknown. Here we report some first mechanistic details. A systematic study of conformation and spin state effects reveals an Fe^{II}-based, hydride transfer, early transition state. A trend of broad range experimental C-H insertion yields (0-88%) of five different C-H bonds was well reproduced and found to originate from the hydride formation capability. Some useful geometry, charge, and energy parameters were reported for the first time to well correlate with barriers. Results suggest a key role of the formation of strong electrophilic iron porphyrin carbene in developing heme-based C-H insertion catalysts for sustainable chemical catalysis and biocatalysis.

MARM 463

Mechanistic study and development of catalytic electron transfer reactions

***Robert A. Flowers**, rof2@lehigh.edu. Lehigh Univ Dept of Chem, Bethlehem, Pennsylvania, United States*

The high degree of sophistication of modern redox-initiated organic reactions is based on the ability to efficiently manipulate and interconvert reactive intermediates such as anions, radicals, cations, and related radical ions through redox processes. Despite the utility of these reactions, chemists have a limited understanding of the important variables in complex reactions that proceed through single-electron reduction and oxidation. As a consequence, the development of efficient catalytic reactions based on these approaches has been limited. The studies presented in this lecture will focus on understanding, improving, and developing efficient catalytic methods based on important synthetic platforms that utilize single electron transfer as a critical step in bond-forming reactions.



MARM 464

Synthesis, characterization, and catalytic activity of aluminum-α-diimine complexes

***Christopher R. Graves**, cgraves1@swarthmore.edu. Chemistry & Biochemistry, Swarthmore College, Swarthmore, Pennsylvania, United States*

The development of new catalytic systems for small molecule transformations that employ non-precious metal complexes is a central challenge in chemistry. Aluminium is one of the most abundant elements in the earth's crust and at ~$2.00/kg, aluminum is ~$10^4$–$10^5$times less expensive than metals such as Pd, Pt, Rh and Ir. Aluminum is therefore an attractive choice for catalyst development because it is readily available, inexpensive, and non-toxic. However, aluminum chemistry has historically been defined by the stability of the +3 oxidation state. The lack of readily accessible multi-electron redox states for common aluminum complexes has limited the applicability of the metal as a catalytic species for processes that depend on oxidation/reduction. The development of aluminum coordination complexes implementing redox-active and non-innocent ligands aims to expand the tool-box of aluminum-based reaction chemistry.
We have been developing families of coordination complexes of aluminium with the classic redox-active ligands α-diimines. α-Diimine ligands of the type Ar-NC(Me)C(Me)N-Ar (Ar = substituted aromatic) were synthesized and their coordination chemistry to aluminum was investigated. Singly ((diimine^{1-})$AlCl_2$) and doubly ((diimine^{2-})AlCl(THF)) reduced a-diimine complexes of aluminium were prepared for ligands incorporating substitution in the *ortho* positions of the aromatic side groups. Aluminum complexes with a-diimine ligands lacking *ortho* substitution incorporated two ligands to give the neutral ligand complexes $[(diimine)_2AlCl_2][AlCl_4]$. All of the complexes were characterized by ^{1}H NMR spectroscopy, X-ray diffraction, and DFT. The redox behaviour of the complexes were investigated using electrochemistry and the cyclic voltamograms showed rich redox behavior. The catalytic activity of the neutral ligand complexes toward the epoxidation of alkenes by peracetic acid will be presented.

MARM 465

Recent advances in the development of Heck-like reactions using heteroatomic electrophiles

***Donald A. Watson**, dawatson@udel.edu. Chemistry/Biochemsitry, University of Delaware, Newark, Delaware, United States*

The discovery and development of Heck-like reactions using hetereoatomic electrophiles will be discussed. These transformations include Silyl-, Boryl-, and Aza-Heck Reactions, which allow for the construction of unsaturated, heteroatomic functional groups using simple alkene starting materials. Synthetic applications and current mechanistic understanding will be discussed.

MARM 466

Zwitterionic N-heterocyclic carbene gold catalyst in a silver-free alkyne hydration reaction with selectivity towards internal alkynes

***Kushan Weerasiri**[1], kcw0008@tigermail.auburn.edu, Graham Dobereiner[2]. (1) Temple, Philadelphia, Pennsylvania, United States (2) Beury Hall Room 344, Temple University, Philadelphia, Pennsylvania, United States*

Zwitterionic N-heterocyclic carbene gold catalyst [(BNHC)Au(SMe_2)] is reported to perform alkyne hydration in the absence of silver and Bronsted acid additives. The hydration shows good regioselectivity, and chemoselectivity towards internal alkynes. While [(BNHC)Au(SMe_2)] is active without silver additives, addition of a silver salt increases reaction rate and decreases selectivity for internal alkyne hydration over terminal substrates.

MARM 467

Synthesis of novel phosphine ligands with an imidazolium tether for use in biphasic reaction media

***Matthew E. Miller**, miller.matthew20@gmail.com, Christopher J. Parnell, Richard J. Rosso. Chemistry, St. John's University, Commack, New York, United States*

One of the most common methods of fine-tuning any catalytic reaction is to alter the ligands around the metal complex. Our laboratory is interested in investigating ligands that produce catalysts that increase catalytic activity and reactivity in biphasic organic/ionic liquid systems.

It has been shown in the literature that ligands having a positively charged moiety remain within the ionic liquid media better than their neutral and anionic analogs. However, the rate of these reactions is still slower than heterogeneous analogs, since much of the reaction chemistry only occurs at the interface between the ionic and organic phases. We have synthesized and fully characterized several imidazolium analogs of diphenylalkylphosphines with different carbon chain lengths between the phosphorus atom and the imidazolium group(s). The separation of the cationic group from the phosphine by a large carbon chain should promote self-

assembly of the phosphines into a micellar or monolayer structures at the interface of the biphasic organic/ionic liquid reaction media; increasing catalytic activity.

MARM 468

Size-dependent morphology of liquid-liquid phase separating aerosol

***Miriam Freedman**, maf43@psu.edu. Penn State, University Park, Pennsylvania, United States*

The chemical and physical properties of aerosol particles that determine their impact on climate are determined in part by their composition, size, shape, and morphology. We have characterized the morphology of submicron aerosol particles composed of organic compounds mixed with ammonium sulfate using cryo-transmission electron microscopy. Particles are made under ambient conditions without the influence of a substrate. Our results for the O:C ratio of the organic compound needed for phase separation to occur are consistent with previous results on supermicron particles. Surprisingly, however, the morphology of some systems is dependent on their size, where small particles are homogeneous and large particles are phase separated. The size at which particles transition from homogeneous to phase separated depends on the drying rate. Even at the slowest drying rates, however, the size dependence is observed, where particles less than approximately 30 nm are homogeneous. This result suggests that the size dependence of the morphology is a consequence of a confinement effect in atmospheric particles, rather than due purely to kinetics. In addition, we unexpectedly observed that the size dependence is a function of the organic to sulfate ratio, where for some compositions, phase separation occurs at all sizes, and at others, phase separation only occurs for larger particles. This result is explained by the mechanism of forming a two-phase system. The size dependence is present for systems that separate through the activated process of nucleation and growth, and absent for systems that separate spontaneously through spinodal decomposition. Finally, we have demonstrated that cloud condensation nucleus activity is dependent on the particle morphology. Phase separated particles with partially engulfed morphologies have the same activation diameter as ammonium sulfate, whereas homogeneous particles have an activation diameter between that of the salt and organic compound. This result indicates that morphology of particles can impact their ability to form cloud nuclei, and therefore affect climate.

MARM 469

Role of coating-surface interactions in controlling the mixing state and morphology of soot nanoparticles

***Alexei Khalizov**[1,2], khalizov@njit.edu, Chao Chen[1], Ogochukwu Enekwizu[2,1]. (1) Chemistry and Environmental Science, New Jersey Institute of Technology, Newark, New Jersey, United States (2) Chemical, Biological, and Pharmaceutical Engineering, New Jersey Institute of Technology, Newark, New Jersey, United States*

Atmospheric aerosols have a very high surface-to-volume ratio when compared to other environmental surfaces. The interactions of aerosol surfaces with trace gas molecules play a major role in modifying both gas-phase and particle compositions in the atmosphere. This presentation will focus on the interaction between condensable vapors and soot nanoparticles, which are fractal aggregates of graphitic spheres that can be mixed with organic and inorganic materials. The morphological and chemical complexity of soot nanoparticles is caused by diverse emission sources and further amplified by aging transformations in the environment. The mechanistic details of these transformations, including the formation of specific mixing states and the extent of morphological changes from the condensation of different chemical compounds will be discussed in connection with current pressing needs to determine the mechanism and timescale of soot aerosol aging, and evaluate associated changes in cloud-forming and optical properties of soot particles. An understanding of soot aging is crucial to reducing uncertainties in climate prediction because soot from incomplete combustion of fossil fuels is a significant contributor to direct climate forcing.

MARM 470

Ions and the ultrafast vibrational spectroscopy and dynamics at mineral-aqueous interfaces

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Interfacial water structure, which can be probed by vibrational sum-frequency generation (vSFG) spectroscopy, is key to many processes. Time-resolved vSFG shows that in the absence of surface charge (pH 2), water at silica surfaces exhibits significantly slower OH stretch vibrational relaxation (~600 fs) compared to bulk. However, at charged silica surfaces (e.g., pH 6), bulk-like fast dynamics (~200 fs) are observed at low ionic strength. This decelerates to ~600 fs, with the addition of NaCl. In parallel, vSFG results demonstrated that silica interfacial water structure is most sensitive to cations at pH=6-8. Consequently, it is unclear whether the observed slowing of the vibrational dynamics is due to the reduction in Debye length, or because of changes in the local hydrogen bonding environment caused by the electrolyte and how this might depend on the identity of the ions. Additional

spectroscopic and time-resolved vSFG experiments on aqueous Al_2O_3 interfaces shed light on the ongoing debate on the role of ions in interfacial water structure and whether the observed behavior is specific to silica/water interfaces or can be generalized to other systems.

MARM 471

Structure and energetics of the Stern layer at mica-water interfaces

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The screening of surface charge by dissolved ions at solid-liquid interfaces—in the region of interfacial fluid known as the electrical double layer (EDL)—plays a recurrent role in surface science, from ion adsorption to colloidal mechanics to the transport properties of nanoporous media. A persistent unknown in theories of EDL-related phenomena is the structure of the Stern layer, the near-surface portion of the EDL where water molecules and adsorbed ions form specific, short-range interactions with surface atoms. Here, we describe a set of synchrotron X-ray reflectivity (XRR) experiments and molecular dynamics (MD) simulations carried out in identical conditions, for a range of 0.1 M alkali chloride (Li-, Na-, K-, Rb-, or CsCl) solutions on the basal surface of muscovite mica, a mineral isostructural to the phyllosilicate clay minerals and one of the most widely-studied reference surfaces in interfacial science. Our XRR and MD simulation results provide a remarkably consistent view of the structure and energetics of the Stern layer structure, with some discrepancy on the fraction of the minor outer-sphere component of Rb. The results of both techniques, along with surface complexation model (SCM) calculations, provide insight into the sensitivity of water structure and ion adsorption to surface topography and the type of adsorbed counter-ion.

MARM 472

Effect of water on the adsorption of CO2 on kaolinite and montmorillonite

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The presence of water molecules, modeled explicitly with Density Functional Theory, leads to significant differences in ΔGads of CO2 on mineral surfaces. The outcomes depended strongly on the clay model (montmorillonite or kaolinite) and on the initial adsorbate-substrate cluster. Small differences in the initial geometry did not produce much change in the adsorption of CO2 on kaolinite, which remained unfavorable, but significantly changed the interaction of this adsorbate with Na-montmorillonite with outcomes as different as physisorption and mineralization. The vibrational frequencies for adsorbed CO2 were compared to experimental data and to calculations in the literature using Molecular Dynamics simulations.
Energy scans for the adsorbate moving away from the surface were performed to determine the activation energy and the rate constant of adsorption, finding a strong dependence on the position and nature of the surface complex as well as the number and distribution of the water molecules with respect to the surface.

MARM 473

Symmetry breaking and photocatalysis of nitrate on TiO_2: Effect of coadsorbed water

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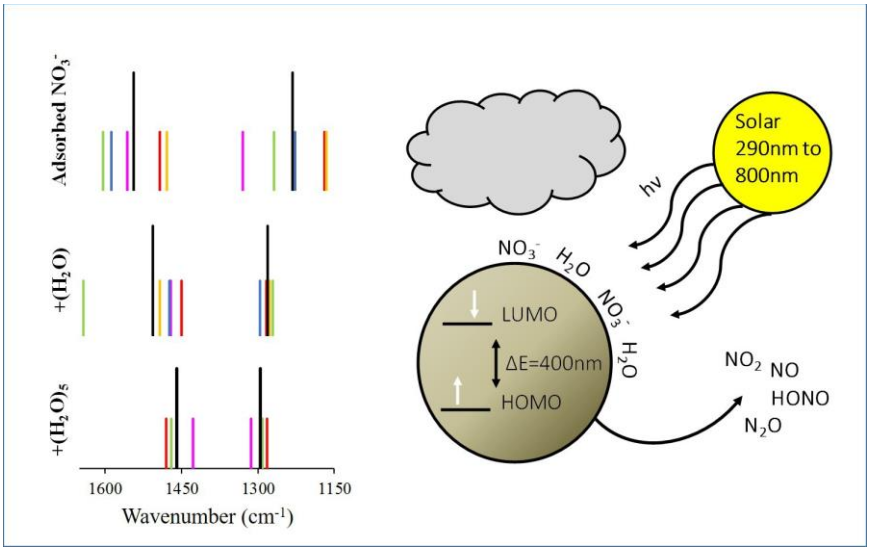
Titanium Dioxide (TiO_2) is a semiconductor component of atmospheric aerosols with a bandgap within the spectral region of solar radiation. Therefore, sunlight photoexcitation can lead to an electron-hole pairs, which can initiate redox reactions on the TiO_2 surface. For instance, the photochemistry of chemisorbed nitrate on TiO_2 has been shown to produce nitrogen oxides (NO_x), HONO and N_2O. In this work, we use vibrational spectroscopy and quantum chemical calculations to investigate the effects of water in the nitric acid coordination onto TiO_2 and its photochemical reaction. Optimizations of chemisorbed nitrates yield several distinct structures in which nitrate losses its D_{3h} symmetry. Our calculations show that, by adding co-adsorbed water to simulate the deliquescent layer of an aerosol particle, the frequencies and bond angles of surface nitrates become more consistent with that of partially solvated nitrate ions. In addition, the investigation of the effect of co-adsorbed water on the photocatalytic degradation of adsorbed nitrates shows no effect on the reaction yield. However, the lower nitrate coverages due to surface water leads to a decrease in the heterogeneous photochemical kinetic constant. Finally, the impact on the co-adsorption of water on the nitrate surface reactions will be discussed in terms of the overall effects on the heterogeneous formation of gaseous products.



MARM 474

Anthracene and pyrene photolysis kinetics in aqueous, organic, and mixed aqueous-organic phases/interfaces

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Phase-separated organic-aqueous mixtures often exist in environmental particulate matter. Many organic compounds are surface-active, and aqueous particulate matter is often coated with monolayers or multilayers of OM. These coatings may provide distinct microenvironments to which PAHs can partition, and in which reactivity may differ from that in the dominant phase. Organic monolayers enhance the surface activity of PAHs in aqueous solution, and heterogeneous ozonation kinetics of PAHs at organic-coated water surfaces can be quite different from those at pristine water surfaces. The potential effects of these organic coatings on PAH photolysis kinetics have not been reported. We have elucidated which factors (e.g. polarity and singlet oxygen concentration) most strongly affect kinetics; determined whether photolysis kinetics in homogeneous organic-aqueous solutions (such as fog and cloud droplets) can be accurately predicted by OM content or some other variable (such as polarity); and have determined the effects of organic monolayers and macroscopic organic phases on PAH photolysis in atmospheric particulate matter such as aqueous-organic aerosols with core-shell morphology. The implications of this work extend beyond atmospheric aerosols to other environments in which aqueous-organic mixtures exist, such as surface waters containing high OM loadings, and ocean surfaces in the presence of organic coatings such as sea-surface microlayers or oil slicks.

MARM 475

Heterogeneous ozonolysis of organic adsorbed on mineral aerosol surfaces

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Atmospheric mineral aerosol provide unique solid-air interfaces on which trace gases such as ozone and volatile organic compounds (VOCs) can react. Prior work has shown that the heterogeneous decomposition of ozone on mineral aerosol decreases with increasing relative humidity due to adsorbed water blocking reactive surface sites. We measured reactive uptake kinetics for ozone decomposition on kaolinite – a representative clay mineral substrate – as a function of relative humidity following pre-exposure to volatile organic compounds including limonene, a-pinene, and catechol. Surface adsorbed organic products were characterized using condensed-phase infrared spectroscopy and GC-MS analysis. The concentration of surface adsorbed organics decreased with increasing relative humidity. At 25% RH, the presence of surface adsorbed organics increased ozone decomposition by two orders of magnitude. The atmospheric implications of mineral-adsorbed organics will be discussed.

MARM 476

Role of the gas-particle interface in the multiphase chemical oxidation of atmospheric organic aerosol

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During atmospheric transport aerosol particles can undergo chemical modification by reaction with gaseous oxidants such as OH and NO_3 radicals. Multiphase chemical oxidation reactions between organic aerosol (OA) particles and oxidants can impact source apportionment, air quality, and the particles' potential to act as cloud condensation nuclei (CCN) and thus climate. A large fraction of the ambient aerosol is organic in nature. However, environmental conditions such as temperature and humidity affect the phase state of the OA particles. Amorphous OA can manifest various phase states such as liquid, semisolid, and solid modulated by ambient conditions, thereby affecting particle viscosity and its interfacial properties. The impact on particle phase and thus interface will in turn affect the oxidation reaction kinetics and resulting particle hygroscopicity. We present experimental results of the OH oxidation of amorphous fulvic acid (FA) aerosol particles at different temperatures and phase states. When oxidized at low temperature in a glassy solid state, the hygroscopicity of FA particles increased significantly. Low-temperature oxidation appears to proceed dominantly at the particle interface, instead of the bulk, promoting the formation of highly-oxygenated particle-bound fragmentation products, which decreases particle molar mass and increases hygroscopicity. To improve our fundamental understanding of multiphase chemical kinetics, we theoretically evaluate the adsorption of gas species on the condensed phase, with a particular emphasis on the impact of temperature on species desorption lifetimes and its influence on the overall reactive uptake process. We apply model-derived sensitivity studies that account for second order surface layer reactions at the interface and changes in desorption lifetimes due to variation in temperature. Lastly, preliminary reactive uptake experiments for temperatures as low as -60 °C will be presented. A detailed understanding of the individual processes governing multiphase chemical kinetics is important for predictive understanding of air quality, health, and climate related issues.

MARM 477

Polymerization of chloroethyl methacrylates: Chain transfer and the carbon-chlorine bond

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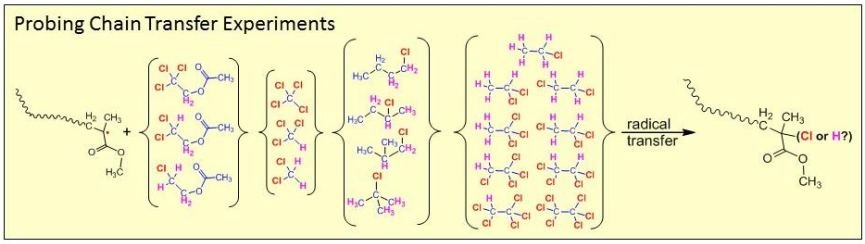
When incorporated into a solvent, the chlorine substituent greatly enhances the range of dissolvable solutes. A similar desirable effect was envisioned for enhancing homogeneous blend formation of methacrylate polymers with other melt-processable polymers toward an application where a refractive index gradient in optical lenses would be fabricated by co-extrusion of compatible polymers. The initial objective of this work was to systematically prepare and evaluate polymers from the monomer series $CH_2=C(CH_3)C(O)OCH_2CH_{3-n}Cl_n$, n = 1,2,3. Two unexpected findings resulted: (1) each monomer produced a crosslinked polymer; (2) the respective crosslink density correlated with the degree of chlorine substitution in the order n=1 > n=2 > n=3. This chlorine substituent effect was investigated by correlation with chain transfer constant measurements on four series of chloroalkyl compounds (depicted below: chloroethyl acetates ($CH_3C(O)OCH_2CH_{3-n}Cl_n$, n = 1,2,3); chloromethanes ($CH_{4-n}Cl_n$, n = 2,3,4) and CD_2Cl_2 and $CDCl_3$ analogs; butylchloride isomers (*n*-, *iso*-, *sec*-, *tert*-) and *tert*-C_4D_9Cl analog; and nine chloroethanes ($C_2H_{n-6}Cl_n$, n = 1-6)) in a methyl methacrylate polymerization. The pattern conveyed by the chain transfer constants and deuterium isotope effects is consistent with a vicinal chlorine effect (i.e. chlorine activation of a vicinal hydrogen for abstraction) to account for the relative chain transfer activities in the four series of model compounds and for the propensity of the chloroethyl methacrylates to crosslink in a bulk free radical polymerization.



MARM 478

Chemistry of high-performance waterborne coatings with improved eco-footprint through the use of self-assembled polymer pigment composites: Chemistry that is truly around us

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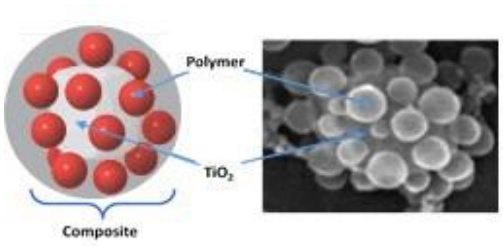
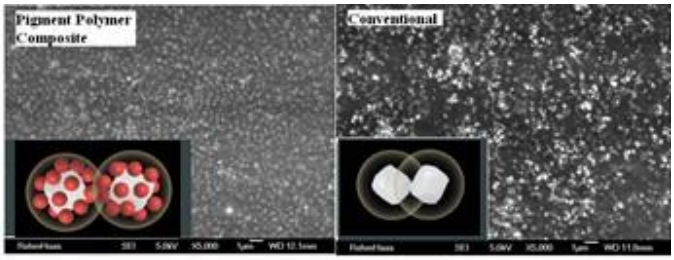
Many people take the coatings around us for granted, not considering the advanced chemistry in a can of paint. In reality waterborne coatings are complex and dynamic multiphase systems, providing critical protection to substrates as well as improved their aesthetics and produced on a massive scale. In the United States approximately 700 million gallons of house paint are produced each year. The environmental impact of these paints has been reduced consistently since the 1940's when up to 70% of the mass of paint applied could be released into the atmosphere as volatile organic compounds (VOC). Far from the solvent borne paints of the past, many waterborne architectural paints of today are Low or Ultra-Low VOC (Often containing <5g VOC/Liter of paint). The performance of these modern waterborne coatings is provided by careful polymer design. The continuous phase of a latex paint is typically a polymer which must coalesce from a dispersion of roughly 150 nm polymer particles under a range of conditions (found in an on your house). These materials are designed to provide a tough film with resistance to stains, mechanical abrasion, UV and other challenges. The polymeric binder also needs to provide adhesion and facilitate a good pigment dispersion. This performance is provided by advanced morphology as well as chemistry such as ambient cure, adhesion promoting monomers, and others. Opacity of this thin film is critical and is typically delivered by 270 nm particles of synthetic rutile TiO2, the performance of which are strongly impacted by dispersion quality. These chemistries as well as the development of commercially successful discrete self-assembled polymer pigment composites and their impact to performance and eco-profile will be discussed.





MARM 479

Conformational study of solvated polyethylene glycol 2000: A molecular dynamics study

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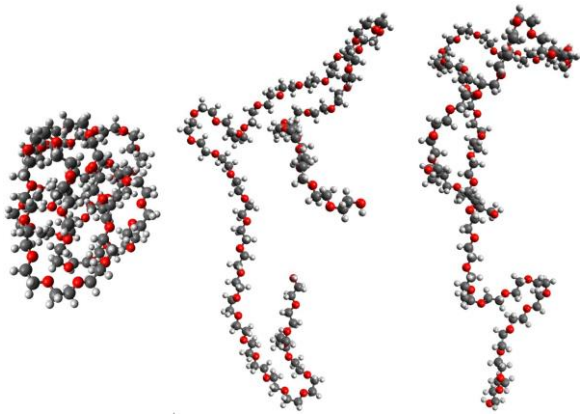
Molecular dynamics simulations of polyethylene glycol (PEG) with molecular weight of 2000 daltons solvated in various solvents were performed with the goal of studying the evolution of the molecular structure as a function of the solvent type. Water, water with 4% ethanol, and ethyl acetate were selected as solvents commonly used in experiments of asymmetric nanoparticles decorated by PEG motifs. The molecular force field used was gromos54A7 in explicit solvents. The PEG chain is very flexible and the polymer undergoes coiling collapsing into a spherically looking structure. The PEG polymeric chain prefers a highly-coiled conformation in water at ambient conditions, reaching this state in approximately 3 ns. PEG in water with 4% ethanol behaved similarly, but the time for the formation of the coiled-like spherical structure was 1-2 ns longer. PEG in ethyl acetate did not form a compact coiled structure. Instead, the polymer displayed a tendency for extending and bending back from the terminals in a process that took 20-30 ns. Inspecting the energies, the radius of gyration, end-to-end distance, orientation order parameter, a principal component analysis showed two distinct structural states in water and in water with 4% ethanol in which the coiled polymer tends to form or not to form hydrogen bonds. The structural evolution in ethyl acetate was more complex, giving rise to a sequence of conformations characterized by different foldings at the chain ends. Elucidation of the PEG structural behavior as a function of solvent will help interpreting the different types of motifs formed on asymmetric nanoparticles used in various medical applications.



Typical structures of polyethylene glycol 2000: PEG in water (left) and PEG in ethyl acetate at two different simulation times (center and right). Not shown, PEG in water with 4% ethanol is visually similar to the structure in water.

MARM 480

Rheological and application properties of non-drip paints

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Paint is a very common yet complex fluid that is required to exhibit a wide variety of chemical and rheological properties in order to meet the needs of the consumer. A good paint may be described as one that applies easily to a vertical substrate and, once dry, maintains itself through typical wear and tear; however, this simple qualitative description is actually a multifaceted quantitative problem for paint manufacturers and raw materials suppliers. Market focus, government regulations, and desired paint properties also vary across different countries, which lead to different paint chemistries and testing protocols for each new product development. This talk will focus specifically on non-drip or thixotropic paints, detailing the additional rheological properties needed to achieve a pudding-like substance that otherwise behaves like a traditional paint. The ingredients within a can of paint that contribute to its application properties is also discussed, with an emphasis on the range of tests used to classify paint appearance (gloss and color), stability, and resistance to weathering, abrasion, and household stains (i.e. coffee, crayons, etc.). Overall, the goal of this session is to inform consumers of the development process behind architectural coatings and to provide insight on the technology contained within a can of paint.

MARM 481

Photoactivated shape changing polymer 4D printing system for flexible actuators

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Current 3D printing technology can print objects with a multitude of materials; however, these objects are static, geometrically permanent, and not suitable for multi-functional use. 4D printing is an emerging additive manufacturing technology that combines 3D printing with smart materials. The 4D printed objects can change their shape over time (4^{th} dimension) by applying heat, pressure, magnetic field, or moisture to the smart materials. 4D printing with a light responsive shape-changing material is beneficial because light is wireless, easily controllable, and causes a rapid shape change of the smart material. Herein, we present several polymeric bilayer actuators fabricated by 4D printing which can reversibly change their shape upon exposure to light. The photoactive layer consists of a newly synthesized linear azobenzene polymer which was printed onto several different support layers to achieve these bilayer actuators. An investigation of the optical and mechanical properties they possess has allowed us to better understand the photomechanical behavior of these devices. This knowledge will enable us to design and fabricate more complex devices and extend their use to applications such as unmanned aerial vehicles, artificial muscles, and biomedical drug delivery platforms.

MARM 482 Withdrawn

Developing an *a priori* metric of triplet separation during singlet fission with density functional theory

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Singlet fission is a promising photophysical process for improving the efficiency of organic optoelectronics, and only recently have the reaction steps of singled fission leading to triplet pair separation been experimentally confirmed. However, there has yet to be a unified description of the mechanism responsible for and indicators of efficient triplet separation. By tracking triplet population dynamics in isolated polymorphs of solution cast 6,13-bis(triisopropylsilylethynyl) pentacene (TIPS-Pn), we found strong evidence for triplet excitation energy transfer as a dominant mechanism for triplet separation. Taking a structural approach to the observed differences in triplet dynamics, the lattice parameters determined for each polymorph enable modelling of TIPS-Pn π-π stacking distance and lateral slip. With models for each processing condition, triplet transfer integrals calculated using density functional theory provide a straightforward metric to evaluate the relative rates of triplet excitation energy transfer between polymorphs. From the results of the model system TIPS-Pn, we propose a generalized method to screen packing motifs of polymorphs of singlet fission materials.

MARM 483

Dual affinity solid-binding peptides for nanoscale organization of Li-ion battery cathode materials

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Recent advances in Li-ion battery performance through the introduction of nanoscale materials into the composition of anode or cathode allow to achieve higher energy storage capacity and energy density owing to faster electronic and ionic transfer and large surface area of electrodes for electrode/electrolyte interactions. But there is a need to develop new methodologies that will allow precise control over the assembly of nanostructured electrodes in order to improve their electrochemical stability and cyclability for the system. Fabrication of nanostructured electrodes through biotemplating presents a novel, cost-effective, and eco-friendly approach, which will allow for precise control over arrangements of active materials into highly organized architectures at the nanoscale, as well as close contact between combined electrode materials with synergistic properties. Specifically, I work on a peptide-templated approach for assembly of heterofunctional cathode materials, which include electroactive material, conductive material, and binder. Using phage display library, I have isolated solid binding peptides (SBP) that have an affinity for one of the promising high-voltage cathode materials $LiNi_{0.5}Mn_{1.5}O_4$ (LMNO). SBP for electroactive material is combined with SBP for multiwall carbon nanotubes (MWCNTs), which are known to improve conductivity of Li-ion battery electrodes, into one multifunctional polypeptide. Our preliminary data indicates that the cathode materials assembled with dual-affinity polypeptide and tested with Li-foil as negative electrode exhibited a decrease in charge transfer resistance, as well as an increase in higher specific capacity during the initial cycles. The research in progress is focused on finding the strongest binding peptides and optimization of system parameters for cathode assembly. Potentially, fabrication of nanostructured electrodes through biotemplating with multifunctional peptides will impart specificity for the target materials, offer a morphological stability for system, and improve cyclability at high discharge rates.

MARM 484

Development of fluorescent and ^{18}F labeled PARP targeted molecular imaging agents

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PARP1 is an enzyme that plays an important role in DNA damage response (DDR) and has been shown to be integral for the maintenance of the genomic integrity for certain types of highly proliferative cancer cells. This reliance on PARP1 has lead to the development of several therapeutic inhibitors, two of which have recently been approved by the FDA for treatment of late stage ovarian cancer. Cancer cells reliant on PARP1 also show much higher expression of the enzyme, which has lead to much interest in the development of PARP1 targeted molecular imaging agents. PARP1 imaging agents have many potential applications including therapeutic drug development in the preclinical setting and patient stratification and treatment monitoring in the clinical setting. The studies presented here follow the development of molecular imaging agents based on olaparib, one of the two FDA approved therapeutic inhibitors, culminating in the fluorescently labeled optical imaging agent PARPi-FL, and the ^{18}F labeled PET imaging agent, [^{18}F]PARPi.

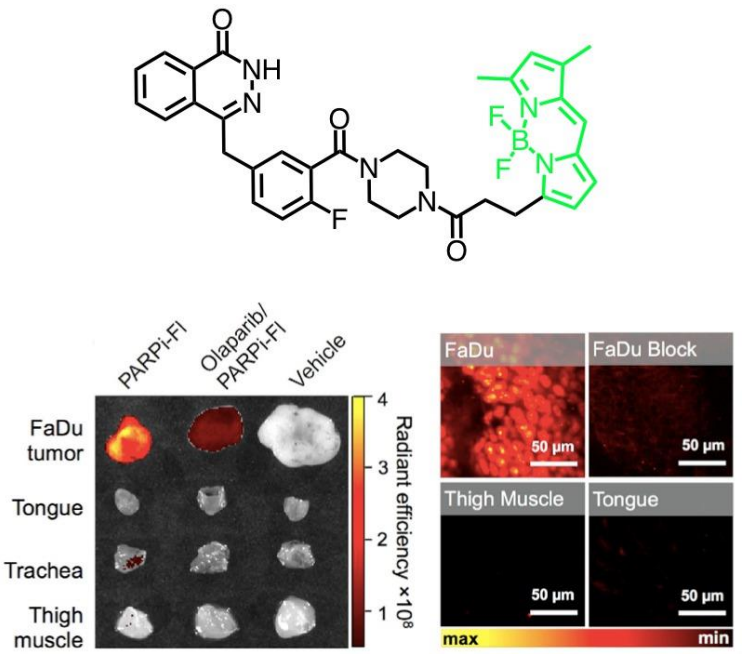

Figure 1. PARPi-FL in FaDu oral cancer squamous cell carcinoma xenografts (OSCC). Top: Structure of PARPi-FL with fluorescent modification in green. Bottom right: whole tissue epifluorescence images. Bottom left: Confocal images of freshly excised tissues.

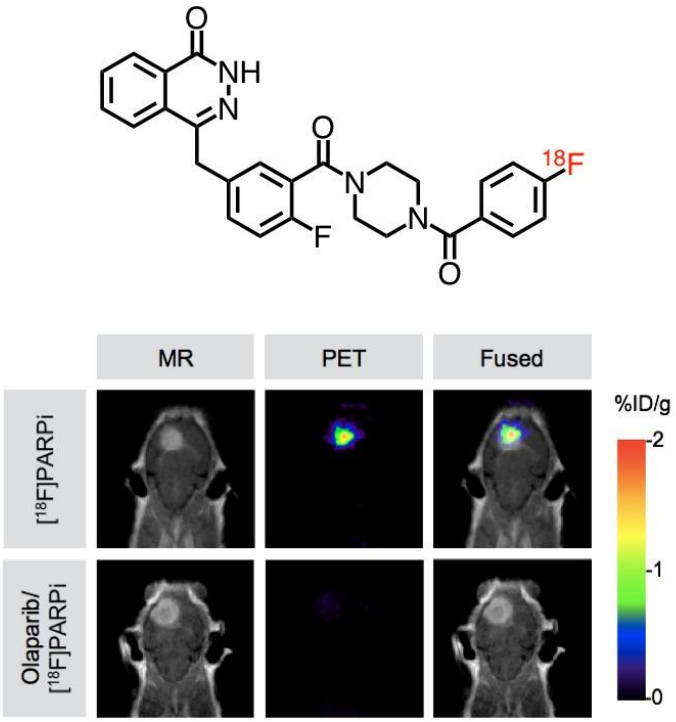

Figure 2. [^{18}F]PARPi in U251 MG glioblastoma multiforme xenografts (GBM). Top: Structure of [^{18}F]PARPi with PET active modification in red. Bottom: PET/MR images of orthotopic GBM model.

MARM 485

Bifunctional chelators: The link between radiometals and radiopharmaceuticals

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Radiometals represent a wide array of radionuclides with decay characteristics well suited to both imaging and therapeutic applications. However, to incorporate these atoms into robust radiopharmaceuticals requires well thought out inorganic chemistry tailored to the individual metal's chemical properties. Therefore, an appropriate metal chelator must be selected based on the desired radiometal. In most cases, a bifunctional chelator is utilized to both bind the radiometal in question and to attach it to a targeting vector of some kind. A number of factors go into deciding the appropriate bifunctional chelator including consideration of both the metal binding properties and the conjugation functionality needed for a specific application. On the chelation side, consideration must be given to the denticity, cavity size, and type of donor groups of the ligand portion of the molecule so that they best match the properties of the radioactive metal cation. On the linker side, attention must be paid to the type of targeting vector desired and the selection of the appropriate coupling chemistry. Both of these components are crucial for attaining a sufficiently stable radiopharmaceutical, in that the radiometal must be tightly bound to the chelator but also that the chelator must remain attached to the drug conjugate. For many common radiometals, the question of ligand choice has largely been settled already, but for some lesser used or up-and-coming radiometals, further research and development is still needed to find the ideal metal-ligand pair. An overview of currently used radiometal-chelator pairs will be given and the process of developing and evaluating a novel chelator will be discussed specifically in reference to zirconium-89.

MARM 486

More efficient reagent for the site-specific modification of proteins and peptides with radiometal chelators

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Site-specific bioconjugation techniques are becoming increasingly popular for the synthesis of immunoconjugates for molecular imaging and therapy. Traditional, random bioconjugation techniques risk blocking the variable region on an antibody, thereby impeding its binding to the antigen. In contrast, site-specific bioconjugation approaches eliminate this issue and provide homogenous species as well, increasing the reliability of data.

One of the more common approaches to site-specific bioconjugation involves the modification of naturally occurring cysteine residues or engineered thiols within antibodies. In order to do this, maleimides are typically used due to the effective Michael addition between thiols and the alkene bond of the maleimide. This coupling is not ideal, however, because the maleimide-thiol linkage is not completely stable under physiological conditions. This instability allows the linkage — along with the radiometal — to exchange with competing endogenous thiols, leading to the accumulation of radioactivity in nontarget organs.

The Barbas Laboratory recently developed phenyloxadiazolyl methylsulfone (PODS) as an alternative to maleimides. This molecule reacts efficiently with thiols, forming a linkage that is more stable under physiological conditions than maleimide-thiol conjugates. Yet four years after the first report, the PODS reagent is still very scarcely used for bioconjugation compared to maleimides. We believe this is because PODS is not commercially available and is relatively difficult to synthesize.

In order to remedy this situation, we have developed a simpler and more accessible synthesis to an analogue of the originally-reported PODS reagent. This method involves a commercially available oxadiazole, minimal use of chemistry equipment, and does not require HPLC purification. With this analogue, we have been able to synthesize two bifunctional PODS-bearing chelators for radiometals: PODS-DFO for ^{89}Zr and PODS-CHX-A″-DTPA for ^{177}Lu. By coupling our PODS reagent with a fluorophore, we were also able to confirm that this molecule can be used for the functionalization of immunoglobulins.

We believe that this method will make the synthesis of this PODS analog more accessible than the original compound, providing biologists and radiochemists better reagents for the synthesis of labeled site-specific immunoconjugates.

MARM 487

Radiometals in imaging and therapy: The Cardinal Health perspective

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Radioisotopes of metallic elements play an increasingly important role in medicine as a component of radiopharmaceuticals used in diagnostic imaging and cancer therapy applications. These radiopharmaceuticals use radiometals selected for their physical properties and availability and are typically incorporated into chelate complexes that allow the combination of the radioisotope with a delivery molecule for transport to the desired target. The chemistry of these metal ion-chelate complexes is driven by the requirement that they are both easy to form and biologically stable. The development of radiometal-based radiopharmaceuticals follows the same clinical trials and regulatory approval processes required for all new drugs. The part that Cardinal Health plays in this development process is not to invent drugs but rather to partner with those who have promising new drug candidates; Cardinal will manufacture and distribute these radiopharmaceuticals so they are available for clinical trials and commercialization. Examples of radiometal-based pharmaceuticals that are of interest to Cardinal Health will be presented.

MARM 488

Impact of FcγRI receptor binding on immunoPET imaging

Cindy Rodriguez[1]*, cindy.rodriguez54@myhunter.Cuny.edu, Delphine Vivier*[1]*, Sai Sharma*[2]*, Pierre Adumeau*[1]*, Brian Zeglis*[3,2]*. (1) Chemsitry, Hunter College, New York, New York, United States (2) Radiology, Memorial Sloan Kettering Cancer Center, New York, New York, United States (3) Ph.D. Program in Chemistry, Graduate Center of the City University of New York, New York, New York, United States*

While antibodies have proven extremely effective vectors for the delivery of diagnostic and therapeutic radioisotopes to tumors, high radiation doses to non-target tissues and poor tumor-to-background activity concentration ratios are major clinical limitations of radioimmunoconjugates. One cause of the accumulation of radioimmunoconjugates in healthy tissues, especially in the spleen and liver, is the sequestration of radiolabeled antibodies by immune cells bearing FcγRI receptors that selectively bind the Fc region of the immunoglobulin. The conformational state of the Fc region is crucial to the interaction with the FcγRI receptor and is indirectly controlled by the heavy chain glycans, a pair of biantennary sugar chains appended to the C_H2 domain of the Fc region. By modifying these sugars, the conformation of the Fc region can be changed into a closed state that impairs FcγRI receptor binding, leading to an 'immune silent' immunoconjugate. Thus, we presuppose that safer and more sensitive immunoPET agents can be obtained from the elimination or reduction of these Fc/FcγRI interactions.
In this investigation, five different trastuzumab-based immunoconjugates bearing altered heavy chain glycans were synthesized and characterized. The ability of these constructs to bind the HER2 antigen was confirmed via flow cytometry experiments with HER2-positive BT474 cells. *In vitro* ELISA tests were used to compare the binding of the conjugates to both human and murine FcγRI receptors. As previously reported, deglycosylation decreases the Fc/FcγRI interaction. Interestingly, site-specific labeling on the heavy chain glycans seems to have the same effect, even if most of the glycans are conserved (^{ss}Tras-DFO$_{\beta G}$). These results were confirmed via *in vitro* binding assays using human and murine macrophages.
Ultimately, combining deglycosylation and site-specific modification (^{ss}Trast-DFO$_{ES}$) could be an effective way to obtained well-characterized immunoconjugates with attenuated Fc/FcγRI interactions. *In vivo* PET imaging studies in healthy and tumor-bearing mice are forthcoming and will allow us to evaluate the impact of this reduced binding on cancer imaging.

MARM 489

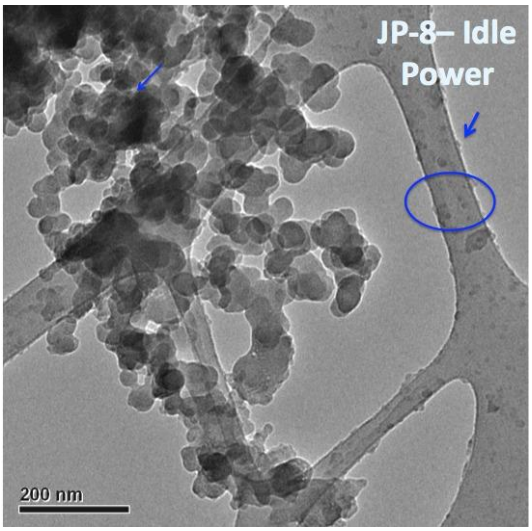
Airport air: What are we breathing?

Randy L. Vander Wal[2,1]*, ruv12@psu.edu, Chung-Hsuan Huang*[2,1]*, Madhu Singh*[2,1]*. (1) Dept. of Energy and Mineral Engineering, Penn State University, University Park, Pennsylvania, United States (2) The EMS Energy Institute, Penn State, University Park, Pennsylvania, United States*

There have been relatively few studies of aircraft and ground support equipment on airport and regional air quality. Transmission electron microscopy (TEM) of jet exhaust particulate matter can provide direct measures of particle size and their change with respect to engine power. Of particular concern are the innumerable small particles produced at idle conditions. Such particles of < 20 nm size can easily reach the deepest recesses of the lung, the alveoli. As the power changes, so too does the particle crystallinity.

Complementing TEM for particle physical size and nanostructure characterization is X-ray Photoelectron Spectroscopy (XPS) for measuring particle surface chemistry, specifically oxygen functional groups such as

phenolic (-OH), carbonyl (-C=O) and carboxylic (-COOH). XPS has also revealed a surprising content of heteroelements including Ti, Ba, Co, Fe etc. at levels of tenths of atomic percent and higher. Particle size, crystallinity and composition each bear health implications for aircraft PM.



TEM image of jet engine soot captured on a lacy grid, under idle power conditions.

Picture of DC-8 aircraft with CFM-56-2C model engines.

MARM 490

Salinity effects on metals desorption in urban streams

Michael D. Kilmer[2]*, michael.d.kilmer@gmail.com, Kristin Kramer*[2]*, Erica R. McKenzie*[1]*. (1) Civil & Environmental Eng., Temple University, Philadelphia, Pennsylvania, United States (2) Civil & Environmental Engineering, Temple University, Nicholson, Pennsylvania, United States*

Soils are exposed to varying levels of salinity from natural conditions (e.g., tidal behavior) or elevated levels caused by human activity (e.g., deicing activities). Urban streams in Philadelphia are exposed to runoff with high salinity levels in the winter months from road salt and brine applications. Additionally, the Delaware River has tidal influences where salinity is variable based on the freshwater discharge into the river.
Batch studies were conducted with four Philadelphia riverine sediments with synthetic surface water; various desorption models were evaluated for best fit. The metals of interest include: cadmium, nickel, cobalt, copper, arsenic, strontium, barium, lead, aluminum, and vanadium. Preliminary results from the first site show that cadmium, nickel, cobalt, copper, arsenic, strontium, and barium have increased desorption with increasing salinity. Lead, aluminum, and vanadium exhibited the opposite trend. All the metals also appear to have two prominent regions of desorption with a rapid initial phase followed by a slow phase until equilibrium is reached. The total metals concentration of strontium and barium were drastically increased from the zero salt condition to the maximum of 17 g/L (2.5XSr, 9XBa). None of the metals exceeded the EPA's listed regulations and recommendations for human and aquatic health, but this data for the first soil was the least impacted by urbanization and industrial activities.

MARM 491

Novel putative propane monooxygenase initiating metabolism of 1,4-dioxane

***Mengyan Li**, mengyan.li@njit.edu, Daiyong Deng, Fei Li. New Jersey Institute of Technology, Newark, New Jersey, United States*

1,4-Dioxane (dioxane) is a groundwater contaminant of emerging concerns given its carcinogenic potential and widespread occurrence. To date, there are more than ten bacterial species that have been isolated to be capable of utilizing dioxane as the sole carbon and energy source. However, tetrahydrofuran (THF) monooxygenase is so far the only group of bacterial enzymes that have been well characterized and studied due to their critical role in initiating the oxidation of dioxane and other cyclic ethers. The gene cluster *thmADBC* encodes four components of the THF monooxygenase. Recent studies demonstrated *thmADBC* is absent in many newly isolated dioxane degraders, which represents a knowledge gap to uncover novel enzymes/genes involved in the biodegradation of dioxane. In this study, we sequenced the genome of *Mycobacterium dioxanotrophicus* PH-06, a bacterial strain exhibiting superior degradation kinetics and affinity towards dioxane. Whole genome sequence using PacBio RS II long-read sequencer unveiled the existence of a novel putative propane monooxygenase gene cluster (*prmABCD*), exhibiting a high similarity to different soluble di-iron monooxygenase genes found in (hydrocarbon-degrading) *Rhodococcus wratislaviensis* IFP2016 (89%) and *Mycobacterium chubuense* NBB4 (87%). Both mRNA sequencing and Reverse Transcription Quantitative PCR (RT-qPCR) analysis have indicated that all four components of this *prmABCD* gene cluster were upregulated when fed with dioxane in comparison with glucose or acetate as the negative control. Furthermore, dioxane biotransformation capability of this putative propane monooxygenase was confirmed in *Mycobacterium smegmatis* mc^2 155 cells heterologously expressing the PH-06 *prmABCD* gene cluster. The expression clones harboring *prmABCD sustain their activity to degrade dioxane and THF after induction, revealing their essential role in the oxidation of cyclic ethers. Identification of this novel enzyme is of great significance to advance our understanding of* dioxane metabolic pathways and develop molecular biomarkers to assess bioremediation potential at contaminated sites.

MARM 492

CO_2 electrolysis using a 3D-printed flow cell and a bismuth-based electrocatalyst

***Stephanie Velardo**, svelardo@udel.edu, Joel Rosenthal. Dept of Chemistry Biochemistry, University of Delaware, Newark, Delaware, United States*

Global energy supply has historically been provided via the burning of fossil fuels. To mitigate environmental concerns related to rising CO_2 emissions, the development of new technologies that can produce fuels from sunlight and CO_2 is of prime importance. Toward this end, we have developed a bismuth carbon monoxide evolving catalyst (Bi-CMEC), that exhibits impressive kinetics and selectively (>90 %) for the reduction of CO_2 to CO. Our prior studies involving, Bi-CMEC were prepared via electrodeposition methods. In this work, we have modified existing drop casting techniques to screen a variety of inexpensive Bi^{3+} salt precursors for CO_2 electrocatalysis. Furthermore, we developed a 3D printed electrolysis flow cell to assess the scalability of our Bi-CMEC systems. This flow device allows for the recycling of electrolyte, encourages faster mass transport, and provides the opportunity for rapid and cost effective prototyping with high precision and accuracy. Our progress with Bi-CMEC screening, optimization and flow-cell design will all be discussed.

MARM 493

Analyzing lipid extraction methods for the production of biodiesel from *Rhodotorula glutinis* and *Cryptococcus neoformans*

***Shannon McGee**[1], shmcgee@cedarcrest.edu, Andre Walther[2], Lindsey A. Welch[1]. (1) Chemical and Physical Sciences, Cedar Crest College, Bethlehem, Pennsylvania, United States (2) Dept. of Biological Sciences, Cedar Crest College, Allentown, Pennsylvania, United States*

Petroleum and fossil fuels are non-renewable, and the burning of these fuels contribute to the expanding problem of global climate change. Biodiesel is a green, renewable energy source that can replace fossil fuels, but cannot compete against petroleum diesel in the economic market. Researchers have begun to study the synthesis of biodiesel from microbial biomass to replace edible oils, which are connected to food security issues. Biodiesel is synthesized by the transesterification of fatty acids into their corresponding fatty acid methyl esters (FAME). *Rhodotorula glutinis* is an oleaginous yeast that has been analyzed by researchers as a source for biodiesel production. *Cryptococcus neoformans* is a widely studied organism due to its pathogenicity. The acapsular mutants that were studied have lost that pathogenicity along with their capsule, and are therefore safer to work with in a laboratory setting. *C. neoformans* strains were analyzed as a viable source for biodiesel production as the species has potential for genetic engineering to increase lipid yield. Across research studies, there are many ways to extract lipids from microbial biomass; however, there is no consensus of the optimal

method for lipid extraction from microbial biomass for the production of biodiesel. This presentation will describe the progress in yielding FAME from *C. neoformans* and *R. glutinis*, as well as various methods to optimize lipid extraction for biodiesel production. The main methods that were tested and compared are microwaving, bead-beating, and lyophilization.

MARM 494

Making connections: High-impact practices for teaching analytical chemistry

***Shirley Fischer-Drowos**, sfischer-drowos@widener.edu. Departments of Chemistry, Biochemistry, & Environmental Science and Sustainability, Widener University, Chester, Pennsylvania, United States*

Analytical chemistry plays an integral role in a number of different disciplines. Often, analysis is taught in a generic fashion. With the success of Process Oriented Guided Inquiry Learning (POGIL) in general chemistry, organic chemistry and physical chemistry, application to analytical chemistry was a logical next step. A consortium of analytical faculty members has developed POGIL materials specifically designed for this field. A description and application of this high impact practice (HIP) is provided. Another high impact pedagogy involves customizing the laboratory experience by combining analytical techniques with other disciplines. Often students with a wide array of majors are enrolled in analytical courses. In this way, specific methods can be adapted to applications and skills of interest. Providing a real world connection in the laboratory tends to make the experience more tangible. In addition to the traditional analytical laboratory experience, an interdisciplinary approach that has been implemented in our curriculum is the connection of biochemistry with analytical to form a specialized laboratory course that addresses the skills of a bioanalyst. A number of experiments were developed integrating the methods needed to work successfully in a graduate or industrial laboratory. A few examples are presented. Some favorable unexpected outcomes in this cooperative learning environment include improved teamwork and extension of these acquired skills into research programs.

MARM 495

Early integration of biochemistry into the analytical curriculum: A simple enzyme kinetics lab exercise for a quantitative analysis course

***John N. Richardson**, jnrich@ship.edu, Tierney Miller, Thomas Frielle, Emily Frieben. Chemistry, Shippensburg University, Shippensburg, Pennsylvania, United States*

We introduce an experiment focusing on a simple enzyme kinetics system (glucose/glucose oxidase) appropriate for use in a first-year quantitative analysis lab setting. Students utilize spectrophotometric methods to (a) generate a standard curve against which they compare assigned unknown samples, and (b) determine the observed order of reaction with respect to the substrate (glucose) using the method of integrated rate laws. Representative data and results will be provided, as well as an overview of several years of actual student results.

MARM 496

Encouraging student engagement in a sophomore-level bioanalytical chemistry laboratory course

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Beginning in 2014, we redesigned an intermediate-level laboratory course typically taught to biochemistry and pre-health students to include a focus on bioanalytical chemistry. Over the past several years, this course has gone through several iterations in an effort to promote independence in the laboratory setting and effective group work skills. In the current course model, students engage in all stages of the scientific process, from proposing an original research question to formally communicating their results to a broad audience. We will describe the evolution of this course over the past several years, the changes we implemented in the most recent iteration of the course during the spring semester of 2017, and our perceived successes of the current course model.

MARM 497

Practical use of ^{13}C benchtop NMR spectroscopy in an undergraduate laboratory

***Robert Espina**[2], robert@magritek.com, Paul Bowyer[2], Hector Robert[2], Andrew Coy[1]. (1) Magritek, Wellington, New Zealand (2) Magritek Inc., San Diego, California, United States*

Traditionally, undergraduate students are introduced to NMR spectroscopy through the analysis and interpretation of ^{1}H NMR spectra. A significant advantage of ^{1}H NMR is the high sensitivity meaning spectra can be acquired very quickly, which is of critical concern in any undergraduate lab. However, complexities in ^{1}H NMR spectra such as signal overlap due to the small chemical shift dispersion, spin-spin splittings, and peak distortions due to strong coupling mean that ^{1}H NMR spectroscopy may be an overwhelming and not the best pedagogical approach to learning NMR, particularly for newcomers to the technique. Furthermore, the issues with ^{1}H spectra are

exacerbated at the low-to-mid field strengths of permanent magnet benchtop NMR spectrometers that many undergraduate labs use. In contrast, ^{13}C NMR can offer a much more straightforward route to be learning NMR, owing to the much simpler and more predictable spectra that it usually provides. The major drawback of ^{13}C is its much lower sensitivity (about four orders of magnitude) compared to ^{1}H. However, recent improvements in the performance and sensitivity of benchtop NMR instruments, combined with the judicious choice of samples, experiments and experiment parameters, mean that practical 1D ^{13}C NMR spectra can be acquired on a benchtop NMR instrument in a few minutes. While the range of practical samples and concentration will be constrained, it may be that ^{13}C NMR can be a valuable and, in many ways, preferable tool for introducing and teaching basic NMR principles. In this paper we demonstrate a 1D ^{13}C-based approach to teaching NMR using several simple but instructive examples limited to total acquisition times of a few minutes, showing how sample and experiment choice can enable 1D ^{13}C NMR to be used in practical ways in a teaching lab.

MARM 498

Real world in the undergraduate analytical lab

***Gregory P. Foy**, gfoy@ycp.edu. York College of Pennsylvania, York, Pennsylvania, United States*

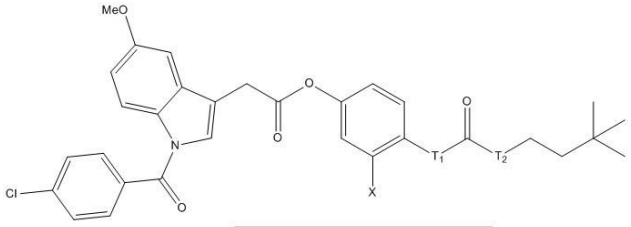
Students want relevant experiences in College, something that they can apply to “Real Life”. In this presentation, the discussion will focus on the development of Real World projects in both the Quantitative Analysis Laboratory course as well as the Instrumental Analysis Laboratory course. The design of the Quantitative Analysis lab first introduces students to the common quant techniques, followed by the Real World project, and the same general design is used in the Instrumental Analytical lab course. This design allows students to experience general techniques and then to design and execute a lab that has real world applications.

MARM 499

Design, synthesis, and testing of bioisosteres of a topical anti-inflammatory Indomethacin prodrug for treating sulfur mustard burns

***Jaya Saxena**[1], jas709@lehigh.edu, C J. Lacey[1], Christophe D. Guillon[1], Laurie B. Joseph [2], Gabriella M. Composto[2], Sherri C. Young[3], Cynthia A. Fianu[1], Jeffrey D. Laskin[4], Diane E. Heck[5], Ned D. Heindel[1]. (1) Lehigh University, Bethlehem, Pennsylvania, United States (2) Ernest Mario School of Pharmacy, Rutgers, New Jersey, United States (3) Muhlenburg College, Allentown, Pennsylvania, United States (4) Rutgers University, New Brunswick, New Jersey, United States (5) New York Medical College, Valhalla, New York, United States*

An ointment prepared from a new indomethacin prodrug (general structure with T_1 and T_2 = O, X = H), known as NDH4338, has shown remarkable effectiveness in accelerating the healing of sulfur-mustard burns in the rodent. NDH4338 possesses a broad range of inhibition of inflammatory enzymes in vitro including COX-1 and COX-2, i-NOS, AChE, and FAAH. It is also effective at quenching free radicals in the DPPH test. In addition, the NSAID portion of the drug is known to be a caspase inhibitor. By replacing oxygens with nitrogens we have generated four new bioisosteres and screened them against the inflammatory targets. Several members of this library exceeded the performance of the parent compound (lower IC_{50}s). Syntheses and inhibition results (*in vitro* and *in vivo*) will be reported.



NDH4338	$T_1 = T_2 = O$	X = H
NDH4781	$T_1 = O, T_2 = NH$	X = H
NDH4784	$T_1 = NH, T_2 = O$	X = H
NDH4787	$T_1 = T_2 = O$	$X = CH_3$
NDH4789	$T_1 = O, T_2 = NH$	$X = CH_3$

MARM 500

Anti-inflammatory and thermal behavior of 1,2,4-triazolo-4-amino imines

*Robert D. Rapp[1], **Christophe D. Guillon**[1], chg3@lehigh.edu, Jaya Saxena[1], Anna Vetrano[2], Cynthia A. Fianu[1], Jeffrey D. Laskin[3], Ned D. Heindel[1]. (1) Chemistry, Lehigh University, Bethlehem, Pennsylvania, United States (2) Robert Wood Johnson Medical School, Rutgers University, Piscataway, New Jersey, United States (3) UMDNJ, Rutgers University, Piscataway, New Jersey, United States*

We have discovered unique anti-inflammatory activity in a family of 1,2,4-triazole-4-N-amino imines. Members of this set suppress induced nitric oxide synthase (iNOS) which is upregulated in vessicated dermal lesions triggered by sulfur mustard insult. A structure-activity study performed on >30 diverse members of the triazole imine family showed that the presence of a cinnamyl imine, a pendant nitro group, and a furyl or thienyl attachment to the triazole core, seemed to enhance the anti-inflammatory properties. Thermal stabilty studies on this drug class revealed a remarkable cleavage mechanism which generated a nitrile and a deaminated triazole. Differential scanning calorimetry pointed to three different mechanisms of thermal fracture depending on the precise structure of the starting triazole imine.

MARM 501

Targeting cancer metabolism using sugar-based small molecules

***Fidelis Ndombera**, fidelis@chem.wayne.edu. Chemistry, Wayne State University, Detroit, Michigan, United States*

Metabolic reprogramming occurs in cancer cells leading to an altered metabolism. Small molecules that block this altered metabolism in cancer or that increase the production of reactive oxygen species (ROS) are emerging as potential anti-cancer agents. This is because increased generation of ROS observed in most cancer cells relative to normal cells suggest that this biochemical property provide a therapeutic window for selective killing of cancer cells using ROS-modulating small molecules. ROS-modulating small molecules such as phenethyl isothiocyanate, piperlongumine and 2-deoxy-D-glucose exploit cancer cell vulnerability to reach lethal ROS levels above the antioxidants protective threshold.
To explore the generality of these observations, we hypothesized that carbohydrate based ROS-modulating molecules would more selectively enhance ROS levels in cancer cells relative to normal cells. Furthermore, cancer cells overexpress glucose (GLUT-1) transporters in order to facilitate enhanced sugar entry necessary to fuel high cancer-cell metabolism. Previous studies have demonstrated that GLUT-1 tolerates substitution at positions 1, 2 and 6 of a glucose molecule. Consequently, we ensured our sugar-conjugated small molecules maintained vital structure-activity relationships with GLUT-1.
Considering that various carbohydrates can be used for cellular energetics or protein N-glycosylation of which interruption can lead to cellular stress, we synthesized and evaluated a library of N-aryl glycosides for induction of ROS and cytotoxicity in H1299 lung cancer cell line. Two N-aryl glycosides (K8 and H8) were identified that induce about 2-fold ROS levels and cytotoxicity in H1299 cells. K8A was recently evaluated in 60 cell lines by the National Cancer Institute and found to inhibit growth in UO-31, NCI H522 and CCRF-CEM. We further showed that the acetylated form of K8 (K8A) activates AMPK, and stabilizes p53 and induce a higher cytotoxicity than 2-deoxy-D-glucose in H1299 cell line. In addition, K8A induces ER stress indicated by up regulation of glucose-regulated protein-78 (GRP-78). Interestingly, initial mechanistic studies suggest that K8A blocks global protein glycosylation in H1299 cells.

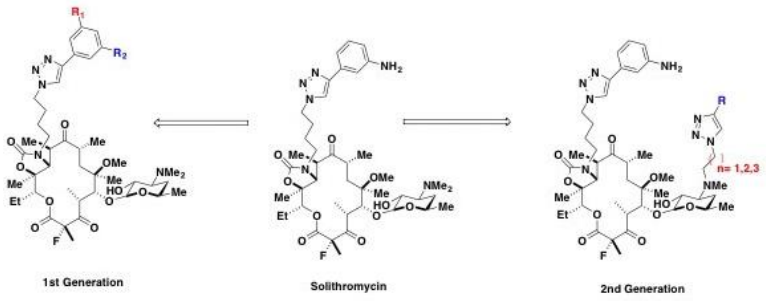
MARM 502

Solithromycin analogs: A click versus *in situ*-click chemistry approaches and antibiotic-resistance benefits

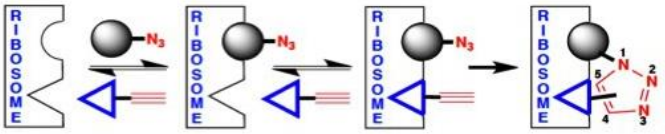
***Samer Daher**, tuf24815@temple.edu. Chemistry, Temple University, Philadelphia, Pennsylvania, United States*

The discovery and development of antibiotics is a success story in medicine wherein countless lives have been saved in the past century. However, there is a crucial need for novel sources of antibiotics to fill the gap of antibiotic resistance. Macrolides are considered to be among the most efficacious drug classes in medicine. For instance, Solithromycin developed in 2005 by Optimer Pharmaceuticals, via Cu(I) catalyzed combinatorial click chemistry, is now in phase 3 clinical trials and has proved to be the most potent amongst ketolides developed to date. Supported by literature evidence, macrolides tend to bind to the 50S subunit of the ribosome and inhibit protein synthesis. For that, we planned to investigate the mode of action prompted by non-covalent interactions: hydrogen bonding as well as pi stacking, which are remarkable features contributing to Solithromycin's potency. Accordingly, structure-activity relationship (SAR) through click chemistry was pursued to synthesize various analogs and test their biological activity via minimum inhibitory concentration (MIC). Alternatively, accessing another library of analogs was achieved via *in situ click chemistry*, in which the ribosomal RNA trigger the coupling of macrolide azide with variety of alkynes to generate several analogs of Solithromycin. This powerful drug discovery platform seems to be promising in selecting potential drug candidates that could enhance the pharmaceutical field. In conclusion, both approaches click and ribosomal *in situ click* are prospective strategies for addressing antibiotic-resistance problem.

First Approach: Synthesis of analogs via click chemistry



Second Approach: Generation of analogs via *in situ click chemistry*



MARM 503

Development of betulin-betulinic acid conjugates as anti-cancer agents

***Subash C. Jonnalagadda**, jonnalagadda@rowan.edu. Chemistry and Biochemistry, Rowan University, Glassboro, New Jersey, United States*

Betulin and betulinic acid are triterpenoid natural products, which can be readily extracted in high quantities from external bark of yellow and white birch trees. Birch tree is native to North America and is also commonly available for purchase as firewood. Betulinic acid is found to exhibit very good activity against few cancer cell lines, and is relatively non-toxic to normal cells. The ready availability and selective cytotoxicity coupled with the favorable therapeutic index have made betulinic acid an attractive and promising *anti*-cancer agent. However, this molecule is almost insoluble in water and shows toxicity only on very few cancer cell lines. We have undertaken a systematic study involving the synthesis and biological evaluation of betulin derived small molecules in an effort towards improving the water solubility as well as the therapeutic profile of the parent natural product. The talk will focus on our synthetic and biological efforts in this project.

MARM 504

SAR development in the start-up and small business environment

***Jay Wrobel**, jaywrobel@gmail.com. Fox Chase Chemical Diversity Center, Inc, Doylestown, Pennsylvania, United States*

Fox Chase Chemical Diversity Center, Inc. (FCCDC, www.fc-cdci.com) was established in Nov., 2008 as an early-stage drug discover working closely with academic laboratories to jointly conduct target validation, hit to lead and lead optimization medicinal chemistry research, based on innovative new findings in pharmacology and biochemistry. Starting with literally nothing in 2008, FCCDC has expanded to a staff of 22 located at two sites in suburban Philadelphia, resulting to date in the design, preparation and submission of ~7,000 NCEs all in the context of multiple research collaborations. The first clinical compound from FCCDC laboratories is FC-4157, for which an IND has been filed and clinical evaluation has now been initiated. An extremely useful resource to FCCDC and multiple other start-ups and small chemical businesses in the region is the Pennsylvania Drug Discovery Institute, a 501(c)(3) non-profit service and outreach organization, which has collected >20,000 reagents and extensive glassware resources, which are freely available to qualified small business and non-profit research organizations.

MARM 505

Discovery Partnerships with Academia (DPAc): A collaborative approach to drug discovery

***Daniel Paone**, daniel.v.paone@gsk.com. GlaxoSmithKline, Lansdale, Pennsylvania, United States*

The Discovery Partnerships with Academia (DPAc) group within GlaxoSmithKline was specifically created to leverage the deep subject matter expertise, mechanistic understanding of therapeutic targets and disease area biology found in academic institutions. Through joint research collaborations, we seek to increase the overall

probability of success towards novel clinical therapeutics. Our general approach, specifics as to what DPAc looks for in a partner, and examples of current collaborations will be presented.

MARM 506

The Moulder Center for Drug Discovery Research: An academic research center with an entrepreneurial spirit

***Benjamin E. Blass**, blassbe@verizon.net. Pharmaceutical Sciences, Temple University School of Pharmacy, Eagleville, Pennsylvania, United States*

The city of Philadelphia is home to dozens of colleges, universities, and business that actively engage in chemical research. Many of these institutions are focused on life science, medicine, and the identification of novel therapeutics. The Moulder Center for Drug Discovery Research, a division of Temple University School of Pharmacy, is a unique institution in the Philadelphia area and the tristate region. As a fully integrated academic drug discovery center, this institution employs the chemical sciences in conjunction with numerous enabling technologies in an effort to identify the next generation of therapeutic agents. Scientists at the Moulder Center work in collaboration with colleagues across the country and around the globe, targeting a multitude of diseases and conditions. This presentation will provide an overview the Moulder Center's operating capabilities and highlight some of our more recent successes.

MARM 507

Academia-industry collaborations: Evolution and new models

***Sree Kant**, sree.kant@pfizer.com. External Science and Innovaton, Pfizer Inc., New York, New York, United States*

The session will highlight the evolution of academia-industry collaboration over time and explore new/emerging models. I will discuss the move from transactional relationships to collaborative partnerships, and the move from project hand-offs to joint incubation and execution of projects. In addition, I will share some of the avenues that Pfizer is exploring or has adopted, in order to drive new emerging science in close collaboration with academia.

MARM 508

Bristol-Myers Squibb/Princeton University academic research collaboration

***Trevor Sherwood**, trevor.sherwood@bms.com. Discovery Chemistry, Bristol-Myers Squibb, West Windsor, New Jersey, United States*

We will present our work from a BMS/Princeton University academic research collaboration

MARM 509

Progress towards developing a mechanistic understanding of base-free transfer hydrogenation catalyzed by Cp*Ir(pyridinesulfonamide)Cl complexes

***Abby R. O'Connor**, oconnora@tcnj.edu. Chem Dept, College of New Jersey, Ewing, New Jersey, United States*

Three-legged piano stool Cp*IrCl complexes (Cp* = pentamethylcyclopentadienyl) bearing pyridinesulfonamide ligands with varying electronic parameters developed by the O'Connor lab are active for the base-free transfer hydrogenation of a variety of substituted aryl and linear ketones and aldehydes, cycloaliphatic and diaryl ketones α,β-unsaturated ketones, diones, β-ketoesters, and biomass derived 5-hydroxymethylfurfural and levulinic acid substrates with 2-propanol at 85 °C. All transfer hydrogenation catalysis was conducted in air without dried and degassed substrates and basic additives are not required for high catalytic activity. The electronic nature of the substrate and Ir complex influence the conversion with respect to time. Control experiments support a homogeneous catalyzed pathway. Variation of the structural rigidity of the ligand framework has been explored and high catalysis activity is only observed with flexible linkers between the sulfonamide and pyridine moieties. Initial NMR studies support the potential for ligand dissociation under catalytic conditions. Here we describe our preliminary mechanistic and kinetic findings to explain why these systems operate under base-free conditions.

MARM 510

Production of secondary phosphines by catalytic cross-coupling reaction

***James M. Camara**, james.camara@gmail.com, Aaron L. Haber. Chemistry, Yeshiva University, New York, New York, United States*

Secondary phosphines are useful precursors to a variety of tertiary and multidentate phosphine ligands through hydrophosphination reactions as well as coupling reactions. Secondary phosphines may be accessed by formation of a P-C bond via cross-coupling reaction. In the presence of a strongly donating supporting phosphine ligand,

copper (I) iodide and carbonate base, we have observed catalytic cross-coupling between aryl iodides and phenylphosphine in refluxing toluene over the course of ca. 24 hours. These reactions proceed cleanly and are highly selective for the production of secondary phosphines over tertiary phosphines. Microwave irradiation at higher temperatures significantly decreases reaction time.

MARM 511

Copper and silver benzoate, aryl complexes, and their implications for oxidative decarboxylative coupling reactions

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Oxidative decarboxylative coupling reactions are gaining recognition as efficient routes to access substituted arenes from inexpensive and readily available carboxylic acid precursors, yet there is little mechanistic understanding of these reactions and their corresponding substrate limitations. This talk will focus on the synthesis and reactivity of phenanthroline-ligated copper and silver benzoate and aryl complexes and their relevance to catalytic decarboxylative coupling reactions.

MARM 512

Microwave-assisted copper-catalyzed amidation of aryl chlorides via concurrent tandem catalysis

*Brice P. Clairmont, Shirley Lin, **Amy H. Roy MacArthur**, macarthu@usna.edu. Department of Chemistry, United States Naval Academy, Annapolis, Maryland, United States*

A method for the copper-catalyzed amidation of aryl chlorides using concurrent tandem catalysis (CTC) has been developed using a multifunctional copper catalyst. The proposed CTC mechanism consists of an initial halide exchange step to form aryl iodides from less reactive aryl chloride substrates. As the aryl iodide intermediate is generated, it is consumed as the substrate in a subsequent amidation reaction to form a new C-N bond. This new method is similar to those previously reported for the copper-catalyzed hydrodehalogenation and cyanation reactions of aryl halides via CTC methodologies. The substrate scope for the amidation reaction and evidence that the reaction occurs through a CTC mechanism will be presented.

MARM 513

Nickel complexes of primary amido-functionalized N-heterocyclic carbene ligands

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The use of bifuctional ligands in transition metal complexes has been demonstrated to increase the reactivity and/or selectivity of these complexes in a range of reactions. A study has been undertaken to examine the reactivity of nickel complexes that are ligated by N-heterocyclic carbene ligands with primary amido functionality. A microwave-assisted protocol has been used to synthesize a series of the ligand precursors. The synthesis of the nickel complexes is accomplished through direct metalation in the presence of potassium carbonate. The characterization of these complexes as well as a preliminary investigation into their reactivity will be discussed.

MARM 514

Secondary bonding interactions to facilitate nitrene group tansfer from mid-valent group VI imidos

***Rick R. Thompson**[2], vmdt60@gmail.com, Lawrence R. Sita[1]. (1) Univ of Maryland, College Park, Maryland, United States (2) Chemistry, University of Maryland, Greenbelt, Maryland, United States*

Recently much interest has been directed towards the develpment of catalysts for the fixation of atmospheric nitrogen toward value-added products and therefore understanding methods for improving the performance of nitrogen-atom transfer (NAT) or nitrene group transfer (NGT) by such systems is crucial to advancing the field. The Mo(IV) imidos, Cp*[N(^{i}Pr)C(Me)N(^{i}Pr)]Mo(NEMe$_3$) (Cp* = eta^5-C$_5$Me$_5$, E = C (**1**), E = Si (**2a**), E = Ge (**3**)), which can be generated from dinitrogen cleavage, have been found to react with 2,6-dimethylphenylisonitrile to cleanly generate the resulting asymmetric carbodiimides, Me$_3$EN=C=NAr (E = C (**5**), E = Si (**6**), E = Ge (**7**)) and the mechanism for this tranformation has been probed. Computational and kinetic studies both support a non-linear trend in rate of reaction amongst the group-14 congeners with the trimethylsilyl derivative being the most active for nitrene group transfer. These results suggest that pi acidity of the EMe$_3$ substituent at the imido nitrogen atom significantly perturbs Mo=N pi-bonding and consequentially, rate of group transfer to organic substrates. This is further substantiated by computational investigation of the same reaction occuring with the hypothetical borylimido species, Cp*AmMo(NBMe$_2$) which showed an even more substantial attenuation of the activation barrier, owning to an empty p-orbital adjecent to the imido nitrogen.

MARM 515

Cerium(IV)-imido complexes: Electronic structures and reactivity

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In general, group 3 metal-ligand bonds, incorporating Sc, Y or the lanthanides are challenging synthetic targets due to their strong change polarization. But they are likewise expected to be reactive for small molecule transformations. We and others have hypothesized that Ce(IV)=E targets should be accessible, due to a higher charge than other group 3 metals and relatively larger metal-ligand covalency. Such Ce(IV)=E moieties should be less reactive and isolable. Furthermore, computational chemistry work has predicted that, in low symmetry settings, such compounds should be stabilized by combinations of both 4f and 5d orbital character. We recently realized the goal of Ce(IV)-ligand multiple bonds in isolation of the first Ce(IV)-imido complex. The structures and reactivity of this and related compounds will be presented.

MARM 516

Materials for organic light emitting diodes

***Nora S. Radu**[1], nora.s.radu@gmail.com, Norman Herron[2,1], Gene M. Rossi[2]. (1) Experimental Station E402/3205F, DuPont Co., Wilmington, Delaware, United States (2) DuPont, Wilmington, Delaware, United States*

Organic light emitting diode (OLED) technology enables vivid color, high contrast, fast response and thin panels with wide viewing angles while consuming less power. We will discuss our recent progress in designing materials that deliver superior OLED device performance.

MARM 517

Copper(II) aryls in catalytic C-O, C-N, and C-C bond formation

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Copper(II) aryls have been proposed as key intermediates in copper catalyzed cross coupling reactions. To address their involvement in C-C, C-N, and C-O bond forming reactions, we describe a family of novel three coordinate copper(II) aryls $[Cu^{II}]$-C_6F_5 supported by ancillary β-diketiminate ligands. Modeling the Chan-Lam-Evans coupling reaction, addition of the phenolate anion PhO^- to $[Cu^{II}]$-C_6F_5 directly affords the diaryl ether PhO-C_6F_5. Mechanistic studies supported by experiment and theory reveal a redox disproportionation of $\{[Cu^{II}](C_6F_5)(OPh)\}^-$ intermediates to give $[Cu^{III}](C_6F_5)(OPh)$ that is unstable towards reductive elimination PhO-C_6F_5.

Crystallographic, spectroscopic, and DFT studies of these three coordinate organometallic copper(II) aryls reveal a unique electronic structure that provides facile bond forming pathways with radicals. For instance, reaction with NO results in C-N bond formation to give [Cu](η^2-ONC_6F_5). We will also describe how these $[Cu^{II}]$-aryl intermediates may be incorporated into radical relay C-H functionalization protocols that allow for the direct transformation of C-H to C-C bonds. These radical based methods allow for the construction of crowded quaternary carbon centers.

MARM 518

Ubiquitin receptors mediate proteasomal processivity

*Mary Cundiff, William J. Dewey, Eden L. Reichard, Nicholas D. Nassif, **Daniel A. Kraut**, daniel.kraut@villanova.edu. Chemistry, Villanova University, Villanova, Pennsylvania, United States*

In eukaryotic cells, proteins are targeted to the proteasome for degradation by polyubiquitination. These proteins bind to ubiquitin receptors, are engaged and unfolded by proteasomal ATPases, and are processively degraded. *The factors determining to what extent the proteasome can successfully unfold and degrade a substrate are still poorly understood.* We previously found that the architecture of polyubiquitin chains attached to a substrate affects the proteasome's ability to unfold and degrade the substrate, with K48- or mixed-linkage chains leading to greater processivity than K63-linked chains. Ubiquitin-independent targeting of substrates to the proteasome gave substantially lower processivity of degradation than ubiquitin-dependent targeting. Thus, even though ubiquitin chains are removed early in degradation, during substrate engagement, remarkably they dramatically affect the later unfolding of a protein domain. How do ubiquitin chains differentially activate the proteasome? One attractive candidate was the ubiquitin receptor Rpn10. Mutation of Rpn10 to prevent ubiquitin binding led to drastic unfolding defects early in the degradation process. Using a destabilized substrate that allowed initial degradation to occur more easily, we found that processivity defects were dependent on ubiquitin chain linkage on the substrate. Similar results were found for the ubiquitin receptor Rpn1, while a double mutant essentially eliminated any ubiquitin-

based activation of the proteasome. We conclude that linkage-based differences allow a substrate to interact with one or more ubiquitin receptors, activating the proteasome's unfolding ability.

MARM 519

Engineering a self-assembling peptide system derived from beta-amyloid

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The misfolding of beta-amyloid protein leads to neurotoxic aggregation in the brain. Amyloid fibrils and neurofibrillary tangles in the brain are hallmarks of Alzheimer's disease progression. The driving force of aggregation of the 40 or 42 residue peptide is an internal domain of seven residues known as the hydrophobic central domain. Our group has developed a novel, self-assembling, dual peptide system derived from this sequence. The novel peptides do not homo-assemble in solution, although rapid hetero-assembly occurs upon mixing. The resulting aggregates have been characterized extensively, including positive ThT fluorescence and beta-sheet secondary structure typical of amyloid aggregates. Beta-sheet composition and morphology can be altered with varying salt concentrations in the buffer and the addition of terminal capping groups. This system has useful applications in the development of novel functional biomaterials, as well as applications in identifying the mechanisms of amyloid toxicity in neurodegenerative diseases such as Alzheimer's disease.

MARM 520

Exploring a role for the ribosome-associated complex in the interplay between environmental stress and prion formation in yeast

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Yeast prions are epigenetic switches that can produce heritable phenotypes. To gain insight into the mechanisms by which cells regulate prion formation, we previously examined the role of the ribosome-associated complex (RAC) chaperones in *[PSI+]* prion formation. The *[PSI+]* prion results from a self-propagating amyloid form of the translation termination factor Sup35, and is manifested phenotypically as elevated levels of nonsense suppression. The RAC consists of the Hsp70 chaperone Ssz1 and the Hsp40 chaperone Zuo1, which anchors the complex onto ribosomes and stimulates the ATPase activity of the Hsp70 chaperone Ssb. Previously we showed that cells lacking Zuo1, and thus lacking RAC function on ribosomes, exhibit higher frequencies of spontaneous and induced *[PSI+]* formation. Cells expressing variants of Zuo1 that are unable to associate with ribosomes, or that are unable to stimulate Ssb ATPase activity, exhibit similarly high levels of prion formation. These findings are consistent with a role for the RAC in chaperoning nascent Sup35 to prevent misfolding of the N-terminal prion domain as it emerges from the ribosome. RAC components can additionally function as transcriptional co-activators for the pleiotropic drug resistance (PDR) pathway, which enhances resistance to various drugs and environmental toxins. Their role in this pathway requires their dissociation from ribosomes. Since a variety of environmental stresses are known to induce prion formation, RAC dissociation from ribosomes under such conditions may facilitate prion formation. Our current work aims to understand the mechanism by which Zuo1 dissociation from ribosomes is triggered in response to stress. We are testing the hypotheses that stress-induced post-translational modification of Zuo1, or interaction with a binding partner, may trigger Zuo1 dissociation from ribosomes to activate PDR. Although we have not yet found post-translational modification of Zuo1 to contribute to PDR activation, overexpression of several proteins facilitates increased drug resistance in a Zuo1-dependent manner.

MARM 521

Defining prion-specific chaperone function in yeast: amyloid diversity as a function of chaperone functional complexity

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Yeast prions are heritable amyloid aggregates of functional proteins. Their propagation to subsequent cell generations is dependent upon the fragmentation of these aggregates by a core set of chaperone proteins. Three proteins make up the core 'prion-chaperone machinery': the J-protein Sis1, the Hsp70 Ssa, and the disaggregase Hsp104, and yet some prions exhibit requirements for additional chaperone activities, indicating that prion-chaperone requirements are heterogeneous. Further, prions can form distinct amyloid structures (amyloid structural polymorphisms), called 'strains' in mammalian systems and 'variants' in yeast, that dictate the intensity of yeast prion-associated phenotypes and stability in mitosis. Recently we and others have uncovered significant complexity in the chaperone requirements of various yeast prions and prion variants, demonstrating that, in

contrast to Hsp104 and Hsp70, which have general roles, J-proteins represent a prion-specific component of the prion-propagation machinery. Most notable has been a direct demonstration that the persistence of the alternative conformations of prions (*i.e*., prion variants) is dependent on the action of different molecular chaperones. This functional specificity was not originally predicted because molecular chaperones are thought to be generalists that recognize common features of misfolded proteins. These findings are particularly significant because they suggest that amyloid structures of alterative prion conformations have unique features that are differentiable by chaperone proteins, and therefore may be exploitable for therapeutic intervention, revealing a previously unappreciated level of additional complexity. Because J-proteins often act as targeting factors for Hsp70s, they may constitute the first chaperone response to the presence of amyloid, but a critical barrier to advancing the understanding of chaperone function in prion biology is that the fundamental chaperone requirements for most yeast prions remain unidentified, precluding a comprehensive understanding of how protein sequences give rise to amyloids with distinct patterns of chaperone interaction.

MARM 522

Prion-like transmission of mutant huntingtin aggregates in *Drosophila* brains

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Huntington's disease (HD) is an inherited neurodegenerative disorder caused by expansion of a CAG repeat region in exon 1 of the huntingtin (Htt) gene. Htt proteins encoded by this mutant gene contain an expanded polyglutamine (polyQ) stretch near their N-termini and are prone to misfolding and aggregation. Accumulating evidence indicates that mutant Htt protein aggregates have prion-like properties—they spread from one cell to another and convert normally-folded Htt proteins into an aggregated state. We have previously shown in the intact Drosophila central nervous system (CNS) that mutant Htt aggregates in olfactory receptor neurons (ORNs) are cleared by neighboring phagocytic glial cells via Draper-dependent phagocytosis. Remarkably, a proportion of these phagocytosed neuronal Htt aggregates reach the glial cytoplasm and effect prion-like conversion of cytoplasmic, wild-type Htt into aggregates (Pearce et al., 2015, Nat Commun). We have demonstrated that mutant Htt aggregates originating in ORNs can also transfer into the cytoplasm of their post-synaptic partners, projection neurons (PNs) and there nucleate aggregation of wild-type Htt. Surprisingly, ORN-to-PN transmission of mutant Htt aggregates also requires Draper, suggesting that glial phagocytosis plays a central role in transferring aggregates between synaptically-connected neurons. Together, these findings indicate that pathogenic Htt aggregates move between individual neuronal and glial cells in intact brains and suggest that phagocytic glia regulate both the clearance and spreading of aggregate neuropathology in the CNS.

MARM 523

Biochemical analysis of protein aggregation in animal models of neurodegenerative disease

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At least nine neurodegenerative diseases have been identified that are caused by the aggregation induced by long tracts of glutamine sequences. One such polyglutamine-containing protein is huntingtin, which is the primary factor responsible for Huntington's disease. A comparative study was carried out looking at the aggregation of the huntingtin exon 1 protein fragment upon transgenic expression in *Drosophila melanogaster* and *Caenorhabditis elegans.* Aggregation was assessed principally using the recently developed fluorescence detection system for the analytical ultracentrifuge as applied to sedimentation velocity experiments, affording detection in complex mixtures under physiologically relevant conditions. Increased aggregation is shown to correlate with increased toxicity for both animal models. Co-expression of the human Hsp70 in *D. melanogaster* showed some mitigation of aggregation and toxicity, correlating best with inclusion body formation. The comparative study emphasizes the value of the analytical ultracentrifuge equipped with fluorescence detection as a useful and rigorous tool in *in situ* aggregation analysis to assess commonalities in aggregation across animal model systems.

MARM 524

Mechanistic insights into β-lactam formation by a non-ribosomal peptide synthetase condensation domain

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Non-ribosomal peptide synthetases (NRPSs) are a class of modular multi-domain enzymes responsible for the synthesis of a wide variety of peptide natural products, many of which are of biological interest. Examples of bioactive NRPS natural products include beta-lactam-containing antibiotics such as the penicillins, cephalosporins, and nocardicins. Whereas the beta-lactam core of the penicillins and cephalosporins is introduced following NRPS assembly of the linear peptide, we found that the termination module (M5) of the nocardicin A NRPS installs the

beta-lactam ring in the nocardicins. M5 takes a serine-containing peptide and facilitates its cyclization to the beta-lactam-containing pentapeptide product pro-nocardicin G. Specifically, it was found that the condensation domain (C), which typically catalyzes peptide bond formation, was responsible for cyclization. This domain, C5, has an unusual third histidine adjacent to a highly conserved HHxxxDG catalytic motif. Based on current knowledge of C domain chemistry and the presence of the atypical residue, a mechanism has been proposed in which ring formation is achieved through acid-base chemistry by way of a dehydroalanyl intermediate. Here we report mechanistic studies to probe the steps of ring formation and to identify the roles of the histidine residues in the active site. Attempts to trap the dehydroalanyl-containing peptide intermediate in the absence of the electrophilic acceptor have demonstrated that ordered binding of both the acceptor and donor substrates in C5's active site must take place for catalysis to occur. In order to probe the first elimination step, a serine-containing peptidyl CoA in which the serine alpha position was deuterated was synthesized and loaded onto the carrier protein of the upstream module. Incubation of this substrate with M5 demonstrated that the generation of the dehydroalanyl residue through elimination of the seryl hydroxyl is reversible. Point mutation studies of the three histidine residues of interest in C5's catalytic motif—His790, His791, and His792—have validated their importance in ring formation in pro-nocardicin G. Specifically, these experiments identified the structural importance of His791 and implicated chemical roles for both His790 and His792.

MARM 525

New enzyme function enabled by photoexcitation

***Todd Hyster**, thyster@princeton.edu. Chemistry, Princeton University, Princeton, New Jersey, United States*

Enzymes are powerful catalysts for asymmetric synthesis as they are capable of achieving activities and selectivities that exceed traditional small molecule catalysts. A encumbrance to the further advance of biocatalysis is the relatively small number of reactions enzymes are capable of catalyzing. In this talk, I will outline our efforts to use photoexcitation to expand the types of reactions accessible to enzymes.

MARM 526

Stereospecific nickel-catalyzed cross-coupling reactions of alkyl alcohol derivatives

***Mary P. Watson**, mpwatson@udel.edu. Chemistry & Biochemistry, University of Delaware, Newark, Delaware, United States*

Transition metal-catalyzed cross-coupling reactions have revolutionized organic synthesis, particularly the construction of bonds to sp^2-hybridized carbons. However, the discovery of analogous reactions of C_{sp3} electrophiles have lagged behind, despite their potential to deliver a range of important targets, including chiral molecules in high enantiopurity. Towards solving this challenge in organic synthesis, we have developed a range of nickel-catalyzed cross-couplings of alkyl alcohol derivatives. In particular, we have developed stereospecific, nickel-catalyzed cross couplings of benzylic carboxylates. These reactions utilize starting materials that are readily available in high optical purity; proceed with high levels of stereochemical fidelity; employ air-stable, functional group tolerance coupling partners, such as aryl boronic acids; and display excellent functional group tolerance. This strategy is also effective for the arylation of allylic electrophiles, and the use of alternative coupling partners to enable borylations. These reactions provide a range of highly enantioenriched products with tertiary and quaternary stereocenters, including molecules important for their biological activity. The optimization, scope, and mechanistic studies of these reactions will be presented.

MARM 527

Enzyme display on *Bacillus subtilis* spores for protein engineering and optimization

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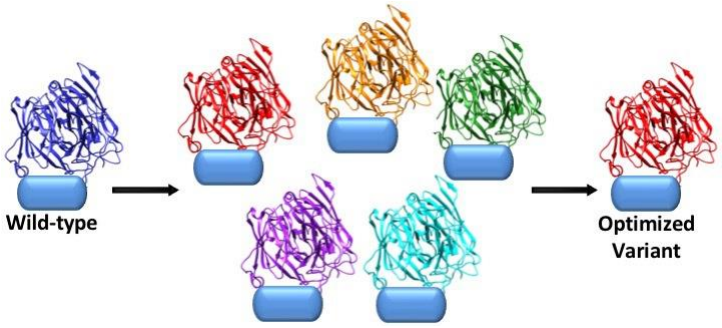
Protein libraries were displayed on the spore coat of *Bacillus subtilis*, and this method was demonstrated as a tool for directed evolution. *Escherichia coli,* yeast, and phage display suffer from protein folding and viability issues. On the other hand, spores avoid folding concerns by the natural sporulation process and remain viable under harsh chemical and physical environments. The naturally occurring *B. subtilis* spore coat protein CotA is a laccase, which

is a copper-containing oxidase. First, CotA is a generalist and it was converted to be specialist by increasing the substrate specificity for ABTS (2,2'-azino-bis(3-ethylbenzothiazoline-6-sulphonic acid) over SGZ (4-hydroxy-3,5-dimethoxy-benzaldehyde azine). A library was created by simultaneously randomizing the 19 amino acids that line the substrate-binding pocket. A Thr260Leu variant (Thr260Leu-CotA) was identified that had a catalytic efficiency [$(k_{cat}/K_M)_{ATBS}$ / $(k_{cat}/K_M)_{SGZ}$] 120-fold greater compared to wild-type after one round of evolution. Next, CotA was evolved for improved activity under high organic solvent concentrations. A CotA random mutation library was screened at 60% dimethyl sulfoxide (DMSO). A Thr480Ala variant (Thr480Ala-CotA) was identified that was 2.38-fold more active than the wild-type CotA after one round of evolution. In addition, Thr480Ala-CotA was more active with concentrations of DMSO ranging from 0-70%. It was also more active than wt-CotA in different concentrations methanol, ethanol and acetonitrile. Finally, an aim was to improve pH stability. The maximum activity is between pH 4 and 5 for the substrate ABTS. However, the activity dramatically decreases at pH 4 after one hour. The activity is not significantly altered at pH 5. A library of approximately 3,000 clones was screened. A Glu498Gly variant was identified to have a half-life of inactivation ($t_{1/2}$) at pH 4 that was 24.8 times greater than wt-CotA. Subsequently, the amino acid substitution was added from the organic solvent mutant. Thr480Ala/Glu498Gly-CotA was constructed and the $t_{1/2}$ was 62.1 times greater than wt-CotA. In addition, Thr480Ala/Glu498Gly-CotA yielded 5.3-fold more product than the wt-CotA.



MARM 528

Validating methanol extraction for the metabolomics of obese patients

Emma J. Robinson[1]*, ejr026@bucknell.edu, Matthew C. Taddeo*[1]*, Xin Chu*[2]*, Weixing Shi*[3]*, Craig Wood*[2]*, Christopher D. Still*[2]*, David S. Rovnyak*[1]*. (1) Bucknell Univ, Lewisburg, Pennsylvania, United States (2) Obesity Institute, Geisinger Clinic, Danville, Pennsylvania, United States (3) Obesity Institute, Geisinger Health System, Danville, Pennsylvania, United States*

NMR is an advantageous technique in metabolomics due to its ability to give spectra with unique fingerprint patterns characteristic of metabolites and to perform intrinsically reproducible measurements. Gradual improvements in protocols for extracting aqueous metabolites from sera while also stripping viral membranes have evolved. But recently, methanol-only extraction has been shown by Gowda and Raftery (2016) to further increase the number and levels of metabolites extracted from a sample. This work characterizes methanol based serum extraction protocols for improved sensitivity and for high lipid conditions. This work tests sensitivity, accuracy and precision of methanol extractions in human sera, fetal bovine sera, and mock sera containing standards. As we intend to apply this method to metabolomics investigations of high BMI patients, robustness of the method for such high-lipid samples was tested, where we have found previously that such samples are prone to phase separation.

MARM 529

Development of electrochemical and fluorescence-based tools for nanomaterials characterization

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The use of nanomaterials for a range of environmental, medicinal, and commercial applications has dramatically increased in recent years. However, the release of these materials into the environment has raised concern over their potential harmful effects necessitating the development of *in situ* tools for nanomaterials characterization. Here we describe the development of electrochemical and fluorescence-based techniques for characterization of spherical silver nanoparticles (AgNPs). Anodic stripping voltammetry (ASV) is a sensitive electrochemical technique for the detection of metal ions and is well-suited for investigation of nanomaterial dissolution properties. Recently established in the literature, particle-impact voltammetry can be used to monitor single nanoparticle redox events electrochemically at ultramicroelectrodes allowing for the determination of ENM size and concentration. ASV studies of the dissolution of silver ions from AgNPs and preliminary particle-impact voltammetry studies of

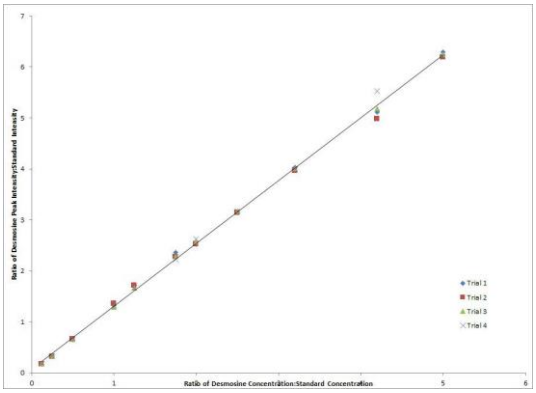
AgNPs prepared in simulated biological fluids (e.g. sweat) will be presented. In addition to their electrochemical properties, AgNPs have a characteristic surface plasmon resonance band between 400 and 500 nm, making them potential energy transfer acceptors for fluorescence resonance energy transfer (FRET) with a variety of commercial dyes (e.g., coumarin derivatives with emission in the same spectral range). The development of a FRET-based assay to probe AgNP aggregation properties will be presented.

MARM 530

Rapid and sensitive quantification of desmosine in body fluids using a stable-isotope labeling and MALDI MS^2

*Pratikkumar Rathod[2,3], Manjeet Kaur[2], Hsin-Pin Ho[2,3], Basant Dhital[1], Marissa Louis[2], Kevin Mark[4], Gregory Boutis[1,5], Jong-Ill Lee[2,6], **Emmanuel Chang**[2,3], echang@york.Cuny.edu. (1) Physics, Brooklyn College/City University of NY, Brooklyn, New York, United States (2) Chemistry, York College/City University of NY, Jamaica, New York, United States (3) Chemistry/Biochemistry, Graduate Center/CUNY, New York, New York, United States (4) Chemistry, LaGuardia Community College, Long Island City, New York, United States (5) Physics/Chemistry, Graduate Center/CUNY, New York, New York, United States (6) Chemistry, Graduate Center/CUNY, New York, New York, United States*

Desmosine and its structural isomer isodesmosine are post-translationally modified amino acids formed from the crosslinking and conjugation of four lysine residues in the elastin protein. Elastin, the molecule that imparts elasticity to tissues such as skin, lung and ligament is the only place where desmosine and isodesmosine are found in nature, and as such, desmosine serves as a biomarker for the presence or pathologic breakdown of elastin. To date, most assays for desmosine rely on LC-MS, requiring extensive sample preparation and chromatographic runs. Here, we present a novel method for quantifying elastin that uses matrix-assisted laser desorption ionization tandem mass spectrometry (MALDI-MS^2) on semi-purified samples using synthetic stable isotope lableled desmosine as an internal standard, and evaluate its analytical capabilities and limitations. Selectivity is obtained by directly interrogating the m/z range associated with unlabeled desmosine and its isotope labeled counterpart. We demonstrate linearity over more than an order of magnitude of concentration (see figure 1), run-to-run reproducibility over a number of weeks and different investigators, and limit of detection into the mid-femtomole range without prior concentration of sample. Finally we show the effectiveness of the method for detecting desmsoine in water, plasma and urine. Sample preparation and instrumental analysis of 10 samples takes about one hour, roughly the same time associated with 1 - 2 comparable LC-MS runs.



MARM 531

Limits of detection for the spectroscopic analysis of pollutants in water samples

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An experiment was designed for a 300-level Analytical Chemistry laboratory to demonstrate quality assurance methods. Nitrate levels in aqueous samples were measured spectrophotometrically utilizing the Griess diazotization reaction. Calibration curves were generated from standard solutions of nitrate. Quality control samples were then run to determine the accuracy of the method. Replicate samples were run to determine the precision of the method. These replicate samples as well as replicate measurements of blank samples were used to determine the signal detection limit, the minimum detectable concentration, and lower limit of quantitation for the method. Ruggedness of the method was also studied by having different students perform the experiment using different instruments and reagents. Results for this specific experiment will be presented, although the general methodology could be applied to a wide variety of analytical measurements and instrumentation.

MARM 532

Taurodeoxycholate aggregation and chiral selectivity for binaphthyl compounds with NMR and ITC

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Micelles formed from the aggregates of taurodeoxycholate (TDC) bile salts are capable of resolving chiral isomers of binaphthyl compounds through micellar electrokinteic capillary chromatography (MEKC). The complex intermolecular interactions that give rise to chiral selectivity in the TDC micelle system are poorly understood. The structural and thermodynamic details of inter-and intra-molecular interactions with TDC and the model chiral analyte 1,1'-binaphthyl-2,2′-diyl hydrogen phosphate (BNDHP) were studied here using NMR and ITC, respectively. Chemical shift analysis of ^{1}H NMR spectra of TDC (3.0 – 80.0 mM) with either isomer of BNDHP revealed ring protons 4-7 constituted the binding edge of BNDHP, and chiral selectivity, as reported by H12 of TDC in the presence of either R- or S-BNDHP, was apparent at TDC concentrations at or above 10 mM, with diminishing chiral resolution above 30 mM TDC. These data indicate more than one aggregation event, with maximal chiral selectivity at about 30 mM TDC. Intermolecular NOESY data revealed NOEs between TDC methyl protons from carbons 18 and 19 with BNDHP ring protons, supporting an antiparallel TDC dimer. S-BNDHP has a prominent NOE with H12 while R-BNDHP interacts with H7, supporting that the isomers approach the dimer from opposite sides. ITC data indicate that the enthalpy difference responsible for chiral selectivity is only about 1 kJ/mole. Together, these data begin to define the complex nature of the molecular interactions that result in chiral recognition in this natural bile salt system.

MARM 533

Progress on NMR metabolomics of Non-Alcoholic Fatty Liver Disease (NA-FLD)

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Within the human body, there are thousands of small molecules (less than about 1500 g mol-1) classified as metabolites, which participate in the biochemistry of homeostasis. It is recognized that the composition of metabolites in individuals can be sensitive to disease states. Recently, metabolite biomarkers for type 2 diabetes (T2D) have been established. Since T2D shares a number of risk factors with non-alcoholic fatty liver disease (NAFLD), it is possible that there are also systematic changes in metabolite levels that correlate with the progression of NAFLD. In this work, we report progress on the NMR metabolomics of human serum obtained from patients exhibiting differing stages of severity of NAFLD. To date, a preliminary set of 55 patient serum samples from middle-aged females of similar age and ethnicity has been studied. Each patient had a varying level of severity of NAFLD; some lacked the disease, while others were spread out upon a spectrum of severity. We note the use of an acetonitrile extraction procedure that has been adapted slightly to handle high-lipid sera. Preliminary results of targeted and untargeted analyses will be presented.

MARM 534

Comparison of orange fuming method against standard methods for development of latent prints on common substrates

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Fingerprints are used in forensic science due to their uniqueness. Fingerprints in their latent state can be lifted with various methods, which vary due to the porosity of the substrate. Cyanoacrylate coupled with luminescent dyes has been the method of choice when observing latent fingerprints on nonporous or semi-porous substrates. A new method, Lumicyano, claims to be able to achieve enhancement in one step. In this presentation, cyanoacrylate coupled with rhodamine 6G is compared to Lumicyano on glass slides, finished plywood, particle board, and porcelain tile. On a visible print, 15 points of minutiae were selected in order to quantify the print. Data suggest that the Lumicyano enhancement method is more effective than the classic cyanoacrylate method on certain substrates.

MARM 535

Chemical measurements in confined liquid films & addressing the urban-rural gap undergraduate research

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At the fluid-solid interface, chemical and physical forces confine fluid molecules, affecting their organization and flow behaviors. The interfacial region often dictates the larger system or device performance, but studying or predicting behavior of the interfacial region is far from trivial. We have developed a dynamic wetting apparatus that allows a more direct and controllable probe of fluid-solid interfaces which is used to examine several model systems including ionic and molecular liquids.

Our group is also active in supporting rural undergraduate students in research experiences. It is well known that participating in genuine reserach activities significantly improves the success of undergraduate STEM students. Statistics from the University of Iowa show a stark contrast in the rates of rural vs. urban students that participate in undergraduate reserach, with 64% of urban student participation in research compared to only 35% of rural students. We provide an outline of a new program to address this disparity.

MARM 536

LCMS and GCMS determination of extraction products of *Moringa oleifera* leaves

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Moringa Oleifera plant is widely known to be rich in nutrients and with many health benefits. In some parts of the world, the plant is used for treatment of various ailments. In this work extraction of the active ingredients in the leaves was carried out. The active ingredient were obtained by refluxing the leaves using both protic and aprotic solvents at variable times. Gas Chromatography Mass Spectroscopy (GCMS) and Liquid Chromatography Mass Spectroscopy (LCMS) were used to analyze both the volatile and non-volatile active ingredients. The major ingredients of Moringa Oleifera were also quantified.

MARM 537

Reaction of artemisinin with DNA bases: LC-MS analysis of key reaction products

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Artemisinin is a sesquiterpene lactone and a popular malaria drug used in Asian subcontinent and some parts of Africa. Understanding the nature and properties of this drug as well as its mechanism of action is very important. New literature suggest that the drug could be used for treatment of various forms of Cancer. In this work, we are investigating possible interaction between Artemisinin and the DNA bases. High Performance Liquid Chromatography (HPLC) and LC-MS were employed as analytical tools to monitor and establish this possible interaction. The results of DNA interaction with other artemisinin derivatives will be discussed

MARM 538

Electrochemical and chromatographic study of Artemisinin and its metabolites

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Malaria is one of the most devastating as well easily controllable infectious diseases in the world. In some parts of Africa and Asia, the Artemisia flowers and seeds provide a strong treatment for malaria attack. Artemisinin is a naturally occurring sesquiterpene lactone containing an endoperoxide bridge capable of generating free radicals. Detailed investigation of the mechanisms of action of this drug is very important. We are investigating the reductive modes of artemisinin after bio-activation using both electrochemistry and chromatography. Several artemisinin reduction intermediates generated after electrochemical reduction were identified using LC-MS. Results of interaction of artemisinin with DNA will also be discussed.

MARM 539

Designing tITP stacking for an in-capillary assay for creatinine

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Capillary electrophoresis (CE) is a low volume, high efficiency technique that is based upon differential migration rates of ionic species. In this work, creatinine, a neutral clinical marker for renal failure, is electrophoretically mixed in-column with picrate, which has an anionic mobility. The resulting nanoliter-volume reaction yields the Jaffé product, which is formed in amounts proportional to the creatinine content of the fluid, is bright red, and can be easily electrophoretically separated from neutral compounds in the reaction mixture. The goal of this project is to optimize the local ionic conditions within the reaction zone(s) to achieve increased sensitivity for the Jaffé product. Some conditions that affect the Jaffé reaction are reactant concentrations, injection lengths, overlap times, and buffer conditions. To enhance sensitivity, transient isotachophoretic (tITP) stacking is employed here to increase the Jaffé product peak height (by decreasing the zone width) as the product is formed within the capillary. Hydroxide is used as a leading anion to promote stacking that allows for about a 10-fold increase in detection sensitivity, allowing quantitative determination of 5 and 0.5mM creatinine in artificial blood serum; experiments to extend this range down to the low end of the “normal clinical range (0.1mM) are ongoing. Counter flow pressure has been investigated towards slowing peak broadening of the Jaffé product. Comparison of simulated (SIMUL 5.0) and experimental transient zone profiles has given insight to the importance of the timing of detection of the Jaffé product. SIMUL allows for frame-by-frame examination of the Jaffé reaction and stacking processes, providing information that cannot be obtained experimentally with a single on-line detector. Examination of the simulated ionic profiles leads to better predictions of the conditions to optimize the in-capillary Jaffé assay.

MARM 540

Development of an easy-to-use, paper-based sensing device for colorimetric detection of formaldehyde

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Formaldehyde is commonly seen in cosmetics and causes severe health issues. It is important to keep track of formaldehyde concentration in the cosmetics people used. An ease-to-use, paper-based formaldehyde sensing device is developed that accomplished detection under 0.05% formaldehyde by weight (the warning concentration suggested by Environmental Protection Agency). The chromogenic detection of formaldehyde involves an organic dye, embedded in paper, that will react to form colored species. The result can be read by naked-eyes with presence of trace formaldehyde in small amount of sample. Previous detection methods were fairly complicated and not practical for customers to use without training or outside lab. The paper-based device will be relatively cheap, for both device and small amount of sample used, and operable by the general public. Furthermore, this device can not only be used to detect formaldehyde in cosmetics, but also in air or solution.

MARM 541

Determination of lead in waterways and drinking water samples by ICP-AES

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The quantification of lead, Pb^{2+}, at 15ppb or less in water should be determined because excess is undesirable and prohibited due to potential toxicity. Lead exceeding 15ppb in drinking water is prohibited by the Environmental Protection Agency (EPA). Inductively coupled plasma-atomic emission spectrometry (ICP-AES) was used to quantify the trace of lead in each water sample and evaluated as either permissible or in violation with EPA set standards. Lead in low doses poses a serious threat to the neurological development of young children. Therefore, drinking water exceeding 15ppb has more toxicity potential.

MARM 542

Integrated emission and absorption spectroscopy experiment for general chemistry

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Emission and absorption spectroscopy are complementary techniques that can be used to demonstrate and reinforce general chemistry concepts. Traditionally, general chemistry students are exposed primarily to absorption spectroscopy in the form of Beer’s law experiments, while emission experiments may involve the study of atomic line spectra utilizing handheld spectrographs or spectroscopes. Technological advances that have made emission and absorption spectrophotometers more portable and affordable allow for more direct comparisons between the two techniques. A 2-week experiment was developed composed of six sections that in different ways explore

emission spectrometry and the complementary technique of absorption spectrophotometry. Parts I and II offer an introduction to the technique of emission spectroscopy as an instrumental method of analysis. Parts III through V emphasize applications of that technique including sample preparation and analysis considerations. Part VI further characterizes emission spectroscopy via comparison with absorption spectrophotometry. All of the experiment sections could be carried out as independent exercises as laboratory time allows or to emphasize a particular content point of instructor interest. The learning objectives for the experiment are included along with detailed overviews of the sections. These include a brief summary of the procedure along with expected student learning outcomes. Typical student experimental results and performance observations are also included.

MARM 543

Comparison of student learning outcomes using mechanism-based and functional group-based approaches in organic chemistry education

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Undergraduate organic chemistry courses traditionally present the material using a functional group-based approach, which often leads students to rely on memorization to learn various reactions. In an effort to better serve the pre-health, natural and life science majors of King's College, a small liberal arts school in Pennsylvania, the organic chemistry courses were reorganized to teach the material according to reaction mechanism. This change placed emphasis on identifying general reactivity patterns and problem-solving skills rather than memorization. Final exam questions were used to evaluate the effectiveness of the reorganization on student learning outcomes. The results of this investigation will be presented.

MARM 544

Get involved with the ACS Division of Chemical Education

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Want to know more about the Division of Chemical Education, learn how you can get more involved with DivCHED, learn about educational resources for chemistry, find out how to apply for travel awards, or meet and network with people from your region, nationally, and around the world who have similar interests? The Division of Chemical Education aims to serve as a means of focusing and enhancing the interest and efforts of all constituencies involved in the teaching and learning of chemistry at every level. If you have an interest in chemistry education, we want you involved in DivCHED. Come visit our poster to learn more about the Division and all we have to offer, meet representatives from the Division, and let us know what you think the Division can do to better meet the needs of our members.

MARM 545

Quantitative analysis laboratory: A new look!

***Susan M. Yochum**, yochum@setonhill.edu. Chemistry, Seton Hill University, Greensburg, Pennsylvania, United States*

This poster will feature key elements of an initiative to enhance student learning in, Quantitative Analysis I & II, the foundational chemistry laboratory courses for first year science majors. The goal of this project was to enhance student learning and retention of techniques and theory by providing resources for pre-lab preparation, post-lab review and for overall reinforcement. *iMovies* were created to capture techniques and chemical demonstrations. Student projects included a career path assignment and a multi-media lab report to enhance interest and comprehension. A learning style inventory was also administered.

MARM 546

Student-created case studies in secondary school science education

***Janet K. Berthel**, berthel@verizon.net. College of St Elizabeth, Morristown, New Jersey, United States*

The use of student-created case studies as an alternative to more traditional research papers and presentations at the secondary school level will be discussed. Merits of the approach include enhanced student interest and engagement, peer-lead instruction, gains in information literacy, and substantive reading plus data analysis within the discipline. Challenges with respect to students' lack of familiarity with the case study format, demands on student and instructor time, and the limited scientific backgrounds of the novice writers will also be addressed. Examples of student work will be presented.

MARM 547

Comparison of Microwave-Assisted Organic Synthesis (MAOS) with Conventionally Heated Over-Pressure Synthesis (CHOPS)

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A new class of synthesis reactor has appeared on the market, which allows for a reaction paradigm similar to that of monomode microwave reactors (i.e., sealed tubes and pressures over the solvent boiling point), but which relies instead upon rapid conventional heating. Several reactions have been examined in a side-by-side comparison of MAOS vs. CHOPS, with an eye toward application in the instructional organic laboratory. Relative merits of each system are discussed, especially with respect to reaction optimization.

MARM 548

Authentic chemistry research in high school

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The Princeton International School of Mathematics and Science (PRISMS) has designed a curriculum that incorporates authentic research into the high school years. In our model, students have dedicated class time of 120 academic hours per year to pursue perform a 2-year project. At the high school level, we expect research to be self-directed under the guidance of a lab director, though not wholly student-proposed. Research work is independent in the sense that each individual student is responsible for searching and reading the background literature, suggesting and conducting experiments, interpreting data, and communicating results. Students may require more guidance and oversight in the initial phases of their research, but should transition toward an independent and active role in generating new ideas from their experimentation and observations.

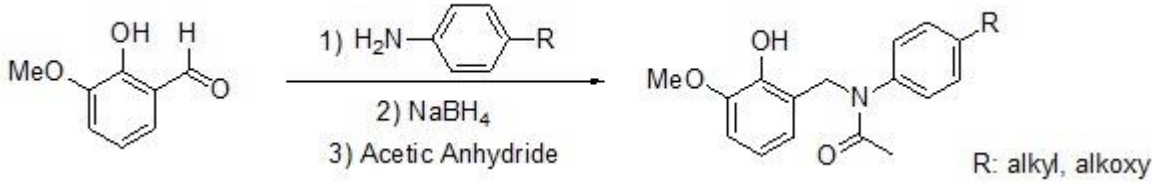
Examples and results of student projects in chemistry will be provided along with a discussion of challenges and lessons learned from implementing an authentic research program in a high school setting.

MARM 549

Further explorations of efficient one-pot three-step reductive amination sequence for the organic laboratory experiment

*Chenyu Zhang, Elenore Wiggin, **Xiaodong Fan**, xfan00@gmail.com. Chemistry, Lafayette College, Center Valley, Pennsylvania, United States*

The reductive amination of *ortho*-vanillin with of *para*-toluidine followed by acylation with acetic anhydride has been reported and practiced in undergraduate organic laboratory experiments. In this study we describe our efforts by applying a series of *para*- substituted aniline derivatives to react with *ortho*-vanillin to explore the scope of the reaction. The experiment allows the students to work and characterize of their own unknown products with IR and ^{1}H NMR.



MARM 550

Extensive studies of iron (III) chloride catalyzed Friedel-Crafts acylation reaction

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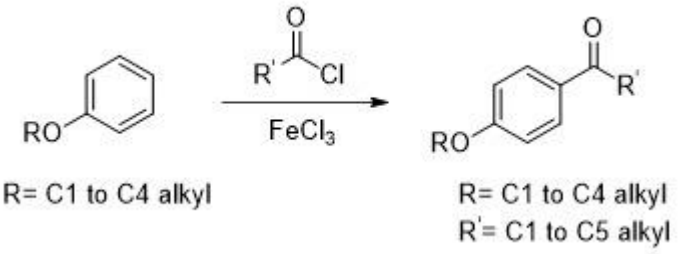
Studies on the Friedel-Crafts acylation reactions using iron (III) chloride as a Lewis acid catalyst have been reported in scientific literature and practiced in undergraduate organic laboratory experiments. In this study we describe our efforts to develop a procedure that includes a wide variety of acid chlorides to react with alkoxy

benzenes to explore the scope of the reaction. The experiment allows the students to work and characterize of their own unknown products with IR and ^{1}H NMR.



MARM 551

Organic chemistry predicting outcomes

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Modeling outcomes in Organic Chemistry is a means to understanding student success; however, there is limited literature on this topic. As an attempt to investigate academic performance, 7,894 students who had taken Organic Chemistry at a large state university with many campuses within a 3 year span were analyzed. General Chemistry I, General Chemistry II, cumulative grade point average, and gender were found to be significant indications for Organic Chemistry performance. Predictions were made and compared using multiple linear regression and generalized linear regression analyses. With every model, there is some degree of uncertainty and assumptions that must be made; therefore, comparing and contrasting two different approaches for modeling student success may provide further insight into the Organic Chemistry classroom.

MARM 552

Bridging chemistry

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A challenge for chemistry instructors is dealing with the limited retention of concepts as students progress from general chemistry courses to organic chemistry, and biochemistry through their freshman, sophomore and junior years. Students struggle grasping more advanced topics because they may see introductory concepts as isolated fragments of information that will not be needed past a given exam. However, as discussions begin to demand implicit understanding of this knowledge, a refresher tool is needed to maintain students actively and efficiently engaged in class. Here in we present a creation of a bridge module encompassing refresher concepts that tie high-school chemistry to general chemistry, general chemistry to organic chemistry, and organic chemistry to biochemistry. The module consists of concept videos tied to active learning problem sets followed by in-class sessions of small groups to discuss the application of these concepts in the advanced courses. Each topic was covered with a video presentation that focuses on problem solving that is well suited for display on mobile devices and an associated active learning project that encourages practice and application of skills developed in that topic. Voluntary student participation was sought from the general, organic and biochemistry class. Students were encouraged to take an online quiz after each set of core topics to assess their readiness in applying the concept to future content. The initial implementation of this module was tested in the Introduction to Biochemistry class and the preliminary data is presented herein.

MARM 553

Authentic/alternative assessment V: Performance of science majors/non-majors on the categorizing grid

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The purpose of this study was to investigate the categorization capacity of college students in a categorizing grid of general chemistry compounds and to compare their classification ability with other categorization schemes like conceptual maps and tables. These studies have been done for several semesters with about 50-60 subjects for reproducibility. Almost all students have showed very little knowledge of the classes of compounds and taxonomic rules. There was not significant statistical difference between the mean scores of majors/non-majors. Since classification is pervasive in nature and science this study is relevant in science education.

MARM 554

Authentic/alternative assessment in chemistry/science education V: The effect of the auto quiz on the achievement of science college students

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The auto quiz is an assessment technique in which the students read, understand, analyze, synthesize and evaluate the assigned topics (e.g. chapter). Then they prepared 15 questions of the most relevant content of the chapter. After they have learned the answers (and reasons for the best or most correct of them) they presented the auto quiz orally to the class. The professor evaluated both the quality of the questions, answers, reasons and examples provided by each student according to the written instructions.

The sample had consisted of about 50 students per semester during several semesters. The students, who prepared, presented and approved one auto quiz per chapter also approved the regular quiz and three exams of the professor with 80% to 100%.

In addition, the auto quiz students also approved the course with 90 to 100%. This constructivist technique was invented and applied by the author and has been very effective in demonstrating the extent of understanding of a topic. There was a significant statistical difference between the mean scores of regular and auto quiz students. This study is relevant for chemical, science education and science in general since this constructivist technique promotes the development of higher cognitive skills, and is relevant for science and science education.

MARM 555

Predicting color appearance of pharmaceutical and cosmetic color additive mixtures using TD-DFT calculations

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Color appearances of color additive mixtures in pharmaceutical and cosmetic formulations can be predicted using a combination of structural predictions from density functional theory (DFT) calculations and excited-state predictions using the time-dependent density functional theory calculations (TD-DFT). These methods were used to investigate the properties of three FDA-certified color additive compounds for externally applied drugs (D&C Red No. 36, D&C Yellow No. 11, and D&C Blue No. 6). Conformational structures were modeled using the molecular mechanics method (MM2) and B3LYP/6-31+G* calculations. The individual molecules were modeled in different solvents; heterodimers and heterotrimers were also modeled to investigate how interactions between molecules affect their optical properties. TD-DFT calculations provided the optical absorbance spectra which then were used to predict the color and appearance of the molecules in solution. Multiple peaks of the singlet excited states calculated were compared to literature and accepted values of visible spectra absorption ranges to assess accuracy of color prediction of mixtures. Batch samples of the mixtures were then prepared in the laboratory to confirm the spectral predictions of the mixed interacting color additive molecules.

MARM 556

Simulations of soap

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Detergents are used in a wide variety of applications, including the study of the structure-function relationship of membrane proteins. In the present study, we are investigating micelle formation in n-dodecyl-β-D-maltoside (DDM) detergents with a longer-term goal of understanding how the nature of the detergent micelle influences the properties of membrane protein solubilization. Molecular dynamics software such as Nanoscale Molecular Dynamics (NAMD) and Visual Molecular Dynamics (VMD) were used to explore the effects of concentration and initial packing configuration on the kinetics of self-assembly of DDM micelles and other associated micelle properties. Simulations included random assemblies of 20, 60, 110 and 200 DDM molecules, pre-formed micelles of 150 and 220 DDM molecules, and a pre-formed inverted micelle of 110 DDM molecules. Results include micelle characteristics such as aggregation kinetics, aggregation number and radius of gyration.

MARM 557

Systematic generation of the Dunham coefficients using symbolic mathematics software

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A mathematical algorithm for algebraically generating the Dunham coefficients for the rovibrational states of a diatomic molecule is spelled out in detail. This algorithm is incorporated into a set of *Mathematica* scripts to generate the terms to any desired order. The coefficients were generated explicitly to 10^{th} order in the smallness parameter, $r_e=B_e/\omega_e$. The computation time increases rapidly with order and schemes to make the computations more efficient are presented. The coefficients to 6^{th} order were optimized non-linearly to achieve agreement with experimental data for $H^{35}Cl$. The potential energy expansion coefficients are statistically significant up to a_{12}.

MARM 558

Unnatural alkanes as models for strained organic compounds

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Following the introduction to structures of organic compounds, students in Organic Chemistry I course are exposed to the concepts of conformers (strain energy, the resulting equilibrium geometries of molecules) and isomers (thermodynamic stabilities). Molecular modeling software, much more easily accessible nowadays, serves as a good learning tool to demonstrate the spacial proximity of atoms in any specific structure model and the consequent adjustments to bond angles, torsional angles and bond lengths that take place as each structure adopts its minimize energy structure. An out of class room project has been developed that requires the students to use this tool and analyze specific structures to (1) evaluate strain among the conformers and the consequence of energy minimization and (2) study highly strained structures, predict isomeric structures that are more stable and verify their prediction. Unnatural alkanes (e.g. propellane) serve as good examples for highly strained compounds. This hands-on assignment has allowed students to spend more time to understand the concept better, improving their performance on the class test following the assignment. This project was also used to teach and assess critical thinking and technical communication skills.

MARM 559

Controlling the charge carrier dynamics in inorganic chalcogenide perovskites by heteroatom doping

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Solar cells based on hybrid organic-inorganic perovskite (HOIP) materials show high solar-energy-conversion efficiency of >22.0%. However, the applications of HIOP materials are significantly limited due to their poor stability and the presence of environmentally hazardous Pb^{2+} ions in them. Recently, all-inorganic chalcogenide perovskite (AICP) materials were suggested as alternative systems for photovoltaic applications. We investigate the geometry, stability, electronic properties, and excited state carrier dynamics in doped and undoped AICP systems. Specifically, $BaZrS_3$ (BZS) and its derivatives namely, $BaZr_{1-x}Ti_xS_3$ (BZTS, x = 0.125, 0.25), $BaZrHfS_3$ (BZHS, x = 0.125, 0.25), $BaZrS_{1.5}O_{1.5}$ (BZSO), and $BaZrS_{1.5}Se_{1.5}$ are modeled using density functional theory (DFT) and hybrid DFT. Calculations indicate that the heteroatom doping can be used for controlling the stability and tuning the band structures of AICP for visible light photovoltaic applications. We use nonadiabatic molecular dynamic simulations to study the excited state charge and energy transfer dynamics and nonradiative electron-hole recombination dynamics in AICP materials. Strategies are devised for controlling the charge carrier dynamics in AICP materials with improved solar-energy-conversion efficiency.

MARM 560

Development of electrochemiluminescent platforms for high-throughput screening applications

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Many biological activities, including cell division, cell death, immune response and intercellular communication rely on a cascade of complex non-covalent interactions between DNA, proteins and other biomolecules. Current efforts in our lab are aimed at development of new platforms to detect and monitor these interactions using a combination of electrochemical and spectroscopic techniques. Toward this end, we are developing the fundamental chemistry required to build multielectrode arrays onto which large biomolecules such as DNA and transcription-factor binding proteins can be immobilized onto optically transparent conducting surfaces. The success of such bioconjugate interfaces is reliant on the use of robust and well-defined linkages that have topologies that we have identified as

being optimal for interfacial charge transfer. Similarly, we have worked to develop methods to incorporate redox and photochemically active probes onto these conducting surfaces and the biomolecules anchored on these platforms. Recent progress on the construction of these platforms and their incorporation into multielectrode arrays for high throughput screening will also be highlighted.

MARM 561

Nitric oxide coordination to a high-spin iron (II) complex with H-bond donors

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The high-spin iron(II) complex [Fe(DIG_3tren)](triflate)$_2$ features a tetradentate tripodal triguanidine ligand with multiple H-bond donors in its second coordination sphere, and is synthesized by reacting the DIG_3tren ligand in acetonitrile with iron(II) triflate. This complex can be used to synthesize the high-spin iron-nitrosyl complex [Fe(DIG_3tren)(NO)](triflate)$_2$ by reaction in acetonitrile with a slight stoichiometric excess of NO. ESI-Mass Spectrometry confirms that this synthesis gives complete conversion using 1% NO in N_2 as the NO source, indicating a strong binding between the NO ligand and the metal atom in this S=3/2 $\{FeNO\}^7$ complex. A similar complex, [Fe(TMG_3tren)(NO)](triflate)$_2$, was previously characterized by Speelman and Lehnert, but our DIG_3tren, unlike TMG_3tren, offers hydrogen-bond donors to potentially stabilize the Fe^{3+}-NO^- resonance structure. Spectroscopic and electrochemical comparisons of the NO complexes show minor differences between the DIG_3tren and TMG_3tren complexes.

MARM 562

Syntheses and structural comparison of [Co(DIG_3tren)X]BPh_4 complexes (X = halide)

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DIG_3tren is a four coordinate tripodal ligand that forms complexes with transition metal ions, including Co^{2+}. The M(DIG_3tren)$^{2+}$ complex can bind to an auxiliary ligand by forming a coordination bond from the metal and by providing hydrogen bond donors from the DIG_3tren arms. Co(DIG_3tren)[BPh_4]$_2$ is a previously reported complex that was reacted with NBu_4X salts in isopropanol to replace one of the tetraphenylborate counter ions with an auxiliary ligand (X=F, Cl, Br), yielding [Co(DIG_3tren)X]BPh_4. The different cobalt complexes of DIG_3tren with different halides as auxiliary ligand were successfully synthesized and their structures determined by X-ray crystallography. The ESI MS of the [Co(DIG_3tren)X]BPh_4 complexes and hydrogen bonding lengths and angles obtained from X ray crystallography are used to compare the strength of different halide anion binding with the cobalt DIG_3tren complex.

MARM 563 Withdrawn

Photo-dissociating ruthenium complexes containing the neocuproine ligand

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The development of new compounds that can selectively target cancer cells is of great interest. Specifically, the development of prodrugs that can be activated under specific conditions such as light or pH, could lead to significant advances in the battle against cancer. Ruthenium complexes containing photo-dissociating ligands have been studied for their activity against cancer cells where the complex only becomes active after ligand loss. To this end, we have prepared multiple ruthenium metal complexes containing the neocuproine ligand (neo), a ligand that undergoes photo-dissociation. We report the synthesis and study of [Ru(bpy)$_2$(neo)]$^{2+}$, [Ru(neo)$_2$(bpy)]$^{2+}$, and [Ru(neo)$_2$(4,4'bpy(OH)$_2$)]$^{2+}$ (bpy = 2,2'-bipyridine; 4,4'bpy(OH)$_2$ = 4,4'-dihydroxy-2,2' bipyridine). Verification of synthesis and structure of each complex was conducted using NMR spectroscopy, infrared spectroscopy, and UV/visible spectroscopy. Cyclic volammetry studies were performed to study the redox properties of these complexes. In addition, pH studies were carried out on the complex containing the 4,4'bpy(OH)$_2$ ligand. The 4,4'bpy(OH)$_2$ ligand contains deprotonatable groups that significantly alter the electronic properties of the complex as a function of protonation state. The photo-dissociative properties of these complexes were studied by shining LEDs of varying wavelengths on the complexes and observing the UV/visible spectra as a function of time.

MARM 564

Synthesis, structure, and catalytic activity of pyridinium based M-NHC complexes

***Roxy J. Swails**, swailsr@lafayette.edu, Stavros Kariofillis, Ryan Cerbone, Allyssa Conner, Melissa Sebold. Chemistry, Lafayette College, Easton, Pennsylvania, United States*

Water soluble catalysts are necessary in order to replace toxic organic solvents with abundant, non-toxic aqueous solvents for catalyzed organic transformations. Toward this effort a series of water soluble imidazolium ligands have been synthesized and used as supporting ligands for M-NHC complexes. The synthesis, structure, and catalytic testing for each complex will be discussed.

MARM 565

***De novo* protein models of binuclear metalloenzymes**

***Amanda J. Reig**, areig@ursinus.edu. Chemistry, Ursinus College, Collegeville, Pennsylvania, United States*

De novo proteins provide a unique opportunity for investigating the structure-function relationships that govern reactivity of binculear metalloproteins in a minimalistic an easily modified scaffold. DFsc is a de novo four-helix bundle protein that is capable of binding a range of divalent metal ions and has been shown to catalyze both oxidation and N-oxygenation reactions in the presence of iron. We have created a series of variants where the active site carboxylate and His residues have been systematically varied in order to understand how individual amino acids affect the structural, spectroscopic, and catalytic properties of the protein. In addition, data indicate that the scaffold is capable of incorporating copper into the active site and initial studies suggest the copper-bound form is capable of performing two-electron oxidation reactions.

MARM 566

Dye molecule-anchored platinum nanocatalysts

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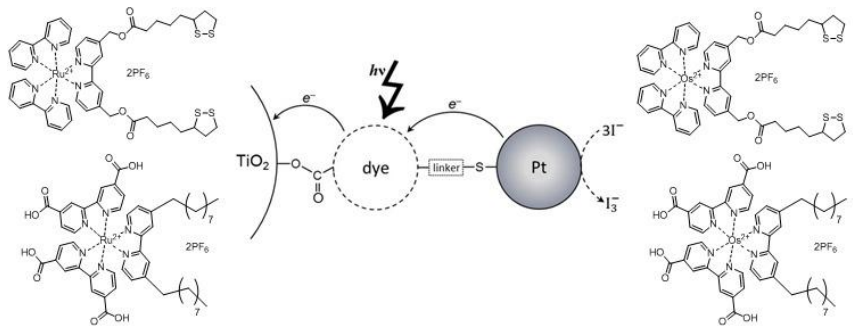
Iodide/triiodide is widely utilized as a redox mediator for dye regeneration in dye-sensitized solar cells (DSSC's) because of many favourable properties, most notably it's low rate of recombination with photoanode electrons. However, the large overpotential (ca.0.5 V) required for efficient reduction of oxidized dye molecules has led to an intense search for improvements or alternatives.

We will present our progress towards a synthetic design aimed at sidestepping the overpotential problem by anchoring a platinum nanoparticle, a known catalyst for the iodide/triiodide redox process, to a Ru(II) or Os(II) dye complex. We have successfully synthesized Pt nanoparticles and functional dye molecules capable of binding to either TiO_2 or Pt. The dyes have two matching bipyridine (bpy) ligands with or without COOH groups for anchoring toTiO_2. The third bpy ligand terminates in either a non-interacting alkyl chain or a 1,2-dithiolane for attachment to Pt. Cyclic voltammetry (CV) of the dyes on a Pt wire confirm that the dye attaches to the Pt exclusively via sulfur. Solar-cells of the TiO_2/dye dimer structure have been successfully assembled and measured. Synthesis, characterization, and studies of both supramolecular assemblies and small molecule comparisons, will be presented along with future directions.



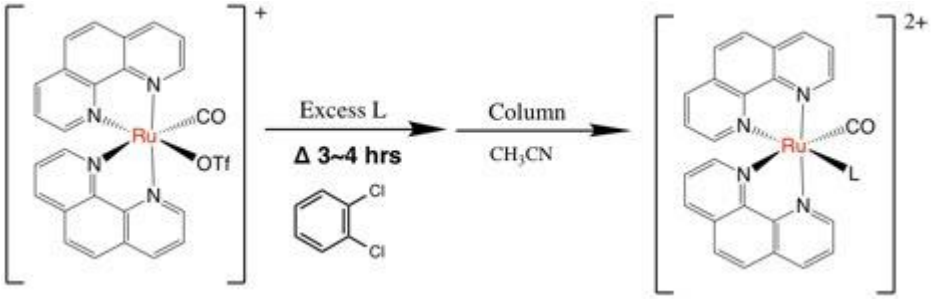
Schematic representation of the dye behaving as a linker between the TiO_2 surface and the Pt nanoparticles framed by the four complexes investigated in this poster.

MARM 567

Synthesis of bis(1,10'-phenanthroline)-carbonyl-ruthenium(II) complexes with varying pyridine ligands

***Armando Seitllari**, armando.seitllari10@stjohns.edu. Chemistry, Saint John's Univeristy, Brooklyn, New York, United States*

The bis-(1,10'-Phenanthroline)-Carbonyl-Ligand-Ruthenium(II), $[Ru(phen)_2CO(L)]^{2+}$, complexes where L is a pyridine derivative ligand, are of interest because they have potential as catalysts for solar energy applications, biosensors for heparin and can also be used as DNA probes. The pyridine ligand derivatives have a higher energy excited state than the standard ruthenium catalyst $[Ru(phen)_3]^{2+}$. The advantage of using these ligands is that they may have longer lived excited states and greater stability. The synthetic process and electronic characterization of these compounds will be discussed in detail.

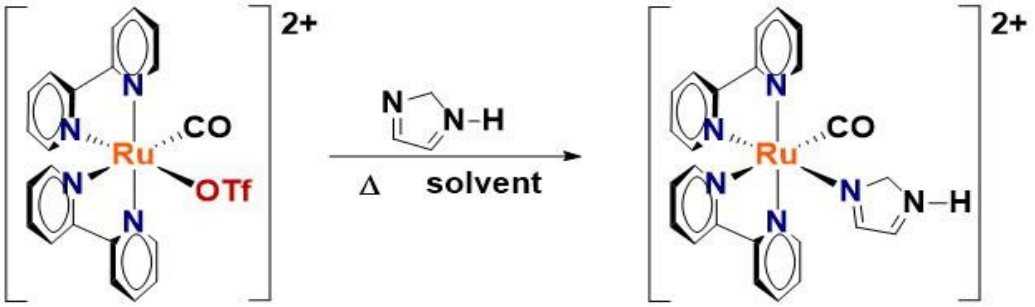


MARM 568

Synthesis of bis-(2,2'bipyridine)-carbonyl-ruthenium(II) complexes with varying imidazole ligands

***Shenell Collins**, shenell.collins12@stjohns.edu. Chemistry, St. John's University, Queens, New York, United States*

The bis-(2,2'-Bipyridine)-Carbonyl-Imidazole-Ruthenium(II) complexes are of interest because they have potential as catalysts for solar energy applications, probes for DNA, and biosensors for heparin. These are new complexes that need to be characterized to determine their electronic properties. Once the ground and excited state properties are understood, these compounds will be screened for use as luminescent sensors. We will discuss the synthesis and electronic characterization of these compounds.



MARM 569

Green synthesis of gold nanoparticles using red azalea plant: An anti-microbial study

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The goal of this researh project is to determin the most efficient method and conditions to synthesize gold-azalea nanoparticles. The red Axalea plant has known antioixidant activity, and works as a surface passivating agent in the synthesis of the gold nanoparticles. Gold-Azalea nanoparticles are of interests due to their ability to generate high sensitive antimicrobial agents. Resistance to antibiotice has posed a serious risk to the population, opening the door for a new antibiotic treatment. A study conducated by Kim et al., concluded that silver nanoparticles were effective growth inhibitors to *E. coli* and *S. aureus,* implying that the silver nanoparticles have antimicrobial properties. In this research project, the Gold-Azalea nanoparticle's antimicrobial ability was tested on *E. coli* and *S. epidermidis*. The green synthesis is of paticular interest as it presents a facile way to synthesize size and shape

controlled nanoparticles, which is important for surface enhanced Raman spectroscopsy. The use of plant extracts is an excellent alternative to the use of harsh chemicals for the gold nanoparticle synthesis. The synthesis is simple, inexpenisive, and ecological with a short time requirement. Details of the protocol and results of charaterization using optical spectroscopy will be presented.

MARM 570

Characterizing the dimerization of N-methyl mesoporphyrin IX *via* fluorometric and UV-vis analysis

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The oligomerization of N-methyl mesoporphyrin IX (NMM) was studied using fluorescence and UV-vis spectroscopy. The NMM concentrations ranged from 0.7 nM to 2.7 μM. Dimerization was found to be the dominant aggregation process characterized by the dimerization constant of $(1.37 \pm 0.08) \times 10^4$ M at 25°C in 10 mM lithium cacodylate buffer with a pH of 7.2. The effects of a variety of salts (specifically NaCl, KCl, LiCl, $MgCl_2$, and $Ca(NO_3)_2$) were studied in the concentration range from 0.7 mM to 100 mM. We discovered that the fluorescence intensity of NMM was largely unaffected by the presence of salts, regardless of the cationic strength or concentration. Characterizing the oligomerization patterns of NMM is crucial to understanding its biological reactivity, such as binding to and stabilizing selectively non-canonical DNA structures of oncogenes and telomeres.

MARM 571

Synthesis and characterization of metallospiroligomers toward the design of artificial metalloenzymes for catalytic oxidation reactions

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The most effective systems for activating carbon-hydrogen (C-H) bonds utilize some of nature's most complex biomolecules. These biological enzymes can cleave C-H bonds with regio- and stereoselectivity that industrial catalysts lack at ambient temperatures. By coupling stereochemically pure bis-amino acids together, we have synthesized rigid ladder-like molecules with desired regio- and steriochemistry. Spiroligomers are synthetic peptidomimetic macromolecules linked through pairs of amide bonds, which, unlike in proteins, prevent conformational rotation, preventing misfolding, and making them more robust compared to natural peptides. Multidentate pyridyl amine based ligands have been being designed and incorporated into the monomeric building blocks. We can couple these monomeric building blocks into macrocycles holding the ligands at fixed distances. The multidentate ligands have open coordination sites that can bind various metal centers. These macromolecular scaffolds are being used as templates for assembly of multi-metal cofactors for catalysis. This allows us to control the steric and stereochemical environment of the active site around the cofactor. Results including synthesis and characterization will be presented.

MARM 572

Characterization studies of an ionic conducting soft-solid electrolyte LiCl:DMF

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The current use of lithium ion batteries is prevalent in every aspect of daily life: cell phones, laptops, electric cars and all have potential safety risks to consumers. The necessity for safer electrolytes is critical in developing solid state electrolytes. Currently, the highest conductivities come from ceramics in the range of 10^{-3} to 10^{-2} S/cm but face the challenge of being brittle and a poor adherent to electrodes. Polymer composite blends can address these physical issues but suffer from poor conductivity in the range of 10^{-7} to 10^{-5}S/cm. The development of soft-solid electrolytes such as LiCl:DMF addresses the physical difficulties of ceramics and improves upon the conductivities seen in polymers with a conductivity in the 10^{-4}S/cm range. In initial studies, the focus was on the Hard-Soft Acid-Base concept that the soft DMF donor does not bind the hard Li+ ions. This results in low-affinity ion channels and high Li ion conductivity. The pressed pellets of LiCl:DMF used in conductivity tests exhibit both bulk and grain boundary resistance, and appears to have a liquid-like interfacial layer between LiCl:DMF grains. An in-depth investigation of the thermal analysis characterization and surface imaging of this compound is discussed to better understand the high conductivity of the co-crystal.

MARM 573

Anti-cancer activity of ruthenium-gold and titanium-gold bimetallic complexes bearing N-heterocyclic carbene ligands

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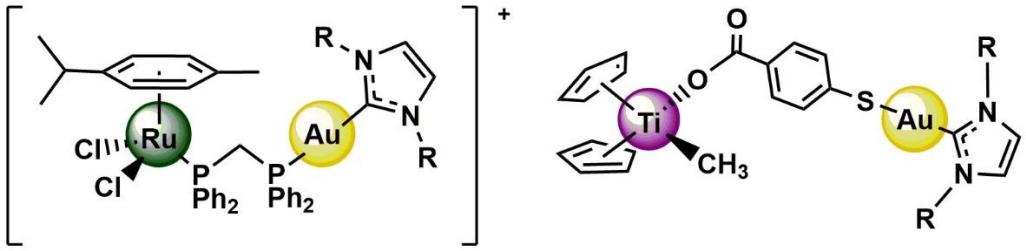
Gold complexes containing N-heterocyclic carbenes (NHC) have emerged as very attractive compounds due to their application as homogeneous catalysts and their potential as anticancer and antimicrobial agents. In the context of cancer research, we hypothesized that the incorporation of two bio-active metal-fragments in the same molecule would improve their activity as anti-tumor agents due to the interaction of the different metals with multiple biological targets (cooperative effect) and/or by the improved chemicophysical properties of the resulting heterobimetallic compound (synergism). Our group at Brooklyn College has reported recently on the preparation of heterobimetallic complexes containing titanocenes [$TiCp_2$] or ruthenium(II) arene derivatives [Ru(p-cymene)Cl_2(dppm)], and gold(I)-phosphane, gold(I)-chloride, gold(I)-thiolate or gold(I)-heterocyclic carbene (NHC) fragments as potential chemotherapeutics for renal, prostate and colon cancer (including relevant *in vivo* studies for renal cancer). Heterobimetallic Ru-Au and Ti-Au compounds containing NHC-gold(I) fragments display cytotoxicity towards specific cancer cell lines and high selectivity, potent antimigratory and, in some cases, antiangiogenic properties. We report here on the synthesis of new Ru-Au (**1**) and Ti-Au (**2**) compounds containing Au-NHC fragments that have already displayed cytotoxicity towards cancer cells in sub-micromolar range or even in nano-molar range while being selective. We expect these new heterobimetallic compounds to be more efficacious both *in vitro* and *in vivo*. Additionally, we will report on preliminary *in vitro* studies of these bimetallic compounds with potential as cancer chemotherapeutics.



MARM 574

Transition metal complexes with n-heterocyclic ligands for MRI and MRS application

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Both magnetic resonance imaging (MRI) and magnetic resonance spectroscopy (MRS) are diagnostic tools that use the properties of protons *in vivo* to generate a signal. Paramagnetic metal ions can enhance these studies, respectively, by generating new interactions with the protons for MRI, or by generating a strong signal for a given paramagnetically shifted resonance of note in MRS, utilizing the changes in the magnetic environment around the metal. Literature has used lanthanide and transition metal complexes to change the magnetic properties of the proton. Our group has focused study on complexes using macrocyclic ligands appended with various pendent groups to form paramagnetic complexes of iron, cobalt and nickel. Different pendent groups can afford the complex different characteristics, such as having observable protons for chemical exchange saturation transfer (CEST) MRI or to change properties including solubility or the charge. Studied here are complexes of benzimidazole and *N*-methyl imidazole pendent groups on aza- and oxaaza- macrocycles coordinated to Fe(II), Co(II), and Ni(II) ions.

MARM 575

Biochemical and spectroscopic characterization of phylogenetically diverse homologs of the antibiotic resistance protein Cfr

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Cfr methylates the C8 and C2 position of adenosine 2503 (A2503) of 23S rRNA, a modification demonstrated to confer resistance to five distinct classes of antibiotics. Cfr is a member of the radical SAM superfamily, requiring a 4Fe4S cluster and an *S*-adenosylmethionine cosubstrate to accomplish methylation of unactivated carbon center(s). Of the Cfr sequences identified to date, there is known diversity in activity and domain architecture. Here we characterize four phylogenetically distinct Cfr homologs, revealing that all harbor a complete iron-sulfur cluster and robust C8 methylation activity towards a 155mer fragment of rRNA. One of these systems harbors a C-terminal extension necessary for full methylation of A2503 at C8, implying a non-essential regulatory role for the additional domain. The domain resembles a stand-alone electron-transfer shuttle and is present in the genome of other Cfr-containing organisms as a separate open reading frame, raising the possibility that accessory protein modulation of activity is a general feature of Cfr catalysis.

MARM 576

Nonaromatic tetrapyrrole complexes for the electrochemical and photochemical activation of dioxygen

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Porphyrin is a ubiquitous and versatile protein cofactor that plays many roles in biology. Despite their ubiquity, porphyrins only represent a subset of tetrapyrrole macrocycles. For example, tetrapyrroles such as porphyrinogens and related derivatives are nonaromatic macrocycles that contain reduced *meso*-carbons and display unique redox and photophysical properties as compared to those observed for more traditional porphyrinoids. In an effort to develop new tetrapyrrole architectures that are easily prepared and structurally robust we have developed a new breed of tetrapyrrole complexes that allows for the photophysical and transition-metal coordination chemistry of porphyrins to be married with the multielectron redox properties of the porphyrinogen. These scaffolds, which contain a single sp^3 hybridized *meso*-position and form core structures that are distinct from more common porphyrinoids are termed biladienes and isocorroles and support an intriguing redox and photophysical properties that make them well suited for applications in small molecule activation and photosensitization. Recent efforts to utilize metal biladiene and isocorrole complexes for the activation of O_2 via electrochemical and photochemical pathways will be presented.

MARM 577

Performance comparison of metal oxide-graphite anodes in the electrochemical oxidation of ethanol, acetaldehyde, and acetic acid

***Arthur T. Poulos**, atpoulos@scicore.org, Rachel Furman, Michael Namer, Vidhi Patel, Peter Poulos, Meher Sahni. SciCore Academy, Allentown, New Jersey, United States*

A number of research groups have attempted to develop an ethanol-based fuel cell using non-precious metal catalysts for the ethanol oxidation steps. Achieving high current density and high conversion is challenging because complete oxidation of ethanol to carbon dioxide is a 12-electron process, with several alternative pathways available, depending on catalyst and reaction conditions. Oxidation of intermediate acetic acid and acetaldehyde to C-1 species are kinetic bottlenecks due to the strength of the C-C bond. One approach to improving the speed of intermediate oxidation is to fabricate anodes consisting of metal oxides adsorbed or attached to inert electrodes. The expectation is that metal oxides in proximity to the positively charged electrode will be driven to higher oxidation states; transient metal oxidants can serve as the primary oxidizing species, assisted by coordination between the metal moiety and the organic substrate (much in the same way that a coordination bridge promotes alcohol oxidation by chromate). Our group has prepared conductive graphite electrodes coated with metal oxides such as Cu_2O and CuO nanoparticles, chromic oxide, vanadium oxide, and others. The various electrodes were compared with respect to anodic response to ethanol, acetaldehyde and acetic acid. Sustained electrochemical oxidation of the three substrates and various electrodes were conducted in a 2-compartment electrolytic cell, and reaction product distributions were determined by gas chromatography, HPLC and spectrophotometry. Several catalysts exhibited high selectivity toward oxidation of ethanol to acetaldehyde; aldehyde condensation reactions interfere with further oxidation, which led us to investigate catalytic conversion of acetaldehyde to acetic acid. The effects of alternative electrode fabrication methods on anodic current and product selectivity were also studied.

MARM 578

Inorganic microwave synthesis: From quadruple bonds to metal-organic frameworks

***Carly Reed**, creed@brockport.edu, Callen Feeney, Marcy Merritt. Chemistry and Biochemistry, The College at Brockport, Brockport, New York, United States*

Microwave irradiation has proved to be an effective synthetic tool for organic, inorganic, and organometallic compounds as well as solid-state and inorganic nanomaterials. The irradiation and thereby direct heating of the sample often leads to shorter reactions times and higher yields sometimes with reduced reactants and solvents, making microwave synthesis a green synthetic pathway.

A series of multiply bonded dirhenium complexes have been synthesized via microwave synthesis. In all cases, the reaction times were reduced from hours to minutes and for many the yields exceeded those of the traditional synthetic pathways. The complexes were characterized using infrared and UV-Vis spectroscopies, elemental analysis, and X-ray crystallography.

The synthesis of metal-organic frameworks (MOFs) in green reaction media using microwave irradiation is currently under investigation as a method to produce MOFs with better catalytic ability. Synthetic methods and yields will be shared.

MARM 579

Modeling the molybdenum cofactor: Synthesis and reactivity of molybdenum quinoxalyldithiolenes

***Douglas R. Gisewhite**, d.r.gisewhite@eagle.clarion.edu, Alexandra Nagelski, Sharon J. Nieter Burgmayer. Bryn Mawr College, Bryn Mawr, Pennsylvania, United States*

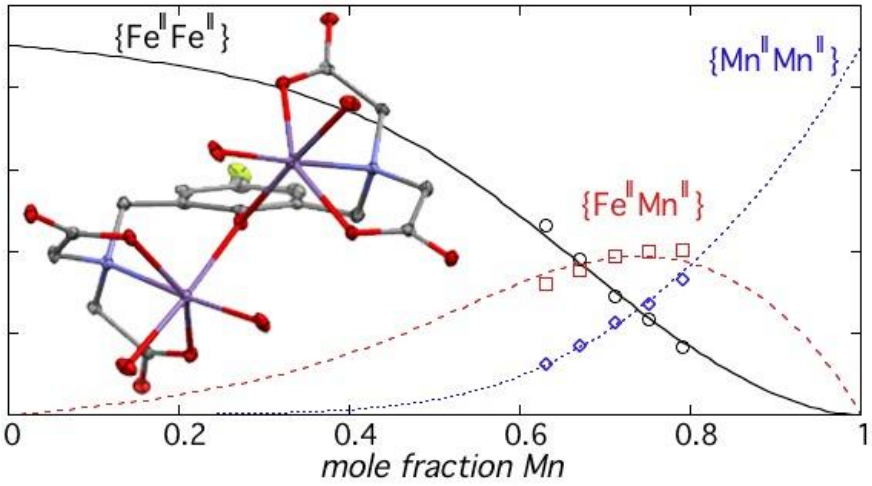
The molybdenum cofactor, Moco, is found in all living organisms, excluding *Saccharomyces cerevisiae,* and participates in global nitrogen, carbon, and sulfur cycles. There is a conserved pterin dithiolene ligand which coordinates molybdenum (Mo) in the cofactor of mononuclear enzymes. Crystal structures of several bacterial molybdoenzymes suggest the pterin dithiolene ligand can exist in both a tricyclic and a bicyclic state. Interconversion of the two states has been thought to play a critical role in the catalytic mechanism of Moco. Therefore, understanding the pyran cyclization and scission, a type of ring-chain tautomerism, is an important aspect of study to understand its role in catalysis. Here, we report the synthesis, characterization, crystal structure, and reactivity to acid of two Moco model complexes with the formula [TEA][Tp*Mo(O)quinoxaline-C(CH_3)$_2$R-dithiolene] where TEA is tetraethylammonium, Tp* is tris(3,5-dimethylpyrazolyl)hydroborate, and R is either methyl or hydroxyl. X-ray crystallography shows two bicyclic models, however, ^{1}H and ^{13}C NMR, UV-Vis, and cyclic voltammetry experiments indicate the hydroxyl group undergoes irreversible intramolecular cyclization producing a pyran ring upon acid addition. Instability created by protonation of the quinoxaline's pyrazine ring encourages pyran degradation yielding pyrrole formation. Analysis of each stable species will be discussed.

MARM 580

Synthetic models of Fe/Mn discrimination by proteins in the ferritin-like superfamily

***William D. Kerber**, will.kerber@bucknell.edu. Bucknell University, Lewisburg, Pennsylvania, United States*

Equilibrium binding of Fe(II)/Mn(II) mixtures to the dinucleating ligand F-HXTA (5-fluoro-2-hydroxy-1,3-xylenediamine-tetraacetic acid) is a model of cofactor assembly in the R2 subunit of class Ic ribonucleotide reductases (R2c) and R2-like ligand binding oxidases (R2lox). The relative stability of bimetallic clusters has been investigated by fluorine NMR, and as predicted by the Irving-Williams series, F-HXTA forms more stable complexes with Fe(II) than with Mn(II). An unexpected thermodynamic preference for the heterobimetallic Fe/Mn cluster was also observed, which could contribute to the selective assembly of metallocofactors in R2c and R2lox. This appears to be a general phenomenon with F-HXTA as other pairs of divalent metal ions exhibited the same effect (Fe(II)/Zn(II), Fe(II)/Mg(II), and Zn(II),Mg(II)). The origin of heterobimetallic cluster stability and the synthesis of 2nd-generation R2c/R2lox models will be discussed.



MARM 581 Withdrawn

Polyketones for hole transport materials

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The achievements in conversion efficiency of Perovskite solar cells have established PSCs as a credible alternative to liquid electrolyte solar cells, but these cells typically contain spiro-OMeTAD, a solid hole transport material (HTM), which is very expensive to fabricate. Polyketones are easily synthesized from carbon monoxide and terminal olefins, and the resulting polymer is reactive making the polymer ideal for post-polymerization functionalization reactions. These functionalized polyketones could yield new materials with unexplored properties such as hole transport activity. Polymers synthesized have been modified with Paal-Knorr reactions to yield new materials which will be explored as HTMs.

MARM 582

Surface chemistry of zinc bromide deliquescence

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Aqueous ionic interfaces are universally abundant and play a critical role in many physical, chemical, biological, environmental and technological processes. Ions at liquid interfaces experience an asymmetric environment that influences interfacial composition, orientation, dielectric forces and transport properties. Probing the electronic structures and interfacial concentrations of aqueous electrolytes at a molecular level is technologically very challenging. Herein we present results using lab-based ambient pressure X-ray photoelectron spectroscopy (LAPXPS) to examine zinc bromide, a salt utilized as an energy storage medium through the use of zinc-bromine flow batteries and in heterogeneous catalysis. The efficiencies of these processes can be directly impacted by the abundance of water in the salts local environment. LAPXPS was employed to study the solid-vapor and aqueous-vapor interfaces of zinc bromide salt under ambient water vapor conditions from < 10^{-7} % to 16 % relative humidity (RH). This humidity range contains the physical transition of deliquescence allowing for the surface chemistry measurement of $ZnBr_2$ as it transitions from solid to an aqueous solution. Zn, Br, and O core shell spectra analyses show clear changes in widths, shifts and relative concentrations as zinc bromide changes phase as a function of RH. These results highlight the powerful utility of LAPXPS to probe changes in electronic structure and chemical composition of salts at solid-vapor and liquid-vapor interfaces.

MARM 583

Measuring the electron scattering cross-section of water vapor using a hydrophobic ionic liquid and lab-based ambient pressure XPS

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Electron interactions with gas phase molecules play a significant role in understanding planetary atmospheric science, radiation damage in biological specimens and plasma science. The total electron scattering cross-section (ESC) is a measure of the interaction between the electron and molecule of interest. Electron collisions with water, the third most abundant molecule in the universe, is an essential process to understand and quantify. Herein we

present results for gas phase water ESC as a function of kinetic energy (KE) using lab-based ambient pressure X-ray photoelectron spectroscopy (LAPXPS). Since a lab-based X-ray source has a constant photon energy, the photoelectron KE was varied by probing a hydrophobic ionic liquid substrate composed of five different elements (F, O, N, C and S) covering a wide KE window. The IL was exposed to water vapor at varying pressures from high vacuum up to 2 Torr while simultaneously taking high resolution XPS spectra. Examining the gas phase attenuation of the XPS peaks for each element allowed for the determination of ESC for water vapor in the KE range of 800-1320 eV complementing previously published photoemission data.

MARM 584

Tetramethylguanidinium amino acid-based ionic liquids: Synthesis, characterization, and evaluation for biochemical applications

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Ionic Liquids (ILs) have shown promising applications in various research fields. In particular, their remarkable properties as highly adaptable and versatile organic solvents mainly composing of ions have seen use in biological systems. The preparation of organic ILs containing 1,1,3,3-Tetramethylguanidine (TMG) and natural amino acid as cation and anion pair, respectively, offers high biological activity and becomes viable alternative to room temperature ILs. Here, we present a study on the potential biocompatibility of amino acid derived ionic liquids (AAILs) containing highly functionalized organic moieties as solvents for biological applications. The characterization of AAILs were validated by comparing experimental vibrational spectroscopy and DFT 6-31G+* quantum chemistry calculations. Further, thermodynamic and unfolding kinetics studies of different proteins (e.g. myoglobin, trypsin, calmodulin) were conducted via electronic spectroscopy measurements to compare the effect of AAIL with respect to traditional ILs. In addition, we examined the interaction of amino acids with corresponding ILs to observe the behavior of the system at higher concentrations.

MARM 585

Conductivity, viscosity, and thermodynamic properties of propylene carbonate solutions in ionic liquids

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Ionic liquids (ILs) are a series of stable, non-flammable, non-volatile organic compounds containing only ionic species. ILs can be adjusted to yield electrolyte solutions with low viscosity and high conductivity for electrochemical energy storage and conversion devices such as lithium ion batteries, fuel cells, and supercapacitors, leading to improved performance in capacity and stability. Propylene carbonate (PC) has been used as a solvent / co-solvent to prepare electrolyte solutions for these energy storage devices. In this work, we have used a series of experimental methods such as calorimetry, gas chromatography, Fourier transform infrared spectroscopy, viscosity and conductivity measurements to characterize the properties of PC / IL solutions and the solvation mechanism. The ILs include 1-butyl-3-methylimidazolium tetrafluoroborate ($BMIBF_4$), 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (BMITFSI), and 1-butyl-3-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (PyrrTFSI). Experimental results demonstrate that the PC / IL solutions possess lower viscosities and higher conductivities, compared with pure ILs. While the thermodynamic properties of the solutions depend on the structures of the molecular ions of the ILs.

MARM 586

Various isomers of ketenylidene cation investigated using ab initio methods

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Ab initio electronic structure theory has been employed to investigate the various stable configurations of ketenylidene cation. This system has been proposed to be found in the interstellar media. The total energies, barrier heights, equilibrium structures and harmonic vibrational frequencies for various extrema points on the surface will be presented. The Coupled Cluster method with single, double and connected triples (CCSD(T)) along with the cc-pVDZ, cc-pVTZ and cc-pVQZ basis are used to investigate this system.

MARM 587

Simultaneously measuring trapped and free carriers using time-resolved infrared spectroscopy

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Solar cells based on organo-halide perovskites have emerged as a promising photovoltaic material. Gaining a better understanding of the organo-halide perovskite's free carrier dynamics can reveal information about the carrier lifetimes and trap state distribution critical to improving the materials performance and stability. However, a complete understanding of the materials photophysics is incomplete due to the limited availability of methods capable of measuring both free and trapped carrier dynamics. Time-resolved photoluminescence (TRPL) spectroscopy has traditionally been used to probe the carrier dynamics of perovskites, but the technique is only sensitive to radiative decay pathways. By using time-resolved infrared (TRIR) spectroscopy in comparison to TRPL we have shown that photogenerated charges relax into free carrier states that have lower radiative recombination probabilities which cannot be observed by TRPL. Furthermore, TRIR measurements also show that trapped carriers exhibit distinct mid-infrared absorptions.

MARM 588

Synthesis of ZnSe:Mn-doped quantum dots for tuning charge carrier lifetimes

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Colloidal quantum dot semiconductors have been the focus of much research due to their uniquely tunable electronic properties. However, surface traps result in short carrier diffusion lengths and poor charge extraction efficiencies. Traditionally, the passivation of surface traps has been approached by modifying core-shell architectures. Our research focuses on establishing the role of Mn^{2+} doping as an alternate method to prolong charge carrier lifetimes. Herein we report the synthesis and characterization by transmission electron microscopy, electron paramagnetic resonance spectroscopy, photoluminescence spectroscopy, and absorbance spectroscopy of ZnSe:Mn doped quantum dots. This work presented will serve as a foundation for future studies addressing energy transfer to acceptor molecules.

MARM 589

Carbon dioxide self-quenching rates

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Vibrational energy transfer between carbon dioxide molecules is important for understanding the thermal properties of the Martian atmosphere. In this work we use transient diode laser absorption spectroscopy to explore self-quenching rates among the lowest few vibrational states of carbon dioxide. Our experiment involves flowing a dilute mixture of carbon dioxide with trace amounts of ozone in krypton or xenon bath gas through a reaction cell. The ozone is photolyzed by a pulsed Nd:YAG laser to create a temperature jump in the gas mixture. The carbon dioxide vibrational state populations shift upward depending on the magnitude of the temperature-jump. The time-evolving, state-selective carbon dioxide populations are measured with a diode laser and the data are fit with appropriate kinetic models. The measurements are repeated over a range of quencher concentrations to allow extraction of the rate coefficients of interest. The goal of this work is to determine all relevant rate parameters with enough precision to develop more accurate Martian upper atmospheric models.

MARM 590

Decrease in activation energy and frequency factor for the intramolecular isomerization reaction of azobenzenes when anchored to ZrO_2 nanocrystalline semiconductor thin films

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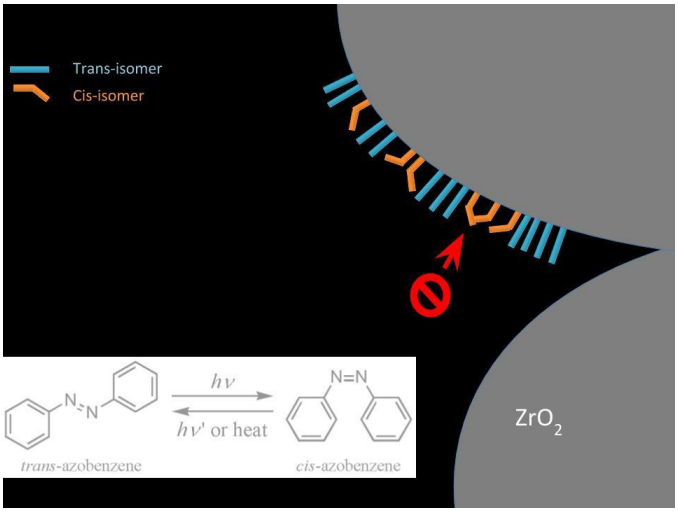
Many contemporary solar fuel devices utilize molecular species that are chemically anchored to nanocrystalline semiconductor thin films. These molecules are typically expected to exhibit similar chemical behavior when anchored to the thin film as when they are dissolved in fluid solution. However, this assumption may not be valid for all types of chemical reactions as the environmental changes that a molecule experiences at the interface may influence chemical reactions in unforeseen ways. In this study, the well-known intramolecular isomerization reaction of azobenzene derivatives is measured in fluid solution and when anchored to ZrO_2 nanocrystalline thin

films. The characteristic absorption spectra of the *cis* and *trans* species are used to quantify the kinetics of *cis* to *trans* isomerization over a range of temperatures. Analysis of the reaction kinetics allows for the activation energy, E_a, and frequency factor, A, to be determined under both solution and interfacial conditions. Notably, the activation energy decreases by more than 25% and the frequency factor exhibits a roughly thousand-fold decrease for the intramolecular reaction when anchored to the thin films, portending the intriguing possibility of the influence of steric hindrance significantly effecting reaction rates at the nanoparticle-solution interface.



Schematic of azobenzene derivatives anchored at the solution-nanoparticle thin film exhibiting steric hindrance of the intramolecular izomerization reaction due to the presence of the nanoparticle itself and other anchored azobenzene molecules.

MARM 591

Without barrier methyl radical transfer from methylco(II)balamin cofactor of vitamin B12 to cysteine in the methionine synthase process

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Calculations models used by the research community to study methylcobalamin vitamin B12 cofactor activation, up until now, have led to serious disagreement between theoretical and experimental data. A calculation of the total energy with geometry optimization and constrained Co-C bond bond length for the base-off CH3- Co(II) model gives the lowest energy barrier for C-Co bond breaking (approximately 20 kcal/mol).
However, with this barrier, a kinetic calculation with fast bond cleavage is improbable. Another contradiction is that the enrgy barrier of the Co-C bond breaking is much higher for base-on species compared to the base-offspecier. Therefore, according to DFT calculations the rate constant of Co-C bond cleavage must have a much lower value for base-on species, when comparing the rate constant of a similar reaction for base-off species. This is a flagrant contradiction with the experimental data, which demonstrates that the rate of reaction of Co-C bond breaking is significantly higher in base-on species, compared with the same reaction rate constant for base-off species. Moreover, the experimental values of kinetic barrier for Co-C bond cleavage in the one-electron reduced base-on methylcobalamin in alcohol-aqua mixtures has been found to be about 7 kcal/mol which is in disagreement with DFT data. On the other hand, the MCSCF geometry optimization of the systems including the dissociated cysteine model and either base-off methylcobalamin specie or the base-on structure (with histidine molecule (imidazole model) as the sixth ligand of the central cobalt) shows Co-C (CH3) bond cleavage without barrier as the first step and CH3 transfer to cysteine as the last step. We conclude, that the histidine-base-on (histidine modeled by imidazole) is effective in CH3 radical transfer from methylcobalamin cofactor to cysteine.The MCSCF results demonstrate, that the correct electronic structure of the methylcobalamin cofactor of vitamin B12 can be obtained only by using methods which take into account the interaction between occupied and unoccupied orbitals causing an effect similar to (vibronic) pseudo-effect Jahn-Teller.

MARM 592

Photochemistry and infrared spectra of biacetyl*water complexes

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Biacetyl ($C_4H_6O_2$) was observed, individually and complexed with water, in inert gas matrices at low temperatures. Infrared spectroscopy was used to determine the structure of the complexes and characterize the photoproducts arising from irradiation using the filtered output of a mercury vapor lamp. Experimental results were compared to the results of density functional theory (DFT) calculations using the M06 method and the aug-cc-pVTZ basis set. The computational data in correlation with the experimental data were used to determine what photoproducts of biacetyl and biacetyl*water complexes occur in inert gas matrices. The photochemistry at wavelengths 400 nm or greater is almost completely quenched in the presence of water. The effects of factors such as concentration, matrix and isotopic substitution on the observed spectra will be discussed.

MARM 593

Luminoprobes study of intramolecular dynamics in kappa-carrageenan-B-type gelatin

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A hydrogel consisting of 0.75 wt% κ-carrageenan, 0.75 wt% B-type gelatin and 0.2M NaCl was synthesized; the phase diagram for the gel was previously determined using NMR, DSC, and UV-Vis spectroscopy. In this work, luminoprobes 2-(dimethylamino)-6-propionylnaphthalene (PRODAN), $Ru(bpy)_3^{2+}$, $Ru(bpy)(dmbpy)(phen)^{2+}$, and pyranine were used to characterize the corresponding phase transitions. PRODAN is a nonpolar molecule and is expected to interact with the macromolecular scaffold of the gel. When increasing the temperature from 5 ^{0}C, PRODAN fluorescence spectrum shifted from lower wavelengths (430 nm) to higher wavelengths (510 nm) as the gel underwent a HBIAPS + SPS to HBIAPS phase transition. This bathochromic shift can be attributed to the latter phase having no hydrophilic domains in which PRODAN could be situated. The PRODAN emission decays kinetics corroborates the above statement. Fluorescence depolarization study of $Ru(bpy)(dmbpy)(phen)^{2+}$ indicates that the positively charged $Ru(bpy)(dmbpy)(phen)^{2+}$interacts with the negative charge of the polymers. Since $Ru(bpy)_3^{2+}$ has the same charge, it is reasonable to assume that it will also interact with the negative charge of the polymers. The emission spectrum of $Ru(bpy)_3^{2+}$ indicates that although $Ru(bpy)_3^{2+}$interacts with the positive charge of the polymers, it resides in the aqueous phase. An Arrhenius plot of the fluorescence decay rate constants of $Ru(bpy)_3^{2+}$ in the gel shows that the probe is not sensitive to the phase transitions that the macromolecular scaffold underwent. Pyranine quenching kinetics indicates that the viscosity of the water pools is the same as that of bulk water. From the aforementioned data, it was concluded that kappa-carrageenan-B-gelatin aqueous gel can be envisioned as a pseudo-static system comprising hydrated macromolecules (responsible for the phase transitions) and “interconnected water pools” (located between macromolecules), the rheological properties of which are very similar to that of pure water.

MARM 594

Intermolecular electron transfer in neat pyridinium ionic liquids

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The impact of solvent dynamics on intermolecular electron transfer has been well studied in neat electron donor solvents such as amines and anilines; however virtually no studies of this sort have been conducted in ionic liquid solvents. The high viscosities of ionic liquids lead to much slower solvent dynamics, and presumably to significant differences in electron transfer to/from these solvents. In this study, steady-state and time-resolved emission methods were used to measure electron transfer quenching between excited-state coumarin electron donors and electron acceptor pyridinium cations in both dilute solution and neat in pyridinium ionic liquids. Stern-Volmer analyses of quenching in dilute solutions of acetonitrile and dimethylsulfoxide showed a wide range of quenching rates for different coumarin dyes that correlated well to estimated free energies of excited-state oxidation. Preliminary time-resolved measurements in neat ionic liquid accepting solvents also show marked differences in quenching rates. In these cases, only local rearrangements, rather than diffusive transport of species is necessary for electron transfer. It is hoped that such experiments, coupled to molecular dynamics simulations will shed new light on solvation structure and dynamics in ionic liquids.

MARM 595

Synthesis, characterization, and evaluation of CoNiP as an electrocatalyst for the hydrogen evolution reaction

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With the high cost of platinum for hydrogen evolution reaction catalysis, significant research has focused on new materials based on cheaper earth-abundant metals such as nickel, iron, manganese, and cobalt. Previous research has shown that nickel-based compounds such as nickel phosphides and nickel sulfides can have favorable electrocatalytic properties competitive with platinum. The mixing of two different transition metals has the potential to further improve the catalytic activities. We considered a mixed-metal phosphide, cobalt nickel phosphide, and investigated this material as a hydrogen evolution reaction catalyst. We synthesized CoNiP with two different methods and confirmed the structure and 1:1:1 Co:Ni:P molar ratio with X-ray diffraction. We used this material to prepare a catalytic electrode and measured the overpotential and Tafel slope and found them competitive with values for platinum and other known materials. Finally we confirmed that significant hydrogen can be generated in a robust manner with low potential using gas chromatography.

MARM 596

Ultrafast vibrational dynamics of perylene diimide solutions during excimer formation

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Understanding the excimeric state in perylene diimide (PDI) derivatives is of importance for solar energy conversion since the excimer may act as either a charge trapping state, or an intermediate for charge transport in solar cells. Recent work has demonstrated that ultrafast mid-infrared (mid-IR) spectroscopy can provide a fundamental understanding of interaction between fixed molecular dimers of PDI molecules. However, the lowest energy conformation of PDI excimers and their role in the solid state remains controversial. We have been able to interrogate this conformational state by measuring diffusion mediated excimer formation in concentrated solutions. We use ultrafast mid-IR spectroscopy to track the evolution of the excimer state by monitoring the perylene ring modes which are sensitive to exciton delocalization over multiple molecules. We then use the excimer vibrational spectrum in the mid-IR region to predict the delocalization and role of the excimer in films of two similar PDI derivatives with different crystal structures.

MARM 597

Rotational dynamics of ionic liquid/acetonitrile mixtures

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Ionic liquids are bulky salts with melting temperatures below 100°C. They have favorable properties such as high thermal stability and low vapor pressure, but the high viscosities of neat ionic liquids limit applications. Binary mixtures of 1-butyl-3-methyl imidazolium tetrafluoroborate and acetonitrile were prepared to reduce the viscosity. Using NMR ^{2}H-T_1 relaxation measurements, we studied the rotational diffusion and its relation to viscosity. Measurements of the cation and acetonitrile rotation compared well to molecular dynamic simulations, allowing interpretation of the structure in the mixtures. Additionally, T_1 and pulsed field gradient measurements were taken of benzene within the ionic liquid/acetonitrile mixtures to study solute dynamics.

A separate study looked into solute dynamics in neat ionic liquids. NMR ^{2}H-T_1 relaxation experiments on the neutral/dipolar/cationic solutes of *p*-xylene/tolunitrile/4-methyl-N-methylpyridinium were conducted to study the effects of solute charge on small molecule rotation.

MARM 598

Visualizing the trimethylamine-N-oxide induced compacted structural ensemble of α-synuclein

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Intrinsically disordered proteins (IDPs) make up an expanding category of proteins and many of which, due to their susceptibility to aggregation, play roles in disease pathogenesis. Moreover their conformational plasticity correlates with a high degree of conformational sensitivity to buffer components and solvent conditions. Here we are focused on visualizing the trimethylamine-N-oxide (TMAO) induced conformational rearrangement of the disease-associated IDP, alpha-synuclein (αS). During Parkinson's Disease pathogenesis, αS self-associates generating neurotoxic fibrillar structures which have long been recognized as post mortem pathological hallmarks of Parkinson's Disease. Previously, distances obtained via single-molecule Förster Resonance Energy Transfer (FRET) have been utilized as constraints in Monte Carlo simulations to generate coarse-grained structural ensembles of IDPs. Expanding on that method, we demonstrate that ensemble FRET measurements from a library of constructs can also be used to build structural ensembles. This library features measurements made with two different FRET probe pair are sensitive on complementary distance ranges. Moreover, we demonstrate that this method can be used to model the ensemble of αS in the presence or absence of TMAO. Despite the observed compaction in the FRET data, our ensembles demonstrate that in the presence of TMAO αS is still disordered. We will expand on this work to visualize the structure of αS monomers during the pathogenic aggregation process.

MARM 599

Mechanism of $Ru(bpy)_3^{2+}$ luminescence quenching by oxygen in water-isopropanol binary system is mixture composition-dependent

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Mechanism of $Ru(bpy)_3^{2+}$ luminescence quenching by molecular oxygen in water-isopropanol binary mixture was studied using a transient absorption laser photolysis technique. In the presence of oxygen, the bleaching of the $Ru(bpy)_3^{2+}$ ground state in water (a polar medium) was monitored at 480 nm; it was found that it did not return back to the initial value on a 0.1 ms time scale. By using fluorimetry, no singlet oxygen was detected in this system, indicating that the quenching occurs via electron transfer. The same experiment performed using isopropanol as a reaction medium produced an opposite result; the bleaching of the $Ru(bpy)_3^{2+}$ ground state coincided with the $Ru(bpy)_3^{2+}$ luminescent decay. Also, a strong emission centered at 1270 nm was detected in the fluorimetry experiment, indicating that the quenching occurs via energy transfer. The singlet oxygen quantum yield was found to decrease in a linear fashion on increasing water concentration in the mixture. This indicates that the reaction mechanism changes from energy transfer to electron transfer as the medium polarity increases. Quenching rate constant for $*Ru(bpy)_3^{2+}$ in pure isopropanol solution was determined to be $(5.4 \pm 0.3) \times 10^9$ M^{-1} s^{-1} and the quenching rate constant for $*Ru(bpy)_3^{2+}$ in pure water was determined to be $(3.1 \pm 0.2) \times 10^9$ M^{-1} s^{-1}. There is no apparent correlation between the quenching rate constant and the reaction mechanism; the related work is in progress.

MARM 600

Pseudobinary mixture comprising (50mol% CH_3CN and 50 mol% 1-butanol) and water: A DSC and photophysical study involving PRODAN luminophore

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The effect of water on the thermodynamic properties of equimolar acetonitrile-butanol mixture was studied using a DSC technique. In the absence of water, at the cooling rate of 5 ^oC min^{-1}, the mixture undergoes regular crystallization at -73.2 ^oC. At the same heating rate, the melting occurred at -48.5 ^oC; the enthalpy of melting was found to be 60.6 J g^{-1}. Adding 5 mol% of water only slightly affected supercooling of the mixture and no apparent water crystallization peak was noticeable in the thermogram; however, the overall enthalpy of melting decreased to 53.7 J g^{-1}. At the water concentration of 21.88 mol%, another peak appeared at -64.8 ^oC in the cooling part of thermogram; it could be ascribed to the water crystallization, however, the corresponding enthalpy is four times less than expected. Increasing the water content to 37.79 mol% resulted in broad ice melting peak, the enthalpy of which was about 50% of that expected. This decrease in enthalpy of melting could be attributed either to the formation of solid complex(es) or very small sized crystals produced; further research is in progress to explain this

unexpected result. To learn about molecular dynamics of this system, the luminoprobe PRODAN was utilized. Temperature-resolved fluorimetry was used to assess the medium ability to solvate PRODAN and the data obtained are found to be in agreement with the DSC data. To complete the picture related to the molecular mobility in this system, the temperature-resolved pulse laser photolysis data were collected as well.

MARM 601

Dendrimer-glutaminase inhibitor conjugates for the treatment of Rett syndrome

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Rett Syndrome (RTT) is a neurodevelopmental disorder most commonly associated with mutations in the X-linked gene that encodes for methyl-CpG binding protein 2 (MeCP2). Glutamate and immune dysregulation mediated by glial dysfunction are known to be associated with both human RTT and RTT genetic rodent models. JHU29 is a potent kidney-type glutaminase (GLS) inhibitor with IC_{50} of 2.7 µM, GLS enzyme is responsible for production of intracellular glutamate via glutamine-glutamate cycle. Hence, GLS inhibitors, such as JHU29, possess therapeutic potential in treatment of RTT syndrome by reducing the extracellular glutamate levels. Previously, we have demonstrated that hydroxyl-terminal PAMAM dendrimers possess intrinsic capacity to target activated microglia and astrocytes, from systemic administration. We hypothesize that conjugating JHU29 drug to PAMAM dendrimers, will improve the solubility/bioavailability, targeting capability, and therapeutic effect of JHU29, which in turn will significantly improve neurobehavioral and neuropathological outcomes in the mouse model of RTT. We prepared D-JHU29 conjugates, and with a high JHU29 drug loading and purity (> 96 %). Conjugation of JHU29 to dendrimers significantly increased the aqueous solubility of this poorly soluble drug. Our preliminary cell studies with LPS-stimulated BV-2 mouse microglial cells indicate that D-JHU29 conjugate reduces extracellular glutamate levels. Primary mixed microglia cultures were grown using *Mecp2*-null brains. After 24 hours of treatment with a glutaminase inhibitor conjugated to a dendrimer (D-JHU29), mixed glial cells showed decreased levels of glutaminase, along with a decrease in various pro-inflammatory markers and an increase in previously deficient anti-inflammatory cytokines. Hippocampal slice cultures confirm and support the cell studies by demonstrating decreased extracellular glutamate 24 hours' post-treatment. Given these results *in vitro/ex vivo*, we administered D-JHU29 in combination with dendrimer-conjugated NAC (D-NAC) weekly to *Mecp2*-null mice. These results demonstrate that conjugation of glutaminase inhibitor (JHU29) to PAMAM dendrimer increases its bioavailability and targeting ability to specific microglial/astrocyte cells. Assessment of the impact of D-JHU29 on other aspects of Rett neuropathology. These studies have significant implications in the development of treatment for RTT syndrome and for in general for neurodevelopmental disorders.

MARM 602

Structure and energetics of solvated lactic-co-glycolic acid oligomers

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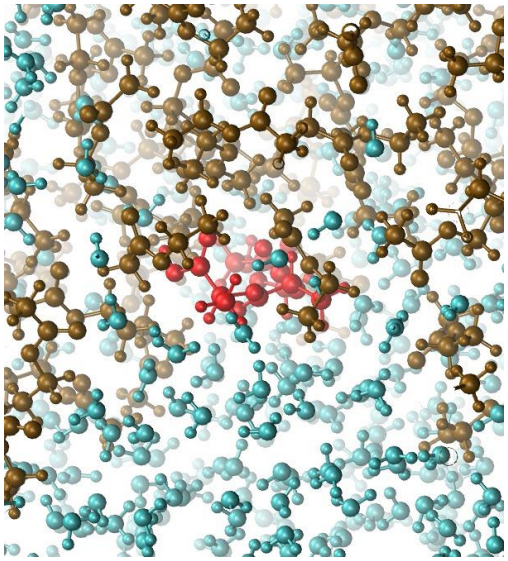
Characteristic shapes of 50:50 lactic-*co*-glycolic acid (LGA) short oligomers are investigated through molecular dynamics simulations at ambient conditions under the Amber12fb force field. An ensemble of 3000 instantaneous structures are selected during the simulation. Subsequently a minimization of the LGA oligomer in a frozen solvent environment is performed. Analysis of the ensemble of minima allows determination of two characteristic oligomer structures, a U-shaped chain and a sigmoid chain. These two types of structures are formed in water, in ethyl acetate (EA), and in their mixture. Water significantly favors the U-shaped oligomers. Meanwhile the oligomers are basically always sigmoid in the mixed water/EA solvent and the molecules are trapped at the solvents interface. The energetics, radius of gyration, end-to-end distance, dihedral angles, and orientational order parameter are some of the studied properties. Structures corresponding to a low energy minimum are less bound to the solvent. A principal component analysis permits a very clear classification if the structures in the ensemble into the U- and sigmoid- shapes. This structural classification should prove important for determining the more efficient lengthening of the polymeric chains and their arrangement in the condensed phase.



LGA oligomer trapped at the water-ethyl acetate interface. Water molecules in blue, ethyl acetate molecules in brown, LGA oligomer in red.

MARM 603

Development of borinic acid polymers as new supported catalysts and multi-stimuli responsive materials

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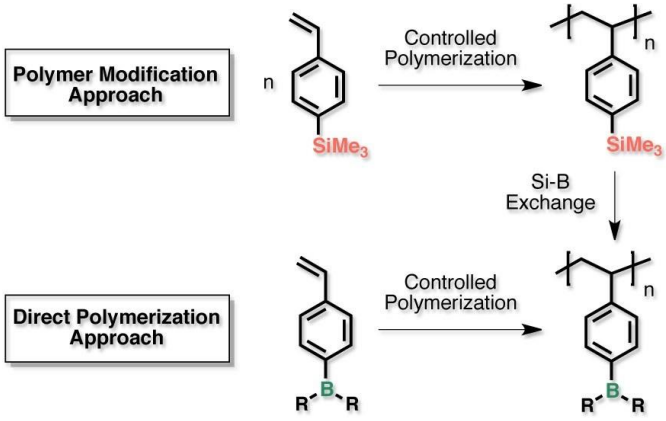
Boron-containing polymers represent a promising class of inorganic and organometallic polymers due to their unique properties. The attachment of Lewis acidic borane groups has been utilized in the development of supported reagents and immobilized catalysts, separation media, sensor systems, stimuli-responsive materials, and biomaterials. Boron-functionalized polymers can be synthesized through direct polymerization of boron-containing monomers or via post-modification procedures (Scheme 1).

In 2014, our group reported the first example of a well-defined borinic acid polymer (PBA) with strong luminescence, high stability, and multiple stimuli-responsive properties. We investigated the role of H-bonding interactions in the self-assembly of these materials into larger supramolecular aggregates and their reversible association with hydrogen bond acceptors. Borinic acids are also of interest as catalysts, for example, in peptide synthesis. This presentation will discuss our current efforts at developing new well-defined borinic acid polymers for catalysis and materials science applications.



Scheme 1. Methods for the synthesis of organoboron polymers.

MARM 604

Ozone uptake on kaolinite as a function of relative humidity and organic coating

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Mineral dust aerosols are ubiquitous particulates that exist within the atmosphere due primarily to dust storms in arid regions. Given their high abundance, mineral dust aerosols have significant impacts on atmospheric chemistry, human health, climate, and biogeochemical cycles. Furthermore, these mineral dusts may serve as a sink for atmospheric ozone, which is closely associated with high levels of pollution in the troposphere. While previous studies evaluated the reactivity of ozone on mineral dust surfaces, there is limited understanding of the effects of relative humidity and volatile organic compounds (VOCs) on atmospheric ozone uptake on these clay surfaces. Using a laminar flow reactor, we measured ozone uptake on kaolinite, an aluminosilicate clay, as a function of relative humidity and VOC pre-coating. Steady state reactive uptake coefficient calculations suggest a decrease in ozone uptake at higher relative humidity, whereas reactions where the kaolinite surface was pre-coated with limonene, catechol, and α-pinene displayed an increase in ozone uptake in comparison to the non-coated surface.

MARM 605

LbL-deposited polyelectrolyte layers as barriers for sustaining release of hydrophilic drugs from hydrogel matrices

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To overcome the fast release of hydrophilic drugs from hydrogel matrices, layer-by-layer (LbL) deposited polyelectrolyte bilayers of poly(allylamine) (PAAm) and poly (styrene sulfonate) (PSS) were evaluated as potential barriers to slow the release. Various hydrophilic low molecular weight drugs were entrapped within alginate microgels (Alg-Ms) surrounded by the LbL PAAm-PSS bilayers, which provide effective diffusion barriers to sustain the release of hydrophilic drugs from a few hours up to 3-day. The spontaneous deposition onto Alg-Ms, after stained with a fluorescent dye, was characterized with fluorescent microscopy. The sustained release from the Alg-Ms coated with PAAm-PSS LbL deposited bilayers was found to be proportional to the number of bilayers, and the release data of the hydrophilic drugs from PAAm-PSS-bilayers-Alg-Ms was found to be diffusion controlled and followed the Fick 2nd law of diffusion. The results indicate that polyelectrolyte bilayers coated Alg-Ms show the potential as controlled release drug-delivery vehicles.

MARM 606

Effect of microstructure on alkaline hydrolysis of poly(3-hydroxybutyrate) films

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Poly(3-hydroxybutyrate) (PHB), an alternative to petroleum-based polymers, are often purified by alkaline treatment. No prior studies have been conducted to determine the impact of alkaline treatment on PHB. The effect of microstructure on alkaline hydrolysis has been studied by varying concentration of base and the temperature. The morphologies of PHB films before and after degradation were evaluated using DSC and FTIR spectroscopy. The hydrolytic degradation study by weight loss measurement revealed that the crystallinity of PHB greatly decreased the hydrolytic ability of PHB. The crystallization of PHB and the effect of base on hydrolysis was investigated by time dependent FTIR spectroscopy. FTIR spectroscopy reveal that the extent of hydrolysis decreased with increasing crystallinity. The crotonic acid was detected as a major product after hydrolysis, confirmed by UV/Visible and proton NMR spectroscopy. The normalized absorbance of the crystalline band at 3010 cm^{-1} band remained constant, suggesting that there is no significant change in crystallinity with degradation. The normalized amorphous band at 1183 cm^{-1} showed a decrease in absorbance ratio, suggesting degradation of the amorphous phase. Our data suggests that alkaline hydrolysis depends on concentration of base and the crystallinity of PHB.

MARM 607

Development of thermometric titration to characterize catalyst supports: Advantages in process control and fundamental understandings of support

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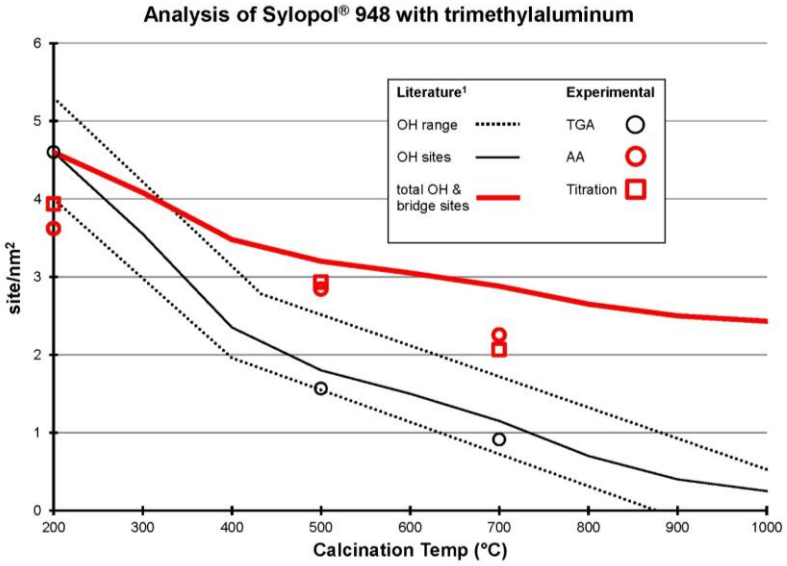
Much of the world's high-density polyethylene is produced in gas phase heterogeneous reactors. This production method relies on the Ziegler-Natta polymerization of ethylene on a high surface area silica catalyst support. These

Ziegler-Natta polymerization centers are anchored to the silica at active sites on its surface, which consist of hydroxyl groups and strained siloxane bridges on the silica surface. In order to produce high-activity polyethylene catalysts on a large scale, the number of active sites on the surface of the silica (expressed as sites/nm^2) must be accurately known. Common methods used to determine this value have disadvantages including labor intensiveness, lack of precision, lack of accurately measuring accessible sites, inability to measure all available active sites, and/or lack of flexibility of the chemical reacting with the surface active sites. We are developing a thermometric titration method to overcome some of these issues. A thermometric titration involves titrating the silica with a reactive compound and using the exothermicity of the reaction as the observable to determine the end point (EP) of the titration. Proof-of-concept experiments show thermometric titration of the silica agrees with atomic absorption (AA) analysis of the silica to quantitate the surface active chemical. Current research involves the analysis of the titration curve to increase the precision of the method.



The surface chemistry of amorphous silica. Zhuravlev model.

MARM 608

Polymer analysis applications of Thermo Fisher Scientific picoSpin NMR spectrometers

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Nuclear magnetic resonance (NMR) spectroscopy has proven to be an invaluable analytical tool for polymer analysis by elucidating molecular structure, studying reaction dynamics, monitoring reaction progress, and gauging product purity. When analyzing polymers using high-field NMR spectrometers, resonance signals often coalesce as broad peaks due to poor molecular rotation and the marginally different chemical environments the polymer repeating units are situated in. To that end, low-field NMR such as the Thermo Scientific™ picoSpin™ 80 NMR spectrometer readily lends itself as a low-cost alternative to high-field instruments with significant savings on both instrument procurement and upkeep, while still generating similar information to what would be obtained from a high-field instrument. In this work, a picoSpin NMR spectrometer was used to obtain a variety of critical polymer data from a diverse group of applications. Information about polymer structure was accomplished through the molecular weight determination of poly(ethylene glycol) (PEG) acetyl triarm and compositional analysis of a polyol. The picoSpin was also used to qualitatively and quantitatively monitor the polymerization of *t*-butyl acrylate with a polystyrene reagent by identifying and integrating the resonance signals associated with the *t*-butyl acrylate monomer. Finally, the picoSpin was used determine the quality of cosmetic product samples by quantitatively determining the percent of polydimethylsiloxane present in the sample.

MARM 609

Investigations of the impact of tetramethylcyclosiloxanes on generation and self-assembly of silver nanoparticles

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Recent years have witnessed a sharp increase in the area of synthesis and mechanistic investigation of controlled self-assembled nanoparticle system because of their applications in selective catalysis, sensing technologies and medical applications. It has been demonstrated previously that the synthetic methods and stabilizing agents up to certain extent dictate the unique property profiles of the nanoscale materials. We have shown that the reaction condition and assembly directing agents play a very critical role in controlling the nanoparticle assembly when generating silver (Ag) nanoraspberries. We were also able to graft such siver nanoraspberries onto multiple surfaces like cotton; activated charcoal and etched glass for medical applications.

In this poster presentation, we present our results of the mechanistic investigations to examine the possible reasons for the self-assembly of silver particles as nanoraspberries. We have performed the reactions of acid catalyze polymerization of 1,3,5,7 tetramethylcyclotetrasiloxane (D_4) without the addition of silver heptafluorobutyrate in order to determine the role of silver in the morphology of the nanoraspberries. It was observed that if tetramethylcyclosiloxanes D_4 nanoparticles were synthesized in presence of heptafluorobutyric acid and not Ag-heptafluorobutyrate, nanoraspberry type structures did not form. We will present the TEM, NMR and IR analysis of the self-assembled siloxanes as well as that of self-assembled silver nanoparticles.

MARM 610

Optical and electronic properties of magic number, mixed ligand gold clusters

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Size dependent optical and electronic properties of novel size gold clusters are at the forefront of research. Nanoparticle semiconductor thin films can absorb high quantities of solar radiation due to their distinct absorption peaks in the visible, ultraviolet, and near-IR regions. The presence of near-IR luminescence in magic number gold clusters is of recent interest for use in biological imaging. The wavelength of emission is ligand dependent influencing the electronic transitions. Magic number particles $Au_{25}L_{18}$ spherical icosahedron structure, $Au_{25}L_{18}$ rod bi-icosahedron structure, and $Au_{144}L_{60}$ spherical icosahedron structure clusters, were synthesized using one phase methods with hexanethiol as the stabilizing ligand. Each gold core was synthesized using hexanethiol, as well as a coumarin derived ligand exclusively, then compared with mixed ligand variations. The electronic transition states of each particle were observed through optical and electrochemical analysis. The clusters were characterized through observation of documented HOMO/LUMO gap using both optical and electrochemical techniques. Au144-clusters indicated quantized double layer charge upon electrochemical analysis. Observation of quenching when coumarin is bound to gold core is observed through fluorescence quantum yield. Transmission electron microscopy was employed to determine particle size and dispersity. The MPCs (Monolayer Protected Clusters) with the hexanethiol stabilizing ligand were then labeled with a coumarin dye via directed ligand exchange. The products of the exchange reaction were then compared with the MPC made from the coumarin ligand. Regions of enhancement in two-photon cross-section analysis indicates possible practical imaging applications.

MARM 611

Synthetic deconvolution of interfaces and materials components in hybrid nanoparticles

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Interfaces between solid-state material systems are critical to a growing number of technological innovations and research fields. Solid-state interfaces can establish pathways for electronic transport, cooperative catalysis, and novel strain-induced properties. Identifying a material system of interest, synthetically generating the interface, and isolating the specific behavior between materials all have associated difficulty, which compounds to obscure our understanding of solid-solid interfaces. Colloidal hybrids, a class of nanostructured materials composed of multiple discrete material domains fused together by solid-state heterojunctions, offer the unique ability to isolate interfaces between nanostructured solids as model systems. However, the number of materials available in colloidal hybrids is limited, due to the incompatibility of synthetic conditions and unfavorable interfaces between material systems. In order for colloidal hybrids to be used as a wide-ranging model for studying interfaces, new synthetic methods,

that circumvent these difficulties, are needed. In this presentation, we will present a generalized, post-synthetic modification method for the transformation of colloidal hybrid particles via sequential anion and cation exchange reactions, which decouples control over interface formation and elemental composition. Using this approach, we establish an array of morphologically controlled, metal-metal chalcogenide hybrid particles, while preserving the original interfaces between domains. Moreover, this chemistry can be extended to engineer new interfaces in novel core-shell hybrid domains, as well as to selectively address and transform one domain, while preserving another, in a three-component hybrid system.

MARM 612

Surface effects of accelerated degradation on pigmented barrier coatings

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Polyester/ether films were synthesized and subjected to accelerated weathering in order to study changes in surface chemistry and correlate those results with alterations in mechanical properties of barrier coatings. A series of films differing in polyether to polyester ratio were loaded with an iron chromium pigment, up to 30% v/v, and subjected to light, heat, and humidity. The increase of the NH/OH and decrease of Amide II regions of specta collected via FTIR indicated changes in functional groups at the coating surface. However, tinsel tests display an increase in elastic modulus indicating coating stiffening throughout the bulk of the coating except for polyether systems. Confocal microscopy was utilized to image the surface and it was discovered that as the polyether coatings increased in pigment loading a higher number of voids in the coating were created from weathering. This in turn caused the integrity of the coating to decrease due to the additional surface area from accelerated weathering.

MARM 613

Metalloporphyrins nanoparticles as an efficient catalyst for olefinic oxidation

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Porphyrin and metalloporphyrin nanoparticles are promising components for advanced material chemistry because of the rich photochemistry and catalytic activity. Self-organized organic nanoparticles (ONP) of metalloporphyrins shows enhanced catalytic activity for the allylic oxidation of cyclohexene using molecular oxygen as oxidizer in aqueous medium under ambient conditions, in contrast to their completely solvated metalloporphyrin in organic solvents. Here we are presenting five different metalloporphyrinoids appended with various thioalkyl groups at the meso position using commercially available porphyrin such as 5,10,15,20-tetrakis(pentafluorophenyl) iron (III) porphyrin, Fe(III)$TPPF_{20}$. The nanoparticles of these porphyrins were prepared by using mixing host guest solvent method (1). The catalytic activity of the nanoparticles of these metalloporphyrinoids is tested for the oxidation variety of organic pollutants and their TON is reported. Our hypothesis is that the difference in their catalytic activity is because of their difference in mechanism from solution phase reaction and the presence of long thiolaklyl chains at the para position of the meso phenyl groups of metalloporphyrinoid may block the access to the central metal atom, where the oxygen is activated.

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