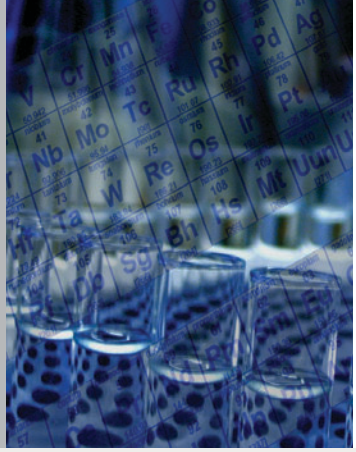
American Chemical Society



MAY 31ST - JUNE 2ND, 2012

UMBC
Baltimore, MD

43rd Middle Atlantic Regional Meeting

Chemistry on the Chesapeake

Sponsored by
The Maryland Section of ACS

UMBC AN HONORS UNIVERSITY IN MARYLAND

ACS Chemistry for Life™

Table of Contents

Participating MARM ACS Sections
(Representing Over 30,000 Members)

Chemical Society of Washington DC (Host of MARM 2011)
Central Pennsylvania
Delaware (Host of MARM 2010)
Lehigh Valley
Maryland (Host of MARM 2012)
Monmouth County
New York
North Jersey
Ocean County
Philadelphia
Princeton
South Jersey
Southeastern Pennsylvania
Susquehanna Valley
Trenton
Western Maryland

43rd Middle Atlantic Regional Meeting
Welcome from the Maryland Section of the American Chemical Society

On behalf of the MARM 2012 Organizing Committee and the Maryland Section of the ACS, we are pleased to welcome you to the 43rd Middle Atlantic Regional Meeting (MARM 2012).The theme of this year's meeting is *Chemistry on the Chesapeake*, reflecting on the diverse research ongoing in the Baltimore area. Symposium topics highlight current research topics, including renewable energy, food and sensory chemistry, and bioanalytical/medicinal chemistry.

We have events for all experience levels from the budding chemists through to senior chemists. Over twenty symposia are included in this year's technical program with more than 450 contributed papers. Speakers come from institutions from across the U.S. and internationally. The program encompasses the fundamental disciplines of chemistry: analytical, biological, inorganic, organic, medicinal, and physical chemistry. In addition, we are honored to host the Remsen Award, which features Dr. Daniel Nocera from MIT, and include a supporting Remsen Award symposium that reflects advances in the chemistry of renewable energy. You will find all symposia take advantage of the enormous talent in the Baltimore/Washington, DC metro area that is rich in national laboratories, universities, and developing chemical technologies. Our program and abstract chairs, Brad Arnold, Ken Cole and Diana Hamilton, deserve your congratulations on putting together this exciting program.

There are workshops for education professionals including several advanced learning techniques that include active learning, online and hybrid course methods. In particular, we have a high school level workshop for students and teachers with an environmental and forensic chemistry focus. We are also sponsoring a Chemagination contest with poster presentation and lunch. Additionally, we are offering several career and leadership (ACS Leadership Institute) workshops, including a unique workshop on Steps for the Chemical Entrepreneur. Furthermore, Shimadzu and Perkin Elmer are offering specialized technical workshops.

We hope that you will visit the MARM 2012 Expo for exhibits by local, national, and international scientific companies. All are invited to attend the other social events, such as the Crab Cake with the ACS Board, Women Chemist Committee luncheon, 50 Year Member luncheon, and Beer Chemistry/Tasting of Local Baltimore Beers. We also encourage you to attend the MARM 2012 Awards Banquet and Remsen Award Lecture Dinner.

We are fortunate to have such generous sponsors, and we are grateful for their contributions. Thanks also to our exhibitors and advertisers, all of whom are listed on the following pages. This meeting would not have been possible without the tremendous effort of the organizing committee and all of the volunteers who give their time and energy. Again, welcome to Baltimore, Maryland and we hope that you will find time to relax and enjoy this opportunity to network and learn.

Yours truly,

Paul Smith and Stephanie Watson
General Co- Chairs, MARM 2012

UMBC

AN HONORS UNIVERSITY IN MARYLAND

Office of the President
University of Maryland, Baltimore County
1000 Hilltop Circle
Baltimore, MD 21250

PHONE: 410-455-2274
FAX: 410-455-1210
VOICE/TTY: 410-455-3233

May 31, 2012

2012 Middle Atlantic Regional Meeting
American Chemical Society

Dear Meeting Participants:

Welcome to the University of Maryland, Baltimore County (UMBC) and to the 2012 Middle Atlantic Regional Meeting of the American Chemical Society. We are delighted to have been selected as the site of this year's regional meeting.

UMBC is recognized for being at the forefront of institutional culture change involving education in science, technology, engineering, and mathematics. For more than two decades, our nationally recognized Meyerhoff Scholars Program has produced large numbers of underrepresented minority STEM graduates, including many young women, who have gone on to complete graduate degrees and become research scientists and engineers. In fact, largely as a result of the Meyerhoff Program, UMBC has become the nation's leading predominantly white institution for producing African American bachelor's degree recipients who go on to complete STEM Ph.D.s. Moreover, faculty in the Chemistry & Biochemistry Department developed the Chemistry Discovery Center where innovative teaching involving small-group, hands-on, student-centered learning has led to much greater student success in introductory chemistry courses (and the techniques are being applied in other fields).

The Baltimore/Washington, D.C. region has one the world's largest concentrations of scientific talent and resources, and we are happy to be a partner in advancing the region's scientific and educational strengths. We also benefit from our proximity to the nation's capital and the headquarters of the American Chemical Society.

I encourage you to see some of the Baltimore area and experience some of its attractions. Also, I invite you to visit the classrooms, laboratories, and other state-of-the-art facilities on our campus. I wish you an enjoyable visit and a productive, stimulating meeting.

Sincerely

Freeman A. Hrabowski

Freeman A. Hrabowski, III
President

KEVIN KAMENETZ
County Executive

On behalf of the people of Baltimore County, welcome to the University of Maryland, Baltimore County for the 43rd Middle Atlantic Regional Meeting of the Maryland Local Section of the American Chemical Society.

Every year, this conference brings together 1,000 chemists, chemical engineers, academicians, graduate and undergraduate students, and related professionals to participate in an important exchange of ideas. This year's meeting will be based around the theme of "Chemistry on the Chesapeake" and feature topics and workshops that highlight research in the Baltimore area ranging from renewable energy to bioanalytical chemistry.

Thank you for visiting Baltimore County for this annual meeting and I wish you best of luck for a productive and enjoyable conference.

Very truly yours,

Kevin Kamenetz

Kevin Kamenetz
Baltimore County Executive

400 Washington Avenue | Towson, Maryland 21204-4554 | Phone 410 887-2450 | | Fax 410-887-4049 | kevin@baltimorecountymd.gov
www.baltimorecountymd.gov

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TTY USERS CALL VIA MD RELAY

A MESSAGE FROM GOVERNOR MARTIN O'MALLEY

Dear Friends:

Welcome to the annual American Chemical Society Middle Atlantic Regional Meeting.

It is one of the great ironies of our times that the very immensity of the problems we face with respect to pandemic flu, global warming, global terror, drought, hunger and poverty, is driving innovation in every sphere of science and technology – particularly in the life sciences.

In Maryland, we believe in the power of the science to revolutionize the way we feed, fuel, and heal our planet. We are at the threshold of brilliant science, innovative technology, and remarkable discoveries – our own cutting edge of history. It's up to us to harness those discoveries and convert them into the jobs and opportunities of tomorrow. Each of you plays an important role in that work. Thank you for your commitment to your work, and for helping us build a better tomorrow.

Please accept my warm wishes for a successful meeting.

Sincerely,

Governor

May 31, 2012

Dear Friends:

I want to extend a warm welcome to everyone attending the American Chemical Society's 43rd Middle Atlantic Regional Meeting. For more than 100 years, the American Chemical Society (ACS) has been a national leader in the field of chemistry. From organizing professional networks and information sharing, to hosting educational and professional gatherings, ACS is committed to supporting scientists within the chemical community.

This year's meeting theme, "Chemistry on the Chesapeake," is especially poignant as Maryland continues to grow and develop as a biotechnology center and cutting-edge research hub. I am proud that Maryland has become a national leader in the sciences, particularly in biotechnology where our state ranks second in the nation. Maryland is home to our nation's premier research facility, the National Institutes of Health, as well two of the finest academic medical centers in the world—Johns Hopkins University and the University of Maryland Medical Centers.

I hope that during you time here you have a chance to see all that Maryland has to offer to our nation's scientific community. Again, welcome to the ACS's 43rd Middle Atlantic Regional Meeting and best wishes for a successful and productive conference.

Sincerely,

Benjamin L. Cardin
United States Senator

UNITED STATES SENATE
WASHINGTON, D.C. 20510

BARBARA A. MIKULSKI
MARYLAND

May 31, 2012

Dr. Stephanie Watson, Co-Chair
Mid Atlantic Regional Meeting
American Chemical Society
Washington, DC 20036-4892

Dear Dr. Watson & Friends:

Greetings to the members and guests of the American Chemical Society on the occasion of your 43rd Annual Middle Atlantic Regional Meeting: *"Chemistry on the Chesapeake"*. Thank you for the kind invitation to share this prestigious event with all of my good friends from the science and academic community. Welcome to all the chemists, chemical engineers, academicians and students who have gathered here at UMBC.

Since its inception, the American Chemical Society has been true to its mission to improve the quality of life for the world's people by advancing your discipline and supporting its practitioners. As the largest scientific society in the world, with 154,000 members, you are uniquely positioned to serve as an intellectual and practical incubator for new ideas and new technologies. The future of our economy and our nation will depend upon our ability to innovate and to win market share. The new ideas and new technologies which you will discover will lead to the jobs of tomorrow for Maryland and for America.

In my role as Chair of the Commerce, Justice, Science Appropriations Subcommittee, I am critically aware that in order to stay competitive our country must continue to invest federal dollars in science and technology as well as technological education. This investment will help create high-paying, high-skill jobs that will preserve our nation's leadership in the global 21st century economy. Rest assured I will always fight to secure robust funding for our nation's scientific programs at facilities such as NIH, NIST, FDA and the NSF.

I know that your deliberations will be cutting-edge and stimulating for everyone who attends. Chemistry is about exploration, discovery and innovation. Perhaps, together we can rekindle the spirit of exploration and discovery that defines our nation and its people.

Sincerely,

Barbara A. Mikulski
United States Senator

ACS Board of Directors

Bassam Z. Shakhashiri, President

University of Wisconsin
Bassam Z. Shakhashiri is a chemistry professor at the University of Wisconsin-Madison. He received his A.B. from Boston University in 1960, his M.Sc. from the University of Maryland in 1965 and his Ph.D. in 1968. He is the first holder of the William T. Evjue Distinguished Chair for the Wisconsin Idea at the University of Wisconsin-Madison, where he has been a professor since 1970. He has been a member of the American Chemical Society since 1961.

Marinda Li Wu, President-Elect

Science is Fun!
Marinda Li Wu is founder and president of Science is Fun! She earned a Bachelors Degree at the Ohio State University in 1971, and Ph.D. from the University of Illinois in 1976. She has been a member of the American Chemical Society since 1970.

Nancy B. Jackson, Immediate Past President

Sandia National Laboratories
Nancy B. Jackson is manager of the International Chemical Threat Reduction Department in the Global Security Center at Sandia National Laboratories. She received her B.S. degree in chemistry from George Washington University in 1979, and her Ph.D. in chemical engineering from the University of Texas at Austin in 1990. She has been a member of the American Chemical Society since 1979.

William F. Carroll, Jr., Chair

Director-At-Large
Bill Carroll is a vice president of Occidental Chemical Corp. He earned a Bachelors degree at DePauw University in 1973, Masters Degree from Tulane University in 1975, and Ph.D. from Indiana University in 1978. He has been a member of the American Chemical Society since 1973.

Madeleine Jacobs, Executive Director/Chief Executive Officer

American Chemical Society
Previously serving as the Editor-in-Chief of Chemical and Engineering News (C&EN), 2004 marks Ms. Jacobs first year as Executive Director of the American Chemical Society. She worked for C&EN from 1969 until 1972 and returned again in 1993. She is a much-honored science journalist, an internationally sought after public speaker, and brings an extensive familiarity and understanding of Society programs, products, and services.

Neil D. Jespersen

Director, District I
Neil D. Jespersen is a Professor at St. John's University. He earned his Bachelors Degree at Washington & Lee University in 1967, and his Ph.D. at Pennsylvania State University in 1971. He has been a member of the American Society since.1968.

George M. Bodner

Director, District II
George M. Bodner is the Arthur E. Kelly Distinguished Professor of Chemistry, Education and Engineering at Purdue University. He earned his Bachelors Degree at the State University of New York, Buffalo in 1969 and his Ph.D. at Indiana University in 1972. He has been a member of the American Chemical Society since1969.

Pat N. Confalone

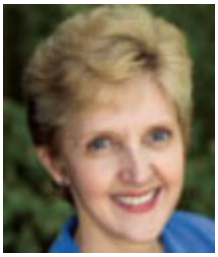
Director, District III
Pat N. Confalone is vice president at DuPont, Global Research & Development, Crop Protection. He earned his Bachelors Degree from Massachusetts Institute of Technology in 1967, Masters Degree from Harvard University in 1968, Ph.D. from Harvard University (R. B. Woodward) in 1970, and Post-Doc at Harvard University (R. B. Woodward) in 1971. He has been a member of the American Chemical Society since 1967.

Larry K. Krannich

Director, District IV
Larry K. Krannich is the Executive Director of the Alabama Academy of Science. He earned his Bachelors and Masters degrees from the Illinois State University, and his Ph.D. from the University of Florida. He has been a member of the American Chemical Society since 1963.

Peter K. Dorhout

Director, District V
Peter K. Dorhout is the dean of the College of Arts and Sciences at Kansas State University, Manhattan Kansas. He earned his Bachelors Degree from the University of Illinois, Urbana-Champaign, and his Ph.D. from the University of Wisconsin, Madison in 1989. He has been a member of the American Chemical Society since 1985.



Bonnie Charpentier

Director, District VI
Bonnie A. Charpentier is vice president at Metabolex Inc. She earned her Bachelors Degree at the University of Houston in 1974, and her Ph.D. in 1981. She has been a member of the American Chemical Society since 1981.

Dennis Chamot

Director-At-Large
Dennis Chamot is the Associate Executive Director of the National Research council, Division on Engineering & Physical Sciences. He earned his Bachelors and Masters Degrees at Polytechnic University in 1964. He earned his Ph.D. at the University of Illinois in 1969, and his M.B. A. from the University of Pennsylvania, Wharton School in 1974. He has been a member of the American Chemical Society since 1964.

Valerie J. Kuck

Director-At-Large
Valerie J. Kuck is an Adjunct Professor at the College of St. Elizabeth Chemistry Department. She earned her Bachelors degree at St Mary of the Woods College in 1961, and her Masters degree at Purdue University in 1965. She has been a member of the American Chemical Society since 1964.

Barbara A. Sawrey

Director-At-Large

Kathleen M. Schulz

Director–at-Large
Kathleen M. Schulz is the President of Business Results Inc. She earned her Bachelors degree at Eastern New Mexico University in 1964, and Ph.D. at the University of Missouri in 1973. She has been a member of the American Chemical Society since 1964.

Kent J. Voorhees

Director-At-Large
Kent J. Voorhees is a professor at the Colorado School of Mines. He earned his Bachelors Degree at the Utah State University in 1965, Masters Degree in 1968, and Ph.D. in 1970. He has been a member of the American Chemical Society since 1967.

MARM 2012 Organizing Committee

General Chairs	Paul Smith	UMBC
	Stephanie Watson	NIST
Program Chairs	Brad Arnold	UMBC
	Ken Cole	NIST
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Workshops/Short Courses	Paul Smith	UMBC
	Alvin Bober	Retired
	Sandy Young	Army Research Laboratory
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	Megan Shanholtz	Johns Hopkins University
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Office of Regional Meetings	Kim Savage	ACS

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http://ndep.us/

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American Chemical Society
Division of Organic Chemistry

http://www.organicdivision.org/

PerkinElmer
For the Better

Join PerkinElmer for an informative workshop at MARM:

May 30, 2012
1:30 PM – 5:00 PM
Room UC115

Presentations for the Workshop include:

- My Sample is Not a Liquid in a Cuvette, Now What Do I Do? (Jeff Taylor)
- How to Choose the Correct UV/Vis/NIR Accessory for Solid Sample Materials Measurement (Jeff Taylor)
- IR: "The Principles and use of an FTIR Microscope (Jeff Taylor)
- Comparative Study: LC-APCI-MS and Offline Ambient Ionization with DSA of Explosives (Josh Wilhide)

In addition, Carl Schwarz will be demonstrating the DSA Tof and Lenny Pitts will demonstrate the NexION.

Don't forget to visit PerkinElmer in Booth #10 at MARM

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Exhibitors at MARM 2012

Agilent manufactures and distributes a complete line of instrumentation serving the clinical, analytical, biotech, environmental, pharmaceutical, forensic science, food and flavor, academia, and all other laboratory markets that have needs for the best in quality, performance, and serviceability in the instruments they purchase. Agilent's manufacturers the world's best selling GC and GC/MS systems, and an entire range of LC, LC/MS, and ICP-MS equipment. Agilent holds market leadership positions in consumables, software, genomics microarrays, reagents, lab automation, support, and compliance services. We offer complete solutions, from sample preparation to data analysis, and can optimize your workflow productivity and performance through automation.

Alfa Aesar, a Johnson Matthey Company, is a leading international manufacturer and supplier of research chemicals, metals and materials. With over 33,000 products listed in its main catalog, Alfa Aesar is the single source for customers' chemical and material needs, from sizes for research to semi-bulk and bulk quantities. The Alfa Aesar Catalog carries organic compounds, high purity inorganics, pure metals, alloys, elements, precious metal compounds and catalysts, rare earths, AA/ICP standards and more. Virtually all products are in stock for immediate shipment.

Aurora Analytics provides expert chemical synthesis and analytical services, with an emphasis on the design and synthesis of small molecules and polymers. Aurora uses its expertise to develop reagents and systems for education, research and diagnostic products. Available products include solid and solution-phase coupling reagents and alcohol biomarkers.

Bruker Daltonics is a leading provider of Separation and Mass Spectrometry instruments for the Analytical Sciences. Our innovative and easy-to-use product families (ESI-TOF, Ion Trap, FTMS, MALDI-TOF, LC, GC, GC-MS, ICP-MS) provide the highest performance, highest value systems for a wide range of small molecule, polymer, and biomolecule analysis applications.

Sample prep workstations, integrated analytical solutions for GC/MS and LC/MS designed to optimize performance, enhance productivity, and extend laboratory capabilities. Since 1967, GERSTEL has enabled analysts to achieve ultra-low detection levels in complex matrices with unequalled preparative capability while dramatically increasing sample throughput and handling difficult sample preparation challenges.

Interchim is a global company which manufactures chromatography products for purification, analytical and sample preparation. The column product range is comprised of Flash, Prep, SPE, UPLC, and HPLC. Instruments for purification include the first flash system to withstand pressures of 435 psi/30 bar. The company has introduced high efficiency flash cartridges which run three times faster than conventional columns.

MicroLab's FS-522 high-resolution laboratory interface provides almost every measurement needed for general chemistry : pH, temperature, pressure, REDOX, conductance, voltage, and more . MicroLab's integrated 360 - 880 nm FASTS pee scanning spectrophotometer simultaneously measures absorbance, fluorescence, scatter, transmission, and turbidity. FASTspec 18 unique in its ability to perform spectrophotometric titrations.

Parker Balston Gas Generators for analytical instruments eliminate the expense and danger associated with high pressure compressed gas cylinders. The inconvenience of changing cylinders and supply interruptions will no longer be a concern. A Parker Balston Gas Generator offers long term price stability and eliminates long-term commitments, contract negotiations and tank rental fees. A continuous supply of consistent purity is available 24/7 without the need for operator attention. Parker Balston offers Gas Generators for a variety of analytical applications including LCMS, GC, FTIR, and NMR. Parker offers global distribution and support.

Perkin Elmer, Inc. is a global leader focused on improving the health and safety of people and their environment. With our analytical instrumentation and leading laboratory services, we focus on improving the integrity and safety of the world we live in.

Rigaku Corporation provides the world's most complete line of X-ray diffraction and X-ray fluorescence instruments and components, including benchtop XRD and XRF systems, X-ray optics and detectors, single crystal diffractometers for chemical crystallography, multi-purpose diffractometers with SAXS and in-plane capabilities, and high-powered WDXRF spectrometers. Founded in 1951 in Tokyo (Japan), Rigaku Corporation is a global leader in X-ray and thermal analysis, automation solutions, and non-destructive testing. Rigaku employs more than 1,100 people in the development, manufacturing, marketing and support.

Rigaku Raman Technologies, a division of Rigaku Corporation, is located in San Jose, California. We are global leaders in the development, manufacturing and sales of handheld portable Raman spectrometers. Our FirstGuardTM is a new breed of Raman handheld instrumentation. Designed to be taken into the factory, warehouse or out in the field for real-time, fast sample measurements. FirstGuard models are 21 CFR Part 11 compliant and available in three different excitation wavelengths 532 nm, 785 nm, and 1064 nm depending on your application needs.

Spectrum manufactures and distributes fine chemicals and laboratory products with quality and delivery you can count on every time; serving chemists in all industries with analytical reagents, solvents, solutions and fine chemicals, including >22,000 TCI America items and >4000 chromatography/ spectroscopy consumables from PerkinElmer. A one-stop lab shop: chemicals, equipment, supplies.

Sigma-Aldrich is a leading Life Science and High Technology company. Our chemical and biochemical products and kits are used in scientific research, including genomic and proteomic research, biotechnology, and pharmaceutical development. Sigma-Aldrich is committed to Accelerating Customer's Success through Innovation and Leadership in Life Science, High Technology, and Service.

Waters

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Waters Corporation, the premium brand in the analytical instruments industry, creates business advantages for laboratory-dependent organizations by delivering practical and sustainable scientific innovation to enable significant advancements in healthcare delivery, environmental management, food safety, and water quality worldwide. Bringing keen understanding and deep experience to those responsible for laboratory infrastructure and performance, Waters helps customers make profound discoveries, optimize laboratory operations, deliver product performance, and ensure regulatory compliance. Pioneering a connected portfolio of separations and analytical science, laboratory informatics, mass spectrometry, as well as thermal analysis, Waters' technology breakthroughs and laboratory solutions provide an enduring platform for customer success.

GENERAL MEETING INFORMATION FOR MARM 2012

REGISTRATION

Registration is available through the MARM 2012 at http://marmacs.org/2012/register.html. Onsite registration will take place in the University Center from:

- Wednesday, May 30 4:00 PM – 6:00 PM
- Thursday, May 31 & Friday, June 1 7:00 AM – 5:00 PM
- Saturday, June 2 7:00 AM – 12:00 PM

LODGING & TRAVEL

UMBC is located just south of the city of Baltimore and 40 miles north of Washington, DC. **From the north,** take Interstate 95 to Route 166 (Exit 47B, Catonsville) or take Interstate 83 to the Baltimore Beltway (I-695, west) and then take Exit 12C (Wilkens Avenue, west); follow the signs to UMBC. **From the south,** take Interstate 95 to Route 166 (Exit 47B, Catonsville); follow signs to UMBC. Baltimore-Washington International Airport is only five minutes away. Bus service is available from downtown Baltimore. AMTRAK and MARC commuter trains serve the nearby BWI Rail Station. Other information is found on the MARM 2012 website http://marmacs.org/2012/directions.html.

A variety of rooms will be available for MARM 2012 (http://marmacs.org/2012/housing.html). Dorm rooms will be available on the UMBC campus: $27+change / night for a double shared or $40 for a double shared with a 3 or 4 day meal plan. Dorm room reservations forms are found on the MARM 2012 website. Undergraduate Housing Award Application is also available. This award is intended to help undergraduate students pay for housing while attending the 2012 MARM meeting of the ACS. Students meeting certain criteria will be given first consideration, but all are encouraged to apply. Blocks of rooms will be available at the: **Holiday Inn Inner Harbor ($150 / night)-**301 West Lombard Street, Baltimore, Maryland 21201; Phone: (410)685-3500 • Fax: (410)727-6169; Reservations: Toll Free: (888)HOLIDAY; www.innerharborhi.com; Easy access to all downtown/Inner Harbor sites; Short drive to/from UMBC (~15-minutes) and **Four Points Sheraton ($115 / night)-**7032 Elm Road, Baltimore, Maryland 21240; Phone: (410)859-3300 or toll free: (800)368-7764; www.fourpoints.com/bwiairport;

SHUTTLE SCHEDULE

Free Shuttles will be available between the meeting locale on the UMBC campus and the Holiday Inn Inner Harbor, Four Points Sheraton at BWI, and the BWI Amtrak/MARC station. Drop-off on campus will be at the ITE Building:

Schedule (for all three locations):

Morning/ Afternoon

Thursday, Friday, and Saturday

7:00AM-10:00AM, Shuttles run continuously
10:00AM-5:00PM, Shuttles come hourly (Approximately on the hour)

Evening

Thursday and Friday

5:00PM-10:00PM, Shuttles run continuously

Saturday

5:00PM-8:00PM, Shuttles run continuously

REFRESHMENTS

A variety of social events and field trips have been planned for MARM 2012. All luncheons and dinners will be held at the University Center 312. The Starbucks in the University Center (first floor) will also be open from 10:00AM to 3:00PM Thursday through Saturday during the meeting for your convenience. In addition, a limited number of boxed dinners will be available Thursday evening. Event tickets may be purchased onsite.

Thursday, May 31

12:00pm - 2:00pm 50 Year Member Luncheon
12:00pm - 2:00pm All You Can Eat Cook-out (University Center, 1st Floor Plaza)

evening

5:30pm - 7:00pm Remsen Award Dinner

Friday, June 1

12:00pm - 1:30pm Women Chemists Committee Luncheon
12:00pm - 2:00pm All You Can Eat Cook-out (University Center, 1st Floor Plaza)

evening

5:30pm - 7:30pm Awards Dinner
8:00pm - 9:00pm Beers of Baltimore Beer-Tasting (Tent, Upper Plaza)

Saturday, June 2

12:00pm - 1:00pm Chemagination Luncheon
12:00pm - 2:00pm All You Can Eat Cook-out (University Center, 1st Floor Plaza)
12:00 pm- 2:00pm Crab (Cup)cake with the ACS Governance/
"Science and Society" Panel Discussion (Tent, Upper Plaza)

evening

7:00pm - 10:30pm Baltimore Harbor Dinner Cruise

Coffee Breaks: Coffee, soft drinks, and light snacks will be available in the UC Ballroom and in the foyer of the ITE Building outside LH 7 and LH 8 in the morning from 9:30AM-10:45AM and in the afternoon from 2:30PM-3:45PM.

Poster Sessions: All poster sessions will take place in the University Center Ballroom. All Happy Hour sessions (5:00pm to 7:00pm) also include hors d'oeuvres and a cash bar for beer and wine.

Thursday	
Analytical Chemistry, Environmental Chemistry, Food and Flavors	1:30pm - 3:30pm
Happy Hour: Biochemistry and Computational Biochemistry	5:00pm - 7:00pm
Friday	
Physical Chemistry, Inorganic Chemistry, Energy and Chemistry Education	9:30am - 11:30am
Nanochemistry and Organic Materials	1:30pm - 3:30pm
Happy Hour: Organic and Medicinal Chemistry	5:00pm - 7:00pm
Saturday	
Undergraduate Research A	9:30am - 11:30am
Chemagination	11:45am - 2:45pm
Undergraduate Research B	3:00pm - 5:00pm

PROGRAM

Symposia and workshops are listed on subsequent pages. The symposium programs formally begin at 8:00 AM on Thursday, May 31st, and they continue throughout the three days of the meeting. Look for those papers that are of interest to you.

EXHIBITION AND SPONSORSHIPS

The Vendor Exhibit Show will be in the Ballroom of the University Center on May 31 through June 2 from 9:00 AM – 7:00 PM on Thursday and Friday and 9:00 AM – 5:00 PM on Saturday. The exhibition area will include the poster sessions and is adjacent to the areas for technical sessions and symposia. Coffee breaks will be held area from 9:00 AM – 11:30 AM and from 1:00 PM – 3:30 PM.

MARM 2012 Awards Summary

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

Marilyn D. Gorman, Teacher Affiliates of the North Jersey Section

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

Malcolm D'Souza, Wesley College, Dover, DE.

The E. Ann Nalley Regional Award for Volunteer Service to the American Chemical Society

Bill Suits, N. Jersey Section

The ACS Division of Chemical Education Mid-Atlantic Region Award for Excellence in High School Teaching

Helena Buzin, Central Bucks High School South Warrington, PA

The Chromatography Forum of Delaware Valley: 2012 Student Award Symposium

Kenton Chodara, Pennsylvania State University

Erin Ennis, Drexel University

Amanda Leffler, Pennsylvania State University

Kendall Sandy, Bucknell University

Brandy Taylor, Bucknell University

The Stanley C. Israel Regional Award

For Advancing Diversity

In the Chemical Sciences

Marilyn D. Gorman

Teacher Affiliates of the North Jersey Section

Marilyn D. Gorman, a career high school chemistry teacher in predominantly urban districts, has stimulated and fostered activities that promote inclusiveness within and outside the classroom.

During the eight years teaching in the Philadelphia School System at West Philadelphia High School (100% students of color) Marilyn volunteered to sponsor students in a Saturday chemistry enrichment program at a nearby university and was part of a neighborhood group where she tutored and chaperoned cultural trips. Serving seventeen years in Abraham Clark High School (70% students of color) in the school district of Roselle, Marilyn mentored scores of students, many of whom are in STEM careers. By volunteering to sponsor events, she engaged students in Science League for Chemistry, Chemistry Olympics, Young Science Achievers Program (YSAP) and ACS Project SEED. YSAP is for students from underrepresented populations in the STEM fields and Marilyn coached students to prepare budgets, design experiments, submit proposals, perform experiments at the school, and write reports under her supervision. All grant recipients presented their results at a ceremony in May where they were judged and monetary prizes awarded. For Project SEED, she not only wrote grants to the ACS to help fund the program, recommended students for the program, helped them write resumes, told them

how to interview successfully with professors, and followed-up during the summer by visiting them at their work sites. Further, she helped them give posters at the end of the summer, helped judge posters at the yearly presentation of students from all over the state, and then encouraged them to apply to colleges and seek scholarships.

The E. Emmet Reid Award

in Chemistry Teaching at Small Colleges

in the ACS Mid-Atlantic Region

Malcolm D'Souza

Wesley College, Dover, DE

Dr. Malcolm J. D'Souza is Professor of Chemistry at Wesley College, in Dover, Delaware. He has published 70 peer-reviewed journal articles, has over 200 abstracts in conference proceedings, and has established a nationally recognized Wesley College Undergraduate Directed Research Program in Chemistry. He has been especially effective at involving undergraduates in his research projects and he has mentored over 100 undergraduate students in the laboratory since 1992, with 47 undergraduate co-authors on his list of peer-reviewed publications. Forty one of D'Souza's students have received merit/recognition awards at national conferences; many are awarded significant scholarships and fellowships, and are accepted in competitive graduate and professional school programs. D'Souza currently serves as Co-Director for

Undergraduate Research on a $17.4-million National Institutes of Health (NIH) IDeA grant to the State of Delaware. In addition to his research in organic chemistry, he also has projects, presentations, and publications in the area of chemometrics, developing commercial databases that assist in the development of new pharmaceutical and agricultural products.

The E. Ann Nalley Regional Award

for Volunteer Service

to the American Chemical Society

William (Bill) H. Suits

N. Jersey Section

Bill graduated from the UW Madison where he played football, participating in the ’60 Rose Bowl. By his senior year he managed a lab and stayed on to train graduate students while building X-ray Scattering equipment. Moving to sales, marketing and customer applications; he worked for Packard Instruments, Varian, Beckman and Dionex until he retired at 58 to care for his wife and help ACS. In various roles he chaired his section, MARM 05, and was the inaugural chair of the MARM Board. As an ACS Career Consultant he has helped hundreds of chemists advance their career and recruited 5 new consultants. He speaks to several groups about networking and career related issues. Bill has organized several large section meeting that drew in excess of 500 attendees.

Serving as section councilor, he served on CPRC, CEPA and LSAC. He also served on the Board of ChemPharma and AIDSfreeAFRICA where he continues as Board Advisor. Bill helps Students@Science and Expanding Your Horizons to find members who will help with educating students from poor areas and create interest in science education.

The ACS Division of Chemical Education (CHED)

Mid-Atlantic Region Award

for Excellence in High School Teaching

Helena Buzin

Central Bucks High School South Warrington, PA

Helena Buzin received a Bachelor of Science Degree in Chemistry with a minor in Mathematics from Wagner College in 1979. After graduating, Helena worked as an analytical chemist for several years. While working, Helena married and had 3 children. She decided to leave industry to take care of her family. Helena then decided to return to school to pursue a degree in education. Helena received her Master of Education Degree in Science from Arcadia University in 1994, and has been employed in the Central Bucks School District since that time.

While teaching all levels of chemistry – from Conceptual through Advanced Placement- as well as Oceanography and Mathematics, Helena continued her education by taking classes in both science and education at St. Joseph's University. During her time in Central Bucks, Helena has initiated collaborative exchanges between her high school chemistry students and elementary/ middle school students. She also developed a

program with Delaware Valley College that affords Advanced Placement students the opportunity to participate in a week-long Organic Chemistry extension course. While at Central Bucks South, Helena developed and implemented a Forensic Science course that emphasizes chemistry and physics in the curriculum. The course culminates in a final assessment of analyzing a crime scene.

Helena is the advisor of Chemistry Olympiad and the National Honor Society as well as the co-advisor of the Science Olympiad team. She also acts as a mentor to new chemistry teachers in the district. She thoroughly enjoys all aspects of teaching and mentoring students, challenging each to work to the maximum of their potential while providing support and encouragement. Helena is proud of influencing students to pursue careers in chemistry, biochemistry and chemical engineering, but the most rewarding part of her job is having students remain in contact allowing her to see their successes.

The Chromatography Forum of Delaware Valley: 2012 Student Award Symposium

The following winners will present their work at the DVCF student award symposium on Friday June 1, 2012 from 3:00 pm to 5:45 pm in UC115. The scheduled presentations are:

- **Kenton Chodara,** Dan Sykes, Pennsylvania State University

  Selection of a Column and Optimization of a Method for the Analysis of Antidepressants in Aqueous Samples using Liquid Chromatography-Tandem Mass Spectrometry

- **Erin Ennis,** Joe Foley, Drexel University

  Is it Better to Separate Charged Enantiomers using Electrokinetic Chromatography With or Without Electroosmotic Flow?

- **Amanda Leffler,** Frank Dorman, Pennsylvania State University

  Analytical Investigation of Synthetic Street Drugs

- **Kendall Sandy,** Tim Strein, Bucknell University

  Probing chiral separation mechanisms with MEKC and NMR: 1-1'-bi-2-naphthol and secondary cholate micelles

- **Brandy Taylor,** Tim Strein, Bucknell University

  Studying MEKC Separation Capabilities of Cholic Acid Micelles with NMR: Effects of pH, Temperature, and Concentration

MARM AWARDS CRITERIA

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

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

Nomination Guidelines:

Purpose: 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.

Nature: The award consists of a medal and a $1,000 grant to support and further the activities for which the award was made. The award also will include funding to cover the recipient's travel expenses to the ACS regional meeting at which the award will be presented.

Rules of Eligibility: Individuals nominated for the award may come from any professional setting: academia, industry, government, or other independent facility. Nominees may also be organizations, including ACS local sections and divisions. The awardees will have increased the participation and leadership of persons from diverse or underrepresented minority group(s), persons with disabilities, or women.

To Nominate: For nomination of individuals, a letter of nomination of no more than three pages and a CV or resume is required. For institutions or corporations, a brief description of the institution or organization must be included. Nominations may also include up to two supporting letters of no more than three pages and up to five different samples of program materials.

For details and most up to date information regarding the award, please refer to the ACS web site: www.acs.org/awards then click on “Other ACS Awards”.

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

Nomination Guidelines:

The E. Emmet Reid Award is administered by the Organizing Committee of the Middle Atlantic Regional Meeting (MARM) of the American Chemical Society for outstanding achievements in teaching chemical sciences at small colleges within the Middle Atlantic Region.

Purpose: To recognize, encourage and stimulate high quality teaching and research at small colleges.

To nominate: Nominations for the Award are made by the Local Sections of the Middle Atlantic Region. The Chairman or Secretary of the Section must sign and transmit the nomination to the MARM Award Committee Chairman. A committee may be appointed to solicit names of candidates for final selection.

No special form is required but the MARM Award Chair must receive the nominee's short curriculum vitae, list of publications, and evaluation of the nominee's achievements as a teacher in a small college. This document should clearly demonstrate the candidate's attributes: the quality of the candidate's teaching; organization and efficiency of lab work; research and/or development work; ability to challenge and inspire students; extra-curricular work in chemistry; courses, meetings, presentations, awards, etc. Seconding letters are not essential but as many as three may be included with each nomination. Letters may include careful evaluations of the teacher's abilities by his superiors, associates, or by local section members.

- The candidate need not be a member of the American Chemical Society.
- The Award committee of MARM will review the candidates and select the nominee.
- The nominee will be presented the Award during the forthcoming MARM. The nominee is expected to deliver a short acceptance speech.

- Unsuccessful candidate's files will be kept active for a period of three years upon receipt of a letter from the nominating section chairman or secretary. Any further updating of the candidates file will be welcomed at that time but are not mandatory.
- The Award will consist of $1,000 and a major award plaque.

The E. Ann Nalley Regional Award
for Volunteer Service to the American Chemical Society

Nomination Guidelines:

Purpose: 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.

Nature and Establishment: This award was instituted in 2006 by ACS President E. Ann Nalley as part of her presidential initiative to recognize ACS volunteerism. It is Dr. Nalley's wish that the award continue in perpetuity at each regional meeting. The award consists of a plaque honoring the recipient with an imbedded medallion commemorating Dr. Nalley.

Rules of Eligibility: A nominee must be a member of the American Chemical Society residing in a local section within the region, and will have made significant contributions to their Region of the American Chemical Society. The volunteerism to be recognized may include a variety of activities, including but not limited to the initiation or sponsorship of a singular endeavor or exemplary leadership in the region. Past and present members of the ACS Board of Directors and staff are ineligible for this award.

Submittal process: For each nominee, a Nomination (which includes a bio or curriculum vitae) and one or two Support Forms must be completed. As indicated in the form, these materials should be completed and forwarded to the *2012 MARM Awards Chair* Merle Eiss**,** meiss32@comcast.net

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

Nomination Guidelines:

Purpose: To recognize, encourage, and stimulate outstanding teachers of high school chemistry in the Middle Atlantic Region. The Middle Atlantic Region of the ACS consists of the following Local Sections:

- Washington DC
- Maryland
- Western Maryland
- Lehigh Valley PA
- Southeastern PA
- Susquehanna Valley PA
- Philadelphia PA
- South Jersey
- Ocean County NJ
- Monmouth County NJ
- Trenton NJ
- Delaware
- Princeton NJ
- North Jersey
- New York (NYC)

Nature: The Award consists of a cash award and a plaque. Reasonable travel expenses to the Regional Meeting at which the award will be presented will be reimbursed. A certificate/plaque may also be provided to the recipient's institution for display. The awardee may be asked to give an address and/or participate in a symposium with other teachers.

Rules of Eligibility: Any individual, except a member of the award selection committee or currently enrolled student of the nominee, may submit one nomination or support form in any given year. Local Sections are especially encouraged to submit nominations for the award. The nominee must be actively engaged in the teaching of chemistry or a chemical science in a high school (grades 9-12) on at least a half-time basis. The nomination should clearly demonstrate as many of the following attributes as possible:

- The quality of the nominee's teaching; unusually effective methods of presentation should be emphasized;

- The nominee's ability to challenge and inspire students;
- Extracurricular work in chemistry or a chemical science by the nominee, including science fairs, science clubs, and activities that stimulate the interest of young people in chemistry and related sciences;
- A willingness to keep up-to-date in the field, as evidenced by the pursuit of a higher degree in chemistry or a chemical science, enrollment in refresher courses and summer institutes, regular attendance at scientific meetings, membership in professional organizations, and other means of self-improvement;
- Evidence of leadership and/or active involvement within the profession.

Required Nomination Components:

1. A completed Nomination Form that consists of...
    - A Nominator Information form
    - A Nominee Information form
    - A Nominator Recommendation letter of not more than 1,000 words submitted by the nominator
2. A curriculum vitae or resume that includes a list of the nominee's honors, professional activities, and additional evidence of service to the profession. This must be limited to no more than two pages and the activities listed must have occurred within the past five years.
3. At least one, but not more than three, letters of support**.** One must be from the teacher's current principal or supervisor. Additional letters of support may be sent by colleagues, members of the American Chemical Society who are familiar with the nominee's achievements, or former students and parents of former students.

Unsuccessful candidates' files will be kept active for a period of one year.

The Chromatography Forum of Delaware Valley – Student Award Symposium

Nomination Guidelines:

The annual CFDV Student Award Symposium provides graduate and undergraduate students with an opportunity to present their research in the field of separation science at the 2012 ACS MARM Meeting, to be held at the University of Maryland, Baltimore County, on May 31- June 2. Presentation of a paper at this symposium enables students to achieve recognition for their accomplishments, as well as developing important career skills and professional contacts.

All students whose papers are accepted for presentation at the Student Award Symposium will receive an honorarium and reimbursement of the undergraduate student registration fee. Each student will also receive a certificate acknowledging his/her accomplishment and commemorating the event, which is sponsored by the Chromatography Forum of Delaware Valley. Though many participants are pursuing separation science as their major course of study, students in the areas of medicine, biochemistry, engineering and organic chemistry have successfully presented papers describing areas of research that involve separations.

Previous awardees are ineligible. For a paper to be given full consideration for presentation at the Student Award Symposium, a title & 250-word abstract should be sent to the address below.

Dr. Mary Selman
Rohto-Mentholatum Research Labs
111 Rock Road
Horsham, PA 19044
Phone: 215-442-1880 x19
E-mail: mary.selman@rmrl.com

MEETING AT A GLANCE

Registration - UC 310

Wednesday: 4:00pm-6:00pm
Thursday: 7:00am-5:00pm
Friday: 7:00am-5:00pm
Saturday: 7:00am-12:00pm

Special Events

Thursday

Remsen Award Lecture "The Artificial Leaf"	7:30pm-9:00pm	LH 5

Friday

"Yeast Metabolism and the Flavor Chemistry of Beer"	6:30pm-7:45pm	LH 5
Beers of Baltimore Beer Tasting	8:00pm-9:00pm	Tent

Saturday

"Crab (Cup)cake" with ACS Governance/"Science and Society" Panel Discussion	12:00pm-2:00pm	Tent

Exposition - UC Ballroom and Ballroom Lounge

Thursday: 9:00am-7:00pm
Friday: 9:00am-7:00pm
Saturday: 9:00am-5:00pm

Oral Technical Sessions

Thursday Morning

Analytical Chemistry	8:30am-11:45am	LH 4
Atmospheric Chemistry	8:10am-12:00pm	LH 5
Frontiers in the Application of Computational Chemistry to Biological Systems A	9:00am-12:15pm	LH 7
Nanomaterials: Self-Assembly and Applications	8:10am-12:00pm	LH 8
Addressing Challenges in Food Analysis Using Emerging Technologies	8:20am-12:00pm	BS 120

Thursday Afternoon

Advances in Chemistry of Fluorescence Measurements and Imaging Techniques	1:30pm-4:45pm	LH 4
Remsen Award Symposium	1:00pm-5:00pm	LH 5
Frontiers in the Application of Computational Chemistry to Biological Systems B	1:30pm-5:00pm	LH 7
Measurements and Methods in Environmental Nanotechnology and Nanotoxicology	1:00pm-5:30pm	LH 8
Organic Chemistry	1:30pm-4:45pm	BS 120

Thursday Evening

Dietary Phytochemicals and Prevention of Metabolic Syndrome	6:30pm-9:00pm	LH7
Remsen Award Lecture	7:30pm-9:00pm	LH 5

BUILDING CODES: BS = Biological Sciences, MEYR = Meyerhoff Chemistry Building, UC = University Center
Lecture Hall (LH) Locations: LH 2, MEYR; LH 4, Academic IV; LH 5, Engineering;
LH 7 and LH 8: Information Technology/Engineering.

Friday Morning

Chemistry in the Chemical Senses A	8:00am-11:30am	LH 4
Renewable Energy A: Metabolic Engineering	8:00am-12:00pm	LH 5
Younger Organic Chemists: The Breadth of Organic Synthesis	8:30am-12:00pm	LH 7
Bioanalytical Chemistry	8:30am-11:45am	BS 120

Friday Afternoon

Chemistry in the Chemical Senses B	1:00pm-4:30pm	LH 4
Renewable Energy B: Biofuels	1:30pm-5:00pm	LH 5
Medicinal Chemistry	1:30pm-5:00pm	LH 7
Computational Chemistry	2:00pm-5:15pm	BS 120
Chromatography Forum of the Delaware Valley Student Awards Symposium	3:00pm-5:45pm	UC 115

Saturday Morning

Mass Spectrometry of Biomolecules	8:20am-12:00pm	LH 4
Contemporary Organic Materials	8:00am-12:00pm	LH 5
Carbohydrates in Drug Design A	8:50am-11:35am	LH 7
Renewable Energy C: Processes and Materials	8:30am-12:00pm	BS 120
Nanochemistry A	8:30am-12:00pm	MEYR 120

Saturday Afternoon

NMR Spectroscopy of Biomolecules	2:00pm-5:20pm	LH 4
Photochemistry	2:00pm-5:30pm	LH 5
Carbohydrates in Drug Design B	2:00pm-4:50pm	LH 7
Inorganic Chemistry	2:00pm-5:15pm	BS 120
Nanochemistry B	2:00pm-5:30pm	MEYR 120

Posters - UC Ballroom

Thursday

Analytical Chemistry, Environmental Chemistry, Food and Flavors	1:30pm-3:30pm
Happy Hour: Biochemistry and Computational Biochemistry	5:00pm-7:00pm

Friday

Physical Chemistry, Inorganic Chemistry, Energy and Chemistry Education	9:30am-11:30am
Nanochemistry and Organic Materials	1:30pm-3:30pm
Happy Hour: Organic and Medicinal Chemistry	5:00pm-7:00pm

Saturday

Undergraduate Research A	9:30am-11:30am
Chemagination	11:45am-2:45pm
Undergraduate Research B	3:00pm-5:00pm

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LH 7 and LH 8: Information Technology/Engineering.

Educational Programming

Thursday

Chemistry Classroom of the 21st Century	8:30am-11:45am	MEYR 120
Best Practices for Successful Online and Hybrid Courses/Innovation in the Chemistry Lab	1:30pm-4:50pm	MEYR 120

Friday

College Text Software: Enhancing Student Learning	8:30am-5:00pm	UC 201
Forensic Chemistry for High School Students	9:00am-12:00pm	LH 8
Environmental Chemistry for High School Students	1:00pm-4:00pm	LH 8

Saturday

Elementary School Teachers STEM Workshop	8:30am-12:00pm	MEYR 371, 372
Active Learning in the Chemistry Classroom	8:30am-11:45am	UC 201
Bringing Forensic Chemistry into the HS Classroom	9:00am-12:00pm	MEYR 120
Elementary School Teachers STEM Workshop	1:30pm-5:00pm	MEYR 371, 372
Active Learning in the Chemistry Laboratory	2:00pm-4:25pm	UC 201
Bringing Environmental Chemistry into the HS Classroom	2:00pm-5:00pm	MEYR120

Chemagination, ***Saturday***

Poster Set-up	11:45am	UC Ballroom
Lunch	12:00pm-1:00pm	UC 312
Poster Judging	1:00pm-2:45pm	UC Ballroom
Chemistry Demos	3:00pm-4:00pm	LH 2 (ALL ARE WELCOME!)
Awards Presentation	4:00pm-5:00pm	UC 312

Career Workshops and Resume Reviews

Thursday

Employment Workshop	8:00am-9:30am	UC 115
Preparing Your Resume	9:30am-11:00am	UC 115
Effective Interviewing	11:00am-12:30pm	UC 115
Individual Resume Review	1:30pm-5:00pm	MEYR 272

Programming for Entrepreneurs and the Business-Minded

Thursday

ACS Leadership Workshop: Fostering Innovation*	1:00pm-5:00pm	MEYR 256

Friday

Panel Discussion: Best Steps for the Chemical Entrepreneur	9:30am-12:00pm	MEYR 120
You Too Can Be an Entrepreneur or Partner with One	1:00pm-5:00pm	MEYR 120

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LH 7 and LH 8: Information Technology/Engineering.

Specialized Technical Workshops*

Thursday

Expanding Your Laboratory Capabilities for the Better, PerkinElmer	1:00pm-5:00pm	UC 115

Friday

Automated Serum to Purified Peptides in 10 Minutes for LCMS, Shimadzu	8:00am-12:00pm	MEYR 272
Automated Serum to Purified Peptides in 10 Minutes for LCMS, Shimadzu	1:00pm-5:00pm	MEYR 272

* require advanced registration; inquire at Meeting Registration (UC 110)

Undergraduate Programming

Friday

Panel Discussion: Careers in Chemistry	9:30am-11:30am	UC 115
Student Networking	6:00pm-	MEYR Courtyard

Saturday

Undergraduate Research Poster Session A	9:30am-11:30am	UC Ballroom
Undergraduate Research Poster Session B	3:00pm-5:00pm	UC Ballroom

Food - General

A light continental breakfast will be available Thursday through Saturday from 7:30am-8:45am in UC 312.

Coffee, soft drinks, and light snacks will be available in the UC Ballroom and in the foyer of the ITE Building outside LH 7 and LH 8 in the morning from 9:30am-10:45am and in the afternoon from 2:30pm-3:45pm.

On each day of the meeting, All-You-Can-Eat Cookouts will be held on the lower plaza in front of the first floor of the University Center (UC) from 12:00 pm to 2:00 pm. Cash is accepted if you did not pre-register.

Starbucks in the University Center (first floor) will be open Thursday through Saturday from 10:00am to 3:00pm for attendees' convenience.

Special Luncheons and Dinners

Thursday

*50/60 Year Member Luncheon***	12:00pm-2:00pm	UC 312
*Remsen Award Dinner***	5:30pm-7:00pm	UC 312

Friday

*WCC Luncheon***	12:00pm-1:30pm	UC 312
*Awards Dinner***	5:30pm-7:30pm	UC 312

Saturday

*Chemagination Luncheon***	12:00pm-1:00pm	UC 312
Crab (Cup)cake with the ACS Governance	12:00pm-2:00pm	Tent, Upper Plaza

** requires an additional fee; inquire at Meeting Registration (UC 110)

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LH 7 and LH 8: Information Technology/Engineering.

MARM 2012 Undergraduate Program

"Life after Graduation" Q&A Panel

Friday 9:30am-11:30am, Room UC 115

Ever wonder what life is like after walking across the stage? Want to know what you can do with your degree? Come hear a range of panelist discuss career options.

Marvourneen Dolor - Consulting Environmental Scientist/Policy Analyst

I am an independent government contractor working with a wholly-owned government corporation housed in the at the U.S. Department of Transportation - the Saint Lawrence Seaway Development Corporation. I provide environmental science and policy advice to the agency's Administrator and senior staff in the areas of ship-borne pollution, climate change adaptation, the National Ocean Policy, and the environmental aspects of international agreements with Canada. I also analyze scientific articles and legal briefs, and use this analysis to draft briefing papers to the Secretary and Deputy Secretary of Transportation.

Carmen Drahl - Associate Editor, Science/Technology/Education, Chemical & Engineering News magazine

Carmen Drahl made the transition to a writing career while earning a Ph.D. in chemistry at Princeton University. Born and raised in New Jersey, she now lives in Washington, D.C. and reports for Chemical & Engineering News magazine. At C&EN she's written about how new medications get their names, explained the science behind a controversial hair-straightening product, and covered the scientific firestorm sparked by an alleged arsenic life form. Her work has been featured on SiriusXM's "Doctor Radio", Radio New Zealand's "This Way Up", and elsewhere. Her coverage has also been recognized by MIT's Knight Science Journalism Tracker.

Robert W. Esmond, J.D., Ph.D. – Director, Sterne, Kessler, Goldstein & Fox P.L.L.C.

Dr. Esmond is an intellectual property attorney who specializes in obtaining patents for the pharmaceutical and biotechnology industry. Dr. Esmond also counsels his clients on various intellectual property matters such as patentability investigations, validity and infringement analyses, freedom-to-operate, and ANDA practice.

Carl Schwarz - Northeast Regional LCMS Sales Team Leader, PerkinElmer

Responsibilities include managing the sales of the LCMS product portfolio in the Northeast Region and mentoring of a chromatography/mass spectrometry sales team in the applications and understanding of LCMS technologies.

Dimitra Stratis-Cullum - Senior Research Chemist, U.S. Army Research Laboratory

Dr. Stratis-Cullum is a senior research chemist at the U.S. Army Research Laboratory. Her research interests are currently focused on synthetic molecular recognition, multifunctional biomaterials, and advanced optical sensor development. Her research program is very multidisciplinary, bringing together chemistry, bioengineering, materials science, and computational physics to enable advanced solutions to chemical, biological and other sensing applications.

Mike Zapf - Scientist, Materials Processing Group, McCormick & Company, Inc. Technical Innovation Center

Since 1976, Mike has held positions primarily in the Analytical Sciences Group in Chemistry, after starting this career in Sensory Science. He had prior experience at the FMC Corporation and Martin Marietta Cement in Baltimore. Later experience was in the organic synthesis of small flavor chemicals, including milliliter to multi-liter scale, analytical chemistry with a statistical background and additional pilot plant work with large scale chromatography and supercritical extractions. Mike holds a BS in Chemistry from Towson University and currently teaching lab at Towson.

"Chit Chat and All That" Student Networking

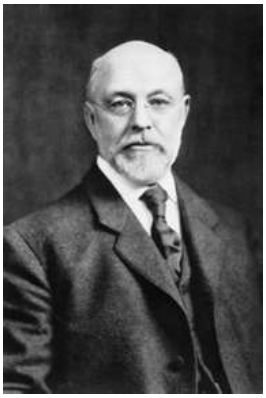
Friday 6pm, Chemistry Courtyard/MEYR 145

Food and friends, what could be better? Grab some pizza, play some games, meet some new people and get new ideas for your student chapter.

Undergraduate Research Poster Sessions

Saturday 9:30am-11:30am and 3:00pm-5:00pm
UC Ballroom

Remsen Award



The Remsen Award was established in 1946 by the Maryland Section of the ACS to memorialize the career of Ira Remsen, the first Professor of Chemistry and second president of the Johns Hopkins University. Remsen Memorial Lecturers are chemists of outstanding achievement, in keeping with Ira Remsen's long and devoted career as an exponent of the highest standards in chemistry. This year's Remsen Award goes to *Dr. Daniel G. Nocera, the Henry Dreyfus Professor of Energy and Professor of Chemistry, at the Massachusetts Institute of Technology*. Before the evening award lecture, an afternoon symposium arranged by Dr. Nocera will be held and includes Christopher J. Chang (University of California, Berkeley), Michelle C. Chang (University of California, Berkeley), Matthew W. Kanan (Stanford University), Tyrel McQueen (Johns Hopkins University), Bart Bartlett (University of Michigan), Joel Rosenthal (University of Delaware), and Shih-Yuan Liu (University of Oregon). For more information, see the program schedule.

Details: **Thursday, May 31, 2012**

Symposium by faculty arranged by Dr. Nocera	1:00 pm- 5:00 pm (ITE/LH5)
Remsen Award Dinner	5:30 pm-7:00 pm (UC312)
Remsen Award Presentation and Lecture	7:30 pm-9:00 pm (ITE/LH5)

Remsen Award Lecture

The Artificial Leaf

Daniel G. Nocera

It has been said for an ideal solar fuels process that the system requirements are:

- Earth-abundant materials
- No wires
- Direct solar-to fuels process.

Two earth abundant catalysts have been discovered that promote the oxygen evolving reaction (OER) and hydrogen evolving reaction (HER). The ability to operate these catalysts under benign conditions (in water at pH 7 and under 1 atm) has enabled the construction of the artificial leaf, which consists of a silicon wafer, coated with the respective OER and HER catalysts. By immersing the artificial leaf in water and holding it up to sunlight causes efficient water splitting; and all of this is done with no wires. The system surpasses the prescription from the community because it also does not rely on a membrane. By constructing a simple, stand-alone device composed of earth-abundant materials, the artificial leaf provides a means for an inexpensive and distributed direct solar-to-fuels conversion process with low-cost systems engineering and manufacturing requirements. The science behind the catalysts and the artificial leaf will be presented.

50 Year Member Luncheon

Thursday, May 31, 2012
University Center 312
12:00 pm to 2:00 pm

Please join us to honor all 50 Year (and some 60 Year) Members of the ACS and listen to speaker Dr. Donald Boesch, UMCES President, Professor of Marine Science and biological oceanographer. He has published two books and 90+ research papers and was appointed by President Obama to the National Commission on the BP Deepwater Horizon Oil Spill and Off Shore Drilling. He will speak on "Environmental Science and the Chesapeake Bay".

Women Chemists Committee Luncheon

"Strengthening American Science Education to Reach World-Class Status."
June Streckfus
Executive Director of Maryland Business Roundtable for Education, Inc.

Friday June 1, 2012
12:00 pm – 1:30 pm
University Center 312

Speaker Biography

June Streckfus has been executive director of the MBRT since its founding in 1992. The MBRT is a coalition of more than 100 leading Maryland businesses that have made a long-term commitment to support education reform and improve student achievement in Maryland.

MBRT has been recognized nationally by The Business Roundtable, the National Alliance of Business, the Public Relations Society of America, and the U.S. Department of Education…and regionally by Maryland educator associations and the Maryland State Department of Education.

A former teacher, county administrator, and U.S. Senatorial state director, June works relentlessly to involve business in the process of school improvement. With a B.S. in education from the University of Maryland and a master's degree and certificate of advanced study in liberal arts from Johns Hopkins University, June's leadership skills, diverse background, and unbending integrity have won her the respect and confidence of corporate executives, educators, government officials, and community leaders.

Streckfus co-chaired the Governor's Science, Technology, Engineering and Math (STEM) Task Force and serves on the Governor's P-20 Leadership Council; MSDE's Educator Effectiveness Panel, Race To The Top Advisory Board, K-12 Assessment Advisory Council; and College of Notre Dame Teacher Education Advisory Board.

Sponsored by the Women Chemist Committee.

MARM 2012 Awards Dinner

Friday June 1, 2012
5:30 pm to 7:00 pm
University Center 312

Please join us to honor all the awardees from MARM 2012:

The Stanley C. Israel Regional Award for Advancing Diversity in the Chemical Sciences
Marilyn D. Gorman, Teacher Affiliates of the North Jersey Section

The E. Emmet Reid Award in Chemistry Teaching at Small Colleges in the ACS Mid-Atlantic Region
Malcolm D'Souza, Wesley College, Dover, DE.

The E. Ann Nalley Regional Award for Volunteer Service to the American Chemical Society
Bill Suits, N. Jersey Section

The ACS Division of Chemical Education Mid-Atlantic Region Award for Excellence in High School Teaching
Helena Buzin, Central Bucks High School South Warrington, PA

The Chromatography Forum of Delaware Valley: 2012 Student Award Symposium
Kenton Chodara, Pennsylvania State University
Erin Ennis, Drexel University
Amanda Leffler, Pennsylvania State University
Kendall Sandy, Bucknell University
Brandy Taylor, Bucknell University

Bill Carroll, Chair of the ACS Board will present the awards and deliver a short talk.

Beers of Baltimore, Seminar and Beer Tasting
Friday June 1, 2012

Seminar

Information Technology/Engineering Building- LH5

6:30 pm -7:45 pm

Chemistry and Biochemistry of the Wort

Stephen Jones, Brewmaster, Oliver Breweries.

A complex series of chemical and biochemical reactions, from the mash tun to the brew kettle, produce a wort that will provide nutrients for yeast fermentation and its many other metabolic pathways, as well as directly determining many of the organoleptic properties of the final product. I will present a brief overview of some of the key aspects of wort production in a brewpub setting.

Yeast Metabolism and the Flavor Chemistry of Beer

Steve Frazier, Brewmaster, The Brewers Art.

The flavor of beer is strongly affected by the yeast strain utilized during fermentation. Although the connection between beer flavor and yeast is intuitive, the ways in which flavor active compounds originate, and the metabolic rationale for their origin, are not always obvious. We, as beer drinkers, are fortunate recipients of the end products of numerous intricate chemical processes involved in yeast fermentative metabolism. Aspects of the chemistry, and biochemistry, of beer flavor will be discussed with respect to the origin of characteristic beer flavors.

Beer Tasting

Tent, Upper Plaza (between Fine Arts Building and Meyerhoff Building)

Come sample some of the hand crafted Belgian beers from The Brewers Art and English ales from Oliver Breweries. The tasting is to start immediately following the seminar. Event registration required.

Stephen Jones graduated from the University of Warwick, Coventry U.K., with Bachelors of Science (Honors) in Biochemistry. He also has a diploma in Brewing from the Institute of Brewing and Distilling, London. Stephen brewed for the Firkin Brewery in Coventry and Loughborough in the U.K. for six years before joining Oliver Breweries in December of 1999.

Steve Frazier graduated with honors in physics in 1988 from the University of California, Santa Cruz, and received an MA in physics from Johns Hopkins University in 1992. He has been brewing with The Brewer's Art since 2002.

Meet the ACS Governance

Saturday June 2, 2012
Noon to 2:00 pm
Tent, Upper Plaza (between Fine Arts Building and Meyerhoff Building)

Improving People's Lives Though the Transforming Power of Chemistry

The Roles of ACS, Science, and Education in Society

Bassam Z. Shakhashiri, President of the ACS, will lead a distinguished panel that will emphasize the vitality of science literacy in our advanced scientific and technological society today. The panel will discuss the critical role of institutions of higher education in advancing science and in serving society. The conversation with the audience will focus on the importance of the chemical science s as key to improving the quality of life around the world. One goal of this session is to inspire members of the audience to pursue careers in research, teaching and public service in keeping with the ACS mission: to advance the broader chemistry enterprise and its practitioners for the benefit of Earth and its people.

Questions for the Panel and Audience:

- What are the grand challenges to science and to education in serving society today?
- What are the roles of institutions of higher education in addressing these challenges?
- Are science, scientists, and educators prepared and ready to address these challenges?
- Are we likely to succeed in convincing society to support us in addressing the challenges?
- Why should anyone pursue a career in the chemical sciences?
- What are the employment prospects in the chemical sciences?
- What can/should we do to raise the public awareness of the importance of chemistry in daily life?

Panelists include:

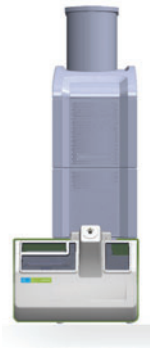
- **Dr. William E. Kirwan**, Chancellor of University System of Maryland
- **Dr. David Wilson**, President of Morgan State University
- **Dr. Freeman A. Hrabowski**, President of UMBC

Boxed lunches and **Crab (Cup)cakes** will be provided.

PerkinElmer
For the Better

Join PerkinElmer for an informative workshop at MARM:

May 30, 2012
1:30 PM – 5:00 PM
Room UC115



Presentations for the Workshop include:

- My Sample is Not a Liquid in a Cuvette, Now What Do I Do? (Jeff Taylor)
- How to Choose the Correct UV/Vis/NIR Accessory for Solid Sample Materials Measurement (Jeff Taylor)
- IR: "The Principles and use of an FTIR Microscope (Jeff Taylor)
- Comparative Study: LC-APCI-MS and Offline Ambient Ionization with DSA of Explosives (Josh Wilhide)

In addition, Carl Schwarz will be demonstrating the DSA Tof and Lenny Pitts will demonstrate the NexION.

Don't forget to visit PerkinElmer in Booth #10 at MARM

SHIMADZU
Excellence in Science

Excellence in Science

Shimadzu has been a world leader in the analytical instrumentation industry for over 135 years. Our goal has always been to find the best solutions for research, development and applications to meet your specific disciplinary needs. And as the preferred vendor of many institutions, our instruments are used by top researchers across the globe, scientists who can count on the stability, experience, and support that only Shimadzu offers.

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- HPLC/UHPLC
- LC/MS/MS
- Particle Size
- Testing Machines
- Thermal
- TOC/TN/TP
- UV-VIS

Workshop: Friday, June 1

8AM – Noon and 1PM – 5PM; 272 Meyerhoff Chemistry Building

We cordially invite you to join us for this informative workshop. Topics include:

- Perfinity Workstation - Automated Serum to Purified Peptides in 10 Minutes for LCMS
- Modern Gas chromatography Techniques – Heart-cut GC, GCXGC
- Choosing the Right Accessory to Maximize the Functionality of Your UV-Vis

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WORKSHOPS

Career Workshops and Resume Reviews / Leadership Workshops

Thursday, May 31, 2012:

- 8:00am-9:30am - UC115 **ACS Planning Your Job Search**: This workshop addresses employment trends and professional values (self-assessment). Then,the process of networking is explored: who is in your network, how to expand it. Strategies such as informational interviewing will be discussed.
- 9:30am-11:00am - UC115 **ACS Preparing a Résumé**: Your resume is a personal introduction and leaves an impression. In this workshop you will learn which personal data format is right for your "marketing plan," and construct a winning resume.
- 11:00am-12:30pm - UC115 **ACS Effective Interviewing**: Many job seekers think their work ends once an interview is secured. Think again! This workshop will examine the entire interview process, types of interviews, frequently asked questions, and how to evaluate an offer.
- 1:00pm-5:00pm - MEYR256 **ACS Leadership Workshop: Fostering Innovation**: We are constantly challenged to come up with new ideas, approaches, and solutions, yet most of us feel ill-equipped to do this effectively. With a systematic and proven process to generate ideas you can lead your team to develop new ideas. Gain the understanding and tools to tap into your own innovation style and stimulate innovative thinking among your committee members. Sponsored by ACS Leadership Advisory Board
- 1:30pm-5:00pm - MEYR272 **ACS Individual Résumé Review:** Description: An ACS Career Consultant will be available to provide individual résumé reviews and career assistance from 1:30 -5:00 pm. You must bring a copy of your résumé. Sign-up will be available at meeting registration.

  All Career Workshops and Resume Reviews sponsored by the ACS Office of Career Management and Development.

SMALL BUSINESS AND ENTREPRENEUR WORKSHOPS

Friday, June 1, 2012:

- 9:30am-12:00pm – MEYR120 **Best Steps for the Chemical Entrepreneur**: Join our wide spectrum of panelists for a facilitated discussion as to best steps for the chemical entrepreneur. Topics discussed will include: creating an organizational structure; various forms of intellectual property and their use as strategic business assets; alternative forms of funding/financing; and factors relating to enterprise success such as technology, customer base, marketing, management. This is your opportunity to ensure the success of your new or planned entity. Panelists include: Konstantina Katcheves (Lonza International)-intellectual property and collaborations, technology transfer, and acquisition; Jacque Allan (Saul Ewing)-

entity formation and steps to prep for exit diligence; Robbie Melton(Tedco)- MD resources for the early stage entrepreneur. Planned by the ACS Division of Small Chemical Businesses (SCHB) and presented by SCHB organizer Gianna Arnold (GArnold@saul.com). Additional support from Saul Ewing LLP.

- 1:30am-5:30pm -MEYR120 **Symposium: You Too Can Be an Entrepreneur or Partner with One**
  - *Introductory Comments:* Bill Suits, ACS Career Consultant, Bedminster, NJ
  - *How a Medicinal Chemist became the CEO of the Year:* Ramesh C. Pandey, Ph.D., GDP Ayurvedic University (GDPAU), New Brunswick Technology Center, New Brunswick, NJ- Importance of the delivery on your commitment(s), which builds the credibility. Focus, Goal and Vision have been the key in my life. A difficult journey: from a scientist to an Entrepreneur/Businessman in bringing the first "Generic Vancomycin" with LyphoMed, partnering with key individuals, surprises with new corporate affiliations, and first herbal product NICOSANTM for the treatment of Sickle Cell Disease (SCD). Choosing the right partners, tenacity, persistence, passion and motivation of the group is important.
  - *Entrepreneurship in Early Drug Discovery Research*, Allen B. Reitz, Ph.D, CEO, ALS Biopharma, LLC, Doylestown, PA- The drug discovery effort worldwide has seen tremendous change in recent years involving high levels of generic substitution, stagnant productivity and innovation, and the globalization of contract research opportunities. However, innovation is coming more frequently from smaller, focused research groups, either in biotechnology companies or at drug discovery institutes affiliated with universities and non-profit research organizations. This talk will focus on best practices in product development and innovation.
  - *The Reality of Entrepreneurship (Not the venture capital kind – the kind where you hang a shingle and start looking for customers)*, Donald Truss, Executive Director Staffing, Students2Science, Inc, East Hanover, NJ-One account: transformation from an analytical chemist to a 30 year business owner, perspectives on the typical entrepreneur and the ideal entrepreneur, lessons learned while assisting hundreds of small business owners with staffing issues, and suggested steps to take if starting a new business
  - *How Can an Incubator Help the Entrepreneur? Some Success Stories*, Ned D. Heindel, Lehigh University, Department of Chemistry, Bethlehem, PA- After four years of declining venture capital support for start-up biopharma companies, the first quarter of 2012 showed a rousing investment to early-stage innovators in the health science space. Investors, however, continue to favor device/diagnostic firms with a prototype in hand or therapeutic firms with a compound in the clinic. The phrases "de-risked investment" and "proof of concept" are on every investor's lips as a virtual requirement for putting funding in play. Comparisons will be presented of the technology plans, financial platforms for a dozen new firms and their products, and how association with an incubator contributed to their respective successes.

Financed by PROF and cosponsored by BGMT, CHAL & SCHB.

BUILDING CODES: BS = Biological Sciences, MEYR = Meyerhoff Chemistry Building, UC = University Center

Lecture Hall (LH) Locations: LH 2, MEYR; LH 4, Academic IV; LH 5, Engineering; LH 7 and LH 8: Information Technology/Engineering.

Online Learning Systems for General and Organic Chemistry

Enhancing Student Learning

Friday, June 1, 8:30 am – 5:00 pm

University Center 201

Each company will give a 20-minute presentation of their online learning system. These presentations will be followed by a hands-on question and answer period where you can ask questions and test out the system for yourself.

General Chemistry	Organic Chemistry
8:30 am – Wiley	1:30 pm – Wiley
8:55 am – McGraw-Hill	1:55 pm – McGraw-Hill
9:20 am – Sapling	2:20 pm – Sapling
9:45 am – Cengage	2:45 pm – Cengage
10:10 am – 12:00 pm: Hands on Q&A	3:10 pm – 5:00 pm: Hands on Q&A

** Please note that food and drink are not permitted in this computer lab. **

High School STEM Education Program

The goal of this STEM Education Symposium is to demonstrate to students advantages of a career in chemistry and to give chemistry teachers tools to enhance their curriculum. There will be separate sessions for students and teachers:

Friday, June 1, 2012 8:30 am to 5:00 pm, ITE/LH8 High School Students and Teachers

Saturday, June 2, 2012 8:30 am to 5:00 pm, ITE/LH8 High School Teachers

The 2012 MARM focuses on the vital theme of Chemistry in the Chesapeake and this conference is led by experts from industry, government and academia. This program will disseminate the latest information in environmental science, forensic chemistry and applied instructional methods. The MARM is dedicated to upgrading the chemistry pedagogy offered to students in the region.

STEM Education Presentations

Morning Session - 9:00 a.m. to Noon

Environmental Chemistry

Speaker:	Dr. Jenn Alosa, Chesapeake Bay Foundation	
	Careers in Environmental Science	*Friday*
Speaker:	Dr. Michael Miller, New Jersey Environmental Protection Administration	
	An Adventure as an Analytical/Environmental Chemist	*Friday*
	Preparing Students to Study Environmental Chemistry in College	*Saturday*
Speaker:	Dr. Ryan Casey, Department of Chemistry, Towson University	
	Intermolecular Forces as a Key to Understanding the Fate of Organic Contaminants	*Friday & Saturday*
Speaker:	Alvin Bober, Retired	
	The Use of Fine Arts Techniques In Teaching Environmental Chemistry	*Saturday*

Lunch - Noon to 1:00 p.m. Included with Registration

Afternoon Session - 1:00 p.m. to 4:00 p.m.

Forensic Chemistry

Speaker:	Dr. Richard Saferstein, Author and Consultant; Former Chief Chemist, New Jersey State Police Laboratory	
	Forensic Chemistry - *Friday*; Teaching Forensic Chemistry - *Saturday*	
Speaker:	Dr. John Butler, NIST	
	Forensic DNA Analysis	*Friday & Saturday*
Speaker:	Jay Tobin, Stevenson University; Former Chief Chemist, Maryland State Police Laboratory	
	The CSI Effect and Forensic Science Careers	*Friday*

The Use of Virtual Labs in Teaching Forensic Science *Saturday*

Sponsored by ACS Division of Chem Ed and Wells Fargo. Questions**:** Please contact either Dr. Sandra K. Young: sandra.young@us.army.mil or Alvin Bober: abober@verizon.net.

CHEMAGINATION CONTEST
MARM 2012

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. 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."* To view a sample ChemMatters magazine visit the national ACS website, acs.org, and look under Education.

In addition to the article, students are asked to design a cover for the magazine. The article must be written as if the student is living in the year 2037, looking back at innovations that have occurred since 2012. The innovation must fall into one of the following categories:

* Alternative Energy Sources
* Environment
* Medicine/Healthcare
* New Materials

The MARM contest will be held Saturday, June 2, 2012 from 12:00 pm to 5:00 pm. The competition will take place on the campus of the University of Maryland, Baltimore Campus (UMBC), Baltimore MD and will consist of the poster session and judging, a chemistry demonstration and awards ceremony.

The preliminary program is as follows:

12:00 – 1:00 pm	Lunch and poster set- up (Room UC 312 and the UC Ballroom)
1:00 – 2:45 pm	Judging
3:00 – 4:00 pm	Chemistry Demonstration (Lecture Hall 2, a.k.a. MEYR 030)
4:00 – 5:00 pm	Awards Presentation

The first place winners in each of the four categories (Alternative Energy Sources, Environment, Medicine/Healthcare, or New Materials) from the local section contests are eligible to compete in the MARM contest. If they cannot attend for any reason, the second place winners can serve as alternates.

The University of Maryland, Baltimore Campus (UMBC) is easily accessible by car or public transportation. Information on transportation, accommodations parking etc. can be found at the MARM website marmacs.org. Event sponsored by the MARM Board.

Regards,
Louise Lawter and Shirish Shah
MARM Chemagination Co-Chairs

Science, Technology, Engineering, & Math (STEM) Education Activities for Elementary School Teachers

Two 3 1/2 -hour hands-on Science, Technology, Engineering, & Math (STEM) education activities for Elementary School teachers sessions are being held on Saturday, June 2 at MARM 2012. These identical sessions will consist of 3 topics relevant to chemistry: computer science/logic, energy topics, and materials/polymers. Attending teachers will perform hands-on labs that they can bring back to their classrooms in part or entirety. Attending teachers will also be given a lab kit (with materials from the experiments performed) to bring back to their classrooms.

Schedule:

Saturday, June 2, 2012 (½ day sessions -you pick which one)(MEYR 371, 372)

AM: 8:30 am – 12 pm

Lunch – AM & PM participants

PM: 1 pm - 4:30 pm

*3 STEM Topics** will be covered along with participation in hands-on activities*:

1. Computer Science plugged and unplugged, Dr. Lisa Marvel, Electrical Engineer, US Army Research Laboratory
2. Energy topics, Dr. Aaron Jackson, Materials Engineer, US Army Research Laboratory
3. Materials/Polymers, Dr. Sandra Young, Materials Engineer, US Army Research Laboratory

** All topics/activities will have documentation to delineate how they connect to state standards.

Sponsored by ARL-NDEP. Questions: Please contact Dr. Sandra K. Young at sandra.young@us.army.mil for additional information.

Kids & Chemistry

Hands-On Science Experiments for 3rd - 8th Grade Students

Saturday June 2 8:30 am to 12:00 pm
Meyerhoff Building (MEYR 302, 310)

Kids & Chemistry is a community-based program that brings together scientists and children to do hands-on science activities. Volunteers include ACS members, ACS Student Chapters, and corporate groups. At the MARM meeting on Saturday, June 2, we are running 3 different experiments:

(1) Chemistry[1]s Rainbow (Best for grades 5-8): Interpret color changes like a scientist as you create acid and base solutions neutralize solutions, them, and observe a colorful chemical reaction.

(2) Jiggle Gels (Best for grades 3-5): Measure with purpose and cause exciting physical changes as you investigate the baby diaper polymer, place a super-absorbing dinosaur toy in water, and make slime.

(3) What[1]s New, CO2? (Best for grades 4-6): Combine chemicals and explore the invisible gas produced to discover how self-inflating balloons work.

3 sessions, you pick one:

Session 1: 8:30 – 9:30 am , Session 2: 9:40 – 10:40 am, Session 3: 10:50 – 11:50 am

Sponsored by ARL-NDEP.

MARM 2012

Program & Abstracts

PROGRAM

Thursday, May 31, 2012 - Morning

Atmospheric Chemistry

Engineering Building, ENGR027 LH5
Financially supported by Division of Environmental Chemistry
Presiding: R. Dickerson

8:10 AM **1.** Impacts of surface-adsorbed organics on tropospheric aerosol surrogates: Heterogeneous ozonolysis and its effects on water uptake. **R. Z. Hinrichs**, L. Woodill, E. O'Neill, A. Kawam

8:40 AM **2.** Material measurement science at NIST for the atmospheric environment. **J. Conny**

9:10 AM **3.** MDE: Monitoring air quality for public health. **J. Hains**

9:40 AM **4.** Sulfate aerosol formation and oxidation pathways: sensitivity to the choice of chemical mechanism employed in simulations. **A. Stein**

10:10 AM Intermission.

10:30 AM **5.** From the stratosphere to air quality: Atmospheric chemistry research at NASA Goddard's Atmospheric Chemistry and Dynamics Laboratory. **K. E. Pickering**

11:00 AM **6.** Atmospheric chemistry research at Howard University: Science, students and opportunities. **W. R. Stockwell**, V. Morris, E. Joseph, B. Demoz, D. Venable, G. S. Jenkins, T. Yu

11:30 AM **7.** Modeling and measurements of atmospheric chemical composition and transport at UMBC. **L. Sparling**

Nanomaterials

Self-Assembly and Applications

Information Technology/Engineering Building, ITE104 LH8
Presiding: S. Stoll

8:10 AM Introductory Remarks.

8:15 AM **8.** Designing bottom-up protein assembly at nanoscale: Towards high density, high payload, quantifiable protein arrays. **J. Hahm**

8:45 AM **9.** Nanostructured energy devices: Manipulating electrons, photons and ions. **L. Hu**

9:15 AM **10.** Three dimensional nanoscale assembly by folding. **D. Gracias**

9:45 AM Intermission.

10:00 AM **11.** Targeted CT nanoprobes for monitoring of cardiovascular diseases. **M. Daniel**, W. Ghann, D. Gardner, O. Aras, T. Fleiter

10:30 AM **12.** Kinetic pathways to the controlled self-assembly of inorganic nanocrystals in solution. **Z. Nie**, J. He, Y. Liu, T. Babu, Z. Wei

11:00 AM **13.** Magnetic hybrid materials for imaging and sensor applications. **A. S. Samia**

11:30 AM **14.** Disrupting interparticle magnetic cross-talk within Fe_3O_4 nanocubes using FePt inclusions. **K. L. Krycka**, C. H. Lai, B. J. Kirby, C. L. Dennis, J. A. Borchers

Food Analysis

Addressing challenges in food analysis using emerging technologies in analytical chemistry and microbiology

Biological Sciences Building, BS120
Presiding: R. Shah

8:20 AM **15.** Investigation of the "pine mouth" phenomena. **L. S. DeJager**, A. Fardin-Kia, S. M. Handy, E. Kwegyir-Afful

8:45 AM **16.** Sequence-based Subtyping and the Systematic Search for a Salmonella Solution. **E. W. Brown**

9:10 AM **17.** Monitoring microbial metabolites by SPME, HSSE and SBSE GC-MS techniques. **R. Marsili**

9:35 AM **18.** Targeted and non-targeted analysis of adulterants. **J. Harnly**

10:00 AM Intermission.

10:20 AM **19.** Validating official methods for dietary fiber definition: Meeting the challenges of knowledge and definition changes. **J. W. DeVries**

10:45 AM **20.** Single-run HPLC-UV-ELSD analysis of tocopherols, sterols and lutein from soybeans. **M. Slavin**, L. Yu

11:10 AM **21.** Analysis of commercial pet food for toxic and heavy metal content. **P. Atkins**, V. Sivakumar, R. Obenauf

11:35 AM **22.** Use of wavelength dispersive X-ray fluorescence and discriminant analysis in the identification of the elemental composition of cumin and vanilla samples and the determination of the geographic origin. **K. Rotta**, W. Roy, C. Zapf, E. Hondrogiannis

Analytical Chemistry, Oral

Academic IV Building, ACIV003 LH4
Presiding: F. Ahmed, D. Davis

8:30 AM **23.** Use of reversed-phase liquid chromatography/mass spectrometry in monoclonal antibody development. **T. Dillon**

8:55 AM **24.** Nitrate contents change during storage in lettuce and cabbage. **J. Huang**, N. Probst, S. Pope, T. Roberts, M. Willis

9:20 AM **25.** Chemical characterization of printing inks using spectroscopic and chromatographic techniques for forensic analysis of questioned documents. **S. A. Kingsbury**, D. K. Shaffer

9:45 AM Intermission.

10:05 AM **26.** DC magnetron sputtered polyaniline-HCl thin films for chemical sensing. **D. A. Boyne**, N. Menegazzo, K. Booksh

10:30 AM **27.** Surface imprinted xerogels for binding tetracycline. **E. E. Mojica**

10:55 AM **28.** Real-time measurement of cell signaling: A quartz crystal microbalance with dissipation monitoring (QCM-D) study on MCF-10A cells. **M. P. Garcia**, J. Chen, A. Shahid, L. Penn, M. Reginato, J. Xi

11:20 AM **29.** High sensitivity terahertz spectrometry: An effective approach for nano- and pico-scale investigation. **A. Rahman**, A. K. Rahman

Chemistry Classroom for the 21st Century

Meyerhoff Chemistry Building, MEYR120
Presiding: W. Lacourse

8:30 AM **30.** Discovery learning: Pedagogy and the classroom. **W. R. LaCourse**

9:15 AM **31.** How learner analytics informs assessment of learning spaces. **J. Fritz**

10:00 AM Intermission.

10:15 AM **32.** Building and sustaining robust STEM cohorts at a community college. **C. J. Foley**, **N. A. Leonhardt**

10:45 AM **33.** Developing a marine biochemistry laboratory stimulates the study of chemistry. **C. Summa**, S. Stuart, C. Nguyen, J. Mathew, **J. W. Ullrich**

11:15 AM **34.** Fostering basic problem-solving skills in chemistry. **F. N. Lugemwa**

Frontiers in the Application of Computational Chemistry to Biological Systems A

Morning

Information Technology/Engineering Building, ITE102 LH7
Financially supported by Division of Computers in Chemistry
Presiding: I. Thorpe

9:00 AM **35.** Calculation of the ionic atmosphere of DNA using 3D-RISM and molecular dynamics. **D. A. Case**, T. Luchko, I. Joung, G. Giambasu, D. York

9:25 AM **36.** Investigating the molecular basis for functional selectivity of G protein-coupled receptors using adaptive biasing techniques. **M. Filizola**

9:50 AM **37.** Activation and desensitization of a glutamate receptor. **A. Y. Lau**, B. Roux

10:15 AM **38.** High accuracy protein active site structures from an integrated quantum mechanics and spectroscopy approach. **Y. Zhang**

10:40 AM Intermission.

11:00 AM **39.** Enhanced sampling in the canonical ensemble for conformational sampling and determining free energies. **B. R. Brooks**

11:25 AM **40.** Hydration in biological computer simulations. **T. Ichiye**

11:50 AM **41.** Insights into the catalytic mechanisms of ribozymes from molecular simulations. **D. M. York**

Thursday, May 31, 2012 - Afternoon

Measurements and Methods in Environmental Nanotechnology and Nanotoxicology

Information Technology/Engineering Building, ITE104 LH8
Presiding: B. Nelson, V. Shah, E. Petersen, B. Marquis

1:00 PM **42.** Evaluating the environmental impact of engineered nanomaterials: An existential conundrum. **D. Y. Lyon**, G. V. Lowry, M. R. Wiesner, K. L. Jones

1:30 PM **43.** Occupational safety in the nanomaterial workplace: Tools and resources for workers and employers. **K. M. Kulinowski**, B. Lippy

2:00 PM **44.** What's up in nano measurements in the environment. **B. Karn**

2:30 PM **45.** Evaluation of *Caenorhabditis elegans* as an alternative animal model for the assessment of nanomaterial toxicity. **P. R. Hunt**, N. Olejnik, R. L. Sprando

3:00 AM Intermission.

3:30 PM **46.** Silver nanoparticle metrology for predicting environmental transformations. **R. I. MacCuspie**

4:00 PM **47.** Development of standardized dispersion methods for the environmental risk assessment of nanomaterials. **J. S. Taurozzi**, V. A. Hackley, M. R. Wiesner

4:30 PM **48.** Titanium distribution in a swimming pool: The case for dissolution. **R. D. Holbrook**, D. Motabar, O. Quinones, B. D. Stanford, S. Snyder

5:00 PM **49.** Impact of nanoparticles on *Nitrosomonas europaea* 19718. **K. Chandran**

Remsen Award Symposium

Engineering Building, ENGR027 LH5
Financially supported by W. R. Grace and Co.
Presiding: G. Meyer

1:00 AM Introductory Remarks.

1:05 PM **50.** CO_2 electroreduction catalysis for sustainable fuel synthesis. **M. Kanan**

1:30 PM **51.** New platforms for conversion of carbon dioxide to chemical fuels. **J. Rosenthal**

1:55 PM **52.** Hydrogen and oxygen evolution with hangman catalysts. **D. Dogutankiper**, D. G. Nocera

2:20 PM **53.** Hydrogen storage by carbon(C)-boron(B)-nitrogen(N) heterocycle materials. **S. Liu**, W. Luo, P. G. Campbell

2:45 AM Intermission.

3:15 PM **54.** Emergent quantum phenomena: New chimie douce methods for the synthesis of strongly correlated materials. **T. M. McQueen**

3:40 PM **55.** Designing metal oxides for high performance, visible-light photocatalysis: Toward solar Z-scheme water splitting. **B. M. Bartlett**

4:05 PM **56.** Building synthetic pathways for production of advanced biofuels in living organisms. **M. C. Chang**

4:30 PM **57.** Illuminating redox chemistry in living systems. **C. J. Chang**

Advances in Chemistry of Fluorescence Measurements and Imaging Techniques

Academic IV Building, ACIV003 LH4
Presiding: Y. Zhang

1:30 PM **58.** Molecular cancer imaging; New diagnostic technologies and beyond. **H. Kobayashi**

2:05 PM **59.** Organic and biosensor indicator dye systems in cellular imaging and drug discovery. **D. Beacham**

2:40 AM Intermission.

3:00 PM **60.** Human CD4+ lymphocytes for antigen quantification: Characterization using conventional flow cytometry and mass cytometry. **L. Wang**

3:35 PM **61.** Monitoring dynamic gene expression changes with quantitative time lapse imaging of GFP expressing NIH 3T3 cells. **M. Halter**, J. Chalfoun, D. R. Sisan, J. T. Elliott, A. L. Plant

4:10 PM **62.** Study of protein unfolding using extrinsic fluorescence compared to classical techniques. **B. Lang**, K. Cole

Analytical Chemistry, Poster

University Center, Ballroom

1:30 - 3:30 PM

63. Extraction of alkylresorcinols (ARs) in food products composed of wheat (*Triticum aestivum*) with the use of a Dionex accelerated solvent extractor (ASE200). **M. D. Holt**, R. Moreau, A. DerMarderosian, N. McKeown, P. F. Jacques

64. Retention mechanisms in HILIC chromatography: Important considerations for robust LC-MS applications. **T. Ascah**, D. S. Bell

65. Microfabrication of single cell hydrogel array for studying cell volume regulation. **J. Heo**, C. Brown, V. Fleischauer, K. Suffoletto, S. Z. Hua

66. Improving the signaling, sensitivity, and affinity of electrochemical, aptamer-based sensors by using ultramicroelectrodes. **M. E. Dávila Morris**, J. Taylor, R. J. White

67. Comparison of α-solanine in organically and non-organically grown russet potatoes. **B. Szychowski**, R. Larsen

68. FT-IR spectroscopic characterization of *Halosimplex carlsbadense* cultures grown in varying conditions. **T. H. Chau**, **D. J. Aurentz**, T. H. Mysliwiec

69. Determination of trace organic constituents in FD&C Yellow No. 6 using solid phase extraction and ultra-performance liquid chromatography. **N. Belai**

70. MALDI typing for discrimination of *Staphylococcus aureus* from *Staphylococcus epidermides* and *E. coli*. K. Abdallah, S. Tokajian, **B. Wex**

71. Determination of elements in color additives by ICP-MS analysis. **N. M. Hepp**

72. Comparison of two spiropyran dyes for use in polymer-based chemical sensors. **S. M. Fetner**, S. E. Stitzel

73. Top-down analysis of intact proteins in complex mixtures. **A. Dhabaria**, J. Cannon, Y. Wang, C. Fenselau

74. Development of a sensitive fluoride sensor. **Y. Hijji**, B. Barare, G. Wairia

75. Amperometric detection of aqueous metals. **W. M. Cunning**, W. R. LaCourse

76. Characterization of curcumin as anion sensor. Y. M. Hijji, **S. Tadesse**, G. Wairia

77. Technical improvements of *in vitro* microdialysis sampling for monitoring bioprocesses. **S. M. Bass**, W. R. LaCourse

78. Optimization and clinical testing of a microwave-accelerated metal-enhanced fluorescence (MAMEF) assay for the detection of *Chlamydia trachomatis*. **J. H. Melendez**, C. Gaydos, C. D. Geddes

79. Evaluation of strategies for small-molecule analysis by MALDI mass spectrometry: What are the caveats and constraints? **J. A. Kelley**, C. C. Lai, L. R. Phillips

80. Assessing changes of cell adhesion using dissipation monitoring. **J. Y. Chen**, A. Shahid, M. P. Garcia, L. S. Penn, J. Xi

81. Amyloidogenic potential of $hIAPP_{22-29}$ is altered by aromatic ring substituents on Phe-23. **E. E. Mojica**, V. Felsen, J. Chinwong, A. A. Profit, R. Z. Desamero

82. Transient absorption measurements for electron transfer in DMPD-coumarin and two coumarin control compounds. **M. Harries**, R. Musat, J. F. Wishart, R. Abdel-Malak Rached

83. The fluorescence quenching of uric acid solubilized in bicontinuous microemulsion by nitrobenzene. **M. O. Iwunze**

84. Effects of Marcellus Shale gas drilling wastewater discharge on trihalomethane formation. **N. Rossi**, Y. Xie, M. Spear

85. Low dose risks from bromate: Drinking water exposures and chemistry and mechanism of risks in rats and humans. **J. A. Cotruvo**, R. J. Bull, J. W. Fisher, D. Delker, Z. Guo, O. Quinones, S. Snyder, C. Ong

86. Electrochemical decomposition of per and poly fluorinated surfactants (PFS) in plating industry wastewater. **J. E. McCaskie**, A. Fath

87. Improved air quality by reducing ammonia emissions from chicken manure. C. Satam, **T. Vinciguerra**, S. Ehrman, R. Dickerson, T. Canty

88. Field methods for rapidly characterizing contaminant leaching from the paint waste. **Z. Shu**, L. Axe, K. Jahan, R. Kandalam V

89. Scanning electrochemical microscopy of biomimetic membranes. **M. D. Sykes**, M. C. Buzzeo

90. A donor-bridge-acceptor of the type $(bpy)_2\ Ru^{II}$ – mcbpy – Pro_1 – Apy – $Ru^{III}(NH_3)_5$ prepared to study electron transfer kinetics in ionic liquids. **A. B. Meloi**, F. Frasca, M. Gohdo, R. Abdel-Malak Rached, J. F. Wishart

91. Role of base excision repair genes OGG1 and APN1 in B[a]P-7,8-dione induced p53 mutagenesis. **Z. Abedin**, M. Louis-Juste, M. Stangl, J. Field

92. Analysis of lead in $PM_{2.5}$ collected at the Kutztown University Air Monitoring Station using graphite furnace atomic absorption spectroscopy. **K. Fillman**, J. A. Palkendo

93. Impact of the Chesapeake Bay climate and boundary layer dynamics on air pollutant concentrations during smog episodes. **D. Goldberg**, C. Loughner, M. Tzortziou, R. Dickerson, J. Stehr, T. Marufu, R. Salawitch, T. Canty, W. Thorn III

94. Reduction of nitrite and nitrate on pyrite. **S. Singireddy**, A. D. Gordon, A. Smirnov, M. A. Vance, M. A. Schoonen, R. K. Szilagyi, D. R. Strongin

95. Tabulation and development of a database of pesticides used in Delaware. **A. Givens**, M. J. D'Souza

96. Determination of lead, mercury, iron and cadmium in rainbow trout from Donegal Lake. **K. Laratonda**, M. R. Luderer

97. Determination of trace metals in venison from white-tailed deer from Western Pennsylvania. **J. Smeal**, **K. Kelly**, M. R. Luderer

98. Reactions of amine and amine radicals with molecular oxygen in atmospheric and combustion chemistry. **A. Voit**, J. Bozzelli

99. Screening of tobacco products for flavor compounds using solid-phase microextraction gas chromatography mass spectrometry. **V. R. Kinton**, M. Thomas, D. Z. Bezabeh, J. Scalese

100. Identification of volatiles in coffee extracts, essences, and distillates by HS-GC-MSD. **T. L. Moore**, J. M. Scalese

101. Development of *in vitro* neuronal cell-based assays for screening food and cosmetic-related compounds. **M. F. Santillo**, P. L. Wiesenfeld

102. Examination of fluoride levels in beverages commonly consumed by children. **J. Rittenhouse**, **M. Staretz**

103. Bioactives-enriched fruit beverage formula for cardio-protection. **K. P. GUNATHILAKE**, H. V. Rupasinghe, N. L. Pitts

104. Antioxidant properties and sensory attributes of four different fruit vinegar beverages. **R. Nandasiri**, V. Rupasinghe, N. L. Pitts

105. Investigation of possible changes of amount and micro structure of iron species within a plant. **S. S. Dehipawala**, A. Y. Djifa, S. Dehipawala

106. Biocatalytic preparation, structural elucidation and biological evaluation of long chain (C_{18}-C_{22}) acylated derivatives of flavonoid glycosides. **.. Ziaullah**, K. S. Bhullar, H. V. Rupasinghe

107. Analysis of coffee for the presence of endosulfan using GC/MS. **W. R. Bringgold**, K. K. Bagga, K. Owens

108. Raman spectroscopic studies of the intermolecular interactions in acetonitrile, propionitrile and butyronitrile solvents. **B. Oloye**

Best Practices for Successful Online and Hybrid Courses / Innovation in the Chemistry Lab

Meyerhoff Chemistry Building, MEYR120
Presiding: L. Montgomery, S. Schaeffer

1:30 PM **109.** Using the QM process to develop and teach quality on-line courses. **W. Rappazzo**

2:00 PM **110.** Analyzing student success in the chemistry classroom by monitoring online homework activity. **C. R. Bowman**, D. B. King

2:30 PM **111.** Challenges and strategies of teaching online and hybrid chemistry courses to community college students. **H. Cost**, **L. Montgomery**

3:00 AM Intermission.

3:20 PM **112.** Organic chemist's development of a medicinal chemistry course. **M. F. Harris**

3:50 PM **113.** Structure identification of carbohydrates and nonnutritive sweeteners: Experimental exercise for undergraduate chemistry laboratories. **A. E. Shinnar**

4:20 PM **114.** How to use the book *African American Women Chemists* to teach chemistry and history. **J. E. Brown**

Frontiers in the Application of Computational Chemistry to Biological Systems B

Afternoon

Information Technology/Engineering Building, ITE102 LH7
Financially supported by Division of Computers in Chemistry
Presiding: A. Mackerell

1:30 PM **115.** Biophysics of a genetic switch: The *lac* operon. **K. A. Sharp**, M. Lewis

2:00 PM **116.** Putting the statistics back in statistical mechanics. **M. R. Shirts**

2:30 PM **117.** How important is charge transfer in biological systems? **D. J. Diller**

3:00 AM Intermission.

3:30 PM **118.** Conformational analysis of antibody CDRs using diffusion maps. **R. Dunbrack**

4:00 PM **119.** Computational chemistry applications in drug discovery: From atoms to gene to clinic: What works, what doesn't. **T. R. Stouch**

4:30 PM **120.** Toxic amyloid ion channels. **R. Nussinov**, H. Jang

Organic Chemistry

Biological Sciences Building, BS120
Presiding: D. Watson

1:30 PM **121.** Theoretical examination of an unusually facile titanium mediated cyclization. **B. N. Hietbrink**, N. Sanford

2:00 PM **122.** Diels-Alder reactions of (*E*)-β-acylacrylic acids and γ-hydroxybutenolides. **W. H. Miles**, B. J. Naimoli, E. M. Cohen, J. S. George

2:30 PM **123.** Krapcho decarboxylation under aqueous microwave conditions. **S. S. Murphree**, J. D. Mason

3:00 AM Intermission.

3:20 PM **124.** PMR 15 type polyimides with non carcinogenic diamines. S. Madaiyan, R. Nair, D. Mathew, S. Pudupadi, **S. Muthusamy**

3:50 PM **125.** New oxyma derivative for amide-forming reactions in water. **M. Kurosu**, Q. Wang, Y. Wang

4:20 PM **126.** Preparation of allyl and vinyl silanes via the palladium catalyzed silylation of terminal olefins. J. R. McAtee, S. A. Martin, **D. A. Watson**

Thursday, May 31, 2012 - Evening

Happy Hour Posters

Biochemistry and Computational Biochemistry
University Center, Ballroom

5:00 - 7:00 PM

127. Thioamide quenching of intrinsic and extrinsic protein fluorescence: Minimalist tools for studying protein dynamics. **J. M. Goldberg**, E. Petersson

128. ^{77}Se enrichment of proteins expands the biological NMR nuclei toolbox. **S. A. Schaefer**, M. Dong, B. Bahnson, C. Thorpe, S. Rozovsky

129. Design, synthesis, and testing of ADP-ribose inhibitors: Chromogenic substrates of bacterial ADP-ribosylating toxins. **S. Parikh**, V. Schramm, K. Clinch, R. Fröhlich, R. Furneaux, J. Harvey, P. Tyler

130. Expression and purification of human PYY(3–36) in *Escherichia coli* using a His-tagged small ubiquitin-like modifier fusion. **C. H. Fazen**, R. P. Doyle

131. Insights into the genomic RNA packaging of simian immunodeficiency virus in chimpanzees. **T. L. Tran**, M. Summers

132. One-step procedure for simultaneous protein precipitation and removal of phospholipids from biological matrices prior to LC/MS analysis. **T. Ascah**, C. Aurand

133. Role of glyceraldehyde-3-phosphate dehydrogenase in the regulation of colony stimulating factor-1 and angiotensin-II type 1 receptor mRNA stability. **M. Khan**, E. Garcin

134. Insights into the structure and function of the soluble guanylate cyclase regulatory domain. **M. R. White**, E. D. Garcin

135. Role of tryptophan-168 in the allosteric regulation of anthranilate synthase from *Streptomyces venezuelae*. M. Ashenafi, **W. Byrnes**

136. Modeling and computational analysis of HIV-1 integrase inhibitors. **B. C. Johnson**, M. Metifiot, Y. Pommier, S. H. Hughes

137. Comparative study of workflows optimized for in-gel, in-solution, and on-filter proteolysis in the analysis of plasma membrane proteins. **W. Choksawangkarn**, N. Edwards, Y. Wang, P. Gutierrez, C. Fenselau

138. Controlled release of neurotrophins and genetically engineered viruses from poly(3,4-ethylenedioxythiophene) (PEDOT)-coated carbon fibers. **C. Kuo**, B. Shim, D. C. Martin

139. Designing of artificial membrane protein maquettes for understanding natural oxidoreductases. **G. N. Goparaju**, H. Saraf, B. A. Fry, B. R. Lichtenstein, G. Kodali, P. Dutton, B. M. Discher

140. Reactivity of nitroxyl (HNO)-derived sulfinamides. **G. Keceli**, J. P. Toscano

141. Latest developments of the CHARMM classical Drude oscillator polarizable force field for proteins. **P. E. Lopes**, A. D. MacKerell Jr.

142. Encapsidation of Rift Valley fever virus as a therapeutic target. **E. Bonyi**, J. Wachira

143. Retroviral RNA promotes gag assembly: RNA as a structural scaffold. **D. Girma**, T. Mathias, Y. Miyazaki, M. F. Summers

144. Mechanism of cytotoxicity of O^2-arylated diazeniumdiolate anticancer agents. **R. J. Holland**, A. E. Maciag, J. E. Saavedra, H. Chakrapani, L. K. Keefer

145. Quantitation of the diazonium ion derived purine adducts of the carcinogens N-nitrosomorpholine, N-nitrosopyrollidine, and N-nitrosopiperidine in cells. **A. C. Brown**, J. C. Fishbein

146. Protein substrate discrimination in the quiescin-sulfhydryl oxidase (QSOX) family. **J. A. Codding**, B. A. Israel, C. Thorpe

147. Site-directed mutagenesis of intrinsic factor and its potential use as a drug delivery agent. **D. Valentin**, R. P. Doyle

148. Elucidating the role of methylated quinolones and N-oxide quinolones in quorum sensing. **P. Anand**, D. B. Hansen

149. FRIENDS: First rigorous ion-exchange numerical design simulator. **N. Pinto**, A. Raim, M. Gobbert, D. Frey

150. Exploring the structural diversity in quinolone quorum sensing molecules. **D. B. Hansen**, A. Agarwal

151. Vibrational Stark effect calculations using quantum mechanical/molecular mechanical simulations. **S. K. Lakkaraju**, A. R. McDonald, A. D. MacKerell

152. Free energetics of polyarginine penetration into model lipid bilayers. **Y. Hu**, S. Patel

153. Allosteric inhibitors alter the dynamic and thermodynamic properties of the RNA polymerase from hepatitis C virus. **B. Davis**, I. Thorpe

154. Probing the interactions between the anti-apoptotic Bcl-2 protein and a new class of rhodanine-based acylsulfonamide derivative inhibitors. **S. Ma**, H. Li, J. Yang, C. Qiao

155. Understanding the molecular origin of synergistic inhibition in the hepatitis C virus (HCV) polymerase. **J. A. Brown**, I. F. Thorpe

156. Using deterministic kinetic modelling to understand the lipid biosynthetic pathway in *Chlamydomonas reinhardtii*. **N. J. Carbonaro**, S. L. Johnson, I. F. Thorpe

157. Free energy profile of base flipping in carcinogen-modified DNA duplexes. **B. Lin**, V. Jain, B. Cho, A. MacKerell, Jr

158. Allosteric dynamics cooperation and its effects on intein catalysis. **M. Cronin**, D. Nellis, J. Zhu, R. Nussinov, **B. Ma**

159. QXD: A new charge-dependent QM/MM interaction potential for simulations of chemical reactions. **E. R. Kuechler**, T. J. Giese, T. Lee, D. M. York

160. Development of pY-stat5 receptor model and virtual screening (VS) of novel stat5a/b inhibitors in prostate cancer (PCa). **E. Gianti**, M. T. Nevalainen, V. V. Njar, R. J. Zauhar

161. Molecular dynamics investigation of DNA-binding foldamers. **A. Abramyan**, Z. Liu, V. Pophristic

162. *Ab initio* quantum chemical study of nonlinear optical properties of aromatic fused rings. **R. Balu**, S. P. Karna

163. 3D modeling of the human apical sodium bile acid transporter (hASBT) based on substituted cysteine scanning mutagenesis (SCAM) profiles. **S. S. Mallajosyula**, P. W. Swaan, A. D. MacKerell Jr.

164. Using molecular dynamics to understand inhibition of NS5B by a novel allosteric ligand. **T. J. Odebode**, I. F. Thorpe

165. Combined quantum and Poisson Boltzmann method for calculating reduction potentials of blue copper proteins. **C. Miller**, T. Ichiye

166. Free energetics of carbon nanotubes association. **S. Ou**, B. A. Bauer, S. Patel

167. Optimization of the CHARMM Drude polarizable force field for DNA. **A. Savelyev**, C. Baker, A. Mackerell

168. Using dynamic importance sampling to explore conformational space in HCV polymerase. **E. Sesmero**

169. Use of single step free energy perturbation to estimate relative binding affinity by fragment modification. **E. Raman**, K. Vanommeslaeghe, A. D. MacKerell

170. Molecular simulations of RNA cleavage transesterification reaction models in solution. **B. K. Radak**, D. M. York

171. Investigations of the impact of ribosomal modification on the binding of the antibiotic telithormycin using molecular dynamics simulations. **M. C. Small**, R. B. Andrade, A. D. MacKerell, Jr.

172. Six-site polarizable model of water based on the CHARMM classical Drude oscillator. **W. Yu**, P. Lopes, A. D. MacKerell

173. Theoretical study of the linear free energy relationships in RNA transesterification reactions. **M. Huang**, **D. York**

Prevention of Metabolic Syndrome by Dietary Phytochemicals

Information Technology/Engineering Building, ITE102 LH7
Presiding: J. Lambert

6:30 PM **174.** Tea intake and markers for metabolic syndrome in US adults. **J. A. Veranrelli**

7:05 PM **175.** Cinnamon polyphenols, insulin sensitivity and chronic diseases. **R. A. Anderson**

7:40 AM Intermission.

7:50 PM **176.** Development of standard reference materials for functional foods and dietary supplements. **M. Bedner**, K. E. Sharpless, L. C. Sander, M. M. Schantz, S. A. Wise

8:25 PM **177.** Prevention of obesity and obesity-related pathologies by dietary polyphenols. **J. D. Lambert**

Friday, June 1, 2012 - Morning

Chemistry in the Chemical Senses A

Morning
Academic IV Building, ACIV003 LH4
Presiding: G. Preti

8:00 AM Introductory Remarks.

8:10 AM **178.** Cracking the code: Translating odorants into olfactory receptor responses. **J. D. Mainland**

8:55 AM **179.** Smelling sulfur: Crucial role of copper in detection of metal-coordinating odorants. **E. Block**, H. Zhuang, H. Matsunami

9:40 AM Intermission.

10:00 AM **180.** Methods to quantify human olfactory perception and examples of results. **C. J. Wysocki**

10:45 AM **181.** Gustatory detection and perception of oral food chemicals. **P. A. Breslin**

Renewable Energy A

Metabolic Engineering
Engineering Building, ENGR027 LH5
Presiding: W. Byrnes

8:00 AM **182.** Session overview: Metabolic engineering of plants and bacteria for biofuel production: Enzymes, genes and pathways. **W. Byrnes**

8:15 AM **183.** Utilization of plants as renewable sources of fuels and chemical feedstocks: The impact of metabolic engineering. **J. M. Dyer**

8:45 AM **184.** Enzyme design for lignin engineering: Innovative modules to redesign plants for next-generation biofuels. **E. Eisenstein**

9:15 AM **185.** Probing plant biomass conversion by the industrially-relevant *Streptomyces* bacteria. **J. K. Sello**

9:45 AM Intermission.

10:00 AM **186.** Quest for hyperthermostable cellulases. **F. T. Robb**, J. E. Graham, D. S. Clark, M. E. Clark

10:30 AM **187.** Construction of a recombinant cyanobacterium for solar hydrogen production. **Q. Xu**

11:00 AM **188.** Two-step liquid hydrocarbon synthesis from carbon dioxide and hydrogen. **D. M. Drab**, M. T. Olsen, D. R. Hardy, H. D. Willauer

Bioanalytical Chemistry

Biological Sciences Building, BS120
Financially supported by Waters Corporation
Presiding: R. White

8:30 AM **189.** Adsorbate-gold bond effect on empirical surface plasmon penetration depth in the near infrared. **L. L. Kegel**, K. S. Booksh, N. Menegazzo

8:55 AM **190.** Label free detection of the bacterial signaling molecule indole by surface-enhanced Raman spectroscopy. **J. F. Betz**, Y. Cheng, G. W. Rubloff

9:20 AM **191.** Comparison of surface reactions on sensor crystals by means of the quartz crystal microbalance. **X. Sha**, X. Xu, C. Sun, L. Alexander, P. J. Loll, L. S. Penn

9:45 AM Intermission.

10:05 AM **192.** Characterizing manufactured extracellular environments for improving *in vitro* cellular biology. **C. R. Anderton**

10:30 AM **193.** Interference effects on the measurement of nanomolar levels of naproxen chemiluminescence in presence of Fenton reaction. **E. Johnson**, **M. Patel**, M. Zdilla, C. Martoff, S. Varnum

10:55 AM **194.** Biosynthetic concatenated labeled peptides are useful alternatives to whole length labeled proteins: Human serum albumin as a case study. **J. Cole**, D. Nanavati, C. Chen, B. Martin, A. J. Makusky, A. Zhu, G. Csako, S. P. Markey

11:20 AM **195.** Electrochemical DNA-based sensors: From benchtop to bedside. **R. J. White**

Younger Organic Chemists

The Breadth of Organic Synthesis

Information Technology/Engineering Building, ITE102 LH7
Financially supported by Division of Organic Chemistry
Presiding: C. Dowd

8:30 AM Introductory Remarks.

8:40 AM **196.** New synthetic methods based on palladium-catalyzed C-H functionalization. **G. Chen**

9:10 AM **197.** Transition metal catalysis of iminium and oxocarbenium ion intermediates. **M. P. Watson**, P. Maity, D. M. Shacklady-McAtee, H. D. Srinivas, S. Dasgupta

9:40 AM **198.** Gold catalyzed intramolecular cyclizations. **Y. Chen**

10:10 AM Intermission.

10:30 AM **199.** How organic synthesis helps an inorganic chemist exploit hydrogen bonding interactions and carve out a niche for her group. **E. T. Papish**, I. Nieto, D. A. Natalie, D. Joseph

11:00 AM **200.** Engineering optical properties of tetrapyrrolic macrocycles for fluorescence bio-imaging. **M. Ptaszek**

11:30 AM **201.** Bacterial conversation stoppers: New methodologies for constructing next-generation anti-infectives. **H. Sintim**

Inorganic Chemistry; Physical Chemistry; Renewable Energy; Chemical Education
University Center, Ballroom

9:30 - 11:30 AM

202. Novel approach to assessing critical thinking skills of general chemistry students. **M. K. Kirk**, A. R. Sherman

203. Effects of the visual complexity of organic chemical notation on reading. **K. L. Havanki**, D. M. Bunce

204. Beyond periodic table: Useful iPad applications in chemistry teaching. **J. Zhang**

205. Evaluation of mini gas chromatographs in the undergraduate organic chemistry laboratory. **E. M. Kleist**, J. D. Fair

206. Zingerone and dehydrozingerone: A new multi-step synthesis project for the second year organic lab. **S. Hirakis**, **J. V. McCullagh**

207. Investigations of 2-(4'-hydroxyphenyl-azo)benzoic acid in various solvents. **F. Akhter**, **M. Arman**, **N. Benson**, **K. Thomas**, **S. Lane**, A. Sidorenko

208. Charge carrier dynamics in SiO_2@Ag@SiO_2 sandwiched nanostructure. **Y. Liang**, Y. Pu, C. Liu, H. Shih

209. Locating the binding sites of Pb(II) ion with human and bovine serum albumins. **A. BELATIK**, S. Hotchandani, R. Carpentier, H. Tajmir-Riahi

210. Magnetic and structural studies of europium sulfide nanostructures. **W. L. Boncher**, S. L. Stoll

211. Evaluation of zinc based metal organic framework for carbon dioxide sequestration. **O. Falola**, J. Matthews, R. Little

212. Synthesis and structure characterization of ionic tributyltin complexes with oxalic acid. **X. Song**, A. Callejas, G. Eng, R. Pike

213. Synthesis, characterization and electrochemistry of chlorinated aromatic [FeFe]-hydrogenase inspired electrocatalysts. **J. J. McCormick**, E. S. Donovan, G. S. Nichol, G. A. Felton

214. Electrochemical mediation of hydrogenase-inspired electrocatalysts: Attempts to lower overpotential. **K. Chen**, E. S. Donovan, G. A. Felton

215. Controlled impregnation of silica colloids with transition metal salts. B. P. Chauhan, **J. Flores**, S. Matam

216. Synthesis, characterization and applications of nickel-silicon gels. B. P. Chauhan, **S. Matam**, **T. Surti**

217. Ruthenium chromophores for anchoring platinum nanoparticles to titanium dioxide semi-conductors in dye-sensitized solar cells. **A. Agushi**, A. Kopecky, E. Galoppini, A. G. Agrios

218. Synthesis and characterization of porphyrin derivatives into the development of a dyad using an Fe8 cluster. **R. Montano**, R. G. Raptis

219. Manganese clusters as potential MRI contrast agents. **W. Hickling**, S. L. Stoll

220. Photophysical and electrochemical properties of bis-cyclometallated transition metal complexes in aqueous and organic media. **M. Patel**, E. Johnson, M. Zdilla, C. Martoff, S. Varnum

221. Synthesis, characterization, X-ray structure and possible anticancer properties of *fac*-$(CO)_3$(neocuproin)Re(picolinate) and *fac*-$(CO)_3$(neocuproin)Re(nicotinate). **B. V. Powell**, S. K. Mandal

222. Synthesis and anticancer properties rhenium(I) aspirinato complexes. **P. Olczak**, S. K. Mandal

223. Small molecule activation and reactivity using low valent chromium (I) supported by a hydrotris(pyrazolyl)borate ligand. **E. S. Akturk**

224. Synthesis and characterization of metal complexes with new steric a-diimine and pyridine(bisanil) ligands in relevance to olefin polymerization. **S. Bhattacharya**, M. M. Millar

225. Pulmonary oxygen toxicity is modulated by its paramagnetic property. **R. Shanklin**

226. Environmental and structural effects on self-assembly of conductive peptide-porphyrin aggregates. **M. Reca**, E. Dahl, J. Gamel, G. A. Caputo

227. Theoretical study of interactions between ferrocene/ferrocenium and imidazolium. **Y. Yang**, L. Yu

228. Continuing development of the CHARMM polarizable charge equilibration force field for phospholipid membranes. **T. R. Lucas**, S. Patel

229. Surface chemistry studies of acrylonitrile on copper, silver, and gold nanoparticles by surface-enhanced Raman spectroscopy. **C. Arble**, S. Bishop

230. Effect of counterions in regulating the self-assembly of hepatitis B viral capsids in solution. **D. Li**, P. Yin, J. E. Sledziewski, T. Li, J. K. Glover, T. Liu

231. Equilibrium and transition states for thiourea using *ab initio* methods. **R. C. Mayrhofer**

232. Correlation analysis of column-density data with surface mixing ratios for O_3 and NO_2 during DISCOVER-AQ. **C. M. Flynn**, K. E. Pickering, L. Pius, Y. Tang, A. Weinheimer, R. Cohen, J. Szykman, G. Chen, L. Lamsal, J. Herman, X. Liu

233. Non-invasive in-depth investigation of skin and other substrates by terahertz scanning reflectometry. **A. Rahman**, A. K. Rahman, B. B. Michniak-Kohn

234. New pincer platforms for CO_2 conversion and small molecule activation. **E. T. Guardino**, J. Rosenthal

235. Ditopic platforms for conversion of carbon dioxide to chemical fuels. **T. Qiu**, J. Rosenthal

236. Carbon dioxide activation by bis-NHC complexes of palladium. **P. W. Ariyananda**, J. W. Eddy, G. P. Yap, J. Rosenthal

237. Towards pyridyl ruthenium capped polystyrene brushes grafted from the surface of reduced graphene oxide sheets. **K. Le**, D. Taylor, Z. Fang

238. High-capacity metal-oxide aerogels for electrochemical charge storage. **P. Gogotsi**, B. P. Hahn, L. Dudek, J. W. Long, D. R. Rolison

239. Synthesis of homoleptic ruthenium 'star' complexes via click reaction. **K. P. Chitre**, E. Guillén, A. Soonjin Yoon, E. Galoppini

240. Characterization of algae bio-oil produced by microwave-assisted pyrolysis: A study of the potential for algae bio-oil as an alternative fuel source. **T. Bender**, D. Austin, **C. T. Santai**

241. Modular functionalization of electrode interfaces for energy catalysis applications. **R. C. Pupillo**, A. Gietter, D. A. Watson, J. Rosenthal

242. Design, evaluation, and optimization of aqueous asymmetric electrochemical capacitors with nanoarchitectured electrodes. **C. P. Hoag**, M. Sassin, J. Long, D. Rolison

Friday, June 1, 2012 - Afternoon

Chemistry in the Chemical Senses B

Afternoon
Academic IV Building, ACIV003 LH4
Presiding: G. Preti

1:00 AM Introductory Remarks.

1:10 PM **243.** DNA-decorated carbon nanotube-based FETs as ultrasensitive chemical sensors: Discrimination of homologues, structural isomers, and optical isomers. **M. Lerner**, S. Khamis, N. Kybert, G. Preti, A. Johnson

1:55 PM **244.** Volatile compounds and disease: Detection of *Aspergillus fumigatus*. **R. Bazemore**

2:40 AM Intermission.

3:00 PM **245.** Genetic influences on body odors in mice and humans. **J. Kwak**, G. Preti, K. Yamazaki, G. K. Beauchamp

3:45 PM **246.** Human pheromones and axillary chemistry: What's known, what's not. **G. Preti**, C. J. Wysocki

Medicinal Chemistry in Academia

Challenges and New Opportunities
Information Technology/Engineering Building, ITE102 LH7
Financially supported by GVK Biosciences Private Limited, AlliChem LLC, APAC Pharmaceutical, LLC, DavosPharma, Eisai Co., Ltd., and Otsuka
Presiding: T. Tsukamoto

1:30 AM Introductory Remarks.

1:45 PM **247.** Adventures in academic probe and drug discovery. **D. M. Huryn**

2:15 PM **248.** Novel therapeutics against *Mycobacterium tuberculosis*. **C. S. Dowd**, E. R. Jackson, G. San Jose, H. Boshoff, K. Kehn-Hall, R. Couch, M. Van Hoek, R. Lee

2:45 PM **249.** Natural products: Continuing sources of inspiration for chemical and biological discovery. **J. S. Schneekloth**

3:15 AM Intermission.

3:30 PM **250.** Small-molecule, anti-cancer BH3 domain proteomimetics: Dual antagonism of the Bak–Bcl-x_L and Bak–Mcl-1 protein–protein interactions. **S. Fletcher**, J. L. Yap, X. Cao, K. Vanommeslaeghe, K. Jung, C. Peddaboina, A. D. MacKerell, Jr, W. R. Smythe

4:00 PM **251.** Development of small molecule prostate specific membrane antigen (PSMA) targeted imaging agents for prostate cancer. **R. C. Mease**

4:30 PM **252.** Oral delivery of the appetite suppressing peptide PYY(3–36) through the vitamin B_{12} uptake pathway. **C. H. Fazen**, T. J. Fairchild, R. P. Doyle

Nanotechnology; Organic Materials

University Center, Ballroom

1:30 - 3:30 PM

253. Next generation surface enhanced Raman scattering (SERS) substrates for hazard detection. E. Holthoff, P. M. Pellegrino, **M. E. Hankus**

254. Synthesis of POSS-MWNT nanohybrid using 'click' chemistry. **H. Ong**, S. Clarke, M. Ginic-Markovic, K. Constantopoulos

255. Effects of gold core interactions within different regimes of thermoresponsive copolymers on stimulus response behavior. **M. Barajas Meneses**, P. Heiden

256. Plasmon-enhanced photophysical properties of carbon nanodots. **R. Taylor**, J. Karolin, C. Geddes

257. Metal-enhanced fluorescence based solvent relaxation. **J. O. Karolin**, C. D. Geddes

258. Sonication induced DNA damage and the role of single-wall carbon nanotubes (SWCNT). **X. Tu**, E. Petersen, M. Dizdaroglu, N. Bryant, M. Zheng

259. Advanced plasmonic surfaces for metal-enhanced fluorescence (MEF). R. Pavlovic, E. Barannikova, B. Mali, **A. I. Dragan**, C. D. Geddes

260. Nanoparticles synthesized from soy protein: Preparation, characterization and application in nutraceutical encapsulation. **Z. Teng**, Q. Wang

261. Screening of various nanoparticles for the removal of lead ions in aqueous samples. **A. J. Porrata-Doria**, A. A. Falade, E. E. Mojica

262. New process for silica conjugated nanoparticles of silver and gold. B. P. Chauhan, S. Matam, **C. Abaid**, **K. Lee**

263. Biphasic synthesis of polymer/inorganic hybrid nanoparticles. **P. Zhang**, J. He, M. T. Perez, Y. Liu, T. Babu, J. Gong, Z. Nie

264. Application of self-assembled amphiphilc peptides containing tryptophan, arginine, and glutamic acid for generation of gold nanoparticles. **A. F. Nahhas**, R. K. Tiwari, K. Parang

265. Based on polarized tubular microflidic device research of *in vitro* calcium phosphate stone formation. **Z. WEI**, P. Amponsah, Z. nie, B. Bandyopadhyay

266. Synthesis of a recyclable nanocatalyst for alcohol amine coupling. **C. Munro**, **P. Cho**, A. Voutchkova-Kostal

267. Self-assembly of inorganic nanoparticle vesicles and tubules driven by tethered block copolymers. J. He, **Y. Liu**, T. Babu, Z. Wei, Z. Nie

268. Development of electrically conductive ink from colloidal metallic nanoparticle systems. **M. A. Olenick**, S. Sweeney, T. S. Snider

269. Crystallization of CL-20 on monolayer surfaces. **J. H. Urbelis**, J. A. Swift

270. Combinatorial approach to the synthesis of novel environmentally benign marine coatings. **N. K. Weise**, P. N. Coneski, P. A. Fulmer, J. H. Wynne, R. F. Cozzens

271. Functionalizing electrode materials via on surface cross-coupling reactions. **A. A. Gietter**, R. C. Pupillo, D. A. Watson, J. Rosenthal

272. Preparation and characterization of glycomic microarrays using surface functionalized catanionic surfactant vesicles : Applications in diagnostics. **N. J. Dashaputre**, P. Deshong, S. R. Raghavan, G. F. Payne

273. Examination of polyoxometalates as possible microbial decontamination agents and subsequent incorporation into electrospun nano-fibrous materials. **S. L. Giles**, P. N. Coneski, J. H. Wynne, R. F. Cozzens, P. A. Fulmer, R. V. Honeychuck, G. L. Weatherspoon, B. T. Rasley

274. Solution-mediated phase transformation of uric acid dihydrate. **J. B. Presores**, J. A. Swift

275. Structure and properties of doped tetraaniline single crystals. **J. Liu**, Y. Wang, R. B. Kaner, D. C. Martin

276. Fabrication of conductive subintestinal submucosa (SIS) for bionic devices: A promising neural interface system. **J. Qu**, B. Shim, C. Kuo, W. Cho, M. G. Urbanchek, N. B. Langhals, P. S. Cederna, D. C. Martin

277. *In vivo* polymerization of poly (3,4-ethylenedioxythiophene) (PEDOT) in living dorsal hippocampus offers a unique approach to increase long-term reliability of the neural interface. **L. Ouyang**, C. Shaw, A. Griffin, C. Kuo, J. Liu, D. Martin

278. Synthesis of potential eco-friendly curcumin derived plasticizers and their effect on the thermal and mechanical properties of polyvinyl chloride. **J. A. Saltos**, **A. Chughtai**, K. Raja

279. Investigation of fluorene p-type materials using a carbon-carbon coupling procedure. **A. Abdullahi**

280. Metal binding properties and applications of curcumin,glucose-polymer conjugates. **A. A. Averick**, S. Guariglia, K. Raja

281. Preparation and characterization of lisinopril-capped gold nanoparticles for molecular imaging of angiotensin-converting enzyme using X-ray computed tomography. **W. E. Ghann**, O. Aras, D. Gardiner, K. Perkins, T. Fleiter, M. Daniel

Renewable Energy B

Bioenergy/Biofuels for Clean Energy

Engineering Building, ENGR027 LH5
Presiding: S. Gregurick

1:30 AM Introductory Remarks.

1:45 PM **282.** Integrating computations with experiments to drive biofuel overproduction. **C. D. Maranas**

2:20 PM **283.** What microbial platforms for producing bio-based chemicals and fuels? **E. T. Papoutsakis**

2:55 PM **284.** Isotope-assisted metabolic flux and pathway analysis of photosynthetic metabolism in diatoms. Y. Zheng, **G. Sriram**

3:30 AM Intermission.

3:50 PM **285.** Microbioreactors for bioprocess development and strain engineering. **H. Lee**, P. Boccazzi, K. S. Lee

4:25 PM **286.** Cellulase engineering and consolidated bioprocessing *Bacillus subtilis* for low-cost production of biofuels and biochemicals. **Y. Zhang**, X. Zhang, C. You, H. Ma

Computational Chemistry

Biological Sciences Building, BS120
Presiding: M. Sellers

2:00 PM **287.** Initial guess generation and dihedral parameter optimization in the ParamChem force field parametrization engine. **K. Vanommeslaeghe**, N. Shen, N. K. Polani, Y. Fan, J. Ghosh, C. Herath, S. Marru, M. Pierce, S. V. Pamidighantam, M. Sheetz, A. D. MacKerell, Jr

2:25 PM **288.** Role of electronic polarizability in the accurate treatment of polyalcohols in an empirical force field. **X. He**, P. E. Lopes, A. D. MacKerell

2:50 PM **289.** Structural and functional consequences of phosphate-arsenate substitutions in selected nucleotides: DNA, RNA, and ATP. Y. Xu, R. Nussinov, **B. Ma**

3:15 AM Intermission.

3:35 PM **290.** Structure-based drug design: Salvianolic acid B as cyclooxygenase-2 inhibitor. **Y. Fang**, Y. Hao, Y. Zhao, X. Gu, W. M. Southerland

4:00 PM **291.** pK_a calculations of protein side chains in explicit solvent using the classical Drude polarizable force field. **X. Zhu**, P. E. Lopes, E. P. Raman, A. D. MacKerell, Jr.

4:25 PM **292.** Understanding the physical mechanisms controlling DNA rigidity: Coarse-grained molecular dynamics simulation study. **A. Savelyev**, C. Materese, G. Papoian

4:50 PM **293.** XPairIt: A software toolkit for smart peptide reagent design. **M. S. Sellers**, M. M. Hurley

Chromatography Forum of the Delaware Valley

Student Awards
University Center, UC115
Presiding: M. Selman

3:00 PM **294.** Is it better to separate charged enantiomers using electrokinetic chromatography with or without electroosmotic flow? **E. J. Ennis**, J. Foley

3:30 PM **295.** Studying MEKC separation capabilities of cholic acid micelles with NMR: Effects of pH, temperature, and concentration. **B. N. Taylor**, T. G. Strein, D. Rovnyak

4:00 AM Intermission.

4:15 PM **296.** Probing chiral separation mechanisms with MEKC and NMR: 1-1'-bi-2-naphthol and secondary cholate micelles. **K. E. Sandy**, T. G. Strein, D. Rovnyak

4:45 PM **297.** Analytical investigation of synthetic street drugs. **A. Leffler**, F. Dorman

5:15 PM **298.** Selection of a column and optimization of a method for the analysis of antidepressants in aqueous samples using liquid chromatography-tandem mass spectrometry. **K. J. Chodara**, D. G. Sykes, M. Gettle, A. M. Zimmermann

Friday, June 1, 2012 - Evening

Happy Hour Posters

Organic and Medicinal Chemistry
University Center, Ballroom

5:00 - 7:00 PM

299. Synthesis and binding studies of anion-responsive pyridine-functionalized calixarenes. A. L. Possanza, F. Liu, G. Chen, K. Houk, **N. Y. Edwards**

300. Enantioselective copper-catalyzed alkynylation of chromene acetals. **H. D. Srinivas**, P. Maity, M. P. Watson

301. Suzuki cross couplings via nickel-catalyzed activation of benzylic C–N bonds. **D. M. Shackladdy-McAtee**, P. Maity, M. P. Watson

302. Enantioselective copper-catalyzed alkynylation of isochroman acetals. **P. Maity**, H. D. Srinivas, M. P. Watson

303. Nickel-catalyzed Heck cross couplings via activation of strong C–O bonds. **A. R. Ehle**, Q. Zhou, M. P. Watson

304. Development of new, physiologically useful nitroxyl (HNO) donors. **D. A. Guthrie**, J. P. Toscano

305. Reaction of pyrroles with *N*-halo compounds: A theoretical study. **M. De Rosa**, H. Kim

306. Selective functionalization of dibromobacteriochlorins leading to non-symmetrical derivatives. **Z. Yu**, M. Ptaszek

307. Preparing allyl silanes via the silyl-Heck reaction. **J. R. McAtee**, S. E. Martin, D. T. Ahneman, K. A. Johnson, D. A. Watson

308. Copper-catalyzed *C*-benzylation of nitroalkanes. **P. G. Gildner**, A. A. Gietter, D. A. Watson

309. Preparation of carbocycles by intramolecular cyclizations of acyllithium equivalents. **P. R. Sharrow**

310. Synthesis, characterization, and structural determination of a lower rim substituted calixarene by using a combination of 1D and 2D NMR experiments. **S. T. Hailu**, P. F. Hudrlik, A. M. Hudrlik

311. Photochromic molecular switches. **K. Flanagan**, K. P. Schultz

312. New heterocycles for metal complexation. **K. R. Hess**, A. W. Addison, M. Sharma, E. C. Duranza, M. Zeller, J. P. Jasinski, A. D. Hunter

313. Electrochemical characterization of Lewis acids in ionic liquids. **G. T. Cheek**

314. N-Glycan analysis on therapeutic antibodies. **C. Toonstra**, W. Huang, L. Wang

315. Using nano mechanical approach to study enzyme catalysis. **W. Du**, L. Zhao, C. Nguyen, K. Zhao, J. Xi

316. Utilizing the vitamin B_{12} uptake pathway for oral delivery of peptides and proteins. **S. Clardy-James**, R. P. Doyle

317. Computational study of substituted 5[H] - phenanthradin-6-ones as poly (ADP-ribose) polymerase-1 (PARP-1) inhibitors by analog and structure based methods. **P. Tigulla**

318. Conformational analysis of nucleosides: A systematic update of PSEUROT using quantum mechanical- and molecular mechanics-derived parameters. **S. M. Graham**, K. M. Ileka, M. Rindfleisch

319. Correlating reactivity to biological activity of halogenated pyrimidine analogues. **K. W. Temburnikar**, N. T. Kim, C. B. Gelbmann, T. Elder, G. Andrei, R. Snoeck, C. Salomon, J. Balzarini, K. L. Seley-Radtke

320. Structural and biological investigations of pyrophosphate coordination complexes. **A. E. Hoffman**, R. P. Doyle

321. Synthesis and biological evaluation of 4,8-didesmethyl telithromycin(5) and 4,8,10-tridesmethyl cethromycin(6): An effort toward addressing antibiotic resistance. **B. S. Wagh**, R. B. Andrade

322. Synthesis and characterization of fatty amide derivatives from gallic acid. **M. D. Lewis**, O. Bakare

323. Chemical analysis and monitoring of biological activities of different fractions of *Taraxacum officinale* in different stages of plant growth. **M. N. Feazell**

324. Novel fluorescent antagonist as a molecular probe in A_3 adenosine receptor binding assays using flow cytometry. **E. Kozma**, S. T. Kumar, S. Federico, K. Phan, R. Balasubramanian, Z. Gao, S. Paoletta, S. Moro, G. Spalluto, K. A. Jacobson

325. Inhibition of system x_c^- transporter-mediated cystine uptake by sulfasalazine analogs. **K. Shukla**, A. G. Thomas, D. V. Ferraris, N. Hin, R. Sattler, J. Alt, C. Rojas, B. S. Slusher, T. Tsukamoto

326. Design, synthesis, and pharmacological evaluation of glutamate carboxypeptidase II (GCPII) inhibitors based on thioalkyl benzoic acid scaffolds. **N. B. Hin**

327. Antioxidant properties of novel NMDA receptor antagonists and radiosensitizers. **Q. N. Nguyen**, B. T. Gaye, J. V. Wallach, Z. Ates-Alagoz, A. Adejare

328. β-Lactam antibiotics: Chemical probes of the glutamate subtype 1 transporter. **R. Martinez**, P. Dunman, S. Rawls, A. Sivakumar, M. Abou-Gharbia, W. Childers, V. Ghidu, B. Rasmussen, S. AlQaradawi, M. Ramanjulu

329. *In vitro* anticonvulsant activity of 2,4-disubstituted phenyl enaminones. **I. O. Edafiogho**, S. B. Kombian, O. Phillips, K. V. Ananthalakshmi, M. G. Qaddoumi

330. Removal of a ricin surrogate from water and reusable medical device surfaces. **P. Kulkarni**, V. M. Hitchins, A. D. Lucas

331. Design, synthesis and biological evaluation of novel Mtb-specific Dxr inhibitors as potential anti-tubercular agents. **G. San Jose**, K. Kehn-Hall, H. I. Boshoff, R. Couch, C. S. Dowd

332. Screening vorozole on a series of human liver cytochrome P450s. **M. A. VanAlstine**, L. Raymond, N. Rayani, K. Sikorski, G. Polson, A. Lian

333. Antagonism of c-myc–max protein–protein interaction with small-molecules. **J. L. Yap**, K. Jung, E. V. Prochownik, S. Fletcher

334. Synthesis and biological evaluation of novel tetracyclic indenoquinoline derivatives as anticancer agents. **S. Chakrabarty**, M. S. Croft, M. G. Marko, G. Moyna

335. Some limits of biocompatibility testing for lipohilic leachates. **A. D. Lucas**, E. A. Gordon

336. Insight into the hydroxylation of quinolone quorum sensing molecules across bacterial species. **E. L. Guevara**, D. B. Hansen

337. MD simulation studies to understand the role of active site residues in lesion processing by thymine DNA glycosylase. **M. S. Noon**, A. D. MacKerell, Jr., A. C. Drohat

338. Wetting properties of ionic liquids. D. Cole, **R. Sperazza**, H. J. Castejon

339. Substrate binding and structure equilibration for the peptide hydrolysis catalyzed by human T-cell leukemia virus type 1 (HTLV-1) protease. **N. Petrillo**, S. Ma

340. Computational simulation of laminaripentaose-producing β-1,3-glucanase (LPHase) catalytic reaction. **X. Zhang**, S. Ma

341. Cyclic and linear homochiral decapeptides containing tryptophan and arginine/lysine residues as Src kinase inhibitors. **A. Nasrolahi Shirazi**, R. Tiwari, D. Mandal, K. Parang

342. Polystyrene supported $AlCl_3$ as a highly chemoselective catalyst for Fries rearrangement of aryl esters. K. Parvanak Boroujeni, **A. Nasrolahi Shirazi**

343. Amphiphilc cyclic peptide $[WR]_4$ as an efficient transporter of negatively charged phosphopeptides. **A. Nasrolahi Shirazi**, R. Tiwari, D. Oh, G. Ye, K. Parang

Saturday, June 2, 2012 - Morning

Contemporary Organic Materials

Engineering Building, ENGR027 LH5
Financially supported by Division of Polymeric Materials: Science & Engineering
Presiding: J. Tovar

8:00 AM **344.** Organic materials research at Johns Hopkins University: Biomedicine, energy and nanoscience. **J. Tovar**

8:15 AM **345.** Synthesis and characterization of functionalized graphite nanofibers. **R. Giuliano**, T. Pellenbarg, J. Hull, E. Borguet

8:45 AM **346.** Comparison of polymer-fullerene heterojunction morphology to bimolecular recombination kinetics. **D. M. DeLongchamp**

9:15 AM **347.** Electrochemical polymerization of conjugated polymers in living tissue. **D. C. Martin**, L. Ouyang, C. Kuo, C. Shaw, A. Griffin

9:45 AM Intermission.

10:00 AM **348.** Poly(thiomethyl methacrylate): Sulfur's effect on polymerization and polymer properties. **A. Snow**, A. Purdy, M. Brindza, G. Beadie

10:30 AM **349.** Sorona® polytrimethylene terephthalate: A renewably-sourced polymer with enhanced performance. **B. W. Messmore**

11:00 AM **350.** Polypeptoids: Synthesis, characterization and materials properties. **D. Zhang**

11:30 AM **351.** Funtional hydrogel materials from self-assembling peptides. **J. P. Schneider**

Mass Spectrometry of Biomolecules

Academic IV Building, ACIV003 LH4
Presiding: S. Jackson

8:20 AM **352.** Communicating concepts and methods in biological mass spectrometry: Development of an introductory tutorial series for the nonspecialist. **J. A. Kelley**, J. Blonder, C. C. Lai, L. Stockwin, T. D. Veenstra, L. R. Phillips

8:45 AM **353.** Use of imaging mass spectrometry to find biomarkers and study time dependent lipid changes in brain trauma caused by controlled cortical impact. **K. Baldwin**, J. Post, L. Muller, D. Barbacci, G. Bull, A. Schultz, B. Cox, A. S. Woods

9:10 AM **354.** Major histoctocompatibility class II^+ invariant chain negative breast cancer cells present unique peptides that activate tumor-specific T cells from breast cancer patients. **O. Chornoguz**, A. Gapeev, M. O'Neill, S. Ostrand-Rosenberg

9:35 AM **355.** Middle out analysis in proteomic workflows. **J. R. Cannon**, C. Fenselau

10:00 AM Intermission.

10:20 AM **356.** Small-volume sample analysis by mass spectrometry: From single cells to high-throughput product screening. **P. Nemes**

10:45 AM **357.** Validation of efficient LC-MS/MS calibration strategies. **M. T. Olson**

11:10 AM **358.** MALDI ion mobility mass spectrometry of biomolecules and non covalent complexes. **D. Barbacci**, S. Jackson, J. Post, K. Baldwin, L. Muller, J. A. Schultz, A. Woods, T. Egan, K. Waters, S. Ulrich, V. Vaughn, M. McCully, E. Lewis

11:35 AM **359.** Unraveling the quagmire of oligonucleotides: Analysis by high resolution mass spectrometry. **J. A. Wilhide**, W. R. LaCourse

Active Learning in the Chemistry Classroom

University Center, UC201
Presiding: H. Perks

8:30 AM **360.** Comparing educational outcomes of a team-based learning approach and a traditional lecture approach to teaching genetics. **S. Caruso**, C. R. Wagner, D. M. Eisenmann, P. J. Farabaugh

8:55 AM **361.** Illustration of unreliability of calculated proton nmr spectra. **D. D. CLARKE**

9:20 AM **362.** Assessing the effect of active learning on student learning outcomes in the chemistry classroom. **L. C. Hodges**

9:45 AM Intermission.

10:05 AM **363.** Organic chemistry and the 'structure-mechanism-reaction' paradigm: Structure knowledge is a powerful predictor of student performance. **S. M. Graham**

10:30 AM **364.** Development and analysis of course and program-level assessment tools and data from general education chemistry and physical chemistry courses. **A. T. D'Agostino**

10:55 AM **365.** Mass, measurement, materials, and more mathematical modeling: The nuts and bolts of let's make an error. **S. A. Sinex**, T. L. Chambers, J. B. Halpern

11:20 AM **366.** Implementing a classroom assessment technique in a large enrollment course. **D. King**

Nanochemistry A

Meyerhoff Chemistry Building, MEYR120
Presiding: M. Daniel

8:30 AM Introductory Remarks.

8:35 AM **367.** Characterization and evaluation of zein/chitosan nanocomplex for encapsulation and controlled release of hydrophilic and hydrophobic nutrients. **Y. Luo**, Q. Wang

9:05 AM **368.** Use of a transferrin-functionalized gold nanoparticle-cored dendrimer for targeting advanced pancreatic cancer. **M. E. Grow**, M. Daniel

9:35 AM **369.** Graphene oxide: A nano catalyst. **G. Bhimanapati**, R. Vander Wal, S. Carranza

10:05 AM Intermission.

10:30 AM **370.** PtSn intermetallic nanoparticle electrocatalysts: Effects of graphene-based supports on electro-oxidation. **C. M. Sims**, A. A. Ponce, Z. Liu, B. W. Eichhorn

11:00 AM **371.** Fabrication and characterization of UV-emitting defect-free 5-10 nm ZnO nanorings. **D. C. Micheroni**, T. S. Ahmadi

11:30 AM **372.** Solvent-free processing methods for formulation of dispersed multi wall carbon nanotube/epoxy composites. **M. L. Gupta**, S. A. Sydlik, J. M. Schnorr, M. Ukaegbu, C. Hosten, T. M. Swager, D. Raghavan

Renewable Energy C

Materials and Processes
Biological Sciences Building, BS120
Presiding: B. Hamadani

8:30 AM **373.** Combined heat and power in automobiles: Utilization of waste engine heat to drive ethanol/water distillation. **J. A. Rudesill**, B. D. D'Alessio, D. D. Frey

9:00 AM **374.** *In situ* studies of organic photovoltaic active layer formation and stability. **L. J. Richter**, N. Shin, M. A. Kelly, A. Herzing, R. Kline, D. M. Delongchamp

9:30 AM **375.** 3D Au–TiO_2 nanoarchitectures for plasmonic photovoltaic applications. P. A. DeSario, **D. E. DeVantier**, J. J. Pietron, L. C. Szymczak, D. R. Rolison

9:55 AM **376.** Fundamental insights to regeneration and recombination with the iodide/triiodide redox mediator relevant to dye-sensitized solar cells. **B. H. Farnum**, G. J. Meyer

10:20 AM Intermission.

10:45 AM **377.** Molecular level control for excited state electron injection and charge recombination at sensitized TiO_2 interfaces. **A. Kopecky**, P. G. Johansson, G. J. Meyer, E. Galoppini

11:10 AM **378.** New organometallic platforms for conversion of carbon dioxide to chemical fuels. **J. L. DiMeglio**, J. Rosenthal

11:35 AM **379.** New multielectron porphyrinoid platform for solar harvesting applications. **A. J. Pistner**, J. Rosenthal

Carbohydrates in Drug Design A

Morning
Information Technology/Engineering Building, ITE102 LH7
Financially supported by Division of Carbohydrate Chemistry
Presiding: L. Wang

8:50 AM Introductory Remarks.

9:00 AM **380.** Advances in the synthesis and sequencing of glycosaminoglycans. **R. J. Linhardt**

9:45 AM **381.** Therapeutic potential of the tumor-associated Thomsen-Friedenreich carbohydrate antigen on nanoparticles. **J. J. Barchi**, S. K. Keay, K. M. Adams, A. Mackerell, S. S. Mallajosyula

10:15 AM Intermission.

10:35 AM **382.** Efficient chemoenzymatic glycosylation remodeling of therapeutic antibodies. **W. Huang**, J. Giddens, L. Wang

11:05 AM **383.** Antivirals from nature: A decade with the cyanobacteria. **C. A. Bewley**

Undergraduate Research Posters A

University Center, Ballroom

9:30 - 11:30 AM

384. Cytochrome P450 functionalized electrodes for *in vitro* diclofenac metabolism. **A. Mugweru**, **E. Cronin**, **M. Mihalenkova**

385. Organocatalyzed reactions of α-acetoxy glycine esters: Toward the asymmetric synthesis of unnatural amino acids. **J. C. Zimmerman**, A. R. Evenson, T. J. Peelen

386. Investigation of the mechanism of the sodium borohydride reduction of benzil. **R. R. Denny**, **T. Nguyen**, T. J. Peelen

387. Novel chemical methodologies for the preparation of betulin derivatives. M. A. Corsello, **C. E. Sleet**, B. J. Penczuk, K. M. Twomey, S. C. Jonnalagadda

388. Morphology of soot aerosol particles by scanning electron microscopy. **X. Wu**, D. A. Bruzewicz

389. Reversible damage and repair of hydrophobic self-assembled monolayers. **S. Phuntsok**, D. A. Bruzewicz

390. Mechanism of ring-contraction of 3H-1-benzazepine to quinoline. **J. Kang**, P. Prasad, S. Karimi

391. Ensuring New York City's water quality: The logistics and procedure learned from a DEP summer internship. **F. Ali**, P. Svoronos, F. Jacques, C. Neptune, P. Meleties

392. Analysis of water samples at the Marine Science Department of New York's Division of the Environmental Protection Agency at Ward's Island. **M. Giwa**, P. Svoronos, N. Yao, F. Jacques, P. Meleties

393. Analysis of compositing samples of various sewage treatment plants at the Newtown Creek facility of New York's Department of Environmental Protection (DEP) Agency. **N. Yu**, P. Svoronos, F. Jacques, A. Negatu, P. Meleties

394. Determination of gallic acid in various beverages using high pressure liquid chromatography (HPLC). **M. Ln**, S. Svoronos, P. Irigoyen, P. Svoronos

395. Spectrophotometric determination of the total amount of antioxidants in juice beverages. **S. Enriquez**, M. M. Moe, S. Svoronos, P. Irigoyen, P. Svoronos

396. Use of the Folin-Ciocalteau method to measure the total amount of antioxidants in tea samples. **K. San**, M. M. Moe, S. Svoronos, P. Irigoyen, P. Svoronos

397. Synthesis of oxyallyl silanes and their application as homoenolate equivalents. **D. Mitchell**, J. Pigza

398. Chemokine production in inflammatory bowel diseases. **R. Loh**, Y. Wu, E. Lin, A. Nguyen

399. Analysis of authentic versus imitation perfumes. **D. M. Miceli**, B. Montalbano, J. Iorio, G. Vaswani, S. Karimi

400. Effect of various compounds on the prevention and degradation of *Staphylococcus aureus* biofilms. **M. M. Moe**, M. Lin, E. Vanegas, N. Gadura, K. LaMagna, D. Maloney

401. Effect of O-acetyl L-carnitine hydrochloride on MDA-MB 231 cells. **D. Dacosta**, M. Regan, R. Sullivan

402. Conjugating silver nanoparticle to the siloxane matrix. **S. Delva**, **M. Chauhan**

403. Reactivity of tris(trimethylsilyl)phosphite (TMSP): Synthesis of a bisphosphonic derivative of bicine. **L. Najjarian**, L. Vargas

404. Synthesis and characterization of efficient Nek2 substrates employing solid phase synthesis procedures. **D. A. Novoa**, S. Kumar

405. Reactivity of tris(trimethylsilyl)phosphite (TMSP): Synthesis of a bisphosphonic derivative of β-alanine. **T. Limdar**, L. Vargas

406. Expression of gamma-synuclein protein in cancer cells. **J. Boroday**, U. Golebiewska

407. Partial sulfonation of polyaniline nanofibers by co-polymerization: Effects of monomer ratio and polymerization initiator. **J. Kaur**, D. M. Sarno

408. Preparation of poly(o-toluidine) as highly porous micron-scale spheres. **D. LaFaurie**, D. M. Sarno

409. Reactivity of tris(trimethylsilyl)phosphite with chloroformates containing electron withdrawing groups. **K. Chavez**, L. Vargas

410. Reactivity of tris(trimethylsilyl)phosphite (TMSP): Synthesis of the bisphosphonic acid of 3-(trifluoromethyl) phenyl chloroformate. **M. Morales**, L. Vargas

411. Synthesis of the fragrance Berryflor using only solid-supported reagents. **C. J. Hogan**, J. Regan

412. Preparation and biological activity of 4-allyl-2-methoxy-6-nitrophenol against four clinically relevant microbes. **B. W. Robinson**, D. A. Abramovitch, F. A. Norris

413. Fluorescence based method for analyzing bacterial membrane permeability. **A. L. Picciano**, **S. M. Misenko**, G. A. Caputo

414. Understanding the mechanisms of copper induced, lipid peroxidation mediated cell death in *Saccharomyces cerevisiae*. **J. Ramlall**, N. Gadura

415. Effect of copper surfaces on endospore-forming bacteria *Bacillus subtilis*. **J. Long**, N. Gadura

416. Comparison of copper mediated toxicity in both *Staphylococcus aureus* and *Escherichia coli*. **P. P. Thu**

417. Genomic toxicity of silver nano particles on *Escherichia coli*. **K. Joseph**, M. Chauhan, M. Tawde

418. Structural and kinetic characterization of glycerolphosphodiesterase activity using a phosphatidylinositol-specific phospholipase C (PI-PLC) active site. **D. M. Strauss**, T. L. Selby

419. Mechanistic characterization of a Ca^{+2} dependent phosphatidylinositol-specific phospholipase C (PI-PLC) from *Streptomyces antibioticus*. **S. Petrovic**, T. L. Selby

420. Ni content of the US nickel coin determined by X-ray fluorescence and visible spectroscopy. **S. Jagdeo**, E. J. Shin, J. H. Shin

421. Application of the laser pointer method to determine the refractive index of solid compounds: Out-in method. **S. Ham**, R. Cho, J. H. Shin

422. Determination of the refractive index of solid compounds by the laser pointer method: Extension method. **J. Lee**, R. Cho, J. H. Shin

423. Photonic crystal fiber bending loss sensitivity for design of fiber sensors. **A. Lee**, **G. Constantinez**, **L. Mora**, D. Kokkinos

424. Use of a microscale freezing point technique to determine the ionization constant of carboxylic acids. **F. Nazumudeen**, P. Irigoyen, P. Svoronos

425. Effects of resveratrol analogues on cell proliferation and migration of mouse melanoma cells. **F. B. Nazumudeen**, M. M. Moe, V. Morris, C. Spatafora, C. Tringali, S. A. Rotenberg

426. Identification of mycotoxin and chemotherapeutics by FDA Northeast Region Laboratory. **F. Nazumudeen**, S. Cox, H. Chauca, J. Obando, P. Svoronos

Saturday, June 2, 2012 - Afternoon

Active Learning in the Chemistry Laboratory

University Center, UC201
Presiding: H. Perks

2:00 PM **427.** Active learning in the chemistry laboratory: The POGIL approach. **F. J. Creegan**

2:25 PM **428.** So you want to revise your laboratory course: What next? **S. E. Van Bramer**, A. Martin

2:50 PM **429.** Going off-recipe: Redesigning cookbook labs for greater pedagogical nutrition. **M. C. Wesolowski**

3:15 AM Intermission.

3:35 PM **430.** Use of critical thinking skills in an undergraduate organic chemistry laboratory: The catalytic hydrogenation of *trans*-methyl cinnamate. **K. J. O'Connor**

4:00 PM **431.** Creating unique undergraduate research projects for nursing majors that investigate the antiproliferative effects of heavy metal compounds on MCF-7, A375, and HFF cells. **A. J. Heston**

Carbohydrates in Drug Design B

Afternoon

Information Technology/Engineering Building, ITE102 LH7
Financially supported by Division of Carbohydrate Chemistry
Presiding: L. Wang

2:00 PM **432.** Functionalized catanionic surfactant vesicles as "artificial pathogens": A new platform for the development of vaccines. **P. DeShong**

2:30 PM **433.** Selective control of N-glycan sialylation via metabolic flux. **K. J. Yarema**

3:00 PM **434.** Personalizing cancer treatment with the aid of glycan array technology. **J. Gildersleeve**

3:30 AM Intermission.

3:50 PM **435.** How NMR spectroscopy reveals the function of the genes for pneumococcal capsular polysaccharide biosynthesis. **C. Bush**

4:20 PM **436.** Glycoconjugate vaccine manufacturing: Lattices and hairy balls. **W. F. Vann**

Inorganic Chemistry
Biological Sciences Building, BS120
Presiding: S. Szalai

2:00 PM **437.** Sequential phenolate oxidation in octahedral cobalt(III) complexes with $[N_2O_3]$ ligands. **M. M. Allard**, C. N. Verani, D. Basu, F. R. Xavier

2:25 PM **438.** Enhanced water stability of carboxylate containing metal organic frameworks via plasma enhanced chemical vapor deposition of perfluorocarbons. **J. B. DeCoste**, G. W. Peterson, M. W. Smith, C. A. Stone, C. R. Willis

2:50 PM **439.** Synthesis of novel low coordinate manganese-nitrogen clusters in quest of water oxidation catalysts. **S. K. Kondaveeti**, S. Vaddypally, M. J. Zdilla

3:15 AM Intermission.

3:35 PM **440.** Iron-based hydrogen evolution catalysts. **C. A. Mebi**, D. Karr, R. Gao

4:00 PM **441.** Pseudorotational rearrangement of ligands at a rhenium(V) pentahydride complex as opposed to simple rotation about a single Re-N bond. G. Birudala, **G. A. Moehring**

4:25 PM **442.** Some chiral copper(II) complexes of piperazine derivatives. **M. A. O'Connor**, A. W. Addison, M. Zeller, A. D. Hunter

4:50 PM **443.** Ligand odyssey: Synthesis and structural characterization of redox-active second and third generation tris(pyrazolyl)borate ligands. **E. R. Sirianni**, G. P. Yap, K. H. Theopold

Nanochemistry B
Meyerhoff Chemistry Building, MEYR120
Presiding: C. Geddes

2:00 AM Introductory Remarks.

2:05 PM **444.** Metal-enhanced fluorescence: Progress towards a unified plasmon-fluorophore description. **C. D. Geddes**

2:30 PM **445.** Quantitative measurement of enzyme activity loss on biofunctionalized gold nanoparticles. **D. E. Gorka**, R. I. MacCuspie, N. O. Savage

2:55 PM **446.** Nanosized semiconductors and metals formed from PMMA ionomers. C. Wu, T. Emge, **M. Hara**

3:20 PM **447.** Synthesis of asymmetric polymer/metal hybrid nanoparticles by interfacial reactions. **J. He**, M. Teresa Perez, P. Zhang, Y. Liu, T. Babu, J. Gong, Z. Nie

3:45 AM Intermission.

4:15 PM **448.** Self assembled nanopillars. **H. JI**, N. Johnson, X. Xu, A. Kojtari, D. Swearer

4:40 PM **449.** Bionanoparticle polymer hybrids and curcumin conjugates for biomedical applications. **K. Raja**, W. Shi, S. Dolai, C. Sun, R. Balambika

5:05 PM **450.** Silicon agents for large scale synthesis of active noble metal nanoparticles. **B. P. Chauhan**, S. Matam, R. Thekkathu, H. Shukla

NMR Spectroscopy of Biomolecules

Academic IV Building, ACIV003 LH4
Presiding: A. Drohat

2:00 PM **451.** Effects of deuteration on NMR parameters of proteins. **V. Tugarinov**

2:30 PM **452.** Tales of two detergents in solubilizing and stabilizing protein for NMR studies. **M. A. Massiah**

3:00 PM **453.** Proteins that switch folds. **J. Orban**

3:30 AM Intermission.

3:50 PM **454.** NMR detection of an RNA structural switch in the HIV-1 leader that regulates genome dimerization and packaging. **X. Heng**

4:20 PM **455.** Carbon detected NMR methods probe folding-upon-binding events involving intrinsically disordered proteins. **S. A. Showalter**

4:50 PM **456.** Molecular recognition by carrier proteins in non-ribosomal peptide synthetases. **D. P. Frueh**, A. Goodrich, S. Mishra, S. Nichols, B. Harden

Photochemistry

Engineering Building, ENGR027 LH5
Presiding: L. Kelly

2:00 AM Introductory Remarks.

2:05 PM **457.** Examing the effects of laser ablation on gold nanoparticles. **D. C. Meier**, R. E. Cavicchi

2:35 PM **458.** Standoff laser-induced fluorescence-backscattered amplified stimulated emission (LIF-BASE) detection of explosive vapors. **J. B. Oleske**

3:05 AM Intermission.

3:20 PM **459.** Probing thermodynamics of pseudo-polymorph conversion in peptides using terahertz spectroscopy. **Z. Ahmed**, D. F. Plusquellic

3:40 PM **460.** Design and construction strategies for assembling artificial redox and light-activatable and light-harvesting proteins. **G. kodali**, L. A. Solomon, T. A. Farid, O. A. Mass, A. Kunche, N. Roach, T. V. Esipova, S. A. Vinogradov, J. S. Lindsey, D. Officer, C. C. Moser, P. L. Dutton

4:00 PM **461.** Multiple photochemical transformations of organic molecules: Juggling with atom connectivity. **D. J. Aitken**, H. Eijsberg, J. Ollivier

4:30 PM **462.** Synthesis and polarity sensing with benzo[ghi]perylene monoimides. **S. J. Manning**, J. A. Arthur, L. A. Kelly

5:00 PM **463.** Photochemical degradation kinetics of 2- and 3-nitrofluoranthene in organic solvent. **S. Gavalda**, R. Arce

Undergraduate Research Posters B

University Center, Ballroom

3:00 - 5:00 PM

464. Synthesis of curcumin incorporated copolymers via ATRP. **F. Pierre Toussaint**, **O. Ajayi**, K. Raja, S. Dolai

465. Synthetic lethal screen to identify genes related to MAM33 in *S. cerevisiae*. **G. A. Roloff**, E. Luvison, M. F. Henry, **M. Azam**

466. Which hydroxyl groups of epigallocatechin gallate (EGCG) are needed for binding to DNA g-quadruplexes? **B. M. Koronkiewicz**, M. F. Bruist, X. Guo, B. Peethambaran

467. Oxidation of alcohols to esters using *N*-bromosuccinimide in aqueous media. **M. C. Stadler**, J. Fair

468. Construction of a coronal discharge ozone generator. **W. H. Miller**, **J. H. Fair**

469. Environmentally friendly synthesis of novel mono-azo and bis-azo dyes using a polymer resin. **A. R. Pulcini**, J. R. Berk

470. Bromine radical ring closure of α-tethered sulfonyl ene-allenes. **J. A. Milligan**, S. S. Murphree

471. Studying the displacement of the chloride leaving group in chloroformate esters. **G. Fernandez-Bueno**, M. J. D'Souza, D. N. Kevill

472. Metal cluster formation in a designed protein scaffold. **E. J. Palovcak**, S. Kondaveeti, M. J. Zdilla

473. Unprecedented azine formation via proton tautomerismof isoquinolyl-1-hydrazones. **K. Cannon**, **S. Lauro**, A. Schmiedekamp, C. Wang

474. Engineering enzyme therapeutics for gluten degradation. **S. Gordon**, E. Stanley, S. Wolf, A. Toland, D. Hadidi, S. Wu, D. Baker, I. Swanson, J. Siegel

475. Convenient strategies to force difficult lactamisations. **B. C. Williams**, K. Q. Ha

476. Investigation into the thermoreversible gelation of polycaprolactone. **J. Monaghan**, I. VonRue

477. Synthesis of four spermidide derivatives using long chain alcohol solvents and coupling of these derivatives to manganese as possible anti-cancer drugs. **B. Begovich**, C. Litchmore, F. C. Mayville, S. E. Hayik

478. Spectroscopic properties of tetracyclines. **M. Rozov**

479. Novel synthesis of high-valent and low-coordinate manganese clusters. **S. F. McWilliams**, S. Kondaveeti, S. Vaddypally, M. J. Zdilla

480. Synthesis and characteristic study of artificial anthocyanidine. **A. Pagan**, J. Kang, J. I. Lee

481. Spectroscopic study of metal complexed anthocyanins from plants for dye-sensitized solar cells. **C. M. Lorenzo**, P. Djan, J. Kang, J. I. Lee

482. Microwave synthesis: Sulfoindocyanine dyes. **R. Matthews**

483. Analysis of caffeine in energy drinks using liquid-liquid extraction and gas chromatography-mass spectrometry. **K. A. Snyder**, K. S. Wendling

484. Calculating partial atomic charges from quantum mechanics: A theoretical study of substituted thiazolidinones and the prediction of their NMR spectra. **K. J. Kober**, K. A. Kistler

485. Impact of plasma membrane unsaturated fatty acid levels on copper surface mediated cell death in *Escherichia coli*. **R. Hong**, T. Y. Kang, N. Gadura

486. Microwave assisted synthesis of cyanine dyes for fluorescence resonance energy transfer. **G. Nyambura**

487. Molecular docking simulations of indoles/ β-cyclodextrin inclusion complexes. **L. Brown**, I. Posey

488. Strongly conjugated hydroporphyrin arrays: Synthesis and optical properties. **C. Pancholi**, J. Nguyen, Z. Yu, S. Zik, M. Ptaszek

489. Novel water-soluble tetrapyrrolic derivatives via “click” reaction. M. Ehudin, **D. Akkad**, R. Arias, C. Toonstra, M. Ptaszek

490. G6PDiagnostic: Point-of-care diagnostic to detect glucose-6-phosphate-dehydrogenase deficiency. **R. Dasgupta**

491. Comprehensive catalase enzyme activity mechanism: Conformer multiplicity and kinetic deviations explained. **J. Rosenblum**, J. P. Mack, W. Schreiber, D. Schnur

492. Construction of an inexpensive in-house Raman spectrometer. **B. Eagleton**, J. Zhang

493. Clicked sweet-curcumin: Modulator of amyloid-β aggregation at ultra-low concentrations. **D. Obeysekera**

ABSTRACTS

Atmospheric Chemistry

1. Impacts of surface-adsorbed organics on tropospheric aerosol surrogates: Heterogeneous ozonolysis and its effects on water uptake

***Ryan Z Hinrichs**, rhinrich@drew.edu, Laurie Woodill, Erinn O'Neill, Alae Kawam.Department of Chemistry, Drew University, Madison, New Jersey 07940, United States*

Surface-adsorbed organics are ubiquitous components of tropospheric aerosols and have the potential to alter aerosol chemical and physical properties. To assess the chemistry of adsorbed organics in the laboratory, we use infrared spectroscopy (DRIFTS) to monitor the adsorption and subsequent ozonolysis of model organics – e.g., catechol and eugenol – on sea salt and mineral aerosol substrates. Adsorption of gaseous organics on sodium halides was controlled by hydrogen bonding interactions, while dissociative adsorption of phenolic functional groups on Al_2O_3 produced surface bound phenolates. Heterogeneous ozonolysis (400 ppb O_3) of surface adsorbed aromatics resulted in ring cleavage (e.g., catechol → muconic acid). Ozonolysis of eugenol proceeded via 1,3-cycloaddition at both the alkene side chain and the aromatic ring, and the relative rates for eugenol versus 2-methoxy-4-propylphenol allowed for quantitative comparison of addition at these two sites. Reaction kinetics were measured as a function of substrate, ozone concentration, and relative humidity.

2. Material measurement science at NIST for the atmospheric environment

***Joseph Conny**, joseph.conny@nist.gov.Surface and Microanalysis Science Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899, United States*

NIST has long worked toward developing measurement science and reference materials to address environmental problems. Presented here is current work by NIST researchers to address needs of the atmospheric chemistry community.

Research on trace atmospheric gases includes the establishment of lower uncertainties in rate constants for the OH reaction. More precise carbon dioxide measurements are acquired with newly-developed photoacoustic spectrometers.

Aerosol research includes accuracy in black carbon measurement and studies of functional groups in secondary organic aerosols. Individual ambient particles are analyzed microscopically to determine how heterogeneity affects optical properties. Photoacoustic and cavity ring-down spectroscopies are used to measure absorption and extinction on various soots and brown carbon. Also studied is the effect of filter substrates on particle absorption. As proxies for atmospheric aerosols, soot-metal oxide particles serve to assess optical properties of internally-mixed particles, and oxidized graphite particles with tunable optical properties serve as various types of brown carbon.

3. MDE: Monitoring air quality for public health

***Jennifer Hains**, jhains@mde.state.md.us.Department of Air Monitoring, Maryland Department of the Environment, Baltimore, MD 21230, United States*

The Ambient Air Monitoring Program at the Maryland Department of the Environment (MDE) works to protect public health by maintaining a statewide network of monitors for O_3, CO, Pb, NO_2, SO_2 and particulate matter and issuing daily air quality forecasts. Along with our monitoring efforts we are interested in understanding the spatial variability of these pollutants and their sources to inform pollution control strategies. We collaborate with nearby universities and federal agencies to investigate the chemical composition of the atmosphere at the surface and in the planetary boundary layer. This

presentation will summarize MDE's ambient air monitoring network and highlight our research collaborations investigating the transport and composition of boundary layer ozone, ozone-precursors and aerosols with ozonesondes launched by Howard University, University of Maryland Baltimore County Lidar and a University of Maryland College Park research aircraft. Special studies investigating meteorological impacts on summertime O_3 events will also be highlighted.

4. Sulfate aerosol formation and oxidation pathways: sensitivity to the choice of chemical mechanism employed in simulations

***Ariel Stein**, ariel.stein@noaa.gov.ERT on assignment to NOAA's Air Resources Laboratory, Silver Spring, MD 20910, United States*

The processes of aerosol sulfate formation are vital components in the understanding of perturbations of earth's radiative balance via aerosol direct and indirect effects. We perform an analysis of the influence of changes in oxidant levels and sulfur dioxide oxidation processes to study the underlying pathways for sulfate formation. Three chemical mechanisms (CBIV, CB05, SAPRC99) are shown to have significantly different responses in sulfate formation when the emissions of NO_x and/or VOC are altered, reflecting different photochemical regimes under which the formation occurs. An analysis of the oxidation pathways that contribute to SO_2 conversion to sulfate reveals substantial differences in the importance of the various pathways among the three chemical mechanisms. These findings suggest that estimations of the influence that changes which perturb SO_2 oxidants have on sulfate abundances, and on its direct and indirect radiative forcing effects, may be dependent on the chemical mechanism employed in the model analysis.

5. From the stratosphere to air quality: Atmospheric chemistry research at NASA Goddard's Atmospheric Chemistry and Dynamics Laboratory

***Kenneth E. Pickering**, Kenneth.E.Pickering@nasa.gov.Atmospheric Chemistry and Dynamics Laboratory, NASA Goddard Space Flight Center, Greenbelt, MD 20771, United States*

Atmospheric chemistry research at NASA Goddard has evolved from being primarily oriented toward diagnosis of stratospheric ozone changes to current activities in air quality. The talk will review the group's research on satellite ozone observations and stratospheric chemical modeling. Tropospheric column ozone has also been derived from satellite data. Tropospheric chemical modeling activities have led to the development of the Global Modeling Initiative (GMI) chemical transport model, the GOCART aerosol model, and a global Chemistry and Climate Model. Data from the OMI instrument are employed in retrievals of tropospheric column amounts of NO2 and SO2 and absorbing aerosol optical depths. The availability of these data has led to an air quality research activity within the group. The talk will provide an overview of the DISCOVER-AQ program, designed to provide data to research linkages between the column amounts of pollutant gases and aerosols obtained from satellite and surface air quality.

6. Atmospheric chemistry research at Howard University: Science, students and opportunities

***William R Stockwell**[1], William.R.Stockwell@gmail.com, Vernon Morris[1], Everette Joseph[2], Belay Demoz[2], Demetrius Venable[2], Gregory S Jenkins[2], Tsann Yu[3]. (1) Department of Chemistry, Howard University, Washington, DC 20059, United States (2) Department of Physics, Howard University, Washington, Dc 20059, United States (3) Mechanical Engineering, Howard University, Washington, DC 20059, United States*

Atmospheric chemistry is now a central discipline in the atmospheric sciences because the impact of air pollution on health and climate. Research involving Howard University students include aerosol measurements made aboard NOAA research vessels (Aerosols and Ocean Science Expeditions, AEROSE); ozone sonde field studies performed across the north Tropical Atlantic and research activi-

ties at Howard University's new field research facility in Beltsville, Maryland. The Beltsville research facility is a unique suburban location where students perform a broad range of studies in areas such as air quality, boundary layer /dispersion meteorology, aerosol physics, ozone dynamics, and LIDAR applications. The Beltsville research supports NASA and NOAA programs. The ground based measurements have been used to ground truth NASA satellite instrument measurements and it supports NOAA programs such as air quality forecasting; the data is being used to test the widely used Regional Atmospheric Chemistry Mechanism, Version 2 (RACM2).

7. Modeling and measurements of atmospheric chemical composition and transport at UMBC

Lynn Sparling, *sparling@umbc.edu.Department of Physics, University of Maryland, Baltimore County, Baltimore, Maryland 21250, United States*

The first part of this presentation is an overview of research in the Atmospheric Physics group here at UMBC. The goals are to reduce uncertainties in climate change forcing due to the radiative impact of clouds, trace gases and aerosols on the energy balance of the atmosphere and their impact on air quality. Experimental work includes the use and development of instrumentation for remote sensing of aerosols and trace gases from satellite, ground-based and aircraft platforms. The second part is a survey of investigations of dynamical transport and mixing processes in different parts of the atmosphere. Examples will include diagnosis of large scale transport processes from observations of stratospheric trace gases, transport of volcanic gases in the upper troposphere, and downward transport of ozone from the stratosphere to the surface. Time permitting, some recent adventures in atmospheric chemical modeling from a beginner's perspective will also be discussed.

Nanomaterials

8. Designing bottom-up protein assembly at nanoscale: Towards high density, high payload, quantifiable protein arrays

Jong-in Hahm, *jh583@georgetown.edu.Chemistry, Georgetown University, Washington, DC 20057, United States*

We evaluate protein adsorption characteristics on chemically homogeneous and heterogeneous polymeric surfaces by employing diblock copolymers, homopolymers, and polymer blends as protein templates. We also carry out for the first time quantitative activity measurements of various enzymes immobilized selectively on one of the domains in microphase-separated block copolymer films. The specific activity of enzymes adsorbed on the diblock copolymer surface are measured and compared quantitatively to that of enzymes in free solution. Protein assembly on chemically modified polymeric nanotemplates is also explored in order to demonstrate the versatility of our new methods in providing a wide range of template size and shape. Our results demonstrate that a wide range of self-assembling, chemically heterogeneous, nanoscale domains in diblock copolymers can be used as basis for high payload, high density protein templates. Subsequently, the resulting protein nanoarrays can serve as novel, high density, high payload, biologically functional substrates in many proteomics applications.

9. Nanostructured energy devices: Manipulating electrons, photons and ions

Liangbing Hu, *binghu@umd.edu.Materials Science and Engineering, University of Maryland College Park, College Park, MD 20740, United States*

Lowering the cost and improving the performance of devices are essential for making renewable energy feasible for everyday applications. In this talk, I will focus on discussing how abundant materials such as paper, silicon and copper can be engineered to create one dimensional nanomaterial networks (***Nano-Nets***) which allow us to manipulate fundamental particles in these energy devices

to ultimately obtain remarkable performance. Conductive Nano-Nets using carbon nanotubes, silver nanowires and copper nanofibers for transparent electrodes in solar cells, silicon Nano-Nets for high performance Li-ion battery anodes, and conductive paper and textiles for ultracapacitors and microbial fuel cells will be discussed in detail.

10. Three dimensional nanoscale assembly by folding

***David Gracias**, dgracias@jhu.edu.Chemical and Biomolecular Engineering, The Johns Hopkins University, Baltimore, Maryland 21218, United States*

Top-down fabrication which is based on lithographic patterning is an extremely precise and mature technology that can be utilized to pattern structures with nanometer scale resolution. Bottom-up paradigms seek to assemble materials and devices from constituent building blocks that interact with each other via physical forces or chemical linkers. In this talk, I will describe the self-assembly of lithographically patterned components into functional devices and materials. The highlight of our approach is that it enables the creation of materials and devices including polyhedral nanoparticles, drug delivery capsules and tissue scaffolds that are precisely patterned in all three dimensions. In addition to static structures, I will also discuss mechanisms to enable chemical stimuli responsive structures that spontaneously reconfigure on exposure to a variety of chemicals including solvents and even enzymes. These have allowed us to create tether-free tools for tissue excision and sampling.

11. Targeted CT nanoprobes for monitoring of cardiovascular diseases

***Marie-Christine Daniel**[1], mdaniel@umbc.edu, William Ghann[1], Daniel Gardner[1], Omer Aras[2], Thorsten Fleiter[3]. (1) Department of Chemistry and Biochemistry, University of Maryland Baltimore County, Baltimore, MD 21250, United States (2) Department of Radiology and Imaging Science and Molecular Imaging Program, National Institute of Health, Bethesda, MD 20892-1088, United States (3) Department of Diagnostic Radiology, University of Maryland Medical System, Baltimore, MD 21201, United States*

Gold nanoparticles (GNPs) conjugated with Lisinopril *via* amine, disulfide and dithiolate linkages were prepared by ligand exchange reaction between citrate-stabilized GNPs and lisinopril or a sulfur-containing derivative. The functionalized GNPs were fully characterized using various techniques. Chemical stability studies in biological relevant media such as phosphate buffered saline (PBS) solution, and in high salt concentration were conducted. Their relative stabilities toward lyophilization and against cyanide-induced decomposition were also investigated. Due to their high stability, lisinopril-thioctic acid gold nanoparticle conjugates were used to assess the targeting of angiotensin converting enzyme (ACE) using X-ray computed tomography (CT). The images obtained clearly indicated targeting of ACE, whose overexpression is associated with development of cardiac and pulmonary fibrosis. Thus the new nanoprobes prepared here will serve as very useful tools for the monitoring of cardiovascular pathophysiologies using CT imaging.

12. Kinetic pathways to the controlled self-assembly of inorganic nanocrystals in solution

***Zhihong Nie**, znie@umd.edu, Jie He, Yijing Liu, Taarika Babu, Zengjiang Wei.Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland 20742, United States*

The controllable self-assembly of nanoscale building blocks into larger specific structures provides an effective route for the fabrication of new materials with unique optical, electronic, and magnetic properties. The ability for nanoparticles to self-assemble as molecule does is opening up new research frontiers in nanoscience and nanotechnology. Great progress has been achieved in the organization of nanoparticles in solutions by tuning the surface chemistry of nanoparticles, as well as the selectivity of solvent quality. To date, most strategies for assembling such nanoparticles mainly relies on thermodynamic control, while there is still lack of kinetic means to realize controllable assembly.

This talk will present a new paradigm to the organization of nanoparticles into a diverse range of complex hierarchical nanostructures by controlling the kinetic pathways of assembly. This nanoparticle self-assembly is solely determined by the kinetic parameters of assembly process.

13. Magnetic hybrid materials for imaging and sensor applications

Anna Cristina S. Samia, *anna.samia@case.edu.Department of Chemistry, Case Western Reserve University, Cleveland, OH 44106, United States*

Nanoscale materials with high surface areas and quantum confinement effects possess unique size and shape-dependent optical, catalytic and magnetic properties. In particular, nanostructured magnets offer innovative prospects in emerging imaging and sensor technologies. The integration of magnetic nanoparticles (MNPs) in composite materials provides added useful functionalities including magnetic assisted separation, magnetic–based imaging and hyperthermia effects. In view of their great potential in bioanalytical applications, recent efforts have been made to combine different types of MNPs into bimodal nanocomposite materials, thereby allowing manipulation by an external magnetic field and simultaneous real time optical visualization. Different morphologies of magnetic hybrid nanocomposite materials have been fabricated in our laboratory. This presentation will provide a general overview of the approaches that have been adopted to prepare multifunctional MNPs such as core-shell magnetic-plasmonic nanostructures, matrix-dispersed MNPs and functional magnetic polymers. These nanostructured magnets are expected to find applications in bioimaging and miniaturized sensor devices.

14. Disrupting interparticle magnetic cross-talk within Fe_3O_4 nanocubes using FePt inclusions

K. L. Krycka[1], *kathryn.krycka@nist.gov, C. H. Lai*[2], *B. J. Kirby*[1], *C. L. Dennis*[1], *J. A. Borchers*[1]. *(1) NIST Center for Neutron Research, Gaithersburg, MD, United States (2) Dept. of Materials Science and Engineering, National Tsing Hua University, Hsinchu, Taiwan Republic of China*

Magnetite nanocubes are highly promising for their use as MRI T_2 contrast agents. 16.1 nm cubes of Fe_3O_4 (Sample A) produce a resistivity of 194 $mM^{-1}s^{-1}$ at 4.7 T, which can be improved to 360 $mM^{-1}s^{-1}$ at 4.7 T by using 14.7 nm Fe_3O_4 nanocubes with 4.1 diameter FePt inclusions (Sample B). Polarization analyzed small-angle neutron scattering is ideal for probing structural and magnetic morphologies [1]. This technique revealed that in powder form Samples A and B saturate to similar magnetic values, yet when the field is relaxed, the nanocubes form magnetic domains of 27.5 $\pm$ 1 nm (> single particle) for Sample A and 16 $\pm$ 1 nm (~ 1 nanoparticle) for Sample B. When solvated to 5 mg/ml only Sample A displays multi-particle magnetic domains of 5-7 nanocubes in length. We speculate that the primary function of the FePt is to disrupt the formation of long-range magnetic domains.

Food Analysis

15. Investigation of the “pine mouth” phenomena

Lowri S DeJager, *Ali Reza Fardin-Kia, Sara M Handy, Ernest Kwegyir-Afful.Center for Food Safety and Applied Nutrition, U.S. Food and Drug Administration, College Park, MD 20740, United States*

Over the past decade, consumers have reported taste disturbances linked to consumption of pine nuts. Between July 2008 and December 2011 the FDA received 482 consumer complaints, prompting a laboratory investigation by the Agency into the cause of the dysgeusia, known as “pine mouth”. Samples of the implicated nuts were analyzed for markers of rancidity (hexanal) and over 400 pesticides including the fungicide cycloheximide. Results of these analyses did not provide any direct correlation between the presence of the analytes and the incidence of “pine mouth”. Recent studies have suggested that the taste disturbance could be linked to *Pinus armandii*, a species of nut that was not commonly found in the US and European markets in the past. As a result, additional testing focused

on differentiation of the species of pine nut samples using fatty acid characterization and DNA-based methods. An overview of analytical methods and findings will be presented.

16. Sequence-based Subtyping and the Systematic Search for a Salmonella Solution

***Eric W. Brown**, Eric.Brown@fda.hhs.gov.Center for Food Safety and Applied Nutrition, U.S. Food and Drug Administration, College Park, MD 20740, United States*

The vast number of *Salmonella* serovars (> 2500) coupled with the highly homogeneous genetic composition of these strains underscores the need for new identification and subtyping strategies. The ability of a subtyping method to assign genetic relationships among outbreak strains is essential for effective epidemiological traceback. DNA sequence-based subtyping approaches provide more rapid and detailed genotypic information about strains. SNP-typing schemes, for example, focusing on hypervariable ORFs or spacer regions in the *Salmonella* chromosome can differentiate clonal lineages of *S.* Enteritidis. When tools for phylogenetic reconstruction are applied, predictive clues to phage-type are also imparted. Other methods shorten the time needed to type *Salmonella* strains. Technology that couples sequence diversity on the *Salmonella* chromosome with rapid mass-spectrometric detection provides detailed information for serological and molecular epidemiological relatedness in a single step. Development of facile typing methods enhances public health by allowing for the timely response and removal of contaminated foods.

17. Monitoring microbial metabolites by SPME, HSSE and SBSE GC-MS techniques

***Ray Marsili**, rmarsili@hotmail.com.Marsili Consulting Group, Rockford, IL 61108, United States*

This presentation will discuss GC-MS sample preparation techniques for detection of microbial metabolites that can generate off-flavors and malodors in foods. Four examples will be presented: (1) mold metabolite profiling from Petri dish cultures to distinguish *Penicillium* molds from non-*Penicillium* molds – a chemotaxonomic study; (2) off-flavor mold metabolites in a club cheese product; (3) identification of musty taint chemicals in casein powder samples; and (4) quantitation of geosmin in a pretzel product.

18. Targeted and non-targeted analysis of adulterants

***James Harnly**, James.Harnly@ars.usda.gov.Beltsville Human Nutrition Research Center,Food Composition and Methods Development Lab, US Department of Agriculture, Agricultural Research Service, Beltsville, Maryland 20705, United States*

A botanical identification method (BIM) is used to determine if a botanical material is the same as authentic, or reference, materials. It returns a binary result: YES, the sample is authentic or NO, it is not. The method requires identification of an inclusivity panel (authentic materials that must always give a positive result) and the exclusivity panel (adulterated or closely related materials that must always give a negative result). With targeted analysis, the adulterant is known and the level of adulteration can be quantified. Non-targeted analysis requires a general statistical process that compares the sample to the mean and variance of the inclusivity panel. A sample is authentic if it lies within the variance limit and adulterated, or not authentic, if it lies outside the variance limit. The level of adulteration is not quantifiable if the adulterant is not known.

19. Validating official methods for dietary fiber definition: Meeting the challenges of knowledge and definition changes

***Jonathan W. DeVries**, Jon.DeVries@genmills.com.Medallion Laboratories/General Mills Inc., Golden Valley, MN 55427, United States*

Nutritionally, dietary fiber is unique. Its benefits relate to its resistance to digestion rather than digestion and absorption. Dietary fiber consists of a complex mixture of digestion resistant components. Serious research on dietary fiber (1950-70) resulted in a definition by Trowell et al in 1976. AOAC International validated Official Methods 985.29, 991.42, 992.16, 993.19, 993.21, and 994.13 to match. As researchers have discovered and elucidated additional dietary fiber sources, there not only has been a perceived need to update the definition of dietary fiber, but to update the supporting methodologies. Recently, the CODEX Alimentarius Commission adopted an international, clarifying, single, concise, definition of dietary fiber that reflects the scientific findings of the past 5 plus decades. AOAC and AACC have validated two all inclusive methods (AOAC 2009.01, 2011.25 AACC 32-45, 32-50) commensurate with this definition. The importance and difficulty of matching in-vitro results to in-vivo results will be presented.

20. Single-run HPLC-UV-ELSD analysis of tocopherols, sterols and lutein from soybeans

***Margaret Slavin**[1], mslavin@gmu.edu, Liangli Yu[2]. (1) Department of Nutrition and Food Studies, George Mason University, Fairfax, VA 22030, United States (2) Department of Nutrition and Food Science, University of Maryland, College Park, MD 20742, United States*

The development and validation of a single extraction procedure and HPLC-UV-ELSD method for the analysis of tocopherols, phytosterols and lutein from soybeans will be discussed. The advantages and limitations of the method will also be reviewed in the context of alternative methods, particularly from the perspective of tocopherols, where the suitability of evaporative light scattering detection has been debated.

21. Analysis of commercial pet food for toxic and heavy metal content

***Patricia Atkins**, patkins@spexcsp.com, Vanaja Sivakumar, Ralph Obenauf.SPEX CertiPrep, Metuchen, NJ 08840, United States*

Consumers have doubled spending on the pet industry over the last decade. The American Pet Products Association reported that in 2009, pet owners in the US spent over $45 billion dollars with $17 billion dollars on pet food purchases.

The melamine pet food scare of 2007 affected millions of people. The illegal supplementation of protein sources with melamine and cyanuric acid caused a lethal complex of compounds that ultimately killed hundreds of pets.

This study determined if a variety of commercial pet foods (both wet and dry food) contained detectable amounts of heavy metal components (Hg, Pb, As, Cr, Co). Samples were uniformly ground using the SPEX SamplePrep Freezer Mill. Samples were digested using high purity nitric acid in a closed vessel microwave unit prior to analysis on ICP & ICPMS. Some samples showed high concentrations of potentially dangerous toxic components.

22. Use of wavelength dispersive X-ray fluorescence and discriminant analysis in the identification of the elemental composition of cumin and vanilla samples and the determination of the geographic origin

Kathryn Rotta[1]*, EHondrogiannis@towson.edu, Walter Roy*[2]*, Charles Zapf*[2]*, Ellen Hondrogiannis*[1]*. (1) Dept of Chemistry, Towson University, Towson, MD 21252-0001, United States (2) Analytical Science Group, McCormick Technical Innovation Center, Hunt Valley, MD 21031-1599, United States*

Wavelength dispersive X-ray fluorescence (WDXRF) was used to measure sixteen elements in 33 cumin spices from 4 different origins and 31 vanilla spices from 3 different origins for the purpose of determining the elemental concentrations to discriminate among the origins as a potential non-destructive screening method. Pellets were prepared of the samples and elemental concentrations were calculated based on calibration curves created using four NIST standards. A separate NIST standard, NIST 1573a (tomato leaves) was used as a validation check. Discriminant analysis was used to classify the samples by their geographical region. Validation of the model with the validation set yielded 100% accuracy for the vanilla samples and 87.5% accuracy for the cumin samples. Successful discrimination with just the seven (for vanilla) or eight (for cumin) elements will allow for higher throughput in the screening of vanilla samples using WDXRF for origin verification in less time.

Analytical Chemistry, Oral

23. Use of reversed-phase liquid chromatography / mass spectrometry in monoclonal antibody development

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Reversed-phase liquid chromatography (RPLC) is a robust technique that has been used for decades in small molecule, peptide, and protein drug development. The use of RPLC for monitoring monoclonal antibody (mAb) product attributes has been under utilized until recent years. Other analytical techniques (ion exchange, size exclusion, hydrophobic interaction, and capillary electrophoresis) are more commonly used for mAb analytics but do not provide direct compatibility with mass spectrometry. Recent interest in utilization of RPLC during mAb development is partially due to the direct compatibility of this technique with high resolution mass spectrometry (MS) and the overall robustness of RPLC. This work describes several applications of RPLC/MS with mAbs including intact glycan profiling, disulfide isoform assessment, isomerization and oxidation analysis, and alignment with process analytical technology (PAT) efforts.

24. Nitrate contents change during storage in lettuce and cabbage

Jinming Huang*, huang@uamont.edu, Nathan Probst, Samuel Pope, Trent Roberts, Mackenzie Willis.Department of Chemistry, University of Arkansas at Monticello, Monticello, Arkansas 71656, United States*

Nitrate and nitrite contents change in fresh lettuce and cabbage during storage were studied. Nitrate concentration was determined by electrochemical method with a nitrate ion selective electrode, while nitrite concentration was determined by Griess assay. Nitrate contents were found to be 1.778, 1.724, 1.109 mg/g for romaine, iceberg, and cabbage respectively. All tested vegetables contained nitrite less than 0.0002 mg/g. Nitrate contents reduced to less than 60% in the homogenized lettuce (romaine and iceberg), while nitrite contents increased more than 1100 fold after 8 days storage at 4 ^{o}C. The nitrate contents decreasing and nitrite contents increasing in homogenized iceberg lettuce were much faster when it stored at room temperature. In contrast, no nitrate contents decreasing and nitrite contents increasing observed in homogenized cabbage during the 8 days cold storage.

25. Chemical characterization of printing inks using spectroscopic and chromatographic techniques for forensic analysis of questioned documents

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The analysis of commercial printing inks, including toner and inkjet media, is important in forensic analysis for the classification and authentication of ink media used in the production of questioned or counterfeit documents. Inkjet inks and toners were examined using a variety of analytical techniques including Fourier transform infrared (FTIR) analysis, pyrolysis-gas chromatography/mass spectrometry (py-GC/MS), elemental analyses including laser-induced breakdown spectroscopy (LIBS), energy-dispersive (X-ray) spectroscopy (EDS), thin layer chromatography (TLC), and several microscopic methods. The spectral profiles obtained from these analyses may then be compared with known standards for the authentication and/or linking with other counterfeit documents. In addition, analysis of laminated (plastic) identity cards provides a unique perspective at their layered construction and the location of encased security features, such as holographic, laser perforation, and radio frequency identification (RFID) features.

26. DC magnetron sputtered polyaniline-HCl thin films for chemical sensing

Devon A Boyne, *dboyne@udel.edu, Nicola Menegazzo, Karl Booksh.Department of Chemistry, University of Delaware, Newark, DE 19716, United States*

Thin films of intrinsically conducting polymers are objects of continuing interest due to their unique chemical and physical properties. Polyaniline (PAni), when doped in an acidic medium, exhibits high conductivity, heavily dependent on the chemical structure and dopant type. In this contribution, a modified dry vapor deposition technique is applied to the preparation of thin films of PAni doped with HCl. This study employs a commercial DC magnetron sputter coater to deposit compressed PAni-HCl powder. Optical and structural characterization (UV-Vis, AFM, FT-IR and XPS) confirm the presence of PAni-HCl and show the films exhibit reduced roughness and continuous thickness. Evidence suggests structural changes and loss of conductivity, not uncommon during PAni processing, does occur during the preparation process. The applicability of these layers to gas sensing was also investigated with SPR spectroscopy. Layers exhibit quantifiable, reversible behavior upon exposure to ammonia gas with theoretical LODs as low as ~0.4 ppm.

27. Surface imprinted xerogels for binding tetracycline

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Different straight chain alkyl alkoxysilanes were used in preparing silica surface based tetracycline (TC)-imprinted xerogels using the sol-gel process. The different formulated surface imprinted xerogels were characterized for TC binding using radioactive labeled (^{3}H) TC. Results showed preferential binding in the ethoxysilane based xerogels in comparison to methoxysilane based xerogels. In addition, a computational approach using the interaction energy (IE) between TC and each alkyl alkoxysilane was used as a rational way of predicting the formulation that will provide the best analytical performance for a given molecularly imprinted xerogel (MIX). Results using Hartree-Fock (HF) calculations showed that there is an increase in IE as the carbon chain increases until an optimum value was obtained at C6 in both alkyl alkoxysilanes. This is in agreement with the experimental results where in the C6 xerogel formulation has the highest imprinting factor.

28. Real-time measurement of cell signaling: A quartz crystal microbalance with dissipation monitoring (QCM-D) study on MCF-10A cells

Marcela P Garcia[1], *mpg36@drexel.edu*, *Jennifer Chen*[1], *Ammar Shahid*[1], *Lynn Penn*[1], *Mauricio Reginato*[2], *Jun Xi*[1]. *(1) Department of Chemistry, Drexel University, Philadelphia, PA 19104, United States (2) College of Medicine, Drexel University, Philadelphia, PA 19104, United States*

Epidermal growth factor receptor (EGFR) plays an important role in cell growth, proliferation, motility, and differentiation. High levels of EGFR are associated with development of breast cancer as its resistance to treatment with cytotoxic drugs. In this study, we examine the role of EGFR and their downstream signaling pathways in human MCF-10A mammary epithelial cells. We used the quartz crystal microbalance with dissipation monitoring (QCM-D) to monitor cellular responses to EGFR signaling in human MCF-10A mammary epithelial cells when treated with epidermal growth factor (EGF). Cellular responses to EGFR signaling were detected based in mass and viscoelasticity of the cells. These responses were associated with EGF-induced biological processes including cytoskeleton remodeling.

29. High sensitivity terahertz spectrometry: An effective approach for nano- and pico-scale investigation

Anis Rahman, *a.rahman@arphotonics.net*, *Aunik K Rahman.Terahertz, Applied Research & Photonics, Harrisburg, PA 17111, United States*

Terahertz spectrometry offers unique capabilities by exploiting the so called “terahertz gap” (~0.1 THz to a few tens of THz). T-ray can penetrate almost all non-metallic objects, thus allows an opportunity to study intrinsic properties of materials in their native environment. For this study a terahertz spectrometer (TeraSpectra, Applied Research & Photonics, Harrisburg, PA 17111) was used. Calibration of the spectrometer and a measurement scheme was carried out by means of the front-end software. The Fourier transform process comprise of a number of different manifestations to suit the versatility of experiments. Further, built-in tools such as Prony frequency spectrum, auto regressive spectrum, and eigen analysis spectrum, allows one to learn details about the molecular properties such as the fine states of Fullerenes, chemical reactions, proteins and detergents in biopharmaceuticals, nanoparticle and ligand properties, label-free DNA hybridization and polymorphism, and others. Some details will be discussed in terms of experimental data.

Chemistry Classroom for the 21st Century

Presiding: W. Lacourse

30. Discovery learning: Pedagogy and the classroom

William R LaCourse, *lacourse@umbc.edu.Chemistry and Biochemistry, UMBC, Baltimore, MD 21250, United States*

The implementation of the Discovery Learning method of instruction was initiated in CHEM 101 in the fall of 2005. The major modification consists of the introduction of weekly two-hour “discovery learning” sessions for all students. In these sessions, students are divided into small groups of four, and they are given carefully crafted worksheets designed to guide them in their development of the ideas and principles that form the basis of the unit being studied. Thus, rather than the instructor promulgating theories, students are asked to develop them on their own (with appropriate guidance from an instructor). Through this method, students become engaged in their own learning and thinking, and they develop supporting skills in teamwork, communication, management, and assessment. Another important learning outcome is that of student responsibility and accountability for their own education. The physical environment and design of the classroom play a significant role in meeting this objective.

31. How learner analytics informs assessment of learning spaces

***John Fritz**, fritz@umbc.edu.Office of Information Technology, University of Maryland Baltimore County, Baltimore, MD 21250, United States*

Can activity be a proxy for engagement? Since 2007, UMBC students earning a D or F use our Learning Management System (LMS) 40 percent less than better performing peers. A similar pattern exists for students comparing their own activity with an anonymous summary of peers earning the same, higher or lower grade on assignments. Correlation is not causation, but are there parallels in physical learning environments using dedicated computer networks, labs, clickers and annotation devices? Can displaying their data back to users support the "flipped" or "inverted" classroom? Like many schools, UMBC has several "smart classrooms," however usage activity is typically reported by building and room, not by course, instructor or student. We've recently analyzed "smart room" usage against class schedules, and are exploring correlation with student grades. This presentation will explore if and how learner analytics might help identify effective practices and practitioners among students and faculty alike.

32. Building and sustaining robust STEM cohorts at a community college

***Candice J. Foley**, foleyc@sunysuffolk.edu, **Nina A Leonhardt**, leonhan@sunysuffolk.edu.Department of Physical Sciences, Suffolk County Community College, Selden, New York 11784, United States*

There is a need for more science, technology, engineering, and mathematics (STEM) professionals for the United States to remain competitive in the increasingly global economy. The attainment of full inclusion of students, from a diversity of backgrounds and achievement levels, in STEM education remains a tremendous challenge. This presentation will highlight a model of effective interprogrammatic collaboration among multiple grant funded STEM initiatives at a community college. Model elements include building a sense of community and belonging, social networking for support and sharing opportunities. In addition, exposure to STEM careers, discoveries and role models are critical. These efforts have coalesced into a model for achieving and sustaining new levels of STEM student collaboration and a strong community of successful STEM scholars.

33. Developing a marine biochemistry laboratory stimulates the study of chemistry

***Christian-Hailey Summa**[2], jwullrich@comcast.net, Samantha Stuart[2], Cong Nguyen[2], Jeffy Mathew[2], **John W Ullrich**[1], jwullrich@comcast.net. (1) Department of Chemistry and Biochemistry, Rosemont College, Rosemont, PA 19010, United States (2) Department of Biology, Rosemont College, Rosemont, PA 19010, United States*

Methods for stimulating interest in chemical research sometimes can be a challenge. We have recently begun building a marine biochemistry laboratory which allows students to explore the fascinating world of marine biology while learning the intricate chemical interactions between marine animals and the aquatic world which they live in. Coral reefs are among the most threatened marine ecosystems in the world. Worldwide surveys paint a sad picture showing that approximately half of the total area of coral reef systems has vanished during the last century. Effective protection of coral reefs is a worldwide concern and Marine Protected Areas (MPAs) have become important platforms for reef management as they promote responsible fishery practice and habitat protection. In addition, coral aquaculture, also known as *coral propagation* is showing promise as a potentially effective tool for restoring coral reefs. The design of the laboratory and coral aquaculture experimental systems will be described.

34. Fostering basic problem-solving skills in chemistry

***Fulgentius N Lugemwa**, ful4@psu.edu.Chemistry, Penn State York, York, PA 17403, United States*

Students learned to manipulate a given equation so that one of the variables is a product of the other two variables and used a triangle to solve a given problem. Problems relating density, mass, and volume; speed of light, frequency and wavelength; moles and liters were attempted using triangles. In addition, a special triangle was constructed to relate the variables and a constant of the ideal gas law equation, and was used to solve ideal gas law problems. This visual representation of the problem helped students to understand the factors that need to be considered and the operations that needed to be performed in the problem-solving process. Over the course of two years, the method was used in four different introductory chemistry classes that had a total of 87 students. More than 80% of the students who use triangles were able to arrive at the correct answers.

Frontiers in the Application of Computational Chemistry to Biological Systems A

Presiding: I. Thorpe

35. Calculation of the ionic atmosphere of DNA using 3D-RISM and molecular dynamics

***David A Case**, case@biomaps.rutgers.edu, Tyler Luchko, InSuk Joung, George Giambasu, Darrin York.Department of Chemistry and Chemical Biology, Rutgers University, Piscataway, NJ 08854, United States*

The ionic atmosphere around highly charged molecules, like DNA, involves the complex interplay of co-ions, counter-ions and water. The reference interaction site model (RISM) uses explicit molecular solvent models to provide an equilibrium sampling of solvent around a solute of arbitrary shape and size. Results are similar to those obtained from explicit solvent molecular dynamics but at a fraction of the cost. We will introduce RISM theory with special attention for thermodynamic qualities, such as preferential interaction parameters and solvation free energies and entropies, and will assess its ability to describe bulk solutions of various aqueous monovalent ions. We then evaluate the distribution of water and ions around a 24 base pair strand of DNA, comparing to MD results and experimental preferential interactions parameters. In both cases RISM gives the correct qualitative behavior and, often, the correct quantitative behavior.

36. Investigating the molecular basis for functional selectivity of G protein-coupled receptors using adaptive biasing techniques

***Marta Filizola**, marta.filizola@mssm.edu.Structural and Chemical Biology, Mount Sinai School of Medicine, New York, NY 10029, United States*

G protein-coupled receptors (GPCRs) are key players in numerous vital biological processes. Over the past decade, the traditional, two-state model of GPCR activity based on which a receptor exists in dynamical equilibrium between an inactive and an active conformation, has been consistently challenged. Mounting evidence suggests that different GPCR agonists acting at the same receptor (or the same ligand in different cellular environments) can activate different signaling pathways. At the molecular level, one possible, simple explanation for this so-called “functional selectivity” is that ligands with varied efficacies can shift the conformational equilibrium of a GPCR towards different receptor states, thus promoting selective activation of intracellular proteins. We have recently designed and tested on prototypic GPCRs a computational strategy that combines different adaptive biasing techniques to enable identification of ligand-specific receptor conformations along pre-determined activation pathways. These structural models can be used for structure-guided discovery of novel ‘biased’ ligands of GPCRs.

37. Activation and desensitization of a glutamate receptor

Albert Y Lau[1]*, alau@jhmi.edu, Benoit Roux*[2]*. (1) Johns Hopkins University School of Medicine, United States (2) University of Chicago, United States*

Ionotropic glutamate receptors (iGluRs) are ligand-gated ion channels activated by glutamate. The binding of glutamate and other synthetic agonist molecules to the extracellular ligand-binding domains (LBDs) of these receptors drives the opening of cation permeable transmembrane pores. Ligand-binding alters the LBD conformational free energy landscape, which provides useful reversible work for opening the gate of the transmembrane ion channel. After activation, the channel can close as a result of conformational rearrangements between LBD subunits that decouple agonist binding from activation in a process called desensitization. Using all-atom molecular dynamics simulations, we computed ligand-binding free energies for a set of different ligands to an AMPA receptor LBD using a methodology formulated on the basis of potentials of mean force. The results for full agonists, partial agonists, and antagonists are compared. We also computed free energy landscapes governing LBD conformational rearrangements important to desensitization. The results are compared with experimental measurements.

38. High accuracy protein active site structures from an integrated quantum mechanics and spectroscopy approach

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We have been developing quantum mechanics methods enabling highly accurate predictions of some 20 widely used spectroscopic properties with theory-versus-experiment correlation coefficient R^2 ~ 0.98. Together with experimental spectroscopic measurements, we have applied such calculations to active site structure refinement and determination for 15 protein systems of wide general interest, covering numerous electronic states, reaction states, and metal environments. Two examples will be discussed. We determined the first atomic level active site structures of myoglobin complexed with HNO, a recently recognized signaling molecule regulating many biological processes, such as vascular relaxation, enzyme activity, and neurological function. Our research also provided the first evidence of two unprecedented mechanisms by which proteins influence ferryl species, key intermediates in many heme enzymes. These results greatly elevate the significance of computational studies in protein structural investigations.

39. Enhanced sampling in the canonical ensemble for conformational sampling and determining free energies

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Progress with the development of improved Self Guided Langevin Dynamics (SGLD) will be presented. Three improvements include: (1) a reweighting procedure to correct for ensemble errors, (2) a SGLDfp method that directly generates a proper ensemble and is size extensive making this method appropriate for larger systems, and (3) a SGLD based replica exchange method (SGLD-REM) has been developed to extend the original method to larger systems. With ordinary molecular dynamics, barrier heights of 10kT are routinely crossed on the 10ns timescale. With SGLDfp this extends to 15kT, and with SGLD barriers heights of 20kT can be routinely crossed. Care is needed with these methods, because barriers as high at 30kT have been crossed, and this has led to unwanted cis-peptide structures in peptide simulations. Calculations of free energies differences, predict protein pKa values, and to generate atomic level structure consistent with electron microscopy data will be presented.

40. Hydration in biological computer simulations

***Toshiko Ichiye**, ti9@georgetown.edu.Department of Chemistry, Georgetown University, Washington, DC 20057, United States*

Water is the most important component of any living organism, and has many unique properties that make substitution of other liquids impossible. However, the ability to treat water properly in simulations of biological systems has been hampered by the potential energy functions used for water and by the computational speeds necessary to improve them. Here, the soft-sticky dipole-quadrupole-octupole (SSDQO) water model is shown to be a computationally fast and yet very accurate model of liquid water. More importantly, simulations with the soft-sticky dipole-quadrupole-octupole (SSDQO) water model are significantly different and more accurate for hydrophilic and hydrophobic solvation, which is important for biological macromolecules. New understanding of hydrophilic solvation is also presented.

41. Insights into the catalytic mechanisms of ribozymes from molecular simulations

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It remains an open question as to how molecules of RNA, which lack the diverse chemical functionality of proteins, can, in some cases, catalyze complex chemical reactions with efficiency that rival some enzymes. In this talk, I will present results from a series of molecular simulations that have mapped out a plausible catalytic mechanism where a divalent metal ion in the active site of the hammerhead ribozyme plays an active role in catalysis, and helps to resolve a long-standing debate over the interpretation of X-ray crystallographic and biochemical experiments. Further, recent computational results that, together with kinetic isotope effect measurements, provide new insight into the nature of the transition state in enzymatic and non-enzymatic phosphoryl transfer reactions.

Measurements and Methods in Environmental Nanotechnology and Nanotoxicology

Presiding: B. Nelson; V. Shah; E. Petersen; B. Marquis

42. Evaluating the environmental impact of engineered nanomaterials: An existential conundrum

***Delina Y. Lyon**[1], delina.lyon@howard.edu, Gregory V. Lowry[2], Mark R. Wiesner[3], Kimberly L. Jones[1]. (1) Department of Civil and Environmental Engineering, Howard University, Washington, D.C. 20059, United States (2) Department of Civil and Environmental Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, United States (3) Department of Civil and Environmental Engineering, Duke University, Durham, NC 27708, United States*

Predicting environmental impact of a chemical requires examining exposure and hazard; however, this approach may not yield useful data for engineered nanomaterials (ENMs) due to the transformations that ENMs undergo when exposed to natural media. When studying fate and transport of ENMs, investigators are stymied by inadequate models that do not account for acquired or lost coatings, ion release, and aggregation. For similar reasons, laboratory toxicity studies of ENMs often differ from effects seen in natural systems. Another challenge is coordinating the exposure and hazard studies to use the same ENMs under similar conditions. While a seemingly simple concept, such an effort requires coordination from all disciplines involved to agree on the logistical and technical parameters. This presentation will outline some of the major issues with predicting ENM impact on environmental systems, including characterizing ENMs, choosing relevant testing systems, and assembling interdisciplinary teams to address ENM risk.

43. Occupational safety in the nanomaterial workplace: Tools and resources for workers and employers

Kristen M Kulinowski[1], *kkulinow@ida.org, Bruce Lippy*[2]. *(1) Science and Technology Policy Institute, Washington, DC 20016, United States (2) The Lippy Group, Baltimore, MD 21228, United States*

As nanomaterial production and use continue to grow, workers and researchers employed in nanomaterial workplaces are among the populations most vulnerable to unwanted health effects due to unintentional exposures. Yet research focused on understanding and addressing occupational safety in these workplaces is scarce. Fewer than 5% of peer-reviewed publications addressing nanotechnology's potential environmental, health, and safety impacts deal with issues of direct relevance to occupational safety and health. This talk will review current knowledge about potential risks, describe employer attitudes toward safety, and introduce practical tools and training materials designed specifically for the nanomaterial workplace.

44. What's up in nano measurements in the environment

Barbara Karn*, bkarn@nsf.gov.Chemical, Biological, Environmental Technology, National Science Foundation, Arlington, VA 22230, United States*

This paper will discuss areas related to the measurements and methods for environmental nanotechnology and nanotoxicology. First, a summary will be given of efforts of a working group under the National Nanotechnology Initiative to identify and coordinate research areas in nanosensors applied to the environment and health. Then a brief overview of selected NSF funded research in nanosensors related to the environment will be discussed. The talk will conclude with a discussion of research needs in methods and measurements for environmental nanotechnology with some reference to nanotoxicology.

45. Evaluation of *Caenorhabditis elegans* as an alternative animal model for the assessment of nanomaterial toxicity

Piper Reid Hunt*, Piper.Hunt@fda.hhs.gov, Nicholas Olejnik, Robert L. Sprando.Department of Toxicology, United States Food and Drug Administration, Center for Food Safety and Applied Nutrition, Laurel, Maryland 20708, United States*

We report the findings of a pilot study designed to evaluate the usefulness of the nematode *C. elegans* as an alternative animal model in assessing nanoparticle toxicity. Advantages of *C. elegans* as a model organism include clear external structures which allow microscopic observation of internal organs in live animals, rapid progress through defined developmental stages, and amenability to genetic and multi-generational analyses. Preliminary results with 10 nanometer silver treatments suggest nanoparticle localization in pharynx, intestine, and eggs, a dose response relationship to larval growth rates, DNA damage, and reduced brood sizes. Organismal uptake of nanosilver was confirmed by ICP-MS. Significantly altered responses were observed with endotoxin contaminated nanoparticle preparations. Analyses are planned to assess the effects of differences in nanoparticle size and charge. If the predictive value of this model is confirmed by animal study results, it will provide a rapid and cost effective method of nanomaterial toxicity analysis.

46. Silver nanoparticle metrology for predicting environmental transformations

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Silver nanoparticles (AgNPs) are the engineered nanomaterial used in the greatest number of consumer products today. However, selecting appropriate materials for toxicity and environmental studies presents a decision – to perform hypothesis testing to gain a fundamental understanding of

nanomaterial behavior based on specific material properties, or to test only the materials predicted to be most environmentally relevant. This talk will present recent findings on how the AgNP surface interacts and reacts with its surrounding environment, including environmental waters, with the aim of better predicting what environmental compartments might be at greatest risk. The main focus will be the role and limits of metrology in understanding and characterizing transformations of AgNPs. By understanding how to characterize AgNP structures and properties, those structures and properties can be related to activities and potential transformations that enable better prediction of how AgNPs might behave if released into the environment.

47. Development of standardized dispersion methods for the environmental risk assessment of nanomaterials

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The evaluation of the environmental and health risks of engineered nanomaterials (ENMs) requires the dispersion of ENMs in relevant matrices (e.g., cell culture media). For ENMs in dry powder form, the source material must first be de-agglomerated in the test medium. The widespread use of ultrasonic treatment for the dispersion of ENM powders is inconsistently applied across laboratories and the lack of standardization has further contributed to observed variability.

We discuss the effect of sonication and medium specific parameters on the stability of ENM dispersions. Results presented here will focus on nanoscale TiO2 in aqueous media, phosphate buffered saline, and cell culture medium (Dubelcco's Modified Eagle Medium).

The optimized dispersion procedures are being issued as publicly available protocols, with the aim of enabling the reproducible dispersion of ENMs in relevant test media intended for Nano-EHS assessment, and the consistent reporting of dispersion preparation and characterization.

48. Titanium distribution in a swimming pool: The case for dissolution

R. David Holbrook[1], *dave.holbrook@nist.gov, Donna Motabar*[1], *Oscar Quinones*[2], *Benjamin D. Stanford*[2,3], *Shane Snyder*[2,4]. *(1) Science and Microanalysis Science Division, National Institute of Standards and Technology, Gaithersburg, MD 20817, United States (2) Southern Nevada Water Authority, Henderson, NV, United States (3) Hazen and Sawyer, New York, NY, United States (4) Department of Chemical and Environmental Engineering, University of Arizona, Tucson, AZ, United States*

The increased use of titanium dioxide nanoparticles (nano-TiO_2) in consumer products has raised concerns about their possible risk to human and environmental health. We report the occurrence, size distribution and behavior of Ti in a typical swimming pool. The [Ti] in the whole swimming pool water samples ranged between 20 and 60 µg/L and increased throughout the sampling period. [Ti] in tap water samples, however, remained relatively consistent, indicating that the [Ti] increase was due to an external source. The filter backwash [Ti] were much higher, suggesting a possible retention of Ti in the filter. The majority of the [Ti] (between 92 and 98%) was found in the dissolved phase, therefore only a minor fraction of the total [Ti] is nano-TiO_2. Although considered relatively insoluble, our results suggest that dissolution of nano-TiO_2 may be the mechanism most responsible for the observed increase in [Ti].

49. Impact of nanoparticles on *Nitrosomonas europaea* 19718

***Kartik Chandran**, kc2288@columbia.edu.Department of Earth & Environmental Engineering, Columbia University, New York, NY 10027, United States*

The rapid commercialization and application of nanomaterials raises concerns about nanoparticles (NPs) entering and impacting biological wastewater treatment plants. Of the different biological processes employed in wastewater treatment plants, nitrification is often the rate determining step. In this study, cultures of *Nitrosomonas europaea*,a widely studied nitrifying organism, were exposed to three different nanoparticles types (TiO_2, ZnO & CeO_2). In response, *N. europaea* cultures exhibited noticeable cell morphology changes. Although NP adsorption onto the cell envelope was not evident, intracellular NP accumulation was observed. Exposure to NPs also negatively impacted metabolic activity and functional gene expression. These results demonstrate that NP exposure could potentially impair wastewater treatment by virtue of interactions with key microbial protagonists at the metabolic and gene expression scales.

Remsen Award Symposium

Presiding: G. Meyer

50. CO_2 electroreduction catalysis for sustainable fuel synthesis

***Matthew Kanan**, mkanan@stanford.edu.Department of Chemistry, Stanford University, Stanford, CA 94305, United States*

Electrolytic synthesis of a C-based fuel powered by a renewable electricity source is an attractive strategy for sustainable fuel production because it enables the use of solar- or wind-derived electricity. To date, however, a CO_2 reduction catalyst that is efficient and functionally stable at high current density has not been developed. We have recently discovered that Cu electrodes prepared by reducing Cu_2O films exhibit catalytic properties that depend on the thickness of the initial Cu_2O film. Electrodes prepared by reducing µm-thick Cu_2O films require 0.5 V less overpotential than polycrystalline Cu for CO_2 reduction to outcompete H_2O reduction in CO_2-saturated aqueous bicarbonate solutions. This feature, combined with a high roughness factor, enables CO_2 reduction geometric current densities near the mass-transport limit at overpotentials less than 0.4 V. Insight into the nature of the active surface for CO_2 reduction will be discussed, as well as mechanistic information available from electrokinetic studies.

51. New platforms for conversion of carbon dioxide to chemical fuels

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The electrochemical reduction of carbon dioxide to carbon monoxide is an energetically uphill transformation. Accordingly, this transformation is an attractive candidate for conversion of solar energy into a versatile and energy rich chemical fuel. Systems that are known to promote this chemistry typically suffer from high overpotentials, low selectivities or require expensive precious metal catalysts. In addressing these shortcomings, we have developed a family of palladium and nickel based electrocatalysts that are supported by dicarbene pincer frameworks. These compounds have been characterized by a suite of analytical techniques and are efficient platforms for the electrochemical conversion of CO_2 to CO. In addition to describing the catalytic properties of these novel architectures, we will also discuss the molecular design principles that engender an efficient CO_2 activation chemistry.

52. Hydrogen and oxygen evolution with hangman catalysts

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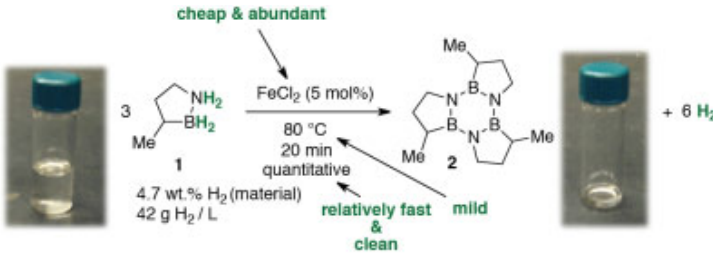
The greatest technological challenge facing our global future is the development of renewable energy. The capture and storage of solar energy at the individual level – personalized solar energy – drives inextricably towards the heart of this energy challenge by addressing the triumvirate of secure, carbon neutral and plentiful energy. Water splitting is a particularly attractive storage mechanism for solar energy. By recombining H_2 and O_2 at a later time, in a fuel cell reaction, the stored solar energy is effectively released. Electrochemical proton reduction for hydrogen generation from carbon neutral energy sources is also an attractive reaction. We have designed and synthesized various Hangman Porphyrins and Hangman Corroles bearing a xanthene backbone as catalysts to manage oxygen evolution, oxygen and hydrogen reduction reactions. These reactions require coupling of *multiple* electrons to *multiple* protons. Hangman catalysts are ideal for these reactions by placing an acid-base group above a redox-active macrocycle.

53. Hydrogen storage by carbon(C)-boron(B)-nitrogen(N) heterocycle materials

Shih-Yuan Liu Liu, *lsy@uoregon.edu, Wei Luo, Patrick G Campbell.Department of Chemistry, University of Oregon, Eugene, Oregon 97403-1253, United States*

The field of chemical hydrogen storage has been dominated by ammonia borane (NH_3–BH_3, AB) and its derivatives. A potential new hydrogen storage platform based on well-defined carbon(C)-boron(B)-nitrogen(N) heterocyle materials is described. I will disuss the development of a liquid-phase hydrogen storage material that is a liquid under ambient conditions, releases H_2 controllably and cleanly at 80 °C, and does not undergo a phase change upon H_2 desorption. Preliminary investigations into the mechanism of H_2 desorption will also be discussed.



54. Emergent quantum phenomena: New chimie douce methods for the synthesis of strongly correlated materials

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Correlated electronic systems, or materials in which electrons show cooperative effects rather than acting independently, are of interest not only for elucidating the origin of emergent behavior arising from simple components, but also due to the practical applications of the resulting physical phenomena. In this talk, I will first discuss the uses of strongly correlated systems in energy applications. I will also show how our development of new 'soft chemistry' methods for the preparation of meta- or kinetically-stable solids, when combined with modern pair distribution function techniques for determining local structure, is allowing us to finally begin to understand how correlated states, such as superconductivity, arise from local interactions of charge, orbital, and spin degrees of freedom.

Further, I will show how our results have profound implications for our understanding of the stability, mobility, and reactivity of ions in all solid state materials.

55. Designing metal oxides for high performance, visible-light photocatalysis: Toward solar Z-scheme water splitting

Bart M Bartlett.*Department of Chemistry, University of Michigan, Ann Arbor, MI 48109, United States*

Solar driven water oxidation for large-scale hydrogen fuel production from semiconductor photoelectrodes has the potential to provide energy on large scale from renewable, sustainable sources. Our research has focused on developing thin film metal oxide photoelectrodes by low-temperature, solution-based processes. Our most promising candidate, $CuWO_4$ has been synthesized by electrochemical deposition from aqueous precursors. The photocatalytic properties of this material were also evaluated by measuring the rate of methanol oxidation when illuminated with visible light, as well as using ferricyanide as a sacrificial electron acceptor. The former result hints that co-catalysts may prevent surface charge-carrier recombination, thereby increasing the rate of water oxidation. The latter result shows promise for overall water splitting at no applied bias using a redox mediator in conjunction with a photocathode for hydrogen evolution.

56. Building synthetic pathways for production of advanced biofuels in living organisms

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Living systems have evolved the capacity to carry out many chemical transformations of interest to synthetic chemistry if they could be redesigned for targeted purposes. However, our ability to mix and match enzymes to construct de novo pathways for the cellular production of small molecule targets is limited by insufficient understanding how chemistry works inside a living cell. Our group is interested in using synthetic biology as a platform to study how enzymes function in vivo and to use this understanding to build new synthetic pathways for the production of pharmaceuticals, nanomaterials, and fuels using living cells.

57. Illuminating redox chemistry in living systems

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The brain requires among the highest levels of metals in the body for normal function, including redox-active copper and iron, but misregulation of these metals is connected to aggregation and oxidative stress cascades that occur with aging and age-related neurodegenerative diseases. We have initiated a broad-based program to study the complex roles of metal ions and redox biology in brain health, aging, and disease by creating new fluorescent and MRI indicators to track metal ions and oxygen and sulfur metabolites in living cells, tissue, and organisms. The design, synthesis, and evaluation of our most recent platforms and their use in molecular imaging will be presented.

Advances in Chemistry of Fluorescence Measurements and Imaging Techniques

58. Molecular cancer imaging; New diagnostic technologies and beyond

***Hisataka Kobayashi**, Kobayash@mail.nih.gov.Molecular Imaging Program, NCI/NIH, Bethesda, MD 20892, United States*

Numerous of molecular imaging (MI) probes have been developed for obtaining *in vivo* target-specific information based on biology. MI probes especially focusing on each modality, each material, or each disease including cancer have been synthesized based on physics and chemistry. New MI probes with unique or multi-functional characteristics have been designed. This talk focuses on (i) MI modalities and signals which employ the full range of the electromagnetic spectra based on physics, (ii) optimized chemical design of MI probes for *in vivo* kinetics based on biology across all physical sizes, (iii) practical examples of new MI probes designed to extract complementary data from targets especially using activatable signaling focusing on cancer detection and characterization. Additionally, based on the similar multi-disciplinary strategy for developing the imaging technology, I will discuss about the newly-developed technology for the highly target-specific cancer therapy, named photo-immunotherapy, which can kill cancer cells leaving normal cells untouched.

59. Organic and biosensor indicator dye systems in cellular imaging and drug discovery

***Daniel Beacham**, dan.beacham@lifetech.com.Molecular Probes, Life Technologies, Eugene, Oregon 97402, United States*

Real-time imaging of physiological and metabolic pathways in cell-based assays remains an enabling technology in the biosciences, augmenting difficult biochemical and proteomic measurements with high-value spatial and temporal information about key analytes and processes underlying cell health, signalling, and SAR in biotherapeutics discovery. This seminar will cover the chemistry of dye-based and genetically encoded biosensor systems evolved for live cell imaging at the Molecular Probes campus of Life Technologies. Topics will include calcium imaging in drug discovery, next generation pH sensor dyes, and novel assays for cell stress, apoptosis, and oxidation. Biosensor and metabolic labeling technologies for autophagic signalling and proteosomal degradation will also be highlighted, with exemplar data and imaging recommendations for scientists from all backgrounds.

60. Human CD4+ lymphocytes for antigen quantification: Characterization using conventional flow cytometry and mass cytometry

***Lili Wang**, lili.wang@nist.gov.Biochemical Science Division, National Institute of Standards and Technology, Gaithersburg, MD 20899, United States*

To search for a biological cell reference material, we characterized commercially available cryo-preserved peripheral blood mononuclear cells (PBMC) and two lyophilized PBMCs, Cyto-Trol and PBMC-NIBSC relative to freshly prepared blood samples. It was found that the antibody bound per cell (ABC) values for CD4 expression on cryopreserved PBMC were consistent with those of freshly obtained blood samples. By comparison, the ABC value for CD4 expression on Cyto-Trol is lower and the value on PBMC-NIBSC is much lower than those of freshly prepared blood samples using flow cytometry and CyTOF™ mass cytometry. By performing simultaneous surface and intracellular staining and cell size measurements in addition to the investigation of the fixation effect on the detected CD4 level on these two cell samples, we concluded that the very lkow ABC value obtained for lyophilized PBMC-NIBSC is largely due to paraformaldehyde fixation; this significantly decreases available antibody binding sites.

61. Monitoring dynamic gene expression changes with quantitative time lapse imaging of GFP expressing NIH 3T3 cells

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Time lapse imaging of cells expressing GFP allows the measurement of dynamic gene expression changes in large numbers of single cells. From automated microscopy images acquired over several days, we quantified fluorescence intensities in individual NIH-3T3 fibroblasts derived from a clonal population that was stably transfected with a tenascin-C (TN-C) promoter driving a destabilized eGFP reporter. The measurements are challenging, requiring robust data acquisition and sophisticated image analysis routines. Advancing the analytical rigor of these measurements is critical. We examined several factors that can influence the quantitative GFP fluorescence measurement such as, stability of illumination, sensitivity to focus, background fluorescence, and photobleaching of the media and tissue culture plate. We have also developed methods to benchmark the analytical performance of the imaging system used to collect the data. We are using these quantitative, dynamic, single cell data to construct predictive models for changes in gene expression activity in the population.

62. Study of protein unfolding using extrinsic fluorescence compared to classical techniques

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The study of protein unfolding is of great importance since melting temperature, T_m, and transition enthalpy are useful indicators of protein stability. Protein unfolding can be measured by a variety of techniques methods such as UV absorbance and differential scanning calorimetry (DSC). Recently, a technique has been developed which uses a fluorescent dye reporter to monitor unfolding. The method, differential scanning fluorimetry (DSF), relies on specific dyes having different fluorescent properties in hydrophilic versus hydrophobic environments. As the protein unfolds, its hydrophobic regions are exposed, thus changing the environment of the fluorescent molecule. In this study, we compare T_m of the proteins using DSC and DSF of model proteins using different reporter dyes. Some of the model proteins we have studied include lactate dehydrogenase, myoglobin, and Rituxamab. While there is generally correlation in the melting temperature between the techniques, there are also important considerations in using the DSF method.

Analytical Chemistry, Poster

63. Extraction of alkylresorcinols (ARs) in food products composed of wheat (*Triticum aestivum*) with the use of a Dionex accelerated solvent extractor (ASE200)

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This research focuses on the extraction process of alkylresorcinols (ARs) from uncooked grains and baked products that have been processed with wheat, corn, rice, and white flour. Previously established extraction methods developed by Ross and colleagues, as well as a semi-automated method involving Accelerated Solvent Extraction were applied to extract ARs within ground samples. Comparison of AR extraction methods have been investigated with gas chromatography and a flame ioniza-

tion detector to quantify AR content. The goal was to validate accelerated solvent extraction of alkylresorcinols (ASE-AR) to the previous manual AR extraction methods. Results for this study as well as a spiking study indicated that it can be comparable to current extraction methods but with less time required. Furthermore, the extraction time for ASE (approx. 40 minutes) is much more convenient than previously methods, which range from 5 hours for processed foods to 24 hours for raw grains.

64. Retention mechanisms in HILIC chromatography: Important considerations for robust LC-MS applications

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Hydrophilic interaction liquid chromatography (HILIC) in conjunction with mass spectrometry (MS) detection has become a powerful tool for the LC-MS analysis of a wide variety of challenging analytes. Applications of the technique have increased dramatically over the past decade, especially for the analysis of polar analytes where reversed-phase chromatography suffers. HILIC conditions employ a high percentage of acetonitrile which enables facilitated solvent evaporation in LC-MS sources and thus often an increase in analyte response when compared to more aqueous based systems. The increased retention of polar analytes afforded by HILIC provides improved selectivity and decreases the impact of endogenous species, often leading to improved qualitative and quantitative analyses. In this report, studies investigating the underlying retention mechanisms dominant in HILIC chromatography are presented and discussed.

65. Microfabrication of single cell hydrogel array for studying cell volume regulation

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Here we present a new method of fabricating single cell array using a polydimethyl siloxane (PDMS) template and photocrosslinkable hydrogel. We constructed the hydrogel array on the glass surface by photopoymerizing a hydrogel precursor solution in the PDMS template. The fabricated array consisted of 25 × 25 circle shape microwells, each of which has ~20 μm diameter. The glass surface within the hydrogel well was coated with fibronectin to promote cell adhesion. Madin-Darby Canine Kidney (MDCK) cells were grown in the hydrogel well array. The occupancy rate of the single cells in the array was higher than 50 %. Cell viability test using Calcein-AM dye showed that most of the single cells were live. This single cell array will be used to screen and analyze the volume regulation of single cells, an essential regulatory function of cells in response to a change of solution osmolarity.

66. Improving the signaling, sensitivity, and affinity of electrochemical, aptamer-based sensors by using ultramicroelectrodes

***Melissa E Dávila Morris**, mdavila1@umbc.edu, James Taylor, Ryan J. White.Department of Chemistry and Biochemistry, University of Maryland Baltimore County, Baltimore, MD 21225, United States*

Electrochemical, aptamer-based (E-AB) sensors are specific, selective, and sensitive capable of detecting target analyte in complex matrices. Here we demonstrate increased sensitivity, improved binding affinity, and signaling properties of E-AB sensors through the use of in-house fabricated gold ultramicroelectrodes (12.5 μm radius) as compared to sensors on commercially available macroscale electrodes (1 mm radius). Specifically, by fabricating sensors employing a 23-nucleotide anti-ATP aptamer on small-area electrodes, we observe a 2-fold signal sensitivity increase and ~5-fold improve-

ment in observed binding affinity (K_d), with ultramicroelectrodes exhibiting a 20 μM affinity while the macro exhibit a K_d of 157 μM. Unexpectedly, we also see a polarity shift in the signaling of the sensor. That is, while macroscale anti-ATP sensors are signal-on, ultramicroelectrode sensors display signal-off behavior. We are currently further investigating this phenomenom but expect that the use of UMEs is a general method to improve E-AB sensor performance.

67. Comparison of α-solanine in organically and non-organically grown russet potatoes

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Glycoalkaloids, such as α-solanine, are naturally produced by plants as part of their defense mechanism against infection, pests, and other harm. This study attempts to quantify the amount of α-solanine in russet potatoes grown organically versus those grown using traditional growing techniques. Based on the compound's role in plant defense, it was hypothesized that potatoes grown organically would contain higher levels of α-solanine. The amount of α-solanine was measured using high performance liquid chromatography. The levels of α-solanine detected were 9.30+/-5.66mg/kg fresh weight in non-organic potatoes and 18.60+/-5.49mg/kg fresh weight in organic potatoes. These results indicate at the 95% confidence level that potatoes grown organically do in fact contain higher concentrations of α-solanine.

68. FT-IR spectroscopic characterization of *Halosimplex carlsbadense* cultures grown in varying conditions

***Tai H Chau**, thc116@psu.edu, **David J Aurentz**, dja5@psu.edu, Tami H Mysliwiec.Division of Science, Penn State Berks, Reading, PA 19610, United States*

Halosimplex carlsbadense is a halophilic archeaon that was isolated from a 250 million year old salt crystal from the Salado formation in New Mexico. The inability to use carbohydrates, amino-acids, fats or nucleic acids as nutrients suggests that *H. carlsbadense* possesses novel catabolic pathways or lacks membrane transport enzymes necessary to utilize such substrates. A detailed growth curve analysis was performed in order to gain more insight and to compare the growth characteristics of *H. carlsbadense* to that of other halophilic microorganisms. Growth of *H. carlsbadense* was optimized in a defined glycerol-acetate medium containing 25% NaCl with a pH of 7.4. A comparative analysis of cultures from optimal and sub-optimal growth conditions was performed to discern differences in the chemical functionality of the cellular population. Variations in the cell surface chemistry of *H. carlsbadense* were analyzed using attenuated total reflectance (ATR) Fourier transform infrared (FT-IR) spectroscopy.

69. Determination of trace organic constituents in FD&C Yellow No. 6 using solid phase extraction and ultra-performance liquid chromatography

***Nebebech Belai**, nebebech.belai@fda.hhs.gov.Office of Cosmetics and Colors, U.S. Food and Drug Administration, Center for Food Safety and Applied Nutrition, College Park, MD 20740, United States*

Color additives must be pre-approved and listed in the Code of Federal Regulations (CFR) before they may be used in products regulated by the U.S. Food and Drug Administration (FDA). FD&C Yellow No. 6 (Y6) is the disodium salt of 6-hydroxy-5-[(4-sulfophenyl)azo]-2-naphthalenesulfonic acid. The dye is manufactured by diazotizing 4-aminobenzenesulfonic acid followed by coupling with 6-hydroxy-2-naphthalenesulfonic acid. Y6 must be batch certified by FDA to ensure compliance with the requirements in 21 CFR 74.706, including specifications for three trace organic constituents: azobenzene (<200 ppb), 1,3-diphenyltriazene (<40 ppb), and 1(phenylazo)-2-naphthalenol (<10 ppm). Currently, these three impurities are determined using solvent extraction and reversed-phase high-performance liquid chromatography. We are exploring a solid phase extraction and ultra-performance

liquid chromatography method for more rapid and accurate determination of the impurities. Our preliminary results will be presented.

70. MALDI typing for discrimination of *Staphylococcus aureus* from *Staphylococcus epidermides* and *E. coli*

Khaled Abdallah, Sima Tokajian, ***Brigitte Wex****, brigitte.wex@lau.edu.lb.Department of Natural Sciences, Lebanese American University, Byblos, None None, Lebanon*

Matrix-assisted laser desorption ionization-time-of-flight mass spectrometry is increasingly used for identification of microorganisms in clinical settings, so called MALDI typing. In order to compete with phenotypic methods of identification, MALDI typing needs to be developed further to characterize bacteria not only to genus and strain level, but also to serotype and antibiotic resistance level. *Staphylococcus aureus* is emerging as threat for outbreaks in healthcare and community settings, particularly the growing number of antibiotic-resistant strains of *S. aureus* is of major concern. We present Maldi protein profiles of fourteen genetically well-characterized, local *S. aureus* isolates. Stringent data analysis and in-house developed software allowed the identification of five peaks (m/z 4823, 6428, 6612, 8903, and 9644) that are common to all *S. aureus* isolates. Compared to *S. epidermides*, three peaks were common in the genus *Staphylococcus*, two peaks common to the strain *S. aureus*, but no peaks were common with *E. coli*.

71. Determination of elements in color additives by ICP-MS analysis

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All certifiable color additives have limiting specifications for lead, arsenic, and mercury. In addition, FD&C Blue No. 1 and FD&C Green No. 3 have limiting specifications for chromium and manganese. It has been impractical to quantify the elements in each different color matrix, so the FDA has used wavelength dispersive x-ray fluorescence (WDXRF) to screen for elements over the specification limits. Interest in reporting quantitative values has led to development of an inductively coupled plasma-mass spectrometry (ICP-MS) method for efficient and reliable quantification of the specified elements at low (~1 ppm) levels. This method is currently being validated using several color additives (both water soluble and insoluble) with the highest demand for certification. Performance characteristics and strategies for overcoming difficulties with mercury and arsenic determinations are described.

72. Comparison of two spiropyran dyes for use in polymer-based chemical sensors

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Molecularly imprinted polymers (MIPs), in combination with spiropyran dyes, are able to be used as a transducing element in chemical sensors for the detection of metal ions. Two spiropyran dyes, 1'-(2-methacryloxyethyl)-6-nitro-spiro[2H-1-benzopyran-2,2'-indoline] (2C dye), and 1'-(6-methacryloxyhexyl)-6-nitro-spiro[2H-1benzopyran-2,2'-indoline] (6C dye) were synthesized and purified by flash chromatography. Structures of the 2C and 6C dyes were confirmed using proton NMR. Each dye has a different length carbon chain that terminates in a methacrylate group to facilitate incorporation of the dye within polymers. Results will be presented that compare the impact that the 2C and 6C dye chain lengths have on the binding ratio of the dye with different metal ions in solution. Results will also be presented that compare how the two dyes respond when incorporated into rigid polymer matrixes with different cross-linker concentrations, which are the basis of the MIP sensors.

73. Top-down analysis of intact proteins in complex mixtures

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Our goal is to develop an effective work flow for analysis of intact proteins using the LC-LTQ-Orbitrap, including front end chromatographic separation and the high resolution analysis of both precursor ions and product ions that is required to assign charge states and thus interpret the spectra. We have used standard proteins to optimize HPLC conditions and to compare three methods for ion activation and dissociation, and extended the method to analyze low mass proteins in cancer cell MCF7 cytosol and E.coli lysate. Cut-off filters and 2D HPLC are evaluated for sample preparation in these complex mixtures. Mixtures were injected onto a C3 column with flow rate of 300nl/min interfaced to an LTQ-orbitrap. The mass range of proteins identified across all experiments ranged from 4.2 kDa to 17.2 kDa . In a cytosol experiment using CID, twenty-five unique proteins were identified with modifications on 10 proteins.

74. Development of a sensitive fluoride sensor

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An imine-based colorimetric anion sensor has been synthesized. Benzothiazole derived salicylidene (Sensor **1**) displayed a highly selective colorimetric and spectrophotometric response to fluoride anion based on deprotonation process. The selective sensing of fluoride over other anions (CN^-, AcO^-, $H_2PO_4^-$, Cl^-, Br^-, HS^-, ClO_4^- anions) has been investigated in CH_3CN by visual color changes, UV–vis and fluorescence experiments. The addition of tetrabutylammonium salts of F^- to the solution of **1** caused remarkable color changes, turning from colorless to orange, which was clearly visible to the naked eye. However, the sensor showed no considerable changes on addition of other mentioned anions. Job's plots indicated the formation of a complex between **1** and fluoride at a stoichiometric ratio of 1: 2 in CH_3CN. The binding constants exhibited **1** as a sensitive and selective sensor for fluoride anions.

75. Amperometric detection of aqueous metals

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Metals are ubiquitous, persistent contaminants often found in the drinking water supply in cationic form. While some species such as Fe^{3+} or Mg^{2+} are essential micronutrients, others such as Pb^{2+} or As^{5+} are very toxic materials. This necessitates the development for a simple, cost effective, accurate, and sensitive method for detection and speciation of metals. Historically, metals detection has been done through optical methods (UV-Visible spectroscopy, Fluorescence, Luminescence, and Atomic Spectroscopy), mass-spectrometry, and electrochemistry. While many different electrochemical methods have been developed to perform these analyses, amperometry is by far the simplest with regards to instrumentation and ease of use. Applying a bi-potential step waveform first reduces and pre-concentrates the analyte on the electrode surface then oxidizes it producing an amplified and measurable current response. This research focuses on the development of a bi-potential waveform to detect Cu^{2+} in water at an Au-RDE using KNO_3/HNO_3 as the supporting medium.

76. Characterization of curcumin as anion sensor

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A simple-to-use colorimetric visual detection of anions(fluoride and Cyanide) using the natural product curcumin [1, 7-bis (4-hydroxy-3-methoxyphenyl) 1, 6-heptadiene-3, 5-dione] has been developed. In acetonitrile detection of fluoride and cyanide was very obvious relative to other anions with a red shift in the absorption at 424 to 75 nm. In 1:1 water acetonitrile, the color change was observed only in the presence of cyanide with a shift to 502 nm. Addition of aliquots of fluoride and cyanide ions to solutions of curcumin induced a well defined color change.and a dramatic change in the UV-vis spectrum. The color change differentiated cyanide, fluoride from AcO^-, $H_2PO_4^-$ from Cl^-, Br^- and ClO_4^- which showed no change.

77. Technical improvements of *in vitro* microdialysis sampling for monitoring bioprocesses

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Microdialysis sampling is a method that takes advantage of selective diffusion of small molecules out of a bioreactor by passing a perfusate fluid through the inside of a low-volume, tubular membrane. The dialysate can be assayed to develop a dynamic concentration versus time profile of the system under study. Microdialysis sampling of a bioprocess provides quenched sample that requires little or no sample preparation. Additionally, this technique does not require sample removal, minimizing sample handling and contamination issues associated with traditional bioprocess monitoring.

The benefits of using a computer programmable pump designed for precision fluid delivery, compared to the commonly used syringe pump, are demonstrated using *in vitro* microdialysis sampling of a carbohydrate-based enzymatic process. The products of the digestion are assayed by *in vitro* microdialysis sampling coupled on-line to high performance anion exchange chromatography and pulsed electrochemical detection.

78. Optimization and clinical testing of a microwave-accelerated metal-enhanced fluorescence (MAMEF) assay for the detection of *Chlamydia trachomatis*

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Chlamydia trachomatis (CT) is the most prevalent bacterial sexually transmitted infection reported to the Centers for Disease Control and Prevention (CDC). To address the need of sensitive and rapid diagnostic tests, we developed a Microwave-Accelerated Metal-Enhanced Fluorescence (MAMEF) assay and report on its optimization and testing with clinical samples. Our data suggest that aluminum "*bow-tie*" structures are as efficient as the gold structures in mediating the lysing and fragmentation of genomic CT DNA as demonstrated by the MAMEF assay. Deionized water is the most suitable buffer for re-hydration of dry swabs and subsequent lysing and MAMEF. Using MAMEF, a detection limit of 10 CFU/mL of CT was achieved in less than 5 minutes total time, which included the sample preparation time. There was an 83% concordance between MAMEF and clinical CT results. Our MAMEF platform is a significant step forward in the development of a point-of-care test for CT.

79. Evaluation of strategies for small-molecule analysis by MALDI mass spectrometry: What are the caveats and constraints?

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Matrix-assisted laser desorption/ionization (MALDI) is a mass spectrometric (MS) method of choice for the efficient and high-sensitivity characterization of biopolymers. However, the utility of MALDI/MS for small-molecule (MW < 800) analysis is much more problematic because the intense matrix signal can often interfere with the analysis. Consequently, MALDI has not been used extensively for the characterization of small molecules. To evaluate selected MALDI/MS methods to overcome or minimize this limitation, we randomly chose compounds (MW 170 - 785) from the Diversity Set of the NCI Chemical Database. All compounds were analyzed on a blinded basis with the stated structure unknown to the analyst. MALDI/MS survey methods included use of 2,5-dihydroxybenzoic acid and pencil lead graphite as matrices as well as direct laser desorption/ionization (LDI). Spectra were evaluated on the basis of their ability to indicate the correct molecular species. The advantages, caveats and constraints of these approaches will be discussed.

80. Assessing changes of cell adhesion using dissipation monitoring

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Cellular de-adhesion induced by epidermal growth factor (EGF) is a critical step of normal embryonic development, wound repair and regeneration, inflammatory response, and tumor cell metastasis. This process of cell de-adhesion exhibits a complex sequence of steps. We have developed a novel method using quartz crystal microbalance with dissipation monitoring (QCM-D) to monitor the changes in cell de-adhesion due to EGF induction in MCF-10A cells. We have successfully monitored changes in adhesion in a monolayer of MCF-10A cells. In addition we have identified the sequence of changes as a rapid de-adhesion step, followed by a transition step, and ending with a slow re-adhesion step. Lastly, we demonstrated the process of cellular de-adhesion process is regulated temporally by the downstream pathways of EGFR signaling. The QCM-D technique can be a useful application in studying other cellular processes and can potentially be a useful in vitro method for drug and biomarker screenings.

81. Amyloidogenic potential of hIAPP$_{22-29}$ is altered by aromatic ring substituents on Phe-23

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Amyloid fibril formation is a complicated process involved in such diseases as Alzheimer, Type II diabetes, Creutzfeldt-Jakob disease and promoted by different factors. One of possible causes of the amyloid fibril formation is pi-stacking of aromatic residues of the amino acids. In our work, we study aggregation of very short peptide fragment NFGAILSS which was determined in previous works as one of the units causing the aggregation in amylin or islet amyloid polypeptide (IAPP). We study the effect of various substituents on the aromatic ring of phenylalanine, which alter electronic structure of the ring. Aggregation rates were determined by using UV turbidity measurements at 405 nm. The result of the experiment showed that substitution on the aromatic ring of phenylalanine has an effect on the rate of aggregation. We also did fluorescence measurements to correlate the turbidity data with changes in the environment of the aromatic ring.

82. Transient absorption measurements for electron transfer in DMPD-coumarin and two coumarin control compounds

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Photoinduced electron transfer (ET) reactions have been extensively studied using model Donor – Bridge-Acceptor syetms. Our work describes kinetic experiments that were performed to study photoinduced electron transfer in DMPD-Coumarin where the DMPD-donor and the Coumarin-acceptor are separated by a single amide bond. This compound along with two controls: Coumarin-Pro-t-Butyl and Coumarin-aminopyridine, were prepared using literature procedure-[1]and were successfully characterized by MS and steady state spectroscopic techniques (UV-vis absorbance and fluorescence). ET kinetics in these compounds were studied in two ionic liquids using picosecond transient absorption. The photoinduced electron transfer reaction involved excitation of the Coumarin at 380 nm followed by reductive quenching from DMPD. Multiexponential kinetics were observed using ionic liquids which could be attributed to slower solvation dynamics in these charged media compared to neutral conventional solvents. Two control compounds were also studied under similar conditions and show no evidence of electron transfer in the fast timescale.

83. The fluorescence quenching of uric acid solubilized in bicontinuous microemulsion by nitrobenzene

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Uric Acid is known to be practically insoluble in aqueous and alcoholic media. However, it exhibits a reasonable solubility in a Bicontinuous Microemulsion system – a 15-fold increase in solubility in this system compared to its solubility in water. The bicontinuous microemulsion used is made up of a three component system – Dodecane-Surfactant-Water. Uric acid solubilized in this system is quenched by nitrobenzene. The obtained fluorescent data do not obey the Stern-Volmer equation. The modified Stern-Volmer equation was therefore used to analyze the obtained data. Only one third (1/3) of this compound is accessible to quenching. The Stern-Volmer quenching constant was calculated to be 229/M. The rest of the physico-chemical information will be discussed.

84. Effects of Marcellus Shale gas drilling wastewater discharge on trihalomethane formation

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This study examined the effects of untreated Marcellus Shale gas drilling wastewater on the formation of brominated trihalomethanes (THMs) in river water. Untreated Marcellus Shale gas drilling wastewater samples and three Pennsylvania river water samples were obtained and tested for bromide and total dissolved solids (TDS). Composites consisting of river water and gas drilling water were treated with chlorine, incubated and tested for THMs.

Results of the bromide testing determined levels in the river samples were below the method detection limits and 982 mg/L of bromide present in the gas drilling water. THM testing results indicated an increase in brominated THMs and total THMs (TTHMs) with additions of gas drilling wastewater. This study suggests gas drilling wastewater containing bromide as a potential factor for previous increases in THM formation in several Pennsylvania drinking water facilities.

85. Low dose risks from bromate: Drinking water exposures and chemistry and mechanism of risks in rats and humans

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This research examined the kinetics and metabolism and mechanisms of carcinogenicity of bromate that is regulated in drinking water at 10 ppb. Kinetics studies demonstrated rapid disappearance of bromate from rat blood *in vivo* and after oral and IV exposures. The 28 day rat studies demonstrated for the first time generation of organobromine compounds occurs *in vivo* in a dose response manner during bromate metabolism. 3-Bromotyrosine modified proteins were shown to accumulate in the rat kidney and testes. Renal tumors in male rats produced at high doses are likely, secondary to an α-2_u-globulin-induced nephropathy, and not observed in humans. Observed effects can be explained by non genotoxic mechanisms. We conclude that bromate cancer data from male rats are not appropriate as a basis for estimating cancer risk in humans.

86. Electrochemical decomposition of per and poly fluorinated surfactants (PFS) in plating industry wastewater

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A system was designed at scale to electrochemically treat plating line waste water and demonstrated that poly and perfluorinated surfactants (PFS) could be eliminated up to 99% efficiency. The treatment also reduced Cr+6 ion in the waste water. The process was effective for PFS in the water in the concentration range 1000 to 20000 microg/l (1ppm-20ppm). The process can be run with automated control system.

The fluorine containing surfactants were decomposed to HF and carbon dioxide under the strong acid electrochemical operating conditions.

A cost effective, analytical test was also developed to determine concentrations of 1H,1H,2H,2H-pol yfluorooctanesulfonate(H4PFOS).

The system is advantageous compared with alternate methods because of the significantly longer service life, higher capacity of the process and reasonable operating costs.

87. Improved air quality by reducing ammonia emissions from chicken manure

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In the Mid-Atlantic region, ammonia from animal husbandry operations is a significant source of particulate matter air pollution. Hale[1] suggested feed controls to reduce ammonia emissions via gypsum-zeolite infusion with crude protein reductions, and a follow-up study[2] calculated a 39% reduction of chicken manure ammonia. This strategy was simulated for May and June of 2002 in areas corresponding to chicken broilers within the Mid-Atlantic Northeast Visibility Union (MANEVU) region. Compared to a base-case scenario without ammonia reductions, a 37.5% decrease of $PM_{2.5}$ over the Delmarva Peninsula was observed, and during moderate $PM_{2.5}$ episodes in this region, six additional hours of compliance (15 $\mu g/m^3$ NAAQS standard) were gained.

Hale, C. E. III. (2005). Symp. State Sci.: Anim. Manure Waste Manage. San Antonio, TX. North Carolina State Univ., Raleigh.

Wu-Haan W., Powers W.J., Angel C. R., Hale III C. E., and Applegate T.J.. (2007). Poultry Science 86:182–190.

88. Field methods for rapidly characterizing contaminant leaching from the paint waste

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Removal of paint from bridges is a significant issue because of the potential release of contaminants and the consequent impact to human health and the environment. Samples from 24 bridges were evaluated with field-portable x-ray fluorescence (FP-XRF) for total concentrations. Other laboratory studies involve leaching experiments including the U.S. EPA toxicity characteristic leaching procedure (TCLP), multiple extraction procedure (MEP). Pb concentrations ranged from 6 mg/kg to 226,000 mg/kg in the paint waste, while Fe concentrations ranged from 7.2% to 99.5%. The elevated Fe concentrations are from the steel grit applied as a blasting agent for removing paint during bridge rehabilitation. Pb along with As, and Cr sorb to iron oxide coatings form on the steel grit surface, which results in reduced leaching. A model is being developed to mechanistically explain the results and will be used for predicting long-term leaching from the paint waste.

89. Scanning electrochemical microscopy of biomimetic membranes

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We seek to better understand the surface interactions that result from drug delivery to cellular membranes. To that end, we are studying biomimetic surfaces on gold substrates by scanning electrochemical microscopy. Tethered bilayers are created through the self-assembly of functionalized thiols and phospholipids and are characterized by cyclic voltammetry, approach curves, and current density area scans. Incorporation of selective protein channels will allow for localized regions of ion transport to be measured. Current work is focused on quantifying membrane formation using electrochemical quartz crystal microbalance and atomic force microscopy.

90. A donor-bridge-acceptor of the type $(bpy)_2 Ru^{II}$ – mcbpy – Pro_1 – Apy – $Ru^{III}(NH_3)_5$ prepared to study electron transfer kinetics in ionic liquids

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Electron Transfer (ET) reactions play a central role in biological processes as well as energy storage and generation applications. Our understanding of ET kinetics is based on experimental studies using model Donor-Bridge-Acceptor (D-B-A) molecules. Here we report on the synthesis of a metal derivatized D-B-A system of the type $(bpy)_2Ru^{II}$ mcbpy–Pro_1–apy$Ru^{III}(NH_3)_5$ where ruthenium metal centers are used as electron donor and acceptor. Steady state absorption spectra of the binuclear molecule showed charge transfer bands at 428 nm and 454 nm which are characteristic of the ruthenium metal centers. HPLC chromatogram of the target molecule showed a peak with a higher retention time compared to the Pro_1Apy$Ru^{III}(NH_3)_5$ starting material and with the spectral data dominated by a broad band around 450 nm characteristic of the ruthenium trisbipyridine metal center. The binuclear

complex thus prepared will be used to study electron transfer kinetics in novel charged solvent media known as ionic liquids.

91. Role of base excision repair genes OGG1 and APN1 in B[a]P-7,8-dione induced p53 mutagenesis

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Benzo[a]Pyrene (B[a]P) is the most common PAH studied. The metabolic product of B[a]P, B[a] P-7,8-dione (BPQ), damages DNA by the generation of reactive oxygen species (ROS). Two DNA repair genes in the BER pathway that repair oxidative damage are *OGG1* and *APN1*. To determine the role of OGG1 and APN1 in BPQ induced mutagenesis, we knocked out both genes in a yeast mutagenesis system for *p53*. We found that there was an increase in the mutation frequency and the number of of G:C/T:A transversions in *p53* treated with BPQ in *ogg1* yeast but the loss of APN1 had no effect. In addition we did not find a strand bias on *p53* treated with BPQ in *ogg1* yeast. These studies suggest that OGG1 is essential in repairing oxidative damage caused by ROS and that the stand bias seen in lung cancer may not be due to the repair of oxidative lesions.

92. Analysis of lead in $PM_{2.5}$ collected at the Kutztown University Air Monitoring Station using graphite furnace atomic absorption spectroscopy

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Ambient $PM_{2.5}$ collected during winter and summer pollution episodes in Berks County, PA were analyzed to determine the mass of lead per volume of air. Currently, two locations in Berks County do not meet the new 2008 Lead NAAQS. Samples were collected in one hour increments by a Beta Attenuation Monitor on a filter cassette. Samples were cut, extracted with trace metal grade acid, and analyzed using Graphite Furnace Atomic Absorption Spectroscopy. From the four pollution episodes analyzed during 2010 and 2011, the average lead concentrations for a one hour sample were typically 0.015 – 0.020 $\mu g/m^3$, with a maximum hourly lead concentration of 0.100 $\mu g/m^3$ for a pollution episode in winter, 2010. The hourly lead mass data was also correlated to wind direction, which consistently correlated to wind directions from the WSW.

93. Impact of the Chesapeake Bay climate and boundary layer dynamics on air pollutant concentrations during smog episodes

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As part of NASA's DISCOVER-AQ air quality campaign, the Delaware II NOAA ship equipped with ozone, nitric oxide and total reactive nitrogen analyzers measured air pollutants during a 10-day experiment in July 2011 over the Chesapeake Bay. Preliminary results show that ozone observations over the bay during the afternoon are often 10% - 20% higher than the closest upwind ground sites. We suggest that a combination of complex boundary layer dynamics, deposition rates, and unaccounted ship emissions are playing an integral role in the regional maximum of ozone over the Chesapeake Bay. Observations from this campaign were also compared to the Community Multiscale Air Quality (CMAQ) model. The model runs showed a regional maximum of ozone over the Chesapeake Bay, but the predictions are often 10-20% higher than observations. This comparison suggests that the boundary layer schemes in WRF and the CB05 chemistry scheme in CMAQ need improvement.

94. Reduction of nitrite and nitrate on pyrite

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Iron-sulfur particles and/or mineral surfaces have been implicated to provide the catalytic active sites for the reduction of dinitrogen on early(Hadean) Earth. We provide a combined kinetic, spectroscopic, and computational modeling study for an alternative source of ammonia from water soluble nitrogen oxide ions. The adsorption of aqueous nitrite(NO_2^-) and nitrate(NO_3^-) on pyrite(FeS_2) and subsequent reduction to ammonia was investigated at 22°C, 70°C, and 120 C. Batch geochemical and *in-situ* Attenuated Total Reflection–Fourier Transform Infrared(ATR-FTIR) spectroscopy experiments were used to determine the reduction kinetics to NH_3 and to elucidate the identity of the surface complexes, respectively, during the reaction chemistry of NO_2^- and NO_3^-. Density functional theory(DFT) calculations aided the interpretation of the vibrational data for a representative set of surface species. We detected the formation of nitric oxide(NO) intermediate on the pyrite surface. NH_3 production from NO_2^- occurred at 70, 120°C and from NO_3^- occurred only at 120°C.

95. Tabulation and development of a database of pesticides used in Delaware

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Approximately 42 percent of the State land is used for agriculture while 13% constitutes residential development. In order to manage pests (insects, weeds, nematodes, rodents), pesticides are used profusely to biologically control the normal pest's life stage. There are two major goals of this project: (1) extract chemical (including 3-D structure) information, log K_{o-w} (octanol-water partition coefficient), vapor pressure, and water solubility data from the manufacture's information packets of 62 pesticides (limited to pesticides whose packets contain a chemical structure) commonly used in Delaware; and (2) to build a database of these pesticides using Bio-Rad's KnowItAll® Informatics System available at Wesley. This research is funded in part, by a National Science Foundation (NSF) EPSCoR grant (EPS-0814251); the National Institute of General Medical Sciences (8 P20 GM103446-12) grant from the National Institutes of Health; a NSF ARI-R2 grant (0960503), and a DESGC NASA Undergraduate Tuition Award.

96. Determination of lead, mercury, iron and cadmium in rainbow trout from Donegal Lake

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The concentration of lead, mercury, iron, and cadmium have been determined in rainbow trout (*Oncorhynchus mykiss*) from Donegal Lake, PA.

97. Determination of trace metals in venison from white-tailed deer from Western Pennsylvania

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The concentrations of mercury, nickel, copper, arsenic, cadmium, lead, manganese, and zinc have been determined in venison from white-tailed deer from Western Pennsylvania.

98. Reactions of amine and amine radicals with molecular oxygen in atmospheric and combustion chemistry

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Recently there has been a report in J. Phys. Chem. letters by da Silva et al.[1] that reactions of amine hydrocarbons radicals with O_2 proceed to products involving double bond formation: an imine plus HO_2•. We studied thermochemistry and kinetics of reactions of several amine and amide radicals with O_2 and subsequent reactions of imines formed with OH and O_2 and transition states. Standard enthalpy, entropy and heat capacities were calculated by B3LYP/6-31G(d,p) DFT and composite CBS-QB3 methods. Kinetic parameters were determined by Transition State Theory and chemical activation reactions of OH addition and O_2 association were analyzed by quantum Rice Ramsperger Kassel analysis for k(E) and Master Equation for pressure falloff. The kinetic analysis yielded elementary reaction rate parameters for modeling reactions of amines and amides in atmospheric and combustion environments.

1, Gabriel da Silva et al.; J. Phys. Chem. Lett., 2012, 3, pp 805-811, DOI: 10.1021/jz300118k

99. Screening of tobacco products for flavor compounds using solid-phase microextraction gas chromatography mass spectrometry

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A rapid method for flavor screening in tobacco products is evaluated. The sample preparation was minimal. Headspace sampling of the different products was performed using solid-phase microextraction (SPME). Different SPME fibers were evaluated for optimun extraction and screening of flavors in tobacco products. Two different capillary columns were investigated in this study. Initial results indicate that the application of SPME GC/MS method has the potential for rapid screening of various flavor compounds in tobacco products. Results obtained from this study will be presented.

100. Identification of volatiles in coffee extracts, essences, and distillates by HS-GC-MSD

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The goal of the present study was to develop a headspace GC-MSD method that allows the Alcohol and Tobacco Tax and Trade Bureau's Nonbeverage Products Laboratory (NPL) to identify specific volatile chemicals in coffee extracts, essences and distillates to make a determination that the product is unfit for beverage purposes by comparing them to the NPL's guidelines. If a product meets the NPL's guidelines, the manufacturer may be able to claim a return on most of the excise tax paid on the alcohol used to produce the product.

101. Development of *in vitro* neuronal cell-based assays for screening food and cosmetic-related compounds

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In vitro cell-based assays using a rat neuron-like cell line (PC12) have been established to evaluate substances in foods and cosmetics that may adversely affect the nervous system. A series of fluorescence assays are being implemented to identify and assess cellular toxicological mechanisms of action including cell viability, oxidative stress, mitochondrial membrane potential, and membrane depolarization-induced calcium influx. The pesticide 2,4-D was less toxic (EC_{10}, 1 mM) than rotenone (EC_{50}, 5 µM). Other compounds tested including mercuric chloride and phenylmercuric acetate had viability EC_{50} values of 30 µM and 9 µM, respectively. Phenylmercuric acetate and rotenone both depolarized mitochondrial membrane potential. Incubation with calcium channel blockers (positive controls) nifedipine and verapamil above 5 µM reduced calcium influx. None of the compounds increased oxidative stress. Ultimately, these in vitro assays may serve a part of high-throughput screening battery that result in the reduction and refinement of animal testing.

102. Examination of fluoride levels in beverages commonly consumed by children

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Excessive fluoride exposure in children can cause dental fluorosis, a condition characterized by defects in the enamel of the teeth. The recommended levels of fluoride intake for children are 0.05-0.07 mg/kg/day. At these levels, there can be a beneficial effect; higher levels, however, can lead to dental fluorosis. It is estimated that 32% of American children have some form of fluorosis. Exposure to fluoride can be due to beverages, food, dietary supplements, and toothpaste. This project focused on examining the concentration of fluoride ions found in beverages commonly consumed by children. High levels of fluoride in some beverages can lead to excessive exposure to fluoride especially if diets are supplemented with fluoride. To assist in preventing dental fluorosis, parents and medical/dental practitiononers need to be made aware of any beverages that may expose children to fluoride levels which may put them at risk for developing dental fluorosis.

103. Bioactives-enriched fruit beverage formula for cardio-protection

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Cranberry (*Vaccinium macrocarpon* L), blueberry (*Vaccinium angustifolium* L.), apple (*Malus domestica* L.) together with ginger (*Zingiber officinale*) and some cardio-protective amino acids, vitamins, and minerals were used for formulation of a functional beverage targeted for potential reduction of the risk of cardiovascular diseases. Bioactive content in fruit juices were increased using reverse osmosis. Ultrasonic assisted extraction was used for ginger. A Physico-chemical properties, sensory properties, antioxidant capacity and ability to inhibit the oxidation of low density lipoprotein (LDL) *in vitro* by the functional beverage were assessed. Total phenolic content, FRAP and percent inhibition of copper-induced LDL oxidation of the ginger extract were 460 mg-GAE/L, 225.58 mg-TE/L and 42.74% respectively. Based on sensory evaluation, fortification of selected functional ingredients at 10% RDI was selected. Phenolic content and *in vitro* antioxidant activities (FRAP and % inhibition of LDL oxidation) of the final functional beverage formulation were 1023.9±45.3 GAE/L, 3113.5±247.8 TE/L, 45.2±9.9%, respectively.

104. Antioxidant properties and sensory attributes of four different fruit vinegar beverages

***Ruchira Nandasiri**, nandasirir@nsac.ca, Vasantha Rupasinghe, Nancy L Pitts.Department of Environmental Science, Nova Scotia Agricultural College, Truro, Nova Scotia B2N2R9, Canada*

Apple, blueberry, cranberry, and tomato are some of the antioxidant-rich fruits widely consumed in North America. Bio-active compounds of above fruits are suggested to have several health benefits. Identification of specific fruits and concentration of acetic acid with consumer acceptable sensory attributes are required to develop and assess potential health benefits of fruit vinegar beverages (FVB). It is hypothesized that specific bio-actives i.e. anthocyanins (blueberry, cranberry), carotenoids (tomato), flavonols and flavanols (apple) present in the selected four FVB could provide specific health benefits. In the current study, sensory properties of four FVB that were prepared from apple, blueberry, cranberry, or tomato with 0.5%, 1.0%, and 1.5% of acetic acid concentrations were assessed using 18 trained panelists. Results indicate there was a significant difference in 0.5% acetic acid concentration compared to other concentration levels ($P<0.05$). Antioxidant capacities of FVB were assessed using FRAP, ORAC and DPPH radical scavenging activity assays.

105. Investigation of possible changes of amount and micro structure of iron species within a plant

***Sumudu S Dehipawala**[1,2], sdehipawala926@yahoo.com, Agoudavi Yao Djifa[2], Sunil Dehipawala[3]. (1) Bio Chemistry, SUNY Stony Brook, Stony Brook, NY 11790, United States (2) Physics, Queensborough Community College, Bayside, NY 11364, United States (3) Physics, Queensborough Community College, Bayside, NY 11364, United States*

Extended X-ray Absorption Fine Structure (EXAFS) and X-ray Absorption Near Edge Spectroscopy (XANES) are well known techniques to study the local environment of atoms in non-crystalline substances. In this study we used Synchrotron X-ray radiation from National Synchrotron Light Source to probe iron species present in different areas of a carrot plant. Samples were collected from different regions of same carrot plant such as roots, stem, mature and young leaves. Samples were then dried at 200^0C and grounded to fine powder. From the height of main absorption edge the amount of iron in each sample was determined. The energy position of the main absorption is sensitive to the chemical nature of the iron compound present in each sample. According to our data, there is no significant difference of chemical nature of iron species in different regions of a carrot plant but the amount of iron varies in each region.

106. Biocatalytic preparation, structural elucidation and biological evaluation of long chain (C_{18}-C_{22}) acylated derivatives of flavonoid glycosides

***. Ziaullah**, ziaullah@nsac.ca, Khushwant Singh Bhullar, H.P. Vasantha Rupasinghe.Department of Environmental sciences, Nova Scotia Agricultural College, Truro, Nova Scotia B2N 5E3, Canada*

Our present investigation describes the regioselective enzymatic acylation of Phloridzin and Quercetin-3-glucoside in high yields with different long chain saturated, mono- and poly-unsaturated fatty acids using immobilized lipase B from *Candida antartica* (Novozym 435®) in acetone at 45 $^oC^{1-3}$. The synthesized esters have been evaluated for their antioxidant capacities and selected biological properties such as antihypertensive, antimelanoma and anti-HIV *in vitro*.

107. Analysis of coffee for the presence of endosulfan using GC/MS

Will R Bringgold[1]*, Kishore.Bagga@drexelmed.edu, Kishore K Bagga*[1]*, Kevin Owens*[2]*. (1) Office of Professional Studies in the Health Sciences, Drexel University College of Medicine, Philadelphia, PA 19102, United States (2) Department of Chemistry, Drexel University, Philadelphia, PA 19104, United States*

Endosulfan has been shown to result in liver toxicity and is a known neurotoxin, subsequently it has raised concerns over its use in coffee production. Before this project, there had been no studies on the detection of endosulfan, or any other pesticides, in the cups of coffee that individuals drink everyday. Several coffee brands and their organic counterparts were investigated for the presence of endosulfan. The coffees were ground into a fine powder, mixed with water and filtered, thus making a cup of coffee. A liquid-liquid extraction was performed on the resulting solution using ethyl acetate. The recovered ethyl acetate extract was analyzed using a GC/MS for endosulfan. The data indicated the absence of any endosulfan above a sensitivity of one part per billion; which is below the accepted daily intake value for endosulfan.

108. Raman spectroscopic studies of the intermolecular interactions in acetonitrile, propionitrile and butyronitrile solvents

Busuyi Oloye*, boloye1@students.towson.edu.Department of Chemistry, Towson University, Towson, Maryland 21252-0001, United States*

Acetonitrile has been widely used as a solvent. However, its structure is still not fully understood. In the present study, we investigated intermolecular interactions of acetonitrile (CH_3CN), propionitrile (CH_3CH_2CN) and butyronitrile ($CH_3CH_2CH_2CN$) with H_2O, Ag^+ and Mg^{2+} ions using Raman spectroscopy. The C≡N stretching in the nitriles, which occurs at about 2200 cm^{-1}, is sensitive to the interactions between the nitriles and the metal ions/H_2O. It was found that H_2O, Ag^+ and Mg^{2+} were attracted to the lone-pair electrons on the CN groups of the acetonitrile, propionitrile and butyronitrile molecules. For all nitriles, the C≡N stretching was shifted to higher wavenumbers by about +6 cm^{-1} with H_2O, +20 cm^{-1} with the Ag^+ ions, and +40 cm^{-1} with the Mg^{2+} ions.

Best Practices for Successful Online and Hybrid Courses / Innovation in the Chemistry Lab

Presiding: L. Montgomery

109. Using the QM process to develop and teach quality on-line courses

Wendy Rappazzo*, wrappazzo@harford.edu.Department of Biology, Harford Community College, Bel Air, MD 21015, United States*

QM (Quality Matters) is a nationally recognized, faculty-centered, peer review process that is used to certify quality online and hybrid courses. The review process utilizes a rubric in order to determine whether a course will receive certification as a quality designed course. The rubric provides an easy tool for instructors to develop, assess, and improve online courses. It consists of eight general standards such as course overview and introduction, assessment and measurement, and learner interaction and engagement. This session will give an overview of the QM process, the rubric, and how it has been used to create and maintain high quality online courses at Harford Community College.

110. Analyzing student success in the chemistry classroom by monitoring online homework activity

***Charles R. Bowman**, bowmancr@drexel.edu, Daniel B. King.Department of Chemistry, Drexel University, Philadelphia, PA 19104, United States*

It is expected that exposure to chemistry problems using online homework will improve student performance in chemistry. A study was conducted to see how student usage of an online chemistry homework system (OWL) correlated with student success in a general chemistry course. Online chemistry homework activity was examined for first-year students taking general chemistry at a mid-size, private university. The six different chemistry problem sets examined were: bond properties; standard molar enthalpy; electronegativity; Lewis dot structures; calorimetry; and stoichiometry. Students' OWL activity was then correlated with their exam grades and their final course grades. Results showed that higher average time spent per problem correlated positively with student success as measured by final grades. However, multiple attempts per problem correlated negatively with student success. Recommendations for instructors are made on how to identify chemistry topics where students may need additional instruction to improve their understanding.

111. Challenges and strategies of teaching online and hybrid chemistry courses to community college students

***Hoa Cost**, hcost@ccbcmd.edu, **Laurie Montgomery**, lmontgomery@ccbcmd.edu.Department of Physical Science, Community College of Baltimore County, Baltimore, MD, United States*

Community college students are extremely diverse in terms of their academic abilities, learning styles, and college course load (full versus part-time). Surges in enrollment and the need for flexible course schedules have lead to an increased demand for online and hybrid chemistry course offerings. Online and hybrid courses pose unique challenges compared to the traditional classroom lecture. Some of these challenges include higher attrition rates and poor success rate. Attrition rates may exceed 50% or higher (per section) and success rates ("C" or better) are on average 10-20% lower than traditional lecture courses. The high withdrawal rate and poor success often stems from the fact that these students often do not recognize the amount of work and commitment needed to take online and hybrid courses. Several strategies have been implemented at the Community College of Baltimore County to help promote student success and retention.

112. Organic chemist's development of a medicinal chemistry course

***Mark F Harris**, mharris@washjeff.edu.Department of Chemistry, Washington & Jefferson College, Washington, PA 15301, United States*

In recognition of the pre-health interests and aspirations of many of the science students at Washington & Jefferson College, a junior/senior level course in medicinal chemistry was developed and has now been offered several times. Courses in medicinal chemistry are still fairly uncommon at small liberal arts colleges such as Washington & Jefferson. Our course serves as a popular advanced elective for both chemistry and biochemistry majors. The author, whose training is in organic chemistry, will describe the steps taken to develop the medicinal chemistry course, as well as the specific structure and content of the class.

113. Structure identification of carbohydrates and nonnutritive sweeteners: Experimental exercise for undergraduate chemistry laboratories

***Ann E. Shinnar**, ann.shinnar@touro.edu.Department of Chemistry, Lander College for Men/Touro College, Kew Gardens Hills, New York 11367, United States*

As part of our undergraduate organic chemistry curriculum, we have developed a laboratory session to identify an unknown sweetener, either natural, semi-synthetic, or synthetic. This experimental exercise, integrated with lecture, illustrates classic chemical reactions of carbohydrates and reveals structural features of nonnutritive, low calorie sweeteners marketed for consumers. Experimental protocols involve a variety of chemical tests for functional groups: Jones' test for alcohols; Beilstein flame test for halogens and alkali metal salts; formation of hydrazones from carbonyls and 2,4-dinitrophenylhydrazine; Tollens test for reducing sugars; ninhydrin reaction for amines. Physical tests include melting point determination and FTIR spectra. Unknown sweeteners comprise: acesulfame potassium, aspartame, sodium saccharin, D-sorbitol, sucralose, and sucrose. For control tests, natural mono- and disaccharides are provided. Identification of the unknown can be completed in one laboratory session. The experiment can also be adapted for other undergraduate laboratories, including biochemistry and general chemistry for allied health sciences.

114. How to use the book *African American Women Chemists* to teach chemistry and history

***Jeannette E Brown**, jebrown5134@comcast.net.retired chemist, unassigned, Hillsborough, New Jersey 08844-4816, United States*

Do you know the name of the first African American Woman to head a department of chemistry? Do you know that an African American woman invented the nitrate explosive detector used by Homeland Security at the airport? Do you know that an African American woman formulated a medicine used to cure Leprosy?

This and other information is found in the book African American Women Chemists. In this paper I will give information about curriculum materials that can be used in the K-12 class room using this book and also how it can be used in college history of science and or women in science courses.

Frontiers in the Application of Computational Chemistry to Biological Systems B

Presiding: A. Mackerell

115. Biophysics of a genetic switch: The *lac* operon

***Kim A Sharp**, sharpk@mail.med.upenn.edu, Mitchell Lewis.Department of Biochemistry and Biophysics, Univ. of Pennsylvania, Philadelphia, PA 19104, United States*

The thermodynamics, kinetics and stochastic behavior of lac repressor-operator-inducer binding have been obtained from recent directed evolution and biophysical measurements. This behavior elucidates the 'design principles' of the lac operon as a genetic switch, and throws light on the principles of allostery and sequence specific recognition of DNA. Application to the design of a better regulatory switch for transgene therapy is discussed

116. Putting the statistics back in statistical mechanics

***Michael R. Shirts**, michael.shirts@virginia.edu.Department of Chemical Engineering, University of Virginia, Charlottesville, Virginia 22904, United States*

Statistical mechanics provides the connection between molecular scale details and macroscopic thermodynamic properties. Traditionally, analytical approaches such as mean field approximations and integral equations have been used to simplify the complicated multidimensional integrals statistical mechanics gives us. This approach breaks down when dealing with the molecular details of biomolecular systems. As computers have become increasingly powerful, they have allowed us over to explore the statistical mechanics of more and complicated biological systems by instead sampling from physical probability distributions. In this talk, I will examine ways that powerful new (and not-so-new!) techniques borrowed from statisticians can be reapplied in physical contexts to accelerate biomolecular simulations and more efficiently analyze the simulation data collected.

117. How important is charge transfer in biological systems?

***David J Diller**, djrdiller@gmail.com.ddiller consulting, East Windsor, NJ 08520, United States*

The vast majority of molecular modeling studies rely on fixed point charges to model electrostatic molecular interactions. In this presentation, we explore the consequences of this approximation. We describe the development of a simple charge transfer model. The model was trained and tested on ab initio quantum mechanical calculations on small molecules. We show that it remains stable on biological molecules and demonstrate that the changes in electrostatic interaction for many protein-ligand complexes are greater than 10 kcal/mol. Finally, we discuss some of the pitfalls encountered and the outstanding issues to make the model practical.

118. Conformational analysis of antibody CDRs using diffusion maps

***Roland Dunbrack**, Roland.Dunbrack@fccc.edu.Fox Chase Cancer Center, Philadelphia, PA 19111-2497, United States*

Antibody structure analysis and structure prediction has long depended on the clustering of the CDR conformations by Chothia et al. in the 1980s and 1990s. We recently performed a clustering of each CDR based on length and conformation using a data set f over 300 antibodies, a dihedral angle metric and an affinity propagation algorithm. Most of Chothia's clusters have held up over time and we have identified several novel clusters. We have used diffusion map methods, developed for analyzing MD simulations, to analyze the structural variation within each cluster. Diffusion maps are a form of multidimensional scaling that projects structural variation onto a small number of coordinates. We show that the probability densities over the diffusion map coordinates for each residue type at a certain position can be used to identify structure-determining residues in a quantitative fashion. This is useful for both antibody structure prediction and design.

119. Computational chemistry applications in drug discovery: From atoms to gene to clinic: What works, what doesn't

***Terry R Stouch**, tstouch@gmail.com.Science For Solutions, LLC, West Windsor, NJ 08550, United States*

Computational chemistry has become an important tool and is integrated into all aspects of drug discovery research. However, successful application to applied drug discovery research is hardly guaranteed and is often dictated primarily by expert insight. Consequently it can be more art form than technology. Improved success requires improved science and more 'informed' software and also more informed application and improved presentation of results. This talk will provide several examples of successful applications (modeling and evaluation of the protein 'targets' of drugs, detailed design of drug structure based on molecular modeling, and application to RNA based 'antisense'

therapeutics) and detail challenges for where we need to improve both in terms of science and in terms of how we apply the science and present results.

120. Toxic amyloid ion channels

Ruth Nussinov, *ruthnu@helix.nih.gov, Hyunbum Jang.Center for Cancer Research, Nanobiology Program, NCI Frederick, Frederick, MD 21702, United States*

The emerging picture from our large-scale simulations of amyloid ion channels is that these toxic ion channels are formed by β-sheets which are highly polymorphic, and spontaneously break into loosely interacting dynamic units (though still maintaining ion channel structures), that associate and dissociate leading to toxic ion flux. This sharply contrasts intact conventional gated ion channels that consist of tightly interacting α-helices that robustly prevent ion leakage, rather than hydrogen-bonded β-strands. In comparison with β-rich antimicrobial peptide (AMP) like protegrin-1 (PG-1), Aβ and PG-1 are cytotoxic, and can form fibrils and dynamic channels which consist of subunits with similar dimensions. These properties support a relationship between amyloidogenic peptides and β-sheet-rich cytolytic AMPs. Our results are further validated by all-D amino acids, as imaged by AFM, tested by electophysiology and by simulations.

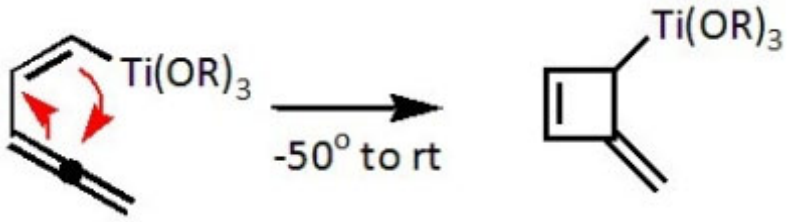
Organic Chemistry

Presiding: D. Watson

121. Theoretical examination of an unusually facile titanium mediated cyclization

Bruce N. Hietbrink, *bruce.hietbrink@gmail.com, Nathan Sanford.Department of Chemistry, Richard Stockton College of New Jersey, Galloway, New Jersey 08205, United States*

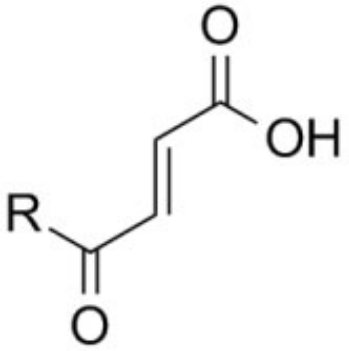
Theoretical tools were used to examine an unexpectedly facile titanium mediated cyclization. While the researchers who first observed this reaction suggested a pericyclic reaction, we demonstrate that it proceeds via a stepwise ionic pathway.

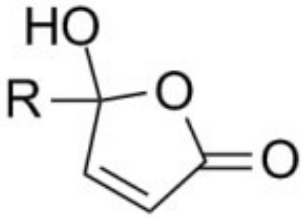


122. Diels-Alder reactions of (*E*)-β-acylacrylic acids and γ-hydroxybutenolides

William H Miles, *Barbara J Naimoli, Evan M Cohen, Jason S George.Department of Chemistry, Lafayette College, Easton, PA 18042, United States*

The Diels-Alder reaction of (*E*)-β-acylacrylic acids and γ-hydroxybutenolides with dienes gave good yields and good regio- and/or stereoselectivity of the corresponding cycloaddition products with the use of Lewis acids.

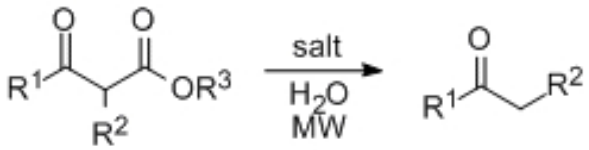




123. Krapcho decarboxylation under aqueous microwave conditions

S. Shaun Murphree, *smurphre@allegheny.edu, Jeremy D. Mason.Department of Chemistry, Allegheny College, Meadville, PA 16335, United States*

The Krapcho decarboxylation is a convenient method to prepare ketone derivatives (2) from the corresponding diesters or ketoesters. Conventional conditions involve the extended heating of the substrate in the presence of sodium chloride in DMSO. Results are presented in which the procedure has been adapted to an aqueous medium under sealed-tube microwave conditions, leading to complete decarboxylation within 30 min. Reaction optimization is also presented, which reveals interesting mechanistic insights.



1 **2**

124. PMR 15 type polyimides with non carcinogenic diamines

Selladurai Madaiyan[1], Regunathan Nair[2], Dona Mathew[2], Sundararajan Pudupadi[3], ***Sarojadevi Muthusamy***[1]*, msrde2000@yahoo.com. (1) Department of chemistry, Anna University, Chennai, Tamil Nadu 600025, India (2) polymers and special chemicals division, Vikram sarabhai Space center, Trivandrum, Kerala 695022, India (3) Department of chemistry, Carleton University, Ottawa, Ontario 1125, Canada*

Though the PMR-15 polyimides, developed by NASA, are easily processed, they undergo extensive microcracking and the monomer methylene dianiline (MDA) is carcinogenic. Bulky groups in the ortho positions to amino group are reported to reduce carcinogenicity.

Hence, in the present study three aromatic diamines with methyl groups ortho to the amino group were prepared and used in the place of MDA to make PMR-15 type of resins. Modified PMR-15 type prepolymers were made by reacting a diamine (3.084 mmoles) with mono-methyl ester of cis-5-norbornene-endo-2,3-dicarboxylic acid (2 mmol) and di-methyl ester of 3,3',4,4'-benzophenonetetracarboxylic acid (2.084 mmole). The structure of the prepared diamines and prepolymers were studied using elemental analysis, FT-IR, ^{1}H-NMR and ^{13}C-NMR spectral techniques. The cure behaviour and thermal stability of the prepolymers were studied using DSC/TGA analysis. Carbon fiber reinforced composites were made. The fiber content, void content, density,Tg and mechanical properties of the composites were studied.

125. New oxyma derivative for amide-forming reactions in water

Michio Kurosu, *mkurosu@uthsc.edu, Qinghui Wang, Yong Wang.Pharmaceutical Sciences, College of Pharmacy, University of Tennessee Health Science Center, Memphis, TN 38163, United States*

An oxyma derivative (2,2-dimethyl-1,3-dioxolan-4-yl)methyl 2-cyano-2-(hydroxyimino)acetate displayed remarkable physico-chemical properties as a coupling additive of amide-forming reactions by using EDCI. Short- to oligo-peptides could be synthesized in water media without measurable racemization. Significantly, a simple acidic and basic water work-up procedure can remove all reagents utilized in the reactions to afford the only coupling products in 80~100 yields. We will present scope and limitations of new peptide-forming reactions in water.

126. Preparation of allyl and vinyl silanes via the palladium catalyzed silylation of terminal olefins

Jesse R. McAtee, Sara A. S. Martin, ***Donald A. Watson****, dawatson@udel.edu.Department of Chemistry and Biochemistry, University of Delaware, Newark, DE 19711, United States*

A high-yielding protocol for the palladium-catalyzed silylation of terminal alkenes using silyl halides will be discussed. This method, which is believed to proceed via a Heck-type mechanism, allows facile conversion of styrenes to *E*-β-silyl styrenes using either TMSI or TMSCl with LiI. Terminal allyl silanes with good *E*:*Z* ratios are also readily accessed from α-olefins by this method. When combined with existing technology, this transformation provides a powerful strategy to selectively functionalize the vinyl or allylic position of terminal alkenes.

Happy Hour Posters

127. Thioamide quenching of intrinsic and extrinsic protein fluorescence: Minimalist tools for studying protein dynamics

Jacob M. Goldberg*, gojacob@sas.upenn.edu, E. James Petersson.Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104, United States*

Quenching of protein fluorescence can be used to monitor protein dynamics or biomolecular associations. This quenching can be interpreted to afford valuable structural information with a resolution that depends on the size of the quenching probe used. We have shown that backbone thioamides effectively quench several fluorophores, including tryptophan and tyrosine, in a distance-dependent manner. We have used this method to monitor the binding of thioamide-containing peptides to the protein calmodulin, protein unfolding in model systems, and other biological processes. Since thioamide analogs of the natural amino acids can be incorporated at any position in the peptide backbone, they can function as a valuable, minimally-perturbing probe of protein interactions.

128. ^{77}Se enrichment of proteins expands the biological NMR nuclei toolbox

Stephanie A Schaefer, *saschaef@udel.edu, Ming Dong, Brian Bahnson, Colin Thorpe, Sharon Rozovsky.Department of Chemistry and Biochemistry, University of Delaware, Newark, DE 19716, United States*

Sulfur, a key contributor to biological reactivity, is not amendable to investigations by biological NMR spectroscopy. To utilize selenium as a surrogate, we have developed a ^{77}Se isotopic enrichment method in heterologous proteins expressed in *E. coli*. We show that selenium-enriched augmenter of liver regeneration (ALR), a flavoprotein that catalyzes the formation of disulfide bonds, is catalytically active. By solving the X-ray structure of the selenium-rich ALR to 1.5 Å resolution, we were able to measure the changes in bond angles and lengths compared to native ALR. In addition, we detect and resolve multiple selenium resonances from numerous cysteine and methionine residues by ^{77}Se NMR. ^{77}Se isotopic enrichment will be useful for biophysical characterization of selenoproteins as well as other sulfur-containing proteins.

129. Design, synthesis, and testing of ADP-ribose inhibitors: Chromogenic substrates of bacterial ADP-ribosylating toxins

Sapan Parikh[1], *Vern Schramm*[2], *Keith Clinch*[3], *Richard Fröhlich*[3], *Richard Furneaux*[3], *Joanne Harvey*[3], *Peter Tyler*[3]. *(1) Chemistry, Manhattanville College, Purchase, New York 10577, United States (2) Biochemistry, Albert Einstein College of Medicine, Bronx, NY 10461, United States (3) Carbohydrate Chemistry, Industrial Research Ltd., Lower Hutt, New Zealand*

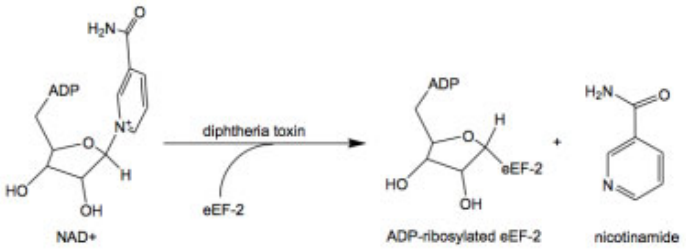


Figure 1: Reaction catalyzed by diphtheria toxin

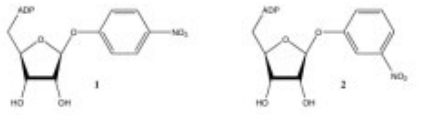


Figure 2: Nucleoside diphosphate analogues **1** and **2**, in which the nicotinamide group has been replaced with 4-nitrophenol and 3-nitrophenol

130. Expression and purification of human PYY(3–36) in *Escherichia coli* using a His-tagged small ubiquitin-like modifier fusion

Christopher H. Fazen, *chfazenj@syr.edu, Robert P. Doyle.Department of Chemistry, Syracuse University, Syracuse, NY 13244, United States*

Human PYY(3–36) (hPYY3–36) is a 34 amino acid hormone that has received a great deal of attention due to its putative effects on appetite regulation. The hPYY(3–36) sequence was modified at the N terminus with an octahistidine tag and Factor Xa protease sequence along with the small ubiquitin-

like modifier (SUMO) tag and expressed in *Escherichia coli*. The fusion protein was purified with a yield of 30 ± 7 mg/L. The SUMO-tagged hPYY(3–36) was digested with two different proteases to return either His-tagged hPYY(3–36) or unmodified hPYY(3–36) that were subsequently purified and characterized.

131. Insights into the genomic RNA packaging of simian immunodeficiency virus in chimpanzees

Thao L Tran[1,2], *lphthaotran@umbc.edu, Michael Summers*[1,2]. *(1) Chemistry-Biochemistry, University of Maryland, Baltimore County, Baltimore, Maryland 21228, United States (2) Howard Hughes Medical Institute, United States*

Human Immunodeficiency Virus (HIV) causes Acquired Immune Deficiency Syndrome (AIDS). Over several decades, AIDS remains a major predicament to public health and social stability. The development of drugs and vaccines to combat AIDS depends on primate model. The genomic RNA of Simian Immunodeficiency Virus from chimpanzees (SIVcpz) found to be closely related to that of HIV type 1 (HIV-1) by phylogenetic analysis. We have utilized computational analysis, gel electrophoresis, and mutagenesis in this study. Computational analysis and RNA sequence alignment uncover that the 5′leader (5′-UTR) of SIVcpz and HIV-1 have similar elements: TAR, poly A, PBS, DIS, and AUG stem-loop. We found the palindromic sequence in DIS is heavily involved in the 5'-UTR dimerization. Further investigation of the structure and the dimerization mechanism of the 5'-UTR in SIVcpz is in progress. This study will broaden the understanding of retroviral evolution and provide insights in retroviral genome packaging.

132. One-step procedure for simultaneous protein precipitation and removal of phospholipids from biological matrices prior to LC/MS analysis

Tracy Ascah, *tracy.ascah@sial.com, Craig Aurand.Supelco/Sigma-Aldrich, Bellefonte, PA 16823, United States*

Endogenous proteins and phospholipids are two of the major causes of matrix effects in LC-MS analyses. The concentration of proteins and phospholipids are often high and variable in plasma and serum samples. Liquid-liquid extraction and solid phase extraction are two commonly used procedures for cleanup of such proteins and phospholipids during the preparation of biological samples. However, both of the procedures involve multiple steps and tend to be time consuming and labor intensive. While the use of protein precipitation affords a faster method for sample preparation, the presence of phospholipids in the sample extracts can significantly impact the quality of the data derived from using this technique. The purpose of this study is to demonstrate the detrimental impact of phospholipid induced matrix ionization suppression when dealing with plasma samples. The techniques compared are standard protein precipitation with organic solvent, and the use of a novel zirconium-based SPE method.

133. Role of glyceraldehyde-3-phosphate dehydrogenase in the regulation of colony stimulating factor-1 and angiotensin-II type 1 receptor mRNA stability

Mohd M. Khan, *mohkhan1@umbc.edu, Elsa Garcin.Department of Chemistry & Biochemistry, University of Maryland at Baltimore County, Baltimore, Maryland MD21250, United States*

Recent investigations revealed that GAPDH binds to the adenine-uridine rich (ARE) areas in the 3'untranslated region (UTR) of the colony-stimulating factor-1 (CSF-1) and of the angiotensin II type 1 receptor (AT1R). On the one hand, GAPDH binding stabilizes CSF-1mRNA, acting as a translational activator, thereby enhancing protein expression in ovarian cancer cells. In contrast, GAPDH was found to decrease the mRNA stability of AT1R and thus the levels of protein expression leading to heart diseases. Thus GAPDH is an example of a broad specificity RNA binding protein able to either destabilize mRNA or enhance translation. Our goal is to elucidate the molecular and structural aspects of GAPDH

interaction with these different mRNAs. Our studies aim to probe GAPDH binding to CSF-1 and AT1R mRNA 3'-UTR by electrophoretic mobility-shift assay, isothermal calorimetry, molecular-modeling, and crystallography, which will help structure-based rational drug design of small molecules to treat cancer and cardiovascular diseases.

134. Insights into the structure and function of the soluble guanylate cyclase regulatory domain

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Soluble guanylate cyclase (sGC) is a heterodimeric protein that acts as the body's main nitric oxide (NO) sensor. sGC binds NO via a ferrous heme within the βHNOX regulatory domain, increasing the catalytic activity several hundred fold as compared to basal levels. We aim to perform structural analysis of NO binding by focusing on truncated β subunit sGC variants, βHNOX and βHNOX-HNOXA. Both constructs were expressed untagged or with an N-terminal MBP tag to determine optimal purification. To study the effect of the HNOXA domain on heme stability, we constructed a βHNOX-HNOXA variant with a Factor Xa cleavage site between the two domains. The untagged proteins express well in *E.coli*, but are difficult to purify. Cleavage of the βHNOX-HNOXA construct was performed; attempts to separate the domains were unsuccessful. Crystallization experiments afforded small crystals that diffracted to 10Å resolution. MBP fusion constructs yielded pure protein with relatively low heme incorporation.

135. Role of tryptophan-168 in the allosteric regulation of anthranilate synthase from *Streptomyces venezuelae*

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Anthranilate synthase (AS) catalyzes the first step in the pathway by which tryptophan is made from chorismate. Previously we characterized the fused AS from *Streptomyces venezuelae* in terms of its kinetic and oligomeric properties. We found that it was active as a monomer and was competitively inhibited by tryptophan. Here our goal was to identify residues comprising the regulatory site. Using sequence alignment and homology modeling, we selected a set of residues for site-directed mutagenesis. We expressed and purified the altered enzymes as His-tagged proteins and characterized them. One mutant enzyme, Trp^{168}□Tyr, was especially interesting. It had K_m-values similar to those of wild-type but had a 6-fold higher $K_i^{tryptophan}$-value and an inhibition pattern that was more mixed-type in character. Binding studies showed that mutation did not alter the strength of tryptophan binding. This suggests that Trp-168 plays a role in communication of the inhibitory signal from regulatory to active site.

136. Modeling and computational analysis of HIV-1 integrase inhibitors

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Recent crystal structures of prototype foamy virus (PFV) intasomes with synthetic viral DNA ends reveal the binding mode of integrase (IN) inhibitors and architecture of the intasome. We generated a model of the corresponding HIV-1 complex based on these PFV IN structures that agrees with earlier crosslinking studies and novel mutagenesis data. We also developed a molecular dynamics (MD)-based approach to computationally evaluate novel compounds. The *in vitro* activities of four clinically relevant compounds against WT IN, Y143R, N155H and G140S/Q148H integrases were used as a training set. Three investigational compounds were docked and subjected to MD simulations, and the

most active compound was accurately identified. Additional MD analysis of other INSTI complexes gave binding energy values that closely match the experimental values of a related compound. These approaches may provide a deeper understanding of how inhibitors interact with the HIV-1 intasome and identify promising scaffolds for second-generation integrase inhibitors.

137. Comparative study of workflows optimized for in-gel, in-solution, and on-filter proteolysis in the analysis of plasma membrane proteins

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Proteomic studies of plasma membrane proteins are challenged by the limited solubility of these proteins and the limited activity of proteolytic enzymes in solubilizing agents such as SDS. In this work, we have evaluated three bottom-up workflows to obtain tryptic peptides from plasma membrane proteins solubilized with 2% SDS. The workflows are in-gel digestion, in-solution digestion, and on-filter digestion. The efficiencies of these strategies, optimized to employ different matrices for trypsin cleavage, were compared using a plasma membrane sample enriched from multiple myeloma cells using a nanoparticle pellicle. On the basis of the number of proteins identified, number of transmembrane proteins identified, hydrophobicity, and spectral count per protein, the workflow that uses in-gel digestion is the most advantageous approach for analysis of plasma membrane proteins.

138. Controlled release of neurotrophins and genetically engineered viruses from poly(3,4-ethylenedioxythiophene) (PEDOT)-coated carbon fibers

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Incorporating biologically active species such as neurotrophins and viruses into conducting polymer coatings has been proven an effective approach to enhance their performance and properties. One strategy has been to entrap these bioactive species into the polymer matrix and release them with externally applied electric fields. In this study, poly(3,4-ethylenedioxythiophene) (PEDOT) doped with nerve growth factor (NGF) or the adenovirus AAV2-GFP was electrochemically deposited on carbon fibers. We found that the rates of release of the NGF and AAV2 from the PEDOT coating could be controlled by voltage applied through the fibers, the chemistry and molecular size of primary dopant, and the environmental pH. The response of cells exposed to the released NGF and AAV2-GFP confirms that bioactive entities were released into the culture system in a controlled manner. These results suggest that bioactively-doped PEDOT on carbon fibers can be potentially used as an intelligent neural interface.

139. Designing of artificial membrane protein maquettes for understanding natural oxidoreductases

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Oxidoreductases are enzymes that perform various processes such as proton coupled electron transfer, energy transduction, catalysis, and transportation of gases etc. Examples of oxidoreductases involved in electron transport are membrane proteins that play role in cellular respiration and photosynthesis. The structural complexity of these biologically important proteins obscures studies on

their structure-functional relationship. We demonstrate that we can design simplified protein models (maquettes) that can reproduce many functional features of the natural oxidoreductases. We are exploring these maquettes for functional fine-tuning and elucidating the structure-function relationship. We have engineered amphiphilic maquettes with different topologies such as homotetramer, homodimer, and a single chain. These maquettes span lipid bilayers and bind 3-6 cofactors to site specifically tailored histidines with inter-cofactor distance of 11-14 Å. We have successfully developed methods to express these maquettes as inclusion bodies in *E-coli*. Our results will include studies on optimizing the purification and characterization of these proteins.

140. Reactivity of nitroxyl (HNO)-derived sulfinamides

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Protein structure and function are known to be altered due to post-translational modifications of cysteine residues. HNO, a potential heart failure therapeutic, targets thiols and results in the formation of disulfide or sulfinamide, depending on the concentration of thiol. We have investigated the reactivity of HNO-induced sulfinamides, which are traditionally considered to be irreversible in peptides and proteins. Our studies in several systems including a small organic molecule, peptides and a cysteine protease indicate that sulfinamides can be reduced back to the free thiol in the presence of reducing agents at physiological pH and temperature. This sulfinamide reduction was examined in both peptides, where a cyclic intermediate analogous to that proposed for asparagine deamidation reactions potentially can contribute, and in a small organic molecule, where the mechanism is restricted to direct thiolysis. We conclude that the contribution from the cyclic intermediate becomes more important in environments of lower dielectric constant.

141. Latest developments of the CHARMM classical Drude oscillator polarizable force field for proteins

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Latest developments of the polarizable CHARMM force field for proteins, based on the classical Drude oscillator, are discussed. Development of the force field includes: (1) determination of bonded and non-bonded parameters of the small molecules that represent the building blocks of proteins; (2) determination of the electrostatic parameters from dipeptides and (3) corrections required to describe properties of larger polypeptides in condensed phase. Application of the force field to the simulation of small polypeptides in aqueous solution is presented. Structural and dynamical properties are compared with available experimental data.

142. Encapsidation of Rift Valley fever virus as a therapeutic target

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Rift Valley fever virus (RVFV) is a *Bunyaviridae*, which are viruses with three negative-strand RNA genome segments. It is a zoonotic pathogen that causes severe illnesses in humans and livestock and for which there are no suitable treatments. Critical to the infectious cycle of RNA viruses is the encapsidation of the genome by the nucleocapsid (N) protein and recently two crystal structures of RVFV N-protein have become available. The goal of this study is to identify, initially through virtual screening, potential anti-RVFV agents that target N-protein. N-protein structures were downloaded from the Protein Data Bank (PDB) and processed for docking simulations with UCSF Chimera. Potential drug-binding cavities were identified with Pocketfinder and virtual screening performed with

AutoDock Vina through the PyRx interface. Potential inhibitors have been identified from the DrugBank database and the NCI Diversity Set II library and will be subjected to further analysis.

143. Retroviral RNA promotes gag assembly: RNA as a structural scaffold

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During the late phase of the retrovirus life cycle the Gag polyprotein assembles at the plasma membrane. We have expressed and purified the capsid and nucleocapsid domains together as a unit (CANC) for the Moloney murine leukemia virus. Viral genome packaging specificity is mediated by the nucleocapsid domain of assembling Gag polyproteins and the RNA packaging element located in the 5′ UTR, known as the Ψ site. The minimum region required for packaging is called the core-encapsidation signal (Ψ--^{ces}). Here, we employ isothermal titration calorimetry and EMSA to characterize the interaction between CANC and Ψ--^{ces}. Our findings suggest that, the Ψ site functions as a RNA structural scaffold that marks nucleation sites for Gag assembly by exposing a cluster of conserved UCUG elements for binding to nucleocapsid domains of assembling viral Gag proteins.

144. Mechanism of cytotoxicity of O^2-arylated diazeniumdiolate anticancer agents

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JS-K and related O^2-arylated diazeniumdiolate prodrugs have demonstrated pronounced cytotoxicity and antitumorigenic properties in a variety of cancer models both *in vitro* and *in vivo*. This study highlights features of the chemical/biological cross-talk of the O^2-arylated diazeniumdiolate signaling cascades.

A consequence of the metabolism of arylated diazeniumdiolate is the depletion of cellular reducing equivalents, GSH, leading to a rise in the cellular oxidation potential as viewed through perturbations of the GSH/GSSG redox couple. This chemical event initiates a myriad of biological events resulting in cell cycle arrest and apoptotsis: a pronounced rise in the steady state levels of endogenous reactive oxygen species, the initiation of stress signaling cascades, mitochondrial/metabolic dysfunction, protein nitration and nitrosation, and DNA strand breaks. In the case of O^2-arylated (bis)diazeniumdiolates, pronounced protein glutathionylation is observed in contrast to their monovalent counter parts. Apparent glutathionylation can form from two independent pathways resulting in structurally distinct modifications.

145. Quantitation of the diazonium ion derived purine adducts of the carcinogens N-nitrosomorpholine, N-nitrosopyrollidine, and N-nitrosopiperidine in cells

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N-Nitrosomorpholine (NMOR), N-nitrosopyrollidine (NPYR), and N-nitrosopiperidine (NPIP) are potent carcinogens and mutagens that have been shown to cause tumors in many animal models. The National Institute of Occupational Safety and Health (NIOSH) employs workplace monitoring for seven nitrosamines including NMOR, NPYR, and NPIP. NMOR and NPYR derived diazonium ion alkylations of guanine and adenine from nucleoside and DNA reactions are well known in the literature and are qualitatively similar. Recent unpublished reactions with nucleosides in our lab have shown

NPYR derived alkylations that are mysteriously 50-80 fold lower than NMOR and NPYR yields. Of the initial adducts in DNA the greatest amounts of alkylation were seen with N7-Gua, O6-Gua, and N3-Ade. Recent work has shown that GM2E1 cells treated with 4mM NMOR for 12-72 hours show all three adducts as a function of dose time. Similar studies for NPYR and NPIP are ongoing.

146. Protein substrate discrimination in the quiescin-sulfhydryl oxidase (QSOX) family

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This work explores the substrate specificity of the Quiescin-sulfhydryl oxidase (QSOX) family to provide enzymological context for investigation of the physiological roles of these facile catalysts of oxidative protein folding. QSOX enzymes are generally unable to form disulfide bonds within well-structured proteins. Use of a temperature-sensitive mutant protein as a model substrate shows that QSOX activity correlates with unfolding. Fusion of this mutant with a more stable protein domain demonstrates that QSOX can selectively introduce disulfides into flexible domains. In terms of intermolecular disulfide bond generation, QSOX is unable to crosslink folded proteins by their surface thiols. However, we demonstrate that flexible protein monomers can be directly coupled by the oxidase. Kinetic experiments and static fluorescence approaches indicate that QSOX does not have a significant protein-binding site. These aspects of substrate discrimination by QSOX family members are rationalized in terms of the stringent steric requirements for disulfide exchange reactions.

147. Site-directed mutagenesis of intrinsic factor and its potential use as a drug delivery agent

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Oral delivery of peptides such as insulin and PYY(3–36) has been successfully achieved by conjugation of these peptides to vitamin B_{12} (B_{12}), thereby utilizing the dietary uptake pathway for the vitamin. Intrinsic factor (IF) is a glycoprotein that carries and protects B_{12} during gastrointestinal passage. Although this protein serves a critical function in the B_{12} uptake pathway, up until now, its use as a delivery agent has not directly been explored. Herein, we describe the site-directed mutagenesis, overexpression, and utilization of IF as a drug delivery agent.

148. Elucidating the role of methylated quinolones and N-oxide quinolones in quorum sensing

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Gram-negative opportunistic bacteria, *Pseudomonas aeruginosa* and *Burkholderia thailandensis* coordinate their pathogenic activities by producing and detecting diffusible signal quorum sensing molecules such as 2-alkyl quinolones (HHQ) analogues. Using a combination of *in vitro* and *in vivo* studies, we have characterized the formation of function of 3- methylation and N-oxide formation in *P. aeruginosa* and *B. thailandensis*. Modifications to HHQ such as methylation and *N*-oxidation directly affect the ability of bacteria to sense such signals. We present studies that show 3-methyl-4-quinolones, molecules produced in *B. thailandensis*, prevent quorum sensing cross-talk between *P. aeruginosa* and *B. thailandensis* indicating that the quorum-sensing molecular structure is highly species specific. Furthermore structural modifications such as *N*-oxide formation also result in significant loss in quorum sensing response. The loss of response in the presence of these molecules indicates a method of potential degradation or down regulation in the cross-talk between the two bacterial species.

149. FRIENDS: First rigorous ion-exchange numerical design simulator

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Innovative separation methods are addressed to fulfill the high separation demands required by biotechnology, namely, protein and peptide purification for biopharmaceutical industry. To accomplish this, a computer-aided optimization methodology for both standard ion-exchange chromatography and also for mixed-mode chromatography is developed, where the ligands on the column packings may exhibit electrostatic interactions as well as hydrophobic interactions and/or hydrogen bonding, and where the role of pH variations is fully accounted for. The implementation of the computer code in a portable message-passing parallel program yields fast full numerical simulations and allows efficient chromatographic system identification and optimization, which goes well beyond any previous attempts at simulations in this area. To summarize, the main aims addressed in this talk are: (1) to develop a computer design and optimization methodology for ion-exchange chromatography that incorporates full numerical solutions and (2) to show the application of this methodology in the context of biotechnology separations.

150. Exploring the structural diversity in quinolone quorum sensing molecules

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The quinolone quorum sensing system is a common form of communication shared by both *Pseudomonas aeruginosa* and *Burkholderia* species. While both bacteria use the same core quinolone structure, these bacteria produce a number of chemically modified quinolones. Using a combination of *in vivo* feeding studies with synthetic quinolones and *in vitro* enzymology in conjunction with LC/FTMS we have demonstrated that a number of modifications occur during the biosynthesis of the quinolone ring while other modifications occur post quinolone ring synthesis. Further more we have demonstrated that some of these modifications serve to attenuate or limit bacteria quorum sensing response.

151. Vibrational Stark effect calculations using quantum mechanical / molecular mechanical simulations

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Vibrational Stark Effect (VSE), the characteristic IR band shift in response to an electric field, is an effective methodology to study changes in the electrostatic environment around a probe. In the event of hydrogen bonding with the environment, experiments require additional NMR studies to sort the electrostatics from other interactions that contribute to observed Stark shifts. We use QM/MM simulations, involving ab initio methods with the CHARMM additive force field, to calculate the stark shift of a methyl-thiocyanate (MtCN) probe between an aprotic (dimethyl sulfoxide) and protic (water, formamide or trifluoroethanol) solvent. By including the interacting solvent molecule in QM calculations, our methods inherently account for all specific chemical interactions. Our simulations satisfactorily reproduce the experimentally observed nitrile blue shift from aprotic to protic solvents. Hence, QM/MM simulations represent a direct technique to calculate VSE and may be employed to probe heterogeneous environments such as proteins and nucleic acids.

152. Free energetics of polyarginine penetration into model lipid bilayers

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Cationic arginine-rich peptides, such as Tat and nona-arginine, are known to transfer into cells via membrane permeation pathways. Their fast membrane penetrating ability is promising as a vector to deliver therapeutic molecules into cells, both in vitro and in vivo. The exact, general mechanism of translocation is still not fully understood or agree upon. Two possible mechanisms are proposed: endocytotic and non-endocytic pathways.

153. Allosteric inhibitors alter the dynamic and thermodynamic properties of the RNA polymerase from hepatitis C virus

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The Hepatitis C Virus (HCV) affects approximately 200 million people throughout the world. There is no cure for this disease and better treatments are sorely needed. The HCV RNA polymerase (gene product NS5B) has become a drug target because of its importance for genome replication. Currently, there are four allosteric binding sites and several inhibitors that can bind to these sites have been identified. However, the molecular mechanisms that underlie allosteric inhibition are unclear from the structural data alone. We employ molecular dynamics simulations and principle component analysis in order to understand how the presence of inhibitors in different allosteric binding sites impacts the structure and dynamics of NS5B. By understanding the structural, dynamic, and thermodynamic changes that accompany ligand binding, we hope to determine the molecular origins of allosteric inhibition in NS5B. This information may aid in the development of novel and more effective inhibitors for NS5B.

154. Probing the interactions between the anti-apoptotic Bcl-2 protein and a new class of rhodanine-based acylsulfonamide derivative inhibitors

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A series of novel rhodanine-based acylsulfonamide derivatives were designed, synthesized, and evaluated as small molecule inhibitors of anti-apoptotic Bcl-2 protein. Among them, two potent compounds were experimentally found to have strong binding affinities with Bcl-2 protein. Docking studies have indicated that both compounds orient similarly at the binding site of Bcl-2, and the calculated relative binding affinities of these small molecule inhibitors correlate well with the experimental results. Energy decomposition analysis of the docked inhibitors and Bcl-2 complex determined that polarization effect plays a very important role in these inhibitors binding. In addition, an amino acid decomposition analysis demonstrated the contributions of individual residues to the interactions between Bcl-2 and its inhibitors.

155. Understanding the molecular origin of synergistic inhibition in the hepatitis C virus (HCV) polymerase

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A major challenge in treating HCV is the emergence of resistance to current treatment regiments. An approach to reducing the rate of drug resistance is increasing the inhibitory effects of small molecules by using them in combination. This study seeks to understand how multiple allosteric ligands can be

used to synergistically inhibit the HCV RNA polymerase (NS5B). Experiments suggest non-additive enhanced inhibition when multiple ligands bind NS5B. We use molecular dynamics simulations to understand the molecular origin of this non-additivity. We hypothesize that the binding free energy measured when multiple ligands bind NS5B simultaneously will be more favorable than the sum of individual ligand binding free energies and that the magnitudes of the computed binding free energies will correlate to the degree of inhibition. Understanding the molecular mechanisms mediating the synergistic inhibition of NS5B may allow such effects to be maximized to inactivate the enzyme.

156. Using deterministic kinetic modelling to understand the lipid biosynthetic pathway in *Chlamydomonas reinhardtii*

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A worldwide effort to find renewable alternatives to fossil fuels is underway. Under certain conditions, algae produce large amounts of lipids that can be converted to biodiesel. However, the lipid biosynthetic pathway of algae is not fully understood. Consequently, we seek to generate a deterministic kinetic model of the lipid biosynthetic pathway in the well-studied microalgae *Chlamydomonas reinhardtii*. This model will incorporate the flow of reactants and products in the pathway, along with concentrations of the substrates and Michaelis-Menten constants for enzymes involved. Key parameters of the model will be manipulated in order to predict optimal mechanisms by which higher levels of lipid production can be induced *in vivo*. As an initial step in performing our analyses, we employ a recently developed kinetic model that describes the full complement of metabolic processes in *C. reinhardtii* in order to extract elements of the model most relevant to lipid production.

157. Free energy profile of base flipping in carcinogen-modified DNA duplexes

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Chemical carcinogenesis are common structural damages in certain specific oncogenes and tumor suppressor genes. Nucleotide excision repair (NER) is the major cellular pathway for removing bulky DNA lesions such as aromatic amines, which are among the most notorious environmental carcinogens. DNA damage recognition in NER is governed by adduct structures and their influences on base pairings at the lesion site as well as the nature of neighboring and distant base sequences. We employed Molecular Dynamics (MD)-based Potential of Mean Force (PMF) calculations to study base flipping at lesion sites to investigate the sequence and lesion effects. Conformations sampled correspond with those observed in NMR experiments for both NOE distance restraints and global structures. Free energy profiles along the base flipping reaction coordinate for the lesions are in agreement with 19F NMR experimental data. The results provided insights into mechanisms of sequence dependent NER.

158. Allosteric dynamics cooperation and its effects on intein catalysis

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Inteins are phylogenetically diverse self-splicing proteins that are of great functional, evolutionary, biotechnological, and medical ihnetrests. It has been shown that intein activity can be regulated by a loop (connecting two beta-strands from the N- and C-terminal intein subdomians of the mini-intein) and by the mutations affecting intein stability (V67L). The effects of loop length and the V67L mu-

tation illustrate the dynamics nature of allosteric regulation of the inteins. We have exmained the inteins's structural dynamics using extensive molecular dynamics simulations, in order to get insights into the correlation of protein dynamics and enzymatic catalysis. We found that stable and active inteins have better dynamics correlations between active site and rest allosteric regions in the intein.

159. QXD: A new charge-dependent QM/MM interaction potential for simulations of chemical reactions

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Frequently, a combined quantum mechanical/molecular mechanical (QM/MM) approach is used to investigate complex reactions in solution. Important to the accuracy of these simulations is the treatment of the non-electrostatic, non-bonded forces, which are most frequently treated with a static Lennard-Jones potential. However, this type of treatment is sub-optimal as it does not allow for physically meaningful changes that occur along a given reaction coordinate such as atoms undergoing drastic changes in partial charge or local chemical environment. This work introduces a charge-dependent exchange and dispersion model, QXD, that couples the non-electrostatic non-bonded QM/MM interactions with the underlying electronic structure in a self-consistent manner. The method is compared with quantum chemical calculations and applied with molecular simulations of reactions in solution that have been well characterized experimentally. Results indicate QXD is more accurate, and considerably more robust than the conventional static Lennard-Jones models, representing a significant advance in state-of-the-art QM/MM simulations.

160. Development of pY-stat5 receptor model and virtual screening (VS) of novel stat5a/b inhibitors in prostate cancer (PCa)

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Prostate Cancer (PCa) is a very common cancer form affecting men in the United States (www.cancer.gov). A biological target implicated in PCa progression is the Signal Transducer and Activator of Transcription 5a/b (Stat5a/b), member of the STAT-Family of Transcription Factors (Tan and Nevalainen, **2008**).

Stat5 activation requires SH2-domain phosphorylation by upstream Protein-Kinases at a conserved Tyrosine, followed by dimerization and nuclear translocation. Recently, Nevalainen et al. identified a small-molecule inhibitor of Stat5a/b dimerization (proprietary work, Thomas Jefferson University).

No crystal structure of human Stat5a/b is currently available (www.rcsb.org). As a keystone of structure-based drug design, we have generated a computational model of pY-Stat5 receptor and implemented a Virtual Screening (VS) workflow for the identification of either more potent analogs of the lead compound or novel chemical classes of inhibitors.

With a view to a "STAT-Family Oriented" approach, our results constitute a foundation for to develop novel inhibitors of Stat5a/b.

161. Molecular dynamics investigation of DNA-binding foldamers

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Foldamers are synthetically derived oligomers that fold into well-defined secondary structures. Some of these oligomers have been programmed to selectively recognize specific sequences in DNA. Some human cancers are caused by overexpression of transcription factors leading to an anomalous gene expression. Therefore ligands that are able of binding DNA in a sequence specific manner and disrupting transcription factor-DNA interactions are of a great interest.

We apply molecular dynamics methods to optimize the design of oligoamides experimentally shown to bind to DNA, by evaluating the influence of the shape of the oligoamide on binding affinity and selectivity as well as the dynamics of DNA upon oligoamide binding. Our aim is to design an oligoamide with appropriate affinity and selectivity for further experimental studies.

162. *Ab initio* quantum chemical study of nonlinear optical properties of aromatic fused rings

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Static and dynamic polarizability $\alpha(-\omega;\omega)$, and second-hyperpolarizability $\gamma(-\omega_4;\omega_1,\omega_2,\omega_3)$, corresponding to dc-electric-field induced Kerr effect (DCKE), intensity-dependent refractive index (IDRI), dc electric field-induce second harmonic generation (EFISH), and third harmonic generation (THG) of benzene, and aromatic fused ring molecules naphthalene, anthracene, and pyrene have been calculated within the framework of *ab initio* time-dependent coupled-perturbed Hartree-Fock using double zeta Cartesian Gaussian basis set with polarization and diffuse functions. The calculated $\alpha(-\omega;\omega)$ and $\gamma(-\omega_4;\omega_1,\omega_2,\omega_3)$ show good agreement with available theoretical and gas-phase experimental data. As expected, the $\gamma(-\omega_4;\omega_1,\omega_2,\omega_3)$ values exhibit the following trend: γ(THG) > γ(EFISH) > γ(IDRI) > γ(static). The linear polarizabilities increase with the number of rings in either dimensions. Whereas, $\gamma(\omega_4;\omega_1,\omega_2,\omega_3)$ increase as the number of rings increases in either dimension, but the magnitude of increase is more pronounced along the molecular chain. The dispersion of $\alpha(-\omega;\omega)$ and $\gamma(-\omega_4;\omega_1,\omega_2,\omega_3)$ due to optical wave length will also be presented.

163. 3D modeling of the human apical sodium bile acid transporter (hASBT) based on substituted cysteine scanning mutagenesis (SCAM) profiles

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hASBT is found to play a key role in the enterohepatic circulation of bile acids. 50% of cholesterol in the body is eliminated by its conversion into bile acids, making hASBT a pharmaceutical target for drugs aimed at lowering cholesterol. Despite its importance no high-resolution structures have been solved for hASBT. Biochemical studies (SCAM) spanning 68% of hASBT, specifically in the proposed exofacial and the transmembrane (TM) regions, have established a 7TM topology for hASBT. These studies also identified residues involved in substrate translocation and sodium sensitivity. Here we describe a computational effort guided by the biochemical SCAM data to build a structural model of hASBT. The computational study involved a sequential fragment assembly based on homology modeling using both bacteriorhodopsin and bovine rhodopsin as templates followed by refinement using explicit and implicit protein-membrane simulations. The final models are compared with the SCAM studies to provide insights into hASBT mechanism.

164. Using molecular dynamics to understand inhibition of NS5B by a novel allosteric ligand

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Hepatitis C Virus (HCV) infects 270-300 million people worldwide, motivating efforts to identify small molecules that may be effective in treating HCV infection. One of the targeted viral enzymes is the RNA Dependent RNA polymerase (NS5B) that plays a vital role in replicating the HCV genome. Our goal is to understand the molecular mechanism of allosteric inhibition mediated by the novel compound AG6, which is the only ligand known to bind to the fingers domain of the enzyme. Studying the mechanisms of allosteric inhibition involving this novel allosteric site may lead to new insights into the mechanisms of allostery in NS5B. Crystallographic data indicate that NS5B can bind simultaneously to AG6 and another allosteric inhibitor in the thumb domain. We use molecular dynamic simulations to understand how changes in the free energy landscape of NS5B mediate inhibitory effects of these allosteric ligands and the mechanisms underlying synergistic binding.

165. Combined quantum and Poisson Boltzmann method for calculating reduction potentials of blue copper proteins

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Accurate and robust calculations of the reduction potentials of the type 1 copper sites in blue copper proteins are necessary due to the vital role these electron transfer proteins play in the biochemistry of many plant and bacterial organisms. The transferability of methods previously developed by Ichiye et al for iron-sulfur proteins is investigated in this work. Here, density functional theory (DFT), at the M06 level, is used to calculate structural and energetic properties of two blue copper redox sites: the four-coordinate plastocyanin site and the three-coordinate laccase site. The reduction potential is a function of the free energy of the reduction reaction, which has contributions from the free energy of the copper site and the protein environment. Diffuse functions on the sulfur atoms were found to be important in iron-sulfur protein calculations, so their inclusion in calculations of the copper site is also considered.

166. Free energetics of carbon nanotubes association

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Carbon nanotubes (CNTs) have been proven for applications in various fields. Experimentally it has been shown that aggregation and improper orientation of CNTs may lead to degradation of the properties and practical performance. In this study we examine the free energetics of CNT association by using molecular dynamics simulation with two (10,10) single-walled carbon nanotubes in non-polarizable (SPC/E) and polarizable (TIP4P-FQ) water force fields. Results suggest that the free energy for the hydrophobe dimerization is reduced in the polarizable water systems. As one nanotube is rotated relatively to the other, the contact surface between CNTs reduces and consequently decreases the depth of the potential well. By decomposing the free energy of tube association it is found that the entropic contribution stabilizes the free energy of association, while the solvent separated configuration contributes the free energy barriers enthalpically. Hydrogen bond network of the solvent is also studied to unveil the mechanism.

167. Optimization of the CHARMM Drude polarizable force field for DNA

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The majority of all-atom force fields for nucleic acids do not account for electronic polarizability, which may preclude realistic description of conformational and thermodynamic behavior of DNA. To represent electronic induction in Molecular Dynamics simulations we use classical Drude oscillators, where an auxiliary massless charged particle is attached to each polarizable atom by a harmonic spring. A multistep parameter optimization scheme was developed in our laboratory to build a consistent Drude polarizable force field for numerous model compounds, including nucleic acid bases, tetrahydrofuran, and dimethylphosphate. Presently, we extend our efforts towards optimizing parameters against larger systems, such as DNA oligonucleotides in a solution. We focus on systematic optimization of the DNA backbone dihedral angle potentials targeting dihedral angle distributions with those obtained from statistical surveys of DNA crystal structures. Simultaneously, fitting is designed to minimize deviations from QM data obtained for model compounds in the gas phase.

168. Using dynamic importance sampling to explore conformational space in HCV polymerase

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Hepatitis C virus (HCV) is a global health concern. Though there are treatments available, they cause many severe secondary effects and are not completely effective. HCV contains a positive sense single-stranded RNA genome and replicates with the aid of RNA dependent RNA polymerase. This polymerase has open and closed conformations. Our goal is to understand how the transition between these conformations occurs in order to determine how allosteric inhibitors stop the replication of HCV. To accomplish this goal we employ the Dynamic Importance Sampling Algorithm (DIMS). DIMS is a pathway finding algorithm that gives information about the intermediate states between defined starting and ending points. The DIMS algorithm will allow us to sample the conformations of intermediates between the open and closed conformations so we can get a better understanding of how this transition takes place, what motions facilitate the transition and what role it plays in enzyme inhibition.

169. Use of single step free energy perturbation to estimate relative binding affinity by fragment modification

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The in-silico SILCS method which involves MD simulation of a protein in a fragment solution identifies binding locations of a limited set of fragments and water on the protein surface. We report a protocol that post-processes SILCS MD sampling data by applying single step free energy perturbation (SSFEP) calculations to rapidly identify chemical modifications leading to enhanced binding affinity. The method involves (i) identifying high probability fragment binding sites, (ii) selection of conformational subspace pertaining to the sites and, (iii) application of SSFEP. The test sets involved single heavy atom substitutions to hydrogens on benzene. The target data for validation included experimental relative hydration free energies of benzene analogues and relative binding free energies of congeneric ligands containing a substituted phenyl group to thrombin and p38 MAP kinase. The SSFEP protocol can identify small fragment modifications rapidly and thus be of utility in fragment based drug design.

170. Molecular simulations of RNA cleavage transesterification reaction models in solution

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Here we employ QM/QM umbrella sampling simulations to probe the free energy surfaces of a series of systems undergoing phosphoryl transesterification under alkaline conditions. Such systems are valuable models for the uncatalyzed process underlying catalytic cleavage of the backbone of RNA. Several simulation protocols using different ionic conditions, water models, and solute Lennard-Jones parameters are compared. The results provide insight into how variation of the nucleophile and leaving group affect the free energy profile for the reaction. Results for a simple RNA backbone model are compared with experiments by Harris *et al.* on the cleavage of the UpG RNA dinucleotide. The calculated and measured free energies of activation match extremely well ($\Delta F^{\ddagger}$ = 19.7 and 19.9 kcal/mol). Solvation is seen to play a crucial role, and is characterized by a network of hydrogen bonds that envelopes the dianionic phosphorane transition state and provides preferential stabilization relative to the reactant state.

171. Investigations of the impact of ribosomal modification on the binding of the antibiotic telithormycin using molecular dynamics simulations

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Microbial resistance presents a challenge in antibiotic development. Telithromycin avoids efflux and drug metabolism resistance, yet dimethylation of N6 of A2058 abolishes its activity, presumably disrupting the desosamine hydroxyl-N1 (A2058) hydrogen bond. To understand this better, Grand Canonical Monte Carlo – Molecular Dynamics (GCMC-MD) simulations of truncated versions of the *E. coli* 50S subunit were performed for wild-type, A2058G, N6-mono/dimethyl mutants. The number of waters within the binding site were allowed to fluctuate during 10,000 GCMC steps, followed by subsequent ribosomal relaxation during 20 ps MD, with this process iteratively repeated until convergence. Probability distributions for the desosamine hydroxyl-N1 (A2058) hydrogen bond show significantly greater sampling of short distances in the wild-type, with the dimethyl mutant showing the lowest sampling of this hydrogen bond and those to N6 of A2058 and nearby A2059 confirming that erm-mediated resistance results from disruption of hydrogen bonds with A2058/9 that are pivotal for binding.

172. Six-site polarizable model of water based on the CHARMM classical Drude oscillator

Wenbo Yu, *wenbo@outerbanks.umaryland.edu, Pedro Lopes, Alexander D. MacKerell.Department of Pharmaceutical Sciences, University of Maryland, Baltimore, MD 21201, United States*

A simple polarizable water model, SWM6, was developed and optimized for liquid phase simulations under ambient condition. Building upon the previously developed SWM4 model, additional sites representing oxygen lone pairs were introduced. Considering the large number of adjustable parameters, simulated annealing together with polynomial fitting were used to perform model optimization. The new water model was shown to yield improved balance between descriptions of single, clustered and bulk phase water. Moreover, the experimental oxygen-oxygen radial distribution was better reproduced, indicating that the new model more accurately describes the local hydrogen bonding structure of bulk phase water. This was further validated by its ability to reproduce the experimental

nuclear magnetic shielding of the water hydrogen atoms in the bulk phase, which is a sensitive indicator of the local hydrogen bonding structure.

173. Theoretical study of the linear free energy relationships in RNA transesterification reactions

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Ribozymes which can catalyze complex biological reactions have aroused great interest, and stimulated much experimental and theoretical effort aimed at gaining a fundamental understanding of their mechanisms. In this work, the mechanisms of RNA transesterification model reactions with different leaving groups have been investigated using the B3LYP/6-311++G(3df,2p)//B3LYP/6-31++G(d,p) level with implicit solvation. Linear free energy relationships have been analyzed between the activation free energy and reaction free energy, and between activation free energy and relative calculated pK_a of the leaving groups. The corresponding linear functions are $\Delta G^{\neq}=0.59\Delta G+26.38$ and $\Delta G^{\neq}=-1.17\Delta pK_a+30.50$, respectively, which indicates a consistent concerted mechanism of the reactions. This work, and related calculations on the sugar- phosphate backbone of RNA, are used as benchmark data for the improvement of simulation models for phosphoryl transfer reactions in solution and in enzyme andribozyme active sites.

Prevention of Metabolic Syndrome by Dietary Phytochemicals

Presiding: J. Lambert

174. Tea intake and markers for metabolic syndrome in US adults

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The present study examines the association between tea consumption (evaluating hot and iced tea independently) and markers for MetS adults in a sample of 6,472 who participated in the 2003-2006 National Health and Nutrition Examination surveys. Tea consumption was evaluated using food frequency questionnaires and 24-hour dietary recalls. Hot tea consumption was inversely associated with markers for obesity, including waist circumference and BMI. In contrast, iced tea consumption was positively associated with markers for obesity and insulin insensitivity. These associations were significant after controlling for age, sex, physical activity, energy intake, sugar intake, and other confounders. Hot tea consumption was also associated with beneficial biomarkers of cardiovascular disease risk and inflammation (increased HDL-cholesterol and decreased C-reactive protein in both sexes), whereas the association with iced tea consumption was again reversed. These results support growing laboratory data which suggest beneficial effects of hot tea against symptoms of MetS.

175. Cinnamon polyphenols, insulin sensitivity and chronic diseases

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Cinnamon polyphenols improve early signs of diabetes and cardiovascular diseases including impaired glucose tolerance, insulin resistance, dyslipedemia, and hypertension. Water soluble cinnamon polyphenols function as antioxidant and anti-inflammatory agents, prevent premature neuronal death, improve brain mitochondrial function, and decrease and reverse tau aggregation associated with Alzheimer's disease. Double-blind placebo controlled human studies report improved fasting serum glucose, triglycerides, total cholesterol and LDL cholesterol in people with type 2 diabetes consuming 1 to 6 grams of cinnamon daily. There are also improvements in blood pressure, fasting glucose, anti-oxidant status and body composition in overweight subjects with elevated fasting

glucose consuming a dried aqueous extract of cinnamon. In rats, cinnamon, in addition to improved insulin sensitivity, leads to increased liver and muscle glycogen and improved cognition. In summary, cinnamon polyphenols increase insulin sensitivity and decrease risk factors associated with diabetes, cardiovascular and Alzheimer's disease.

176. Development of standard reference materials for functional foods and dietary supplements

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The National Institute of Standards and Technology (NIST) has been working with the National Institutes of Health Office of Dietary Supplements and the Food and Drug Administration Center for Drug Evaluation and Research to produce Standard Reference Materials (SRMs) for dietary supplements. This complements the NIST program to produce food-matrix SRMs in support of the Nutrition Labeling and Education Act; many of the food SRMs have values assigned for 'functional' moieties such as vitamins and nutrient elements. The drivers behind our activities and the status of the materials will be reported. The food and dietary supplement SRMs are intended for the same purposes as other natural-matrix SRMs, namely: (1) to validate the accuracy and precision of new analytical methods, and (2) to provide quality control for analysis of similar materials.

177. Prevention of obesity and obesity-related pathologies by dietary polyphenols

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Polyphenols are an abundant secondary metabolite in plant-based foods. Many laboratory and epidemiological studies have suggested that these compounds may have disease preventive effects. Obesity is a rapidly growing public health concern, and obesity-induced inflammation appears to play a key role in the development of diabetes, heart disease, and cancer. Research in our laboratory using a mouse models of obesity have indicated that polyphenolic compounds from green tea (catechins) and cocoa (procyanidins) can modulate high fat-diet induced obesity, hyperglycemia and systemic inflammation. Enzyme studies indicate that these compounds modulate obesity and inflammation by inhibiting the digestion of dietary triglycerides and phospholipids, and inducing fatty acid oxidation in the skeletal muscle. In the case of green tea these effects are enhanced by combination with voluntary exercise. Our results provide key pre-clinical mechanistic data that may aid in the development of dietary polyphenols as preventive agents for obesity and obesity-related pathologies.

Chemistry in the Chemical Senses A

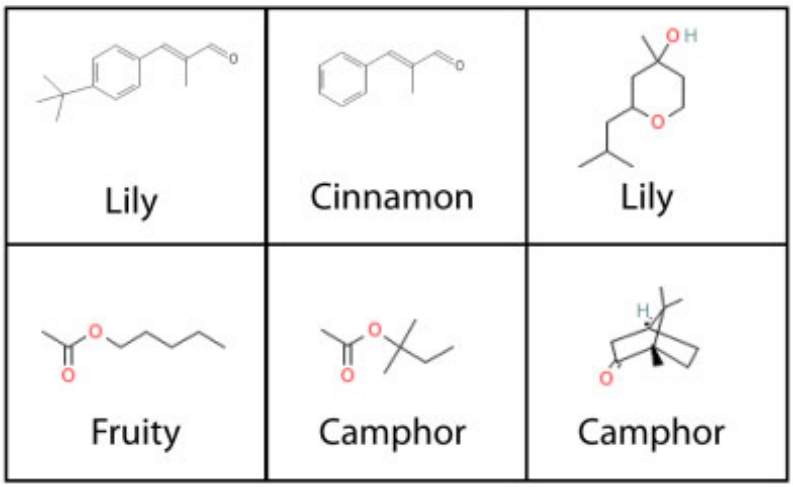
Presiding: G. Preti

178. Cracking the code: Translating odorants into olfactory receptor responses

***Joel D Mainland**, jmainland@monell.org.Monell Chemical Senses Center, Philadelphia, PA 19104, United States*

A fundamental problem in any sensory system is mapping the physical properties of a stimulus to perceptual characteristics. In vision, wavelength translates into color; in audition, frequency translates into pitch. By contrast, the mapping from chemical structure to olfactory percept is unknown.

In other words, there is not a scientist or perfumer in the world who can view a novel molecular structure and predict how it will smell. Here we will discuss current efforts to remedy this problem.



179. Smelling sulfur: Crucial role of copper in detection of metal-coordinating odorants

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In 1887, Emil Fischer wrote that concentrations of thiols of 0.05 ppb are “clearly perceptible to the sense of smell” (1). Spider monkeys can detect 0.001 ppb ethanethiol. Strong-smelling thiols are present in skunk scent, armpit odor, skunky-smelling beer, and male mouse urine, as well as in markers for otherwise odorless natural gas. Until now very little has been known about how low molecular weight sulfur compounds are sensed, although it has been suggested that metalloproteins are involved. Evidence will be presented for the central role of copper in detection of metal-coordinating odorants, including thiols, by a specific mouse olfactory receptor, MOR244-3 (2).

1. Fischer, E.; Penzoldt, F. “Über die Empfindlichkeit des Geruchssinnes” *Justus Liebigs Ann. Chem.* **1887** , *239*, 131-135.

2. Duan, X.; Block, E.; Matsunami, H.; Zhuang, H., et al. “Crucial role of copper in detection of metal-coordinating odorants” *Proc. Natl. Acad. Sci. USA*, **2012** , *109* (9), 3492-3497.

180. Methods to quantify human olfactory perception and examples of results

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Olfaction plays a significant role in the appreciation of ingested foods and beverages; however, olfactory perceptions are uniquely individual because myriad factors influence detection of and response to odors/aromas. Genetics, sex, age, reproductive status, the environment, experience, cognitive bias, personality traits, and more all influence odor perception. It is, however, possible to evaluate and quantify these personal experiences. Methods exist for determining whether a person can smell an odorant and if so its perceived intensity, hedonic valance, odor quality, effects of exposure on

perception of the odor and potential influences on the perception of other odors. These methods are discussed and examples of actual results are presented.

181. Gustatory detection and perception of oral food chemicals

Paul A.S. Breslin, *breslin@aesop.rutgers.edu.Department of Nutritional Sciences, Rutgers University/ Monell Center, New Brunswick, NJ 08901, United States*

Gustatory detection and perception of food stimuli has been shaped by evolution to meet our nutritional needs. We detect and respond to macronutrients and several micronutrients to guide our ingestion and to many anti-nutrients (toxins) to guide our rejction and avoid posioning. An array of trans-membrane receptor proteins in the oral cavity and pharynx serve each category of stimuli. Stimulation may result in conscious taste perception, automatic like or dislike of the stimulus, physiological responses to stimulation, or all of these at once. Taste is also naturally combined with other sensory modalities to form flavor, the handle by which we identify and recognize all foods as we form our associations with them.

Renewable Energy A

Presiding: W. Byrnes

182. Session overview: Metabolic engineering of plants and bacteria for biofuel production: Enzymes, genes and pathways

W. Malcolm Byrnes, *wbyrnes@howard.edu.Howard University College of Medicine, United States*

183. Utilization of plants as renewable sources of fuels and chemical feedstocks: The impact of metabolic engineering

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Modern society is heavily dependent on fossil oils as a source of fuels and chemical feedstocks, but increased demand for oil, decreased production, and escalating costs have stimulated significant interest in developing more sustainable alternatives. While there are many potential sources of energy including solar, wind, nuclear and hydroelectric, plants are particularly attractive as fossil oil alternatives because they can supply energy-dense, carbon-based molecules that are compatible with existing liquid fuels (e.g., gasoline, diesel, jet fuel, etc.), as well as provide feedstocks for the petrochemical industry. However, the main limitation of using plants in this regard comes down to cost. In this seminar I will describe how metabolic engineering is being used to increase the yields of oil in plants, as well as for the introduction of novel metabolic pathways for production of industrially important fatty acids, and how both strategies can significantly improve the overall economics of plant utilization.

184. Enzyme design for lignin engineering: Innovative modules to redesign plants for next-generation biofuels

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We aim to design novel enzymes to control the polymerization of lignin in plants, assess the effect of designed catalysts on lignin structure, and evaluate their ability to improve degradation of lignocellulosic biomass. Our strategy is to generate designs in several stages for timely analysis in plants. In the first stage, substrate binding proteins will be constructed from a variety of scaffolds that optimize the stability of a protein bound bcarbon monolignol radical for attack by the 4-O phenoxy group of a guaiacyl chain. Second stage catalysts will be designed to bind the transition state leading to the

desired b-O-4 linkage, precluding the formation of transition states for undesired coupling reactions. The third stage of enzyme design will add mechanisms to facilitate the conversion of quinone methide intermediates to specific b-aryl ether products. Our interdisciplinary strategy will afford a valuable tool for an integrative analysis of *in planta* lignin assembly.

185. Probing plant biomass conversion by the industrially-relevant *Streptomyces* bacteria

***Jason K. Sello**, jason_sello@brown.edu.Department of Chemistry, Brown University, Providence, RI 02912, United States*

The search for a renewable energy source to act as an alternative to fossil fuel is of global importance. The use of plant biomass as a source of low-value carbon that can subsequently be used to produce high-value biofuels has shown great potential. Most attention is focused on the conversion of the cellulose component of plant biomass, however, this process is impeded by the presence of lignin, a complex aromatic polymer found in the cell walls of plants. The means to effectively and efficiently degrade lignin would enhance the ability to harness the energy stored in plant biomass into a usable fuel. This lecture will address the use of ligninolytic species of *Streptomyces* bacteria as lignocellulose biorefinery.

186. Quest for hyperthermostable cellulases

***Frank T Robb**[1], frobb@som.umaryland.edu, Joel E Graham[1], Douglas S Clark[2,3], Melinda E Clark[2,3]. (1) Department of Microbiology and Immunology, University of Maryland, Baltimore, MD 21202, United States (2) Calvin Hall, Energy Biosciences Institute, Berkeley, CA 94720, United States (3) Department of Chemical and Biomolecular Engineering, University of California, Berkeley, Berkeley, CA 94720, United States*

Growth on crystalline cellulose is rare in the Archaea, and not reported in isolates growing above 81 ºC. In order to determine whether stable consortia of hyperthermophiles can deconstruct cellulose, a sediment sample was collected from a continental geothermal source , at 94ºC, in Nevada. Primary enrichment at 90ºC in mineral media with pulverized *Miscanthus* as sole carbon source was followed by enrichments utilizing filter paper as sole carbon source. A three part culture capable of deconstructing Avicel at 94° C was obtained. A consortium of three novel Crenarchaeotoa was sequenced, and resulted in the expression of a novel endocellulase of unprecedented thermostability. (Graham et al, (2011) Nature Comm doi: 10.1038/ncomms1373). Expression and analysis of the proteins from the genome of Candidatus *S. cellulolyticum* suggests that the optimal growth temperature of this strain is close to 100° C. A cellulase with optimal activity at 113°C was described.

187. Construction of a recombinant cyanobacterium for solar hydrogen production

***Qing Xu**, qnx@nist.gov.NIST (formerly of the JCVI), Gaithersburg, MD, United States*

Cyanobacteria can photolytically split water to support hydrogen production through hydrogenase catalysis. However, one major drawback of this process is that their H_2-evolving hydrogenases are extremely sensitive to oxygen. To develop an O_2-tolerant biophotolytic system, new O_2-tolerant NiFe-hydrogenases need to be identified. Since the oceans harbor an abundance of microorganisms with H_2-production capability, we searched the metagenomic data of the global marine planktonic microbes for new NiFe-hydrogenases. One of the new hydrogenases identified from the ocean was cloned from environmental DNA samples. This hydrogenase demonstrates extraordinary thermostability and O_2-tolerance. To achieve heterologous expression of the [NiFe] hydrogenase in cyanobacteria, its two structural genes (*hynS* and *hynL*) along with accessory genes were cloned under an IPTG-inducible promoter and introduced into the host *Synechococcus elongatus* PCC7942. The

heterologously-expressed HynSL hydrogenase was found to be active. This is the first report of active [NiFe] hydrogenases expressed in the cyanobacterial host.

188. Two-step liquid hydrocarbon synthesis from carbon dioxide and hydrogen

David M. Drab[1], *david.drab.ctr@nrl.navy.mil*, *Matthew T. Olsen*[1], *Dennis R. Hardy*[2], *Heather D. Willauer*[3]. *(1) Division of Materials Science and Technology, NRC Postdoctoral Research Associate, US Naval Research Laboratory, Washington, DC 20375, United States (2) Nova Research Inc., Alexandria, VA 22308, United States (3) Division of Materials Science and Technology, US Naval Research Laboratory, Washington, DC 20375, United States*

Global reliance and future reduction of available fossil fuels presents scientists with a unique challenge and an opportunity to develop new processes and technologies to meet current and future energy demands and also minimize impact on the environment, specifically carbon dioxide emissions. Processes that utilize CO_2 from the environment could be envisioned as CO_2-neutral and, since carbon dioxide is readily available from the air, seawater, and as a byproduct of many industrial energy-producing processes, it could serve as an abundant chemical feedstock for production of energy-rich hydrocarbons such as jet fuel.

This presentation discusses a two-step synthetic approach for CO_2-to-fuel. Carbon dioxide and hydrogen are first reacted over an iron-based catalyst to produce light olefins, which are subsequently oligomerized over a nickel-supported catalyst to liquid hydrocarbons. The effects of scaling and integrating the two steps on the overall conversion and selectivity to C_9-C_{16}hydrocarbon fraction are presented.

Bioanalytical Chemistry

Presiding: R. White

189. Adsorbate-gold bond effect on empirical surface plasmon penetration depth in the near infrared

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Surface plasmon resonance (SPR) based sensors are widely used for detection of analyte binding to recognition elements on the sensor surface. The technology strives toward improved sensitivity by various means such as development of novel plasmonic materials with shallower penetration depth and extension into the near-infrared(NIR) region. Thus, tailoring of surface sensitivity by penetration depth and bulk sensitivity by wavelength of SPR may be achieved. We present a more accurate method for determining penetration depth of SPs on gold while working in the NIR with a novel variable angle NIR-SPR accessory. Generally, penetration depth is calculated from shift in SPR wavelength for given adsorbate thickness. We demonstrate the importance of including an additional factor for the SPR-shift due to adsorbate bonding. This effect is amplified for thin layers of adsorbate and materials with small penetration depth such as nanostructures. The presented techniques offer greater optimization of bulk and surface sensitivity.

190. Label free detection of the bacterial signaling molecule indole by surface-enhanced Raman spectroscopy

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Indole is a small aromatic molecule that is used as an intercellular signal by more than 85 species of Gram positive and Gram negative bacteria. Indole has been linked to spore formation, virulence fac-

tor production, and increased antibiotic resistance within a bacterial population. We report the label-free detection using surface-enhanced Raman spectroscopy (SERS) of indole in M9 minimal media at concentrations similar to those produced by bacteria. SERS substrates created by galvanic displacement of thermally evaporated aluminum by chloroauric acid are evaluated against commercially available gold SERS substrates. The label-free detection of bacterial signaling molecules in culture media creates the exciting possibility of directly monitoring the state of a bacterial population using a rapid and simple analytical method. Given that several important signaling molecules in plants and animals are derived from indole, this result also offers the possibility of studying intercellular communication within and between many different species.

191. Comparison of surface reactions on sensor crystals by means of the quartz crystal microbalance

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The quartz crystal microbalance (QCM) is used increasingly in the development of tailored surfaces for various applications. The QCM can monitor a wide range of chemical reactions at surfaces, including those composed of numerous steps each conducted under different conditions. Different starting surfaces are available as piezoelectric sensor crystals, and a flow cell system allows the introduction of different reaction solutions in sequence. We used the instrument to develop a multi-step procedure to covalently immobilize protein molecules by means of native chemical ligation. During this process, the limitations of the QCM technique emerged and tactics were developed for circumventing such problems as undesired surface adsorption, the changes in instrument response due to change in solution alone (aside from chemical reaction), and the small size of frequency changes for certain chemical reactions. Useful complementary verification techniques that could be conducted outside the flow cell of the QCM were identified.

192. Characterizing manufactured extracellular environments for improving *in vitro* cellular biology

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The extracellular environment that cells experience initiate numerous biophysical and biochemical pathways. Despite the fact that the extracellular environment has a very large impact on cell response, *in vitro* cellular biology studies often do not take into account whether model environments are chemically and physically translatable to those that cells would experience *in vivo*. This oversight has major implications in the biomanufacturing communities involved in areas such as drug development and stem cell engineering. The inadequate toolset to understand the chemical, structural, and mechanical properties materials present to cells is perhaps the principal reason the extracellular environment is largely ignored in cell biology. Here, complementary surface characterization methods, which include time-of-flight secondary ion mass spectrometry (ToF-SIMS) and atomic force microscopy (AFM), are used in conjunction with more traditional bioanalytical techniques (fluorescence microscopy) to understand the physicochemical features of the extracellular environment that influence cell responses.

193. Interference effects on the measurement of nanomolar levels of naproxen chemiluminescence in presence of Fenton reaction

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In our present work, a new chemiluminescence method was developed to determine naproxen. It was a Fenton-based chemiluminescence assay of naproxen in pharmaceutical and artificial urine samples. In specific, with respect to naproxen concentration, interference study included 100-fold excess of vitamins, heavy metals, sugars, potassium, sodium and phosphate.

We have also presented data elucidating the mechanism for naproxen reacting with oxidants such as hydroxyl radical (OH•) produced via Fenton chemistry. Quantification of the hydroxyl radical production and resulting NAP oxidation products were obtained by studying the optical properties of the system and isolating the oxidation products using High Pressure Liquid Chromatography (HPLC). It was found that the chemiluminescence intensity was proportional to the concentration of naproxen ranging from 4.0 ng mL^{-1} to 60.0 µg mL^{-1} with SD of ±1.04 for three repeated measurements of 20.0 ng mL^{-1} NAP and the detection limit was 4.0 ng mL^{-1}.

194. Biosynthetic concatenated labeled peptides are useful alternatives to whole length labeled proteins: Human serum albumin as a case study

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Absolute quantification of proteins using isotope dilution mass spectrometry can be accomplished through the quantification of the peptides generated during proteolytic digestion. The internal standard employed is a biosynthetic ^{15}N, ^{13}C-Lys/Arg protein with a concatenated sequence of five HSA signature peptides with six native amino acid intervening sequences providing proteolytic equivalence to full-length native proteins. Fully ^{15}N-labeled HSA was used for comparison. Human urine samples were processed through an LC-MS/MS assay to correlate with an accepted immunoturbidometric assay. No further cleanup was performed prior to analysis with the LC-MS/MS. Quantification was done using a calibration curve of the ratio of the area under the peaks.

We show that LC-MS/MS with the biosynthetic concatemer and ^{15}N-labeled HSA produced similar absolute quantification as the immunoturbidometric assay. Biosynthetic concatemers can be assembled using peptide sequences from one or more proteins, allowing for a broad spectrum of analytes to be quantified.

195. Electrochemical DNA-based sensors: From benchtop to bedside

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Electrochemical DNA-based sensors have emerged as a potentially promising sensor platform, with examples reported to date for the rapid detection of nucleic acid, protein and small molecule targets. These sensors, which comprise a surface appended, redox-tagged DNA probe, are based on specific, binding-induced changes in the structure and dynamics of this probe. These changes, in turn, alter the efficiency with which the attached redox tag transfers electrons with the electrode, thus gener-

ating signal without the need for exogenous reagents. The specificity of these interactions and the relative paucity of electrochemical interferents allow these sensors to work even when challenged in complex sample media, such as whole blood, without requiring any sample processing. Sensors are optimized by varying parameters such as the sensor fabrication protocols, probe geometries, electrode size, and interrogation methods, allowing the transition of the sensor platform for real-time,continuous monitoring of small molecules.

Younger Organic Chemists

Presiding: C. Dowd

196. New synthetic methods based on palladium-catalyzed C-H functionalization

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Our lab is interested in addressing some of the challenging issues in the C−H functionalization field: the functionalization of unactivated sp^3 hybridized C−H bonds, the development of synthetically useful C−H functionalization protocols, the application of these methods to difficult synthesis problems. Specifically, the talk will be focused on the development and synthetic application of a series of picolinamide-directed palladium-catalyzed functionalization of C−H bonds at remote positions.

197. Transition metal catalysis of iminium and oxocarbenium ion intermediates

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We will describe new transition metal-catalyzed reactions of electrophilic intermediates to enable new reactions and enantioselective transformations. We have discovered a nickel(0)-catalyzed cyclization of *N*-benzoyl aminals to deliver isoindolinones, a heterocyclic scaffold present in numerous natural products and therapeutic targets. Via this reaction, readily available aminal precursors are transformed to a variety of isoindolinone products in synthetically useful yields. Our mechanistic studies are consistent with addition of the electron-rich nickel catalyst to an iminium ion intermediate. We have also developed a new strategy to control enantioselectivity in additions to cyclic oxocarbenium ions, a long-standing challenge in asymmetric catalysis. This route efficiently converts readily available, racemic acetals to valuable enantioenriched alpha-substituted oxygen heterocycles, important scaffolds in bioactive molecules. Use of a chiral copper(I) catalyst and Lewis acid promoter delivers alpha-substituted isochromans and chromenes in high yields and enantioselectivities. Our working model for enantioselectivity will be presented.

198. Gold catalyzed intramolecular cyclizations

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Gold-catalyzed bond-forming reactions via activation of carbon-carbon pi-bonds have recently emerged as useful chemical transformations for organic synthesis. Due to its soft Lewis acidic nature, gold catalyst activates carbon-carbon triple bonds by withdrawing (“pulling”) electron density from the carbon-carbon pi bond. Our interest in new synthetic methodology development for biologically interesting heterocyclic and carbocyclic compounds using late transition metal catalysis has inspired us to explore new facile synthetic routes to such molecules. Our recent progress on new synthetic methodology development to 1-amino isoquinolines and indenones by gold catalyzed intramolecular cyclization reactions will be described. More than twenty 1-amino isoquinolines and indenones have been prepared in good to excellent chemical yields (up to 96%). A proposed reaction mechanism will be discussed.

199. How organic synthesis helps an inorganic chemist exploit hydrogen bonding interactions and carve out a niche for her group

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We have used organic synthesis to place hydrogen bonding groups both near and far from the metal center. In tris(triazolyl)borate (Ttz) ligands, bulky derivatives had not been synthesized prior to our work. We have made several bulky Ttz ligands and thus placed hydrogen bond acceptors at sites distal from the metal center, to better mimic interactions between metal bound histidines and H+ donors in enzymes. More recently, we have been working on dihydroxybipyridine (dhbp) ligands, where through synthesis we can vary the location of the OH groups. Hydroxyls groups proximal to our metal center(s) can act as hydrogen bond donors when protonated, or hydrogen bond acceptors when deprotonated. This also leads to pH being a switch for turning on or off water oxidation catalysis with our dhbp metal complexes. With both dhbp and Ttz ligands, the hydrogen bonding groups have a dramatic impact on bio-inspired chemical reactivity.

200. Engineering optical properties of tetrapyrrolic macrocycles for fluorescence bioimaging

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Tetrapyrrolic macrocycles possess a set of unique optical properties which make them attractive candidates for applications in fluorescence *in vivo* imaging. In this regard particularly attractive are hydroporhyrins – synthetic analogs of photosynthetic pigments. Here we will discuss our synthetic efforts towards developing of hydroporphyrin derivatives with properties optimized for *in vivo* multicolor imaging. We designed, prepared, and characterized a series of strongly coupled hydroporphyrin dyads with bathochromically-shifted absorption and increased fluorescence quantum yields. We also developed a series of weakly-coupled hydroporphyrin dyads, where whole series can be excited with the common wavelength, and each individual dyad exhibits distinctive, well resolved emission band. Finally, we examined a new motif for aqueous solubility of hydroporphyrins. Taken together, results presented here provide the basis for development of new generation of molecular probes for various areas of multicolor, fluorescence medicinal imaging.

201. Bacterial conversation stoppers: New methodologies for constructing next-generation anti-infectives

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Bacterial communication (also called quorum sensing) controls virulence and biofilm formation. Current efforts in our laboratory have focused on the synthesis of new chemical scaffolds to quench bacterial communication. In this talk, the facile synthesis of polycyclic compounds, using tandem reactions and remote C-H insertion reactions, using N-O tethered diazo moieties will be discussed.

Inorganic Chemistry; Physical Chemistry; Renewable Energy; Chemical Education

202. Novel approach to assessing critical thinking skills of general chemistry students

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A first-semester assignment, an introduction to descriptive chemistry and chemical references, was employed to assess students' critical thinking abilities. Each student chose an element, and researched and reported specified data, such as uses and melting point. Students then created costumes depicting their elements. The culmination of the assignment was the in-class presentation of the costumes and three clues to aid in identifying the elements.

AACU VALUE Rubrics were modified to assess critical thinking in four skill categories as demonstrated on this assignment. The percent of students (N = 45) meeting the benchmark of 2 on a 4-point scale was 88.9% for locating sources, but only 60.1% for producing a visual display.

This novel approach provided a baseline for assessing development of chemistry students' critical thinking.

203. Effects of the visual complexity of organic chemical notation on reading

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Organic chemistry equations are used to explicitly illustrate the relationships among organic molecules participating in a chemical reaction. In visually simple equations, relationships among the molecules are straightforward. However, when the visual complexity of the molecules increase, locating relevant relationships can become more difficult because of demands on cognitive resources. This study investigated how visual complexity of chemical equations affects the viewing patterns of students and instructors during reading. Participants were eye tracked while reading high/low visual complexity pairs of organic chemistry equations for comprehension. Analysis of eye fixation patterns suggests that the viewing patterns are affected by the complexity of the equations. When compared to the viewing patterns for visually simple equations, participants reading visually complex equations exhibit longer fixation durations, a greater number of fixations, and a longer sequence of fixations. These results have implications for the design of teaching innovations, assessments, and support materials for organic chemistry.

204. Beyond periodic table: Useful iPad applications in chemistry teaching

***Jiangyue Zhang**, lzhang@immaculata.edu.Chemistry, Immaculata University, Immaculata, PA 19345, United States*

The new generation Apple products, iPhone, iPod, iPad, have been very successful among American youth including college students. It may be possible to convert this entertainment gadget to a useful teaching tool. A number of iPad applications related to chemistry are reviewed and evaluated. From getting the most functional periodic table to finding scholar articles electronically and portably using iPad, it has a potential to enhance students' experience not only in the classroom but also the chemistry learning process.

205. Evaluation of mini gas chromatographs in the undergraduate organic chemistry laboratory

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The use of gas chromatography in undergraduate organic chemistry classes has been incorporated into several laboratory exercises. This project aims to allow a more modern approach to product identification and quantitation at the undergraduate level. Several existing laboratory exercises have been modified to ensure laboratory objectives are met. Successful application of the mini GC as well as its limitations will be discussed.

206. Zingerone and dehydrozingerone: A new multi-step synthesis project for the second year organic lab

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This work describes the multi-step synthesis of zingerone and dehydrozingerone used in our second semester organic lab curriculum. The target compounds are formed from vanillin using aldol condensation followed by transfer hydrogenation. The individual steps proceed in high yield. Unlike previous experiments , this version completes the aldol condensation in a single lab period and avoids the use of pyrophoric hydrogenation catalysts and hydrogen gas during hydrogenation. During the the synthesis, thin-layer chromatography, extraction, recrystallization are used. Column chromatography is used to purify the products. H-1 and C-13 NMR Spectroscopy, IR-Spectroscopy, Gas-Chromatography and TLC comparison to commercial samples are used to analyze product purity. Together, all of these factors make the project an excellent review of the techniques covered over the two-semester Organic Chemistry laboratory course. The experiment has received considerable positive feedback from our students who have enjoyed the beautiful sweet and spicy ginger-like smell of the products.

207. Investigations of 2-(4'-hydroxyphenyl-azo)benzoic acid in various solvents

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The interaction between 2-(4-hydroxyphenyl-azo) benzoic acid (HABA) and four solvents (pyridine, chloroform, tetrahydrofuran (THF) and 1,4-dioxane) were investigated. Previous work synthesized supramolecular assemblies (SMA) with the polymer poly(styrene-block-4-vinylpyridine) (PS-PVP) and HABA. The SMA was observed through FT-IR to have hydrogen bonding interactions between HABA and certain solvents (chloroform, THF, and 1,4-dioxane). Molecular modeling and UV-Vis experiments were conducted to study the HABA solvent interactions. Pyridine was specifically selected as the model for PS-PVP. Analyzing the solutions using UV-Vis confirmed that chloroform, THF, and 1,4-dioxane is capable of forming hydrogen bonds with HABA. In addition, pyridine and HABA created an intermediate. The intermediate was not observed in the other solvents. This observation was further supported by modeling studies which showed H-bond formation between HABA and pyridine.

208. Charge carrier dynamics in SiO_2@Ag@SiO_2 sandwiched nanostructure

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The charge carrier dynamics for SiO_2@Ag@SiO_2 sandwiched nanoparticles with various SiO_2 shell thickness were investigated. Due to interband transition of 4*d* electrons to the 5*sp* band of Ag nanoparticles take place when UV light irradiation, time-resolved photoluminescence spectra measurement was utilized with the Rhodamine B as the probe to quantitatively analyze the electrons transfer between Ag and SiO_2 shell. A decrease in electron transfer rate constant was observed for SiO_2@Ag@SiO_2 sandwiched nanoparticles with increasing SiO_2 shell thickness, this probably because the oxidation process of electrons captured by the vicinity oxygen was impeded by the outer silica. Besides, the photocatalytic activity of SiO_2@Ag@SiO_2 sandwiched nanoparticles was also found keep decreasing with increase the shell thickness. However, the suitable SiO_2 shell thickness could perform repeated and recycled photocatalysis in long-term course because it can instead protect the sensitive Ag nanoparticles from desquamating during such a photocatalystic reaction.

209. Locating the binding sites of Pb(II) ion with human and bovine serum albumins

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We located the binding sites of Pb(II) with human serum (HSA) and bovine serum albumins (BSA) at physiological conditions. FTIR, UV-visible, CD, fluorescence and X-ray photoelectron spectroscopic (XPS) methods were used to analyse Pb binding sites, the binding constant and the effect of metal ion complexation on HSA and BSA stability and conformations. Structural analysis showed that Pb binds strongly to HSA and BSA *via* hydrophilic contacts with overall binding constants of $K_{Pb\text{-}HSA}$ = 8.2 (± 0.8) x 10^4 M^{-1} and $K_{Pb\text{-}BSA}$= 7.5 (± 0.7) x 10^4 M^{-1}. The number of bound Pb cation per protein is 0.7 per HSA and BSA complexes. XPS located the binding sites of Pb cation with protein N and O atoms. Pb complexation alters protein conformation by a major reduction of α-helix from 57% (free HSA) to 48% (metal-complex) and 63% (free BSA) to 52% (metal-complex) inducing a partial protein destabilization.

210. Magnetic and structural studies of europium sulfide nanostructures

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Europium sulfide nanowires have been synthesized via hydrothermal and solid-state routes with tunable morphologies. Changes in magnetic properties have been studied by manipulating particle size and aspect ratio, as well as by probing their band structures with electron doping, via gadolinium incorporation. Effects resulting from single-crystalline and polycrystalline composition are examined, as well as controllable non-stoichiometry.

211. Evaluation of zinc based metal organic framework for carbon dioxide sequestration

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Zinc based metal-organic frameworks (MOFs) derived from the linkers, 2,2› (ethylenedioxy)dibenzoic acid and 2,2›-[1,3-phenylenebis(methylenedioxy)] dibenzoic acid, have been synthesized and evaluated for use in the sequestering of carbon dioxide (CO_2). CO_2 absorption properties of the MOFs were evaluated using a standard gravitated method. The MOFs exhibited a significantly greater uptake of CO_2 as compared to that of N_2 and O_2. The linkers and MOFs were characterized using ^{1}H-NMR,^{13}C-NMR, FE-SEM, TGA and FT-IR.

212. Synthesis and structure characterization of ionic tributyltin complexes with oxalic acid

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Triorganotins have been well established as having various biological activities. Our hypothesis is that ionic triorganotin derivatives will have better solubility therefore better biological activity. Synthesis of the ionic tributyltin complexes involve the reaction of oxalic acid, a diprotic carboxylic acid, with bis(tributyltin) oxide in the presence of dicyclohexylamine (complex **1**) and dibutylamine (complex **2**). A polymeric ionic tributyltin complex with four Tin nuclei in the repeating monomeric unit was obtained from the synthesis with dicyclohexylamine. The structure of the complexes was characterized by Infrared and multi-nuclear NMR(^{1}H, ^{13}C and ^{119}Sn) spectroscopies and confirmed by X-ray crystallography for complex **1** . The ionic complex consists of two anionic moieties and two dicyclohexylammonium as the counterions. All tin atoms in the two complexes have the common trans-trigonal bipyramidal geometry with three butyl groups in the equatorial plane and two O atoms at axial position.

213. Synthesis, characterization and electrochemistry of chlorinated aromatic [FeFe]-hydrogenase inspired electrocatalysts

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The synthesis, characterization and electrochemistry of increasingly chlorinated μ-benzenedithiol-$Fe_2(CO)_6$ electrocatalysts are presented. These catalysts take structural inspiration from the active-site structure of [FeFe]-hydrogenases. The use of increasingly electronegative thiolato bridges is probed, to anodically shift the potential required for the catalysts to undergo reduction. These electrocatalysts must be reduced prior to entering into a catalytic cycle that produces hydrogen from weak acid sources (acetic acid, pKa = 22.3 in acetonitrile).

214. Electrochemical mediation of hydrogenase-inspired electrocatalysts: Attempts to lower overpotential

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Inter- and intra-molecular mediation of electron transfer to an [FeFe]-hydrogenase active-site inspired electrocatalyst has been explored. Metal-centered mediators show greater promise than or-

ganic mediators, although appropriate tuning of the reduction potential of the metal-center mediator remains an outstanding challenge. A successful mediator will allow for a lowering of the overpotential of hydrogen production by acting to relay electrons to the active catalytic site, akin to the use of multiple [4Fe4S] clusters in the native enzyme.

215. Controlled impregnation of silica colloids with transition metal salts

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Transition metal containing nanocomposites of silica are of tremendous interest due their various applications as catalysts, sensors, optomagnetic and photonic materials. In recent years, various strategies have been developed to hybridize silicon based materials with transition metals as well as metal and/or semiconductor nanoparticles. Our group also has been exploring new avenues to produce silica-TM hybrids in controlled and predictable fashion.

In this poster, we will describe a new method, which involves self-gelification/ polymerization of aminoalkoxysilanes with transition metal carbonyls to produce metal complex nucleated silica gels. The characterization studies of the hybrid materials were carried out using UV-vis., IR and NMR, Atomic Force Microscopy, and Electron Microscopy (SEM and TEM). Results of our efforts to introduce the ligand exchange reactions of entrapped metal carbonyls with phosphine's and other coordinating ligands will also be discussed.

216. Synthesis, characterization and applications of nickel-silicon gels

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The covalent attachment of metal complexes and metal nanoparticles to polymerizable monomers can be a very attractive route to produce covalently attached metal containing gels and polymeric materials. An intense interest is devoted to activities in this area of research because of the potential applications of such materials in the fields such as drug delivery, catalysis, electronics, photonics, optoelectronics, sensing, and bio-imaging.

Our strategy is very simple and involves one step synthesis of such materials via the coupling reaction of a bi-functional gel precursor and a novel metal complex. In this presentation, we will describe the synthetic strategy to obtain homogeneously Ni- impregnated silicon gels, which are obtained by the reaction of Ni-complexes with sol-gel precursors during the gelification process. We will also present a comparative study of the gelation of various Ni-complexes and their characterization by various spectroscopic techniques along with exploration of the catalytic activities of these gels.

217. Ruthenium chromophores for anchoring platinum nanoparticles to titanium dioxide semi-conductors in dye-sensitized solar cells

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A ruthenium bis-bipyridyl complex was synthesized with one bipyridyl ligand possessing two carboxylic acid groups to bind to TiO2 semiconductor surfaces in dye-sensitized solar cells (DSSCs) and with the other bipyridyl ligand functionalized for binding to platinum nanoparticles. The purpose of this ruthenium complex was to closely associate platinum nanoparticles to study electron transfer and regeneration properties of DSSCs. Initially, a bipyridyl ligand with two alkyl-thiol groups for binding

to platinum was synthesized, but these thiol groups were not stable. An alternative binding group for platinum was investigated. Stability concerns were addressed with the use of two lipoic acid esters in the bipyridyl ligand. The dye was successfully synthesized and bound to TiO2 films in DSSCs.

218. Synthesis and characterization of porphyrin derivatives into the development of a dyad using an Fe8 cluster

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We propose the synthesis of artificial antennas to improve the efficiency of photovoltaic cells. These antennas need an electron donor and an electron acceptor. We have a family of $Fe_8(\mu_4\text{-}O)_4(\mu\text{-}pz^*)_{12}X_4$ complexes that have been demonstrated to be a very good electron acceptors. These molecular clusters can accept up to four electrons. If we compared with a widely use fullerene molecule, Fe8 clusters can accept two electrons at energies lower than the needed for fullerene to accept the first electron. We predict that more than one electron can be accepted using the available electron donors. For an electron donor we plan to use metalloporphyrins of either Zn, Cu or Fe derivatives. After the addition of any of these metalloporphyrins we can observe the coordination with the already synthesized $Fe_8(\mu_4\text{-}O)_4(\mu\text{-}pz^*)_{12}$(3-HO-pyridine)$_4$. Spectroscopic data indicate the presence of metalloporphyrins coordinating with the Fe8 cluster.

219. Manganese clusters as potential MRI contrast agents

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We have studied the use of manganese clusters as an MRI contrasting agent alternatively from the gadolinium and iron oxide agents in use presently. These clusters have favorable relaxations when compared to gadolinium and also present favorable alternatives in agent delivery. Work here is presented on relaxation studies, different manganese clusters and the corresponding synthesis, and cytotoxcity results.

220. Photophysical and electrochemical properties of bis-cyclometallated transition metal complexes in aqueous and organic media

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Luminescent cyclometalated transition metal complexes have captured the interest of many scientists, principally as triplet emitters in organic light emitting diode devices[1], and increasingly for potential applications in biological and chemical sensing[2] and bioimaging.[3] Although the photochemical properties of such complexes have been the subject of intensive investigation, their behavior in aqueous media remains largely unexplored with the exception of $[Ru(bpy)^3]^{2+}$.

We will be presenting a comprehensive comparative study of $[Ru(bpy)_3]^{2+}$ (bpy = 2,2'-bipyridine and its derivatives), $Ru[3,4,7,8\text{-}(CH_3)_4phen]_3^{2+}$ and $Ir(ppy)_2(bpy)^+$ electrochemical and photophysical properties in organic and aqueous media. This will include investigation into the stability of the Ru(III) and Ir(IV) of respective complex in aqueous solution using approach of chemical oxidation.

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221. Synthesis, characterization, X-ray structure and possible anticancer properties of *fac*-$(CO)_3$(neocuproin)Re(picolinate) and *fac*-$(CO)_3$(neocuproin) Re(nicotinate)

***Brent V Powell**, brpow3@morgan.edu, Santosh K Mandal.Chemistry, Morgan State University, Baltimore, Maryland 21251, United States*

Picolinato and nicotinato complexes are of importance because many of them have been proposed as anti-diabetic drugs. We have been studying the chemistry of rhenium(I) (tricarbonyl) diimine complexes during the past several years. We have found that rhenium(I) picolinato and nicotinato complexes can be synthesized quantitatively from the reactions of the corresponding pentylcarbonato complexes with picolinic and nicotinic acid, respectively, according to eq 1:

fac-$(CO)_3$(α-diimine)ReOC(O)OC_5H_{11} + HOA → *fac*-$(CO)_3$(α-diimine)ReOA +

$C_5H_{11}OH$ + CO_2 (1)

(HOA = picolinic or nicotinic acid)

In this presentation, we would like to describe the synthesis, characterization, X-ray structures and possible anticancer properties of the picolinato complex, *fac*-$(CO)_3$(neocuproin)Re(picolinate) and nicotinato complex, *fac*-$(CO)_3$(neocuproin)Re(nicotinate).

222. Synthesis and anticancer properties rhenium(I) aspirinato complexes

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Transition metal asprinato complexes are of importance because such complexes exhibit glucose-lowering activity for treating type 2 diabetes and cytotoxicity against numerous cancer cell lines. We have synthesized rhenium(I) aspirinato complexes quantitatively from the reactions of the corresponding pentylcarbonato complexes with aspirin according to eq 1:

fac-$(CO)_3$(α-diimine)ReOC(O)OC_5H_{11} + HOA → *fac*-$(CO)_3$(α-diimine)ReOA +

$C_5H_{11}OH$ + CO_2 (1)

(HOA = aspirin or acetylsalicylic acid)

In this presentation, we would like to describe the synthesis, characterization, X-ray structures and anticancer properties of the aspirinato complexes, *fac*-$(CO)_3$(α-diimine)Re(aspirinate), where, α-diimines are 2,2′-bipyridyl, 1,10-phenanthroline, and substituted 1,10-phenanthrolines.

223. Small molecule activation and reactivity using low valent chromium (I) supported by a hydrotris(pyrazolyl)borate ligand

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The $(Tp^{tBu,Me}Cr)_2$ (μ-η ^{1}:η^1 -N_2) complex has been synthesized and structurally characterized. It contains a bridging end-on bonded dinitrogen ligand with a N-N distance of 1.240(12) Å. This Cr(I) dinitrogen complex shows reactivity towards a variety of small molecules. Examples include various azides producing $Tp^{tBu,Me}Cr$(NR) imidos, elemental sulfur yielding the corresponding $Tp^{tBu,Me}Cr$ (η ^{2} -S_2) persulfido, and nitrous oxide yielding the $(Tp^{tBu,Me}Cr)_2$ (μ-O)$_2$ complex.

224. Synthesis and characterization of metal complexes with new steric a-diimine and pyridine(bisanil) ligands in relevance to olefin polymerization

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Brookhart *et.al.* have reported late transition metal complexes of *a*-diimines as excellent catalysts for olefin polymerization. Subsequently, Brookhart *et.al.* & Gibson *et.al.* have reported independently the metal complexes from pyridine(bisanil) compounds as highly efficient catalysts for the same purpose. Since the discovery of pyridine(bisanil) iron and cobalt complexes by Gibson *et.al.* and Brookhart *et. al.*, an immense amount of work has been done on improving the catalytic activities and understanding the mechanism of catalysis by these complexes. It is well established that high steric bulk at the *ortho*-positions of the parent aniline provides highly linear polymers. In our laboratory, we have synthesized and characterized *a*-diimines and pyridine(bisanil) native ligands, as well as metal complexes, starting with 2,4,6-tricyclohexylaniline. In this poster we present a detail of the synthesis and characterization of the native ligands and selected metal complexes with the aforesaid ligands.

225. Pulmonary oxygen toxicity is modulated by its paramagnetic property

***Radford Shanklin**, dshanklin@mbl.edu.Department of Biochemistry, Marine Biological Laboratory, Woods Hole, Massachusetts 02543-0511, United States*

Hyaline-membrane-disease (HMD) is often lethal in newborns. Bilateral cervical vagotomy (BCV), a standard model for HMD, has short median/mean survival. Extent of pulmonary disease varies in different gas mixes [*Biol.Neonat.*20:140,1972]. A slower model, thoracic restraint (TR) on the thorax of newborn rabbits was used in chambers with 100% oxygen with or without magnets with a varied field to +1200 gauss. Parallel experiments with adult female white mice eliminated TR-distress. Rabbits ($p<0.0001$) and mice ($p=0.015$) survived longer in magnetized-oxygen. HMD was twice as severe in rabbits($p<0.0001$), similar in mice. The rate of lung injury per hour in magnetized-oxygen is lower; rabbits: 1.3728%-to-1.7969% (ratio=1.3088); mice: 0.8634%-to-1.2617% (ratio=1.462). Magnetized-oxygen enhances survival; nevertheless, the rate of lung injury is reduced 24%, rabbits, 31% mice. Toxic effects of oxygen are reduced systemically and in lung by weak magnetic field influences on inherently paramagnetic oxygen.

226. Environmental and structural effects on self-assembly of conductive peptide-porphyrin aggregates

***Michael Reca**, recam88@students.rowan.edu, Erin Dahl, Jillian Gamel, Gregory A Caputo.Department of Chemistry and Biochemistry, Rowan University, Glassboro, NJ 08028, United States*

We investigated novel peptide/porphyrin systems for potential applications in organic solar cells. Meso-tetra(4-sulfonatophenyl)-porphyrin (TPPS) and meso-tetra(4-carboxyphenyl)-porphyrin TPPC successfully self-assembled with a 22-residue peptide containing 3 cation-rich porphyrin binding motifs. Previous work has shown that similar TPPS/peptide systems form excitonically coupled J-aggregates with varying effectiveness across acidic to neutral pH levels. Here we report preliminary results indicating strong effects of ionic strength and TPPS/TPPC coupling on the self-assembly using absorbance spectroscopy. The ionic strength studies corroborate a negative correlation between ion concentration and J-aggregate formation, implicating an electrostatic component in assembly. Addition of TPPC into TPPS at low pH appears to enhance excitonic coupling between porphyrins and higher order aggregation. The system also exhibits pH sensitivity with J-aggregate formation only present below pH 4.

227. Theoretical study of interactions between ferrocene/ferrocenium and imidazolium

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The combination of room-temperature ionic liquids and ferrocene is promising to develop the next-generation nanoelectronic materials. As a first attempt to study the solvation of ferrocene/ferrocenium in imidazolium-based ionic liquids, systematic investigations of intrinsic interactions between ferrocene/ferrocenium and imidazolium in the gas phase are performed with the dispersion-corrected density functional theory. Preliminary calculations reveal degenerate strong interactions of ferrocene with imidazolium in the T-shape and the tilt binding modes. As expected, due to the electrostatic repulsion, no stable binding interaction is captured between ferrocenium and imidazolium although the dispersion interaction exists between the molecules. Binding energies, structures, and electrostatic potentials are characterized. The electronic structures are analyzed with the Natural Bond Orbital method. The solvent effect is further addressed using the continuum solvation model. Due to the involvement of the aromatic structures, the current study also shed valuable insight on π-interactions from a physical chemistry point of view in general.

228. Continuing development of the CHARMM polarizable charge equilibration force field for phospholipid membranes

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Lipid membranes are an essential component of biological systems and play host to a wide variety of proteins and other species. Therefore, it is crucial that to properly represent biologically relevant systems, the lipid membrane must be correctly modeled. Previous generations of polarizable charge equilibration lipid force fields, although successful at reproducing several experimental properties for dipalmitoylphosphatidylcholine and dimyristoylphosphatidylcholine bilayers, failed to predict area per lipid values during NPT simulations and resulted in membrane constriction. Ab intio interactions energies between head group analogs dimethylphosphate and tetramethylammonium were calculated at the MP2/6-31++(2d,p) level of theory and compared with those calculated using modified CHEQ force fields. The current force field includes refinements to the Lennard-Jones non-bond interactions between headgroup atom types O2L (phosphate oxygen) and NTL (choline nitrogen) which mediates headgroup spacing. This modification allows a DPPC bilayer to maintain an area per lipid near the experimental value of 63 $Å^3$.

229. Surface chemistry studies of acrylonitrile on copper, silver, and gold nanoparticles by surface-enhanced Raman spectroscopy

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Acrylonitrile has two functional groups, the olefinic C=C group and the nitrile C≡N group, available for bonding with metal atoms. The C=C group can be bonded via its π-system which results in a decrease of the stretching by 50-150 cm^{-1}, whereas the C≡N group may be bonded via its lone pair electrons on the N atom or via its π-system of the C≡N group. Low concentrations of acrylonitrile were added to explore its bondings with Cu, Ag and Au nanoparticle surfaces of 20 to 40 nm. In comparison to liquid acrylonitrile, the peaks associated to the vibrational assignments of C=C at 1609 cm^{-1} were shifted to 1598 cm^{-1} indicating “mild” coordination to metal through the C=C bond. Broad peaks were observed between 2050 and 2100 cm^{-1}, depending on the kind of metal, which are attributed to π-coordination of the C≡N group.

230. Effect of counterions in regulating the self-assembly of hepatitis B viral capsids in solution

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Highly charged bio-macromolecules with size in nanometer scale can also be treated as macroions. In these bio-macroionic systems, electrostatic interactions are fundamental to various phenomena, especially in regulating nucleic acids (DNA and RNA) condensation and folding, maintaining protein ternary structure and directing the assembly of viral capsids. Our recent studies have shown macroions in solution can slowly self-assemble into spherical hollow vesicular structures in solution due to counterion-mediated attraction and hydrogen bonds. Similar phenomena have been noticed for Hepatitis B viral capsid formation, although the major driving forces are contributed to hydrophobic interactions. By using small angle X-ray scattering (SAXS), we noticed that small counterions closely distributed around HBV capsids and the counterion mediated attraction is critical to the formation of HBV capsids. Our findings may help people better understand the nature of protein-protein interactions, especially the charge effect, in solution.

231. Equilibrium and transition states for thiourea using *ab initio* methods

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Thiourea is a potential molecular species that may be detected in the interstellar media. This work will present calculations of the various equilibrium structures that have been completed for this molecular system using CCSD(T) method with the cc-pVTZ basis. Also calculations on the possibility of the migration of the hydrogen atom from the nitrogen atom to the sulfur atom will be presented.

232. Correlation analysis of column-density data with surface mixing ratios for O_3 and NO_2 during DISCOVER-AQ

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The first deployment of the DISCOVER-AQ project was conducted during July 2011 in the Baltimore-Washington region. The P-3B aircraft performed in situ sampling of the trace gases O_3 and NO_2 over surface air quality monitoring sites. These surface sites were also equipped with ground-based Pandora UV/Vis spectrometers. Satellite observations for tropospheric O_3 and NO_2 from Aura/OMI and forecasts of O_3 and NO_2 from an experimental version of the Community Multi-scale Air Quality model were provided during the deployment. A correlation analysis was performed between the P-3B, Pandora, OMI, and CMAQ O_3 or NO_2 tropospheric column amounts and the surface data for each site. The values of the correlation coefficients obtained for the model are generally larger than those for the observations, indicating that the model surface is more connected to the overlying column than the observations were. However, both model and observations demonstrate larger correlation coefficients for O_3 than NO_2.

233. Non-invasive in-depth investigation of skin and other substrates by terahertz scanning reflectometry

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The non-ionizing nature of T-ray offers an opportunity to investigate both the surface and the sub-surface of biological tissues (e.g., skin) in a non-invasive fashion. It eliminates radiation damage of sensitive tissues while be able to probe disease conditions in the deeper layers leading to an effective real-time diagnostic tool. Measurement of permeation kinetics and dose is important in several areas such as in the study of penetration behavior of an active ingredient through human skin or other tissue. Two critical factors are: the concentration gradient of permeating ingredient across the depth of skin and the kinetics of such permeation. In this study, a terahertz scanning reflectometer (TeraScanR, Applied Research & Photonics, Harrisburg, PA) was used for direct quantitation of analytes across the thickness of stratum corneum and permeation kinetics of active ingredients. Two analytes, hydrocortisone and caffeine were investigated. Some details will be discussed in terms of experimental data.

234. New pincer platforms for CO_2 conversion and small molecule activation

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The reduction of carbon dioxide by two electrons to generate carbon monoxide is an energetically uphill transformation with implications for solar fuel production. Accordingly, we have developed a suite of compounds consisting of $[PDC^{R}PdL](PF_6)_2$, (R= methyl, ethly, isopropyl, cyclohexyl, and mesityl L= acetonitrile, pyridine, and t-butylisocyanide), where PDC^{R} is a pyridine bridged N-heterocyclic carbene pincer ligand. These compounds have been characterized by NMR and IR spectroscopies. Furthermore, X-ray crystallography has permitted the solid-state structures of these complexes to be determined. VT-NMR and IR experiments have allowed for the thermodynamics and kinetics of small molecule binding by this family of complexes to be probed. The subtle interplay between ligand electronics and molecular cleft accessibility will be discussed in terms of catalyst design for CO_2 conversion.

235. Ditopic platforms for conversion of carbon dioxide to chemical fuels

Tian Qiu, *tianqiu@udel.edu, Joel Rosenthal.Department of Chemistry and Biochemistry, University of Delaware, Newark, DE 19716, United States*

Carbon dioxide is a key contributor to global climate change but also a potentially valuable C_1 synthon for production of fine and commodity chemicals. Furthermore, electrochemical CO_2 reduction presents a prime strategy for renewable energy storage via production of liquid fuels. Accordingly the development of catalysts that can efficiently activate CO_2 in the presence of water and protons is a major area of development. Along these lines, we have prepared and structurally characterized a series of functionalized nickel macrocycles containing ancillary Lewis-basic residues. The ditopic nature of these systems allows for orthogonalization of the CO_2 binding and redox sites, thereby allowing these platforms to selectively activate CO_2 in the presence of acid. Accordingly, these new systems display fine faradaic efficiencies for reduction of carbon dioxide. The synthesis and electrochemical properties of these systems will be presented.

236. Carbon dioxide activation by bis-NHC complexes of palladium

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Given the alarming rise of atmospheric CO_2 levels and the unrelenting global demand for liquid, the catalytic conversion of CO_2 to energy rich substrates is an important area of research. In addressing this area, we have developed several palladium complexes supported by chelating dicarbene ligand scaffolds and surveyed the ability of these platforms to serve as electrocatalysts for the conversion of CO_2 to CO. By varying the identity of the supporting ligands the ability of these platforms to activate CO_2 can be tuned with ease. The synthesis, spectroscopy and reactivity of these systems will be presented.

237. Towards pyridyl ruthenium capped polystyrene brushes grafted from the surface of reduced graphene oxide sheets

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Graphene based assemblies are currently being explored with the goal of gaining new insight on the fundamental photophysics of these materials. Our approach is to graft polystyrene brushes from the surface of chemically reduced graphene oxide sheets. The polystyrene brushes are end capped with a pyridyl ruthenium complex. Furthermore, we have systematically altered the length of the polystyrene brush. These systems are rigorously characterized by NMR, IR, XPS, AFM, SEM, GPC, fluorescense and CV.

238. High-capacity metal-oxide aerogels for electrochemical charge storage

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Electrically conductive metal-oxide aerogels are highly porous three-dimensional architectures that contain a network of solid nanoparticles suspended through void space. Such materials have high surface areas (typically 100–600 m^2/g) and a large electrode/electrolyte interface beneficial for the kinetics of electron/cation insertion reactions and the magnitude of electrochemical charge stored thereby.[1] Previously Long *et al*. demonstrated facile processing routes for downselecting nanocrystalline iron oxide (FeO*x*) phases from a parent FeO*x* aerogel.[2] We are now extending this work to explore the ion-insertion properties of certain FeO*x* phases derived from a sol–gel approach (i.e., Fe_3O_4, γ-Fe_2O_3) and optimizing the performance of such materials through the deliberate incorporation of structural defects.

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239. Synthesis of homoleptic ruthenium ‘star’ complexes via click reaction

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Homoleptic ($[RuL_3]^{2+}$), ruthenium(II) complexes carrying rigid bpy-triazole-anchor linkers for attachment to semiconductor surfaces were synthesized using the azide/alkyne-“click”-reaction. The

two star-shaped complexes **StarK-Ipa** and **StarK-pBn** were comprised of 2,2'-bipyridine ligands that are 4,4'-disubstituted with 1,2,3-triazole bridges terminating with isophthalic (Ipa) or *p*-benzoic (pBn) methyl ester groups, respectively. The complexes were prepared by complexation of the bpy-triazole-anchor ligands synthesized by click reaction, whereas click-reactions of the azide- or ethynyl-substituted Ru bipyridyl complexes with ethynyl- or azide-substituted anchor groups were not successful. Titration with acid showed a ~2-fold increase in fluorescence for both **StarK-Ipa** and **StarK-pBn** . Also, complexes **StarK-Ipa** and **StarK-pBn** were bound to semiconducting TiO_2 and insulating ZrO_2 nanoparticle films. The ZrO_2 films, following excitation at 485 nm showed a broad fluorescence band whereas the fluorescence was fully quenched on TiO_2.

240. Characterization of algae bio-oil produced by microwave-assisted pyrolysis: A study of the potential for algae bio-oil as an alternative fuel source

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Algae are a fast-growing, renewable, and sustainable source of biomass feedstock. Algae biomass was converted into bio-oil using microwave-assisted pyrolysis (MAP). Algae-derived bio-oils have been shown to have comparable physical properties of petroleum diesel, including density, viscosity, and heating value. During this research algae biomass collected from pure (*Chlorella vulgaris* and *Scenedesmus*) and mixed (filamentous green algae) cultures were each subjected to MAP, in which different algae-derived bio-oils were produced. The crude algae-derived bio-oils as well as biodiesel were characterized in terms of density, viscosity, and heating value determined using O_2 bomb calorimetry. Heating value averages with standard errors were diesel 45.75±0.05 MJ/kg, biodiesel 39.39±0.06 MJ/kg, and algae-derived bio-oil 30.83±2.05 MJ/kg. With further upgrading or blending of the bio-oil in order to reduce its viscosity, the results from this study provide support for the use of algae biomass as an alternative fuel source.

241. Modular functionalization of electrode interfaces for energy catalysis applications

Rachel C. Pupillo, *rcp@udel.edu, Amber Gietter, Donald A. Watson, Joel Rosenthal.Department of Chemistry and Biochemistry, University of Delaware, Newark, DE 19716, United States*

Catalysts are currently being designed to promote the energetically uphill conversion of carbon dioxide to fuels, as a means to store renewable energy inputs. Much focus has been directed at the design and synthesis of homogeneous molecular electrocatalysts for such transformations, however, studying such systems is complicated by diffusion of both catalyst and substrate to an electrode surface. Anchoring of discrete molecular catalysts onto an electrode surface eliminates many of these complications and allows for electrocatalyst efficacy to be probed more effectively. We have developed a general method to tailor inexpensive electrode interfaces for a variety of electrochemical applications. This two-step method takes advantage of our ability to graft a monolayer of properly substituted aryl-diazonium derivatives directly onto conducting supports followed by an appropriate chemical transformation to afford arrays of modified molecular wires. The fabrication and electronic properties of these well-ordered interfaces will be discussed.

242. Design, evaluation, and optimization of aqueous asymmetric electrochemical capacitors with nanoarchitectured electrodes

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Carbon fiber-paper-supported carbon nanofoams are ideal electrode platforms for electrochemical power sources due to such inherent attributes as high specific surface area, high electronic conductivity, a size-tunable through-connected pore network, and a "plug-and-play" macroscopic form fac-

tor. To enhance the electrochemical functionality of carbon nanofoams, we have developed simple, scalable electroless deposition protocols that generate conformal, nanoscale coatings of charge-storing metal oxides on the carbon surface. For example, exposing the carbon nanofoam to sodium permanganate produces a nanoscale manganese oxide (MnO*x*) coating. The metal oxide coating increases the capacitance of the carbon nanofoam 2-to-10 fold without significantly affecting its high-rate capabilities. Prototype aqueous asymmetric electrochemical capacitors (ECs) containing these metal oxide–carbon nanofoam electrodes provide operating voltages approaching 2 V, specific energy of 14 W h kg^{-1} and a 10 s charge–discharge. In addition, we also explore more practical issues related to this EC design, including the down-selection of separators and electrolytes.

Chemistry in the Chemical Senses B

Presiding: G. Preti

243. DNA-decorated carbon nanotube-based FETs as ultrasensitive chemical sensors: Discrimination of homologues, structural isomers, and optical isomers

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We have explored the abilities of all-electronic DNA-carbon nanotube (DNA-NT) vapor sensors to discriminate very similar classes of molecules. We screened hundreds of DNA-NT devices against a panel of compounds chosen because of their similarities. We demonstrated that DNA-NT vapor sensors readily discriminate between series of chemical homologues that differ by single methyl groups. DNA-NT also discriminate among structural isomers and optical isomers, a trait common in biological olfactory systems, but only recently demonstrated for electronic FET based chemical sensors.

244. Volatile compounds and disease: Detection of *Aspergillus fumigatus*

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Repulsion to odor produced by rotting matter is a safety mechanism most animals possess to avoid disease. Recognition of this relationship between disease and odor pre-date recorded thought. Taken a step further, identification and measurement of volatile chemicals produced by specific pathogens provide a means for early disease diagnosis. In this study volatile chemical profiles collected from the headspace of *Aspergillus fumigatus* (a pathogenic fungus that causes invasive pulmonary aspergillosis, allergic bronchopulmonary aspergillosis and chronic fungal sinusitis) contained a large abundance of the sesquiterpene farnesene (3,7,11-trimethyl-1,3,6,10-dodecatetraene) and, depending on extraction time and sorbent material, other farnesene isomers and sesquiterpenes such as bisabolene (methyl-4-(6-methylhepta-1,5-dien-2-yl)cyclohex-1-ene). When human lung cells were cultured externally and infected with *A. fumigatus*, farnesene was also detected in each model lung system.

245. Genetic influences on body odors in mice and humans

Jae Kwak[1], *jaekwak@hotmail.com, George Preti*[1,2], *Kunio Yamazaki*[1], *Gary K Beauchamp*[1]. *(1) Monell Chemical Senses Center, Philadelphia, PA 19104, United States (2) Department of Dermatology, School of Medicine University of Pennsylvania, Philadelphia, PA 19104, United States*

Individual mice and humans can be recognized by a unique odor signature (odorprint) that is, in part, genetically determined. Among the genetic bases for individual odorprints, major histocompatibility complex (MHC) genes have been demonstrated to influence body odors in mice and humans. Animal studies suggest that odorprints regulated by MHC are robust despite other genetic and environmental perturbations. Additional genetic components have been shown to affect individual odor

signatures. Variation in the structure of the major urinary proteins (MUPs) is extensive in wild mouse populations, which has been reported to be involved in individual recognition, inbreeding avoidance, and evaluation of genetic heterozygosity of potential mates. In humans, the ATP-binding cassette transporter subfamily C member 11 (ABCC11) gene has been shown to be associated with the production of axillary odor components. In this presentation, we will discuss the effect of these genetic components on odorprints in mice and humans.

246. Human pheromones and axillary chemistry: What's known, what's not

George Preti[1,2]*, preti@monell.org, Charles J Wysocki*[1]*. (1) Monell Chemical Senses Center, Philadelphia, PA 19104, United States (2) Department of Dermatology, School of Medicine University of Pennsylvania, Philadelphia, PA 19104, United States*

Body odors are the focal point for the consumer product industry and academics interested in human scent. Although deo-products have been around for more than 100 years, the compounds which produce underarm odor have only been known since 1991. Pheromones were first sought and defined for insects in 1959. Many insect and some non-human mammalian pheromones release a specific reaction: e.g., a definite behavior or developmental process. Evidence supports the production of human chemosignals, but they are not sex attractants, as suggested by advertisements. The nature and biogenesis of the volatile compounds which characterize the axillae has been studied; they are a mixture of C_6-C_{12} normal, branched, unsaturated, and hydroxy-organic acids as well as smaller amounts of olfactory potent thio-alcohols. The acids, including (E)-3-methyl-2-hexenoic acid are present in microgram quantities in many individuals. Progress in linking axillary components to physiological/ pheromonal affects and transmitting of individual identity will be described.

Medicinal Chemistry in Academia

Presiding: T. Tsukamoto

247. Adventures in academic probe and drug discovery

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Sequencing of the human genome ushered in a new focus for biomedical research – instead of identifying genes, now efforts are aimed at understanding the function of those genes and their products. Small molecule probes are ideal tools to interrogate these biological systems, and can serve as starting points for drug discovery efforts. Medicinal chemists working in an academic setting have an opportunity to make significant impact in this area of research, particularly when the targets are proteins and systems that are not well understood, are involved in rare or neglected diseased and /or may benefit from access to highly specialized expertise in chemistry, biochemistry or biology. Efforts at developing probes to answer key biological questions in the areas of rare infectious diseases, difficult to treat cancers and neurological diseases will be highlighted, as will the challenges encountered.

248. Novel therapeutics against *Mycobacterium tuberculosis*

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Tuberculosis (TB), caused by *Mycobacterium tuberculosis* (Mtb), is one of the world's deadliest infectious diseases. Emergence of drug-resistant strains of Mtb and co-infection with HIV has made TB both difficult and expensive to treat. New TB therapies are needed to shorten treatment and be effective against all strains and metabolic states of the organism. Development of inhibitors of 1-deoxy-D-xylulose-5-phosphate reducto-isomerase (Dxr), an essential enzyme for Mtb, is a novel approach toward the development of a new TB chemotherapy. Natural product fosmidomycin inhibits Dxr, kills other organisms reliant on this enzyme, but is not effective against Mtb. The goals of our work are to: synthesize lipophilic prodrugs of fosmidomycin and its analog FR900098 that kill Mtb, and to rationally design inhibitors that will specifically inhibit the enzyme. Combining these approaches should yield molecules active and potent against Mtb. Our progress in each of these areas will be described.

249. Natural products: Continuing sources of inspiration for chemical and biological discovery

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Natural products continue to be a source of inspiration for chemists and biologists alike. From a pharmacological perspective, biologically active natural products modulate protein function in diverse and often unanticipated modes. Furthermore, they can provide insight into the mechanism of disease progression and treatment. Recent estimates suggest that natural products serve as the inspiration for some 50% of all oncology drugs from the 1940s to date. From a chemical perspective, natural products provide unusual and unprecedented chemical architectures that serve as the inspiration for novel synthetic methodologies in addition to providing novel chemical material for further study. This talk will detail two case studies of biologically active natural products: fellutamide B, a neurotrophic peptide aldehyde, and mitragynine pseudoindoxyl, an analgesic rearranged indole alkaloid. The role each molecule has played in chemical and biological study will be discussed.

250. Small-molecule, anti-cancer BH3 domain proteomimetics: Dual antagonism of the Bak–Bcl-x_L and Bak–Mcl-1 protein–protein interactions

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Over-expression of the anti-apoptotic Bcl-2 proteins, particularly Bcl-x_L, Bcl-2 and Mcl-1, leads to tumor initiation and progression. The cell survival function of these proteins is a direct result of their ability to sequester the α-helical BH3 "death" domain of the pro-apoptotic Bcl-2 proteins, which include Bak and Bax. Accordingly, the development of small-molecule BH3 mimetics is now a well-established strategy toward the identification of novel, anti-cancer therapeutics. However, for this approach to be effective, the BH3 mimetic must be able to engage both Bcl-x_L/Bcl-2 and Mcl-1, otherwise the tumor will demonstrate resistance. Starting from a previously-reported BH3 mimetic that exhibits micromolar activity against the Bak–Bcl-x_L complex in vitro, we have conducted a structure–

activity relationship study of the backbone of the mimetic, and enhanced the inhibitory activity ten-fold. Furthermore, our new compounds demonstrate disruption of both the Bak–Bcl-x_L and Bak–Mcl-1 complexes in whole cells, and they induce apoptosis.

251. Development of small molecule prostate specific membrane antigen (PSMA) targeted imaging agents for prostate cancer

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Prostate cancer (PCa) is the second leading cause of cancer-related death in men. More accurate staging of PCa would lead to better treatment decisions resulting in improved clinical outcomes. Prostate-specific membrane antigen (PSMA) is a type II integral membrane protein expressed on the surface of PCa cells, particularly in androgen-independent, advanced and metastatic disease. This talk traces our efforts in the development of PSMA inhibitors based on the glutamate-urea scaffold as imaging agents for a variety of modalities, including positron emission tomography (PET), single photon emission computed tomography (SPECT) and optical imaging. Our agents consist of either small radiohalogenated ureas totally confined to the PSMA binding site or larger molecules containing a linker that tethers chelated radiometals or fluorescent moities to the outside of the protein. Both types have detected PSMA-positive tumors in experimental PCa. Initial clinical studies also clearly identify known and suspected sites of metastatic PCa.

252. Oral delivery of the appetite suppressing peptide PYY(3–36) through the vitamin B_{12} uptake pathway

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Injections of PYY(3– 36) have shown positive effects on appetite regulation. With nearly 400 million adults worldwide considered obese, these positive effects have sparked an increased interest in PYY(3– 36) research, including release profiles, receptor targets, and medicinal applications. A major area of interest is oral delivery of PYY(3– 36) that can display clinically relevant weight-loss outcomes in what would be a highly patient compliant route. The vitamin B_{12} (B_{12}) pathway has already been successfully used for oral delivery of other peptides including erythropoietin and insulin, but the quantity delivered has been below clinically relevant levels. Herein, we present synthesis, purification, characterization, and clinically relevant in vivo oral delivery of B_{12}–PYY(3– 36) conjugates.

Nanotechnology; Organic Materials

253. Next generation surface enhanced Raman scattering (SERS) substrates for hazard detection

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Sensitive and accurate methods are needed for the detection and identification of hazardous materials (chemical, biological, and energetic) in field. Such a sensing capability has wide spread impact to the US military and first responder communities. Surface enhanced Raman scattering (SERS) is increasingly becoming a reputable technique for the real-time, dynamic detection and identification of hazard materials. We will discuss the utilization of commercially available next generation SERS substrates for the detection of energetic materials. Known concentration of energetic materials jet printed into the SERS sensing surface using a precisely calibrated system. Preliminary efforts towards an innovative biomimetic SERS sensing platform will be discussed.

254. Synthesis of POSS-MWNT nanohybrid using 'click' chemistry

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Multi-walled carbon nanotubes (MWNTs) are functionalized with an alkyne group using toluene-2,4-diisocyanate in an attempt to react with azide functionalized polyhedral oligomeric silesquioxane (POSS) to form a nanohybrid using 'click' chemistry. FTIR spectroscopy and NMR analysis were utilized to follow the introduction of the alkyne- and azide- groups onto their respective particles as well as their eventual consumption in the final POSS-MWNT nanohybrid product. This approach provides a simple and convenient route to effectively synthesize a nanohybrid not just from MWNTs and POSS, but a wide variety of nanoparticles using 'click' chemistry.

255. Effects of gold core interactions within different regimes of thermoresponsive copolymers on stimulus response behavior

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Thermoresponsive polymers and copolymers are characterized by a Lower Critical Solution Temperature (LCST), which is usually approximated by cloud point (CP) measurements. At the LCST thermoresponsive polymers polymer undergoes a coil-globule transition, which is useful for temperature controlled drug delivery. In this work we bonded thermoresponsive polymers to gold nanoparticle cores at different locations in the polymer backbone to study the effects of bonding regime on the cloud point temperature and the transition window. Copolymers of di(ethylene glycol) methyl ether methacrylate (DEGMA) and Acrylic Acid (AA) were prepared by RAFT polymerization, and then the AA was modified with cysteamine to give pendant thiols at different locations in the copolymer. Thiol placement altered the stability of the gold nanoparticles and their thermal response properties. The causes and effects of these differences are discussed.

256. Plasmon-enhanced photophysical properties of carbon nanodots

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Luminescent Carbon NanoDots (CND) are a recent addition to the list of allotropes of carbon, i.e. to the family of fullerenes, graphene, nanotubes, Diamond etc. CND's are highly fluorescent, relatively easy to synthesize, and are thought to have a low toxicity, with subsequent potential downstream applications in cellular imaging, optoelectronics and photodynamic therapy, to name but just a few. In this poster contribution we report the steady-state and time-resolved fluorescence properties of CND's of different sizes. In an attempt to further amplify the luminescence of the CNDs, we further demonstrate that the CND fluorescence can be plasmon-enhanced, by the close-proximity to silver nanoparticle. Furthermore, we present that these CND's can also be a sensitizer for singlet oxygen thus making them suitable for photodynamic therapy (PDT).

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257. Metal-enhanced fluorescence based solvent relaxation

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We describe the effects of several well-known polarity sensitive probes localized in the near-field of silver nanoparticles, which support metal-enhanced fluorescence (MEF). In a previous model describ-

ing the effects of fluorophores close-to plasmon supporting nanoparticles, it has been suggested that a blue spectral shifts in the emission spectra is present, due to modifications in the fluorophores radiative decay rate relative to the solvent relaxation time. However, recent works have shown that this model is indeed incorrect. Our experimental and theoretical considerations support the theoretical model for MEF, as postulated by Geddes, whereby non-radiative transfer to close-proximity nanoparticles, affords for the particles themselves to radiate the coupled quanta. Given the quick coupling time and rapid coupled system radiative lifetimes, traditional fluorophore-solvent relaxation in the near-field is not observed. With the attention that MEF has recently received our findings are of a fundamental nature for understanding enhanced plasmon mediated emission.

258. Sonication induced DNA damage and the role of single-wall carbon nanotubes (SWCNT)

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Sonication is known to produce oxygen-derived species such as hydroxyl radical and hydrogen peroxide that can produce oxidatively induced damage to DNA. Oxidatively induced damage to DNA bases has been well-studied and the reaction mechanisms have been resolved. GC-MS methodologies have been developed to both qualitatively and quantitatively measure the DNA lesions. Here, the GC-MS methodology is adopted to investigate the DNA damage from sonication in the presence and absence of SWCNT. Surprisingly, we found that the overall DNA damage is reduced in the presence of SWCNT, particularly for DNA lesions formed by the reductive pathway. The protective role of SWCNT observed in this work suggests a contrary view to the general belief and provides addtional information on the toxicity of the material.

259. Advanced plasmonic surfaces for metal-enhanced fluorescence (MEF)

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There has been a significant literature in the last 5 years on the use of metallic nanoparticles to favorably enhance the luminescence properties of close-proximity fluorophores. These favorable properties include enhanced emission (Fluorescence, Phosphorescence, Chemiluminescence), enhanced dye photostability as well as directional non-isotropic emission. In this poster presentation we describe the development of a highly enhancing plasmonic surface, which has been readily applied to the widely used 96-well plate format, that can enhance fluorescence signatures > 50 fold and Chemilumescence HRP-catalyzed emission > 1000-fold. Given that both fluorescence and Chemiluminescence technologies are entrenched throughout the Biosciences today, then our new surfaces are likely to find notable impact.

260. Nanoparticles synthesized from soy protein: Preparation, characterization and application in nutraceutical encapsulation

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Nanoparticles were synthesized from soy protein, one of the most abundant and widely utilized plant proteins, for nutraceutical and drug encapsulation. The preparation process consisted of dispersion, desolvation, drug incorporation, crosslinking and evaporation. The role of each procedure was systematically investigated by means of particle size, size distribution, and zeta potential as well as morphology observation. Curcumin as a model drug was encapsulated successfully into the nanopar-

ticles, evidenced by Fourier transform infrared spectroscopy and X-ray diffraction patterns. The average size of the curcumin-loaded nanoparticles was 220.1 to 286.7 nm, and their zeta potential was around -36 mV. The highest encapsulation efficiency and loading efficiency achieved were 97.2% and 2.7%, respectively. The release of curcumin in phosphate buffer saline followed a biphasic pattern. Possible mechanisms of the formation of nanoparticles as well as the incorporation of curcumin were discussed based on the data obtained from this study.

261. Screening of various nanoparticles for the removal of lead ions in aqueous samples

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Nanomaterials are materials possessing grain sizes on the order of a billionth of a meter (nanometer). Nanomaterials possess unique, beneficial chemical, physical, and mechanical properties and they have been used for a wide variety of applications. They have been used as a remediation material in removing pollutants such as chlorinated solvents (polychlorinated biphenyls) and heavy metals (chromium). In this study, nine commercially available nanomaterials have been screened for removal of lead ions (Pb2+) in aqueous samples. Fixed amount of the nanomaterials were added to Pb2+ solution of known concentration. The amount of the Pb2+ that bound to the nanomaterials was determined using atomic absorption spectroscopy (AAS). The effect of pH and the presence of humic acid on the aqueous solution containing the metal ions was also performed to determine the optimize conditions in the removal of lead out of the aqueous solutions.

262. New process for silica conjugated nanoparticles of silver and gold

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The optical and electronic properties of the nanoparticles are highly dependent on their size, morphology, surface and the media of stabilization. Due to this reason, the quest for new synthetic routes to produce nanoobjects is a very worthy endeavor. In recent years we have been investigating new efficient, general and high yielding methodologies to noble metal particles at nanometer size regime for applications in the field of catalysis, optoelectronic devices, targeted drug delivery etc.

In this presentation, we will communicate our primary investigation of a very efficient synthesis and characterization of resulting metallic silica nanocomposites in high yields. In this process, we will demonstrate a very efficient and controlled polymerization/gelificaion of a bis-alkoxy aminosilane to produce silver and gold silica nanocomposites in one pot. In addition, we will also present the reduction studies of the gel nucleated metals salts to produce nanoparticle redispersible powders of nanosilver and nanogold.

263. Biphasic synthesis of polymer/inorganic hybrid nanoparticles

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Asymmetric multicomponent nanoparticles (AMNPs) with the synergetic properties can serve as building blocks for the sophisticated functional materials and devices. We described a biphasic synthesis of polymer/inorganic AMNPs using interfacial reactions. Briefly, by separately dissolving the inorganic precursors (e.g. $HAuCl_4$) and monomers (e.g. aniline, methoxyaniline, and ethoxyanline) in two immiscible solvents, their reaction occurred at the interface can thus generate the AMNPs. In aniline system, the multiple morphologies of polyaniline/Au asymmetric nanoparticles, including

lollipop, dumbbell, and frog-egg shapes, can be obtained by varying the concentration of precursors and monomers. While, for hydrophobic monomers (methoxyaniline and ethoxyanline), patchy hybrid nanoparticles with controlled dimensions can be prepared. The liquid-liquid biphasic synthesis method meets the urgent need for a synthetic strategy capable of preparing hybrid AMNPs with fine-tuned structural and compositional complexities. Our approach is simple, versatile, cost-effective, and scalable for synthesizing large quantities of AMNPs with tunable size, shape, composition and morphology.

264. Application of self-assembled amphiphilc peptides containing tryptophan, arginine, and glutamic acid for generation of gold nanoparticles

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A number of linear (e.g., $(REW)_3$, $(WRE)_3$, $E_3W_3R_3$, $(WEWR)_3$) and cyclic (e.g., $[REW]_3$, $[E_3W_3R_3]$) amphiphilic peptides were synthesized using Fmoc/tBu solid-phase peptide synthesis. The tryptophan residue in the peptides acted as a reducing agent. The direct dissolution of the peptides except $(WEWR)_3$ into an aqueous solution of $AuCl_4^-$ led to the formation of gold nanoparticles showing maximum absorption at 550 nm and change of the solution color from yellow to red. The peptides formed diverse self-assembled nanostructures in water (2 mM) as shown with Transmission electron microscopy. The peptides did not show any significant cytotoxicity after 72 h incubation with human ovarian adenocarcinoma (SK-OV-3), breast cancer (MDA-MB-231), and leukemia (CCRF-CEM) cancer cells at a concentration of 50 µM. Cellular uptake studies indicated that $(REW)_3$ was not able to improve the delivery of fluorescence-labeled lamivudine significantly possibly because of the presence of negatively-charged glutamate and limited cellular uptake.

265. Based on polarized tubular microflidic device research of *in vitro* calcium phosphate stone formation

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Calcium phosphate (CaP) deposition is a hallmark of many diseases, such as nephrolithiasis and atherosclerosis. In this study, we developed a strategy to mimic the process of CaP stone formation in human renal tubules, in order to reach a new level of understanding of such biologically controlled crystallization. We demonstrated the in-situ deposition of calcium phosphate stones on the inner surface of proximal renal tubules, suggesting that the cellular tubular structures potentially offer an in vivo-like environment for the real-time observation of kidney stone formation. This strategy can be generalized to culture and form other types of cellular tubular structures, such as salivary tubular cells in the microfluidics. The combined 3D cell culture in microfluidics and in-situ deposition of CaP stones opens up a new route to address the molecular or cellular origins in the occurrence of some CaP stone related diseases such as nephrolithiasis.

266. Synthesis of a recyclable nanocatalyst for alcohol amine coupling

Catherine Munro, ***Philip Cho***, *Adelina Voutchkova-Kostal.Chemistry Department, George Washington University, Washington, DC 22314, United States*

Alcohol amine coupling is a reaction of high interest to the pharmaceutical industry for the synthesis of active pharmaceuticals. Catalytic alcohol amine coupling has been reported using several homogeneous transition metal catalysts. The homogeneous catalysts however, are not recyclable and this limits the scalability of the process. Here we report on the rational development of a recyclable nano-

catalyst for alcohol amine coupling of benzylic alcohols. The nanocatalyst consists of palladium and silver nanoparticles supported on the anionic clay hydrotalcite (HT). The catalysts were synthesized by reduction of metal salts adsorbed on the HT and characterized by TEM, AFM, Powder XRD, and EDX. The extensive characterization facilitates rational understanding of the relationship between composition, electronic parameters, nanoparticles size, surface area, and catalytic activity. This approach will be further applied to optimizing the cayalytic activity and incorporating tandem CH functionalizations.

267. Self-assembly of inorganic nanoparticle vesicles and tubules driven by tethered block copolymers

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The self-assembly of nanoparticles (NPs) leads to the formation of new generation of functional materials and devices. With the organization of nanoscale building blocks, the collective properties (such as plasmonic properties) which are distinguished from individual particles or bulk materials can be obtained. In this poster, we present a rational design of a new type of amphiphilic "colloidal molecules" (ACMs) that are made from nanoparticles tethered with amphiphilic linear block copolymers (BCPs) on the surface. In selective solvent, the ACMs assembled into vesicles when BCPs with a long hydrophobic block or NPs with large diameters were used. On the other hand, tubular assemblies were obtained for ACMs comprising BCPs with a shorter hydrophobic block and NPs with smaller sizes. The interparticle spacing between neighboring particles can be finely tuned by using BCPs with different molecular weight and subsequently adjust the plasmonic properties of the self-assembled structure.

268. Development of electrically conductive ink from colloidal metallic nanoparticle systems

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Colloidal metallic nanoparticle systems are of interest due to their suitability in a variety of applications. For instance, some nanoparticle systems can be layered onto a variety of surfaces with extraordinary control, in some cases self-organizing into thin films only one or two atomic layers thick. This gives rise to a conductive metallic multilayer that could be used in electronic or catalytic applications. Here, modification of previously reported techniques has yielded a transition-metal based "ink" that exhibits a measurable electrical conductivity upon drying. The viscosity of the ink can be tailored for use on a variety of surfaces, and further modification of ink properties may be possible through variation in the identity or stoichiometry of the metal source. Once the electronic characteristics of this "nanoparticle ink" are optimized, it may show promise for use in lithography or sensing and as an improvement over currently used "conducting glues."

269. Crystallization of CL-20 on monolayer surfaces

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Cl-20 is a high-energy secondary explosive with applications in the fields of propellants and pyrotechnics. Its performance and stability can be affected by structural properties including crystal phase (polymorphism), morphology, internal defects and particle size. The development of crystallization methods that can control one or more of these physical aspects offers several potential advantages. CL-20 crystallization on functionalized trimethoxysilane monolayers in an array of solvents was ex-

amined. The effect of template-directed nucleation on crystal orientation, preferred morphology, phase and nucleation density will be discussed.

270. Combinatorial approach to the synthesis of novel environmentally benign marine coatings

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The accumulation of undesirable marine organisms, has been an obstacle to seafaring vessels for centuries. In addition to high costs from increased fuel consumption, removal of these fouling agents is also a severe economic burden. Increasing regulations of traditional marine coatings have put emphasis on alternative coating systems that are environmentally benign. In this work, quaternary ammonium salts have been incorporated into low surface energy polymer backbones to provide an active antimicrobial defense mechanism. Furthermore, hydrolysable moieties have been incorporated into these polymers in order to provide “renewable” antimicrobial activity to the coating system as the coating slowly erodes in a controlled manner. Because of the extended lifetime and slow hydrolysis rate of these systems, a unique method of monitoring hydrolysis was developed. Synthesis, characterization, and hydrolysis kinetics of these systems will be discussed.

271. Functionalizing electrode materials via on surface cross-coupling reactions

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The modification of electrode-surfaces with redox-active molecules is an important area of research in modern electrochemistry, with potential impact in fields ranging from alternative fuel production to advanced sensing materials. Control of the molecular topology of these devices at the electrode-catalyst interface of these devices is essential. However, current methods for preparing well-defined functionalized electrodes remain highly limited.

Expanding the utility of previously reported carbon electrodes modified with mono-layers of phenylacetylene, we have developed conditions for on-electrode cross-coupling reactions to prepare well-defined functionalized electrodes. Conditions for both Sonagashira and Glaser couplings have been developed, and the modified electrodes have been characterized using a variety of electrochemical and surface analysis techniques. These carbon-carbon bond-forming reactions offer the ability to prepare highly complex, well-defined modified electrode surfaces. The results of our preliminary studies using simple redox active probes, as well as comparison of these techniques to previous systems will be discussed.

272. Preparation and characterization of glycomic microarrays using surface functionalized catanionic surfactant vesicles : Applications in diagnostics

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Formation of glycomic microarrays has been accomplished by deposition of catanionic surfactant vesicles on hydrophobically-modified chitosan (HMc). Deposition of catanionic surfactant vesicles on HMc surface was characterized by incorporating a lissamine rhodamine dye. The vesicles remained adhered to the HM chitosan surface after washing with buffer solution. Detergent washing studies indicated that vesicles remain intact on this surface. Vesicles that were functionalized with glycocon-

jugates were deposited on the HM chitosan surface to prepare glycomic microarrays. Lectin binding studies show that the carbohydrates on the vesicle surface are available for binding. Concanavalin A (Con A) binding to vesicles functionalized with glucose, and peanut agglutinin (PNA) binding to vesicles functionalized with lactose were studied and observed to be selective to respective binding components. Vesicles incorporated with lipooligosaccharide (LOS) of *Neisseria gonorrhoeae* showed specific binding with an antibody specific for the LOS. Application of this methodology to diagnostic reagents will be discussed.

273. Examination of polyoxometalates as possible microbial decontamination agents and subsequent incorporation into electrospun nano-fibrous materials

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Synthesized Wells-Dawson structure type polyoxometalates (POMs) with hetero-metal substitutions have been incorporated into polymer matrices in prior studies for surface chemical decomposition. These challenges consisted of pesticides and organics residing on painted surfaces. These same materials have been subjected to antimicrobial challenges followed by incorporation into polymer matrices for electrospinning. The polymer matrices are electrospun onto a surface and form fibrous mats which exhibit high surface areas. These novel fibrous materials of POMs were created by electospinning the polymer/POM mixture to create a surface covered with fibers that were then subjected to microbial challenges. The fibrous materials are to be incorporated onto surfaces, which would ultimately be utilized in applications such as air filtration. Neat POM solutions and the fibrous materials were examined for decontamination challenges against a variety of pathogens and are reported herein. The fibers were also characterized using a variety of surface analysis techniques including SEM.

274. Solution-mediated phase transformation of uric acid dihydrate

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Uric acid, a product of protein metabolism, is the most abundant organic component in human kidney stones. Different forms of uric acid occur under physiological conditions: anhydrous uric acid (UA), uric acid monohydrate (UAM), uric acid dihydrate (UAD), and various salts such as monosodium urate monohydrate (MSU). Solution-mediated phase transformation of UAD to UA may be important in the physiologic deposition of kidney stones, since compositional analysis of numerous kidney stones reveals that UAD is rarely found in the absence of UA. The specific objective of this study was to investigate the transformation kinetics of the metastable hydrate to the thermodynamically stable uric acid, and to identify factors which affect these changes. This study explored the transformation process in model aqueous solutions as well as model urine solutions. The effect of impurities to the transformation process was also investigated.

275. Structure and properties of doped tetraaniline single crystals

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Conjugated small molecules, oligomers, and polymers are useful for applications such as conducting biomedical interfaces, organic transistors and photovoltaics. Highly ordered semiconducting organic

oligomer crystals are of great interest for their potentially higher conductivity and as models for fundamental studies of structure- property relationships and charge transport mechanisms. Here we examine the structure and properties of doped tetraaniline single crystals prepared with a solvent exchange method. Well-defined tetraaniline nanowires, nanoribbons and nanoplates have all been fabricated by choosing suitable dopants. Powder X-Ray diffraction and low dose electron diffraction techniques are employed to resolve the packing structure in single crystals of these various morphologies. Packing models are built to correlate experimental results to crystal structures. Electrochemical impedance spectroscopy has been used to characterize the electrical properties of these single tetraaniline nanowire/nanoribbon/nanoplate on microelectrodes using two-probe techniques.

276. Fabrication of conductive subintestinal submucosa (SIS) for bionic devices: A promising neural interface system

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Here we report the design and realization of a regenerative peripheral neural interface (RPNI) system made of poly (3,4-ethylenedioxy-thiophene) (PEDOT) and subintestinal submuscosa (SIS). The system consists of three parts -- SIS, PEDOT and metal electrode—stacked together and then wrapped around living muscle and neural cells somewhat like a burrito. The morphology, electric properties and biocompatibility of this RPNI system was studied with scanning electron microscopy, electric impedance spectroscopy and PC12-TurboGFP cell viability tests. The results indicate that these materials have the electrical and biological properties needed to function as stable interface between peripheral nerves and wires for bionic arms and legs. As this system combines the advantages of traditional indirect and direct neural interface systems, we are now testing its ability to transmit signals in a rodent model in-vivo.

277. *In vivo* polymerization of poly (3,4-ethylenedioxythiophene) (PEDOT) in living dorsal hippocampus offers a unique approach to increase long-term reliability of the neural interface

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Chronic implantation of neural probes in the central nervous system is usually accompanied by the growth of an insulating glial scar that encapsulates the implant, resulting in impedance increase and signal loss. Previously we proposed that the *in vivo* polymerizing of a conducting polymer, poly (3, 4-ethylene-dioxythiophene) (PEDOT), can potentially circumvent glial sheath and reconnect the probe with the neurons. Here we report the evaluation on the effects of this method on living rodent brain function with a behavioral model, delayed alternation (DA). The rodents were implanted with a localized delivery/electrode system and the polymer was directly deposited *in vivo* at different healing stages. The electric properties were examined by cyclic voltammetry and electrochemical impedance spectroscopy. The influence of polymerization on hippocampus function was evaluated by the DA task training. The interactions between the polymer and neural tissue were examined with immunohistochemistry and scanning electron microscope.

278. Synthesis of potential eco-friendly curcumin derived plasticizers and their effect on the thermal and mechanical properties of polyvinyl chloride

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Plasticizers are widely used for their effectiveness reducing hardness, density, glass transition temperature (t_g), and volume resistivity of polymers. Among its limitation, plasticizers have been reported to migrate out of polymer systems, making them less flexible and less efficient. They are associated with reproductive and developmental toxicity in humans, and with negative environmental impact on plants and animals. Curcumin, the active ingredient in curry spice turmeric, is rigid in structure with two phenolic groups that can be modified covalently. The eco-friendly plasticizers are based on curcumin-(cu) and tetrahydro curcumin-(thc), and reacted with stearic acid and bromododecane to produce (cu & thc)di-esters and di-ethers respectively. They are blended to two polymers: PVC and Polystyrene in percentages of 35%, 45% and 55%, to test their effectiveness inducing depression of t_g of polymer/plasticizer system. These will be compared to control samples of DBP. These plasticizers are potentially better from ecological and toxicological viewpoints.

279. Investigation of fluorene p-type materials using a carbon-carbon coupling procedure

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The synthesis of a fluorene-based compounds was investigated as luminescent for p-type materials. Interest in polyfluorene derivatives has increased because of their high photoluminescence quantum efficiency, high thermal stability, and their facile color tunability, obtained by introducing low-band-gap co-monomers. Research in this field has increased significantly due to its potential application in tuning organic light-emitting diodes (OLEDs). We made use of a Sonagashira-type cross-coupling reaction to attach an ethynyl substituent onto the fluorene moiety. This product was in turn used to couple with a boronylated compound. The synthesis and characterization of this product will be discussed.

280. Metal binding properties and applications of curcumin,glucose-polymer conjugates

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The phytochemical curcumin has been reported as having a number of medically important properties, including anti-inflammatory, antioxidant, anti-cancer, and chelation activity. However, curcumin's viability as a therapeutic is hampered by characteristics such as poor water solubility and bioavailability. A new approach to increasing curcumin's utility is to conjugation to a polymer. There are several benefits to this approach, including greatly increased water solubility, increased activity from the polyvalent effect, and the ability to attach targeting groups.

Our group found that conjugating curcumin to polymers causes precipitatation in the presence of a metal that curcumin binds. This project exploited this property to test a wide range of metals for binding with curcumin. We found that curcumin had surprisingly high specificity for toxic metals, and that the curcumin,sugar-polymer conjugate is a potential chelating agent for metal poisoning and toxic-metal site remediation.

281. Preparation and characterization of lisinopril-capped gold nanoparticles for molecular imaging of angiotensin-converting enzyme using X-ray computed tomography

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Overexpression of angiotensin-converting enzyme (ACE) has been associated with various cardiovascular diseases. ACE inhibitors, such as lisinopril, have shown a favorable effect on patient outcome for individuals with heart failure or systemic hypertension. Thus targeted imaging of ACE would be of crucial importance for monitoring its expression in tissues. In this respect, lisinopril-coated gold nanoparticles were prepared to provide a new type of probe for targeted molecular imaging of ACE by X-ray computed tomography (CT). The functionalized gold nanoparticles were fully characterized using various techniques. Chemical stability studies in biological relevant media were also conducted. Results from *in vivo* experiments revealed that the functionalized gold nanoparticles specifically targeted ACE in the region of the lungs and heart. This new nanoprobe could therefore serve as a cardiac imaging agent for evaluating the severity of heart failure and monitoring the progression of various cardiovascular diseases.

Renewable Energy B

282. Integrating computations with experiments to drive biofuel overproduction

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In this talk, we will describe efforts that integrate computations with experiments to drive metabolic overproductions. We will briefly introduce the OptForce procedure for suggesting and prioritizing genetic manipulations that overproduce a targeted chemical and highlight results for maximizing the availability of the flavonone precursor malonyl-CoA and the identification of chain-specific pathway interventions leading to fatty acid overproduction in *E. coli* along with experimental results. Next, we will switch gears and demonstrate how the same bilevel optimization framework can be used to assess the optimality characteristics of microbial communities. Ultimately, all developed tools and models will be integrated within the recently unveiled MetRxn knowledgebase. We will discuss current features of the MetRxn knowledgebase of standardized metabolite and reaction information web-resource and highlight how it can used to speed up the process of building and correcting organism-specific metabolic models and prospecting for novel production pathways.

283. What microbial platforms for producing bio-based chemicals and fuels?

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Most strain development for bio-based fuels chemicals using metabolic engineering and synthetic biology is currently based on the *E. coli* and yeast platforms, solely based on the superior genetic tools available for these organisms. If one however considers bioprocessing characteristics of major economical impact, like substrate utilization and biocatalytic/biophysical traits, a different, more diverse picture emerges. Substrate utilization is perhaps the most profound parameter that affects process economics, simply because substrate costs typically exceeds 60% of the whole process cost. There exist organisms that use a much broader spectrum of hexoses, pentoses, oligo and polysaccharides, including cellulosics, as well as waste gases (syngas, CO_2, CO), all the same time with hardly any carbon catabolite repression. What can we learn from these organisms and how can we use synthetic-biology strategies to engineer superior strains for efficient biobased processes to produce chemical and fuels?

284. Isotope-assisted metabolic flux and pathway analysis of photosynthetic metabolism in diatoms

*Yuting Zheng, **Ganesh Sriram**, gsriram@umd.edu.Department of Chemical and Biomolecular Engineering, University of Maryland, College Park, MD 20742, United States*

Photosynthesis is vital toward converting solar energy and atmospheric CO_2 into biofuels and biochemicals. However, it is inherently an inefficient process due to the difficulty of concentrating CO_2 around RuBisCO, the enzyme that catalyzes the first step of carbon assimilation in photosynthesis. Diatoms, a class of marine algae, supposedly possess efficient photosynthetic mechanisms and are hypothesized to operate biochemical "CO_2 pumps" to enhance photosynthetic rates. However, direct metabolic evidence of such CO_2-pumping pathways and the measurements of flux through them are lacking. To address this gap in knowledge, we performed isotope-assisted metabolic flux analysis on the model diatom *Phaeodactylum tricornutum*. For this, we fed several isotopically labeled carbon sources to this organism and employed mass spectrometry and metabolic network modeling to trace the path of CO_2 through photosynthetic metabolism. This presentation will discuss our results and the insights provided by them toward engineering diatoms and algae for biofuel production.

285. Microbioreactors for bioprocess development and strain engineering

***Harry Lee**, harrylee@pharyx.com, Paolo Boccazzi, Kevin S Lee.Pharyx, Inc., Boston, MA 02119, United States*

Conducting microbial fermentation experiments under controlled conditions is essential for bioprocess optimization and for generating data to develop and validate of metabolic models in strain engineering. These experiments typically use bench top stirred tank bioreactors, which are flexible general-purpose tools, however their laborious set-up and operation limits experimental throughput. We have developed a microbioreactor platform with the control capabilities of a stirred tank bioreactor, but in a scalable form factor for performing multiple experiments in parallel. Consumable microfluidic bioreactors can be customized for different applications including anaerobic fermentation for biofuel process development, and continuous culture for strain engineering.

286. Cellulase engineering and consolidated bioprocessing *Bacillus subtilis* for low-cost production of biofuels and biochemicals

***Y-H Percival Zhang**[1,2], Xiao-Zhou Zhang[2], Chun You[1], Hui Ma[2]. (1) Dept of Biological Systems Engineering, Virginia Tech, Blacksburg, VA 24061, United States (2) CBP project, Gate Fuels Inc, Blacksburg, VA 24060, United States*

Consolidated bioprocessing is a low-cost biomass processing by integrating cellulase production, cellulose hydrolysis, and sugar fermentation into a single step. Our ultimate goal is to develop ready-to-use *B. subtilis* strains that can hydrolyze pretreated cellulosic materials better than natural cellulolytic strains and produce a variety of desired products with high yields. We have achieved: (i) the creation of the first and second generation recombinant cellulolytic microorganisms; (ii) enhanced endoglucanase activities on solid cellulose by directed evolution; (iii) simple DNA assembly by prolonged overlap extension PCR; (iv) enhanced microbial cellulose hydrolysis by displaying trifunctional mini-cellulosome on the cell surface; and (v) the creation of synthetic metabolons for facilitating metabolite channeling in competing metabolic pathways. To achieve high-product yields under anaerobic conditions, we have designed cofactor-balanced synthetic pathways for the production of lactate, fumurate, ethanol, isobutanol, and fatty alcohols. In this talk, we will update our advances in this project.

Computational Chemistry

Presiding: M. Sellers

287. Initial guess generation and dihedral parameter optimization in the ParamChem force field parametrization engine

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ParamChem is a computational environment to optimize empirical force field parameters for drug-like molecules. Compounds of interest are first processed by the CHARMM General Force Field (CGenFF) program for automatic atom typing and assignment of parameters and charges by analogy. While this functionality has found widespread use, the accuracy of the resulting parameters is inherently compromised by the limited transferability of force field parameters. Therefore, ParamChem features a Graphical User Interface (GUI) that allows the user to perform QM Potential Energy Scans on selected dihedral angles and fit the associated dihedral parameters to the resulting QM target data using a highly efficient fitting algorithm. Additionally, work on optimizing charges as well as bond, angle and improper dihedral parameters is in progress.

288. Role of electronic polarizability in the accurate treatment of polyalcohols in an empirical force field

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The CHARMM polarizable force field based on the classical Drude oscillator model has been extended to acyclic polyalcohols, such as ethylene glycol and glycerol. Parameter optimization was performed to reproduce experimental and quantum mechanical data for gas phase properties such as geometries, conformational energies, vibrational spectra, and dipole moments as well as for condensed phase properties like heats of vaporization, molecular volumes, and hydration free energies. The inclusion of explicit electronic polarizability allows for more accurate treatment of intramolecular conformational energetics and the balance between intra- and intermolecular hydrogen bonding interactions, and overcomes the difficulties encountered in CHARMM additive force field due to the need to overestimate molecular dipoles to compensate the implicit polarization effect in condensed phase. The presented force field will allow for simulation studies of polyalcohols in biological systems and provides a basis for ongoing developments towards a polarizable force field for carbohydrates.

289. Structural and functional consequences of phosphate-arsenate substitutions in selected nucleotides: DNA, RNA, and ATP

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A recent finding of a bacterial strain that can rely on arsenic instead of phosphorus raised the questions of if and how arsenate can replace phosphate in biomolecules that are essential to sustain cell life. We selected essential nucleotides to computationally probe if arsenate can retain the structural and functional features of phosphate nucleotides. Hydrolysis of adenosine triarsenate provides 2-3 kcal/mol less energy than ATP hydrolysis. Arsenate DNA/RNA interacts with proteins less strongly

than phosphate DNA/RNA. We observed that the weaker arsenate RNA-protein interactions may hamper rRNA assembly into a functional ribosome. We further compared the experimental EXAFS spectra of the arsenic bacteria with theoretical EXAFS spectra for arsenate DNA and rRNA. Our results demonstrate that while it is possible that dried GFAJ-1 cells contain linear arsenate DNA, the arsenate 70S ribosome does not contribute to the main arsenate depository in the cell.

290. Structure-based drug design: Salvianolic acid B as cyclooxygenase-2 inhibitor

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Over expression of cyclooxygenase-2 in oral mucosa has been associated with head and neck cancer (HNC). Celecoxib is non-steroidal anti-inflammatory cancer therapeutic drug, which selectively inhibits cyclooxygenase-2 but is cardio-toxic. Molecular modeling has been carried out on structures of cyclooxygenase-2 bound with substrate and inhibitors. The structural comparison of those complexes indicated that celecoxib and substrate occupy the same binding-site in cyclooxygenase-2, indicating a competitive inhibition. Based on the fact that Salvianolic acid B (Sal-B), a leading bioactive component of an herbal medicine, could inhibits cyclooxygenase-2 similar to celecoxib, the Sal-B has been docked into cyclooxygenase-2 in the same binding-site of celecoxib. Docking result showed that Sal-B is not only a good fit in the celecoxib binding-site but can also form more H-bonds with the protein. These results are expected to contribute to the development of cyclooxygenase-2 targeted therapy for HNC. This work was supported by NIH/RCMI Grant 8G12 MD007597.

291. pK_a calculations of protein side chains in explicit solvent using the classical Drude polarizable force field

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pK_a values of ionizable groups are based on their intrinsic proton affinities in combination with their environments. Shifts in pK_a's from intrinsic values, e.g. molecules in solution, can occur in the wide range of environments of various polarities as those offered by proteins. It is generally accepted that additive force fields largely lack the ability to accurately model the full range of polar environments in proteins, which may, in part, be the underlying cause for error in pK_a estimates based on free energy calculations. Using pKa as an end-point observation, we determine whether a polarizable model can offer a more accurate prediction of pKa shifts. Presented are the first explicit-solvent calculations of side-chain pKa's for Asp, Glu, and His in Ribonuclease A using the CHARMM classical Drude polarizable force field. Comparisons with the CHARMM additive force field are also presented.

292. Understanding the physical mechanisms controlling DNA rigidity: Coarse-grained molecular dynamics simulation study

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Double-stranded DNA is among the stiffest biopolymers, whose bending propensity crucially influences many vital biological processes. It is not fully understood which among the two most likely forces, electrostatic self-repulsion or base pair stacking, plays a dominant role in determining the DNA›s unique rigidity. Different theoretical and experimental studies to date have yielded contradictory re-

sults on this issue. We address this important question by means of Molecular Dynamics (MD) simulations using both atomistic and coarse-grained force fields. Particularly, our accurate coarse-grained model for the double-stranded DNA with explicit mobile ions, derived systematically from underlying atomistic MD simulations, is utilized in the present study. Using two independent sets of calculations, we found that electrostatic and non-electrostatic effects play a comparable role in maintaining DNA›s stiffness. Our findings differ substantially from predictions from existing theories for DNA rigidity and may indicate that a new conceptual understanding needs to be developed.

293. XPairIt: A software toolkit for smart peptide reagent design

***Michael S Sellers**, michael.s.sellers.ctr@us.army.mil, Margaret M Hurley.Weapons and Materials Research Directorate, U.S. Army Research Laboratory, Aberdeen Proving Ground, Maryland 21009, United States*

Recent advances in automated discovery and synthetic library science show great promise for the development of recognition elements with improved stability, affinity, and specificity. Here we present the modeling portion of an iterative experimental/computational study to produce high affinity peptide binders to the Protective Antigen (PA) of *Bacillus anthracis*. The result is a general usage, HPC-oriented, Python-based toolkit built upon powerful third-party freeware, which is designed to provide a better understanding of peptide-protein interactions, and ultimately predict and measure new smart peptide binder candidates.

We present an improved simulation protocol with flexible peptide and protein docking, coarse grain and atomistic models, on-the-fly molecular dynamics, and explicit water representation. Candidate peptides are docked with the Anthrax Protective Antigen and Lethal Factor, and binding locations and affinities are reported.

Chromatography Forum of the Delaware Valley

Presiding: M. Selman

294. Is it better to separate charged enantiomers using electrokinetic chromatography with or without electroosmotic flow?

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Electrokinetic chromatography (EKC) is a separation technique used to separate neutral compounds via a pseudostationary phase (PSP) into which the compounds can differentially partition. Charged compounds including charged enantiomers can also be separated by EKC via such differential partitioning, although these separations have received less attention. The separation of charged enantiomers via EKC is compared under conditions of either high or low (suppressed) electroosmotic flow (EOF) with a PSP whose electrophoretic mobility is either large and counter-electroosmotic or zero or nearly so. Thus all the permutations of conventional EKC and reverse-flow electrokinetic chromatography (RF-EKC) are considered, although the experimental emphasis will be on those involving suppressed EOF. In particular, the benefits of suppressed EOF on resolution and migration time are examined for pharmaceutical enantiomers of varying hydrophobicity. Chromatographic figures of merit are compared for each approach and applications are explored.

295. Studying MEKC separation capabilities of cholic acid micelles with NMR: Effects of pH, temperature, and concentration

***Brandy N Taylor**, bnt001@bucknell.edu, Timothy G Strein, David Rovnyak.Chemistry, Bucknell University, Lewisburg, Pennsylvania 17837, United States*

Micelle-forming bile salts are effective pseudo-stationary phases for chiral separations of binaphthyl compounds with Micellar Electrokinetic Capillary Chromatography (MEKC). We systematically investigated cholate micelles interacting with R,S-1,1'-binaphthyl-2,2'-diylhydrogenphosphate (BNDHP) as a model analyte. We varied pH, temperature, and concentration of BNDHP while monitoring the chiral resolution obtained with MEKC and chemical shifts with ^{1}HNMR. As cholate monomers aggregate and BNDHP molecules sample the micelle aggregate, changes in BNDHP chemical shifts give the CMC of cholate ca. 13-14 mM at pH 12; the CMC decreases at higher pH and increases with temperature, suggesting that higher pH and lower temperature could improve chiral separations in MEKC. S-BNDHP concentrations from 50-400 μM (pH 12.8) produced cholate CMCs from 10 mM to 8 mM, respectively, indicating that S-BNDHP may participate in stabilizing cholate aggregates. These data show that NMR can aid investigations of the multi-variable landscape of chiral separations.

296. Probing chiral separation mechanisms with MEKC and NMR: 1-1'-bi-2-naphthol and secondary cholate micelles

***Kendall E Sandy**, kes028@bucknell.edu, Timothy G Strein, David Rovnyak.Department of Chemistry, Bucknell University, Lewisburg, PA 17837, United States*

This work is aimed at understanding the mechanistic aspects of chiral separations with bile salts, one of nature's chiral selectors, using Micellar Electrokinetic Capillary Chromatography (MEKC). NMR studies with binaphthyl-2,2'-diyl-hydrogen-phosphate (BNDHP) are able to detect a preliminary aggregate of cholate at 7mM and a primary micelle at 14mM., but chiral MEKC separation does not occur until above 14mM. However, studies with R,S-1-1'-bi-2-napthol (BN) are only sensitive to a second CMC value between 35-40mM cholate, consistent with higher concentrations of cholate needed to resolve R/S-BN. The analyte may play a larger role than simply being a "guest" in the bile salt micelle, modulating the CMC by actively participating in micelle formation. We have probed the interactions between BN and cholate using NMR. The H6 proton of BN is an effective reporter of secondary micelle formation and predicts chiral separation. Ultimately, NMR allows better mechanistic understanding of chiral interactions with cholate.

297. Analytical investigation of synthetic street drugs

***Amanda Leffler**[1], aml357@psu.edu, Frank Dorman[2]. (1) Department of Forensic Science (Chemistry), The Pennsylvania State University, University Park, PA 16802, United States (2) Department of Biochemistry and Molecular Biology, The Pennsylvania State University, University Park, PA 16802, United States*

Synthetic drugs, or "legal highs", are entering the drug market faster than they can be restricted. Analysis of such designer drugs and the determination of their individual compounds may help ban their production and illegalize their use. A quick and efficient extraction method will benefit analysts by increasing the amount of evidence that can be processed in a given time.

This presentation will discuss the development of an extraction method of drug compounds from various commercial media, followed by separation using gas chromatography with mass spectrometric detection (GC-MS). The developed chromatographic method provides qualitative and quantitative analysis of synthetic compounds in the samples based on the use of appropriate standards. A preparatory HPLC method for the fractionation of multi-component samples and the use of direct infusion MS/MS in further identification of unknown samples will also be discussed. This method could reduce the time a new drug is on the market.

298. Selection of a column and optimization of a method for the analysis of antidepressants in aqueous samples using liquid chromatography-tandem mass spectrometry

***Kenton J Chodara**, kjc257@psu.edu, Dan G Sykes, Melissa Gettle, Alicia M Zimmermann.Department of Forensic Science, The Pennsylvania State University, State College, PA 16802, United States*

Antidepressants are psychiatric medications taken with the intent to alleviate mood disorders. These drugs and their metabolites enter the environment as a byproduct of use, and may pose a danger to human and environmental health. No environmental regulation of these compounds currently exists in the USA. A selective and sensitive detection method is necessary for developing regulation.

This presentation will discuss methodology developed for detection and identification of a variety of antidepressant drugs and their metabolites. High Pressure Liquid Chromatography on fused-core silica phases provides analyte separation, and an electrospray ionization triple-quadrupole mass spectrometer employing Multiple Reaction Monitoring is used for detection. Samples are preconcentrated using solid-phase extraction using an HLB cartridge.

This study examines the effect of column composition on separation. Column compositions include C8, C18, phenyl-hexyl, and amide. Parameters such as efficiency, asymmetry, and selectivity will be considered for optimization. Waste water samples will be used for validation.

Happy Hour Posters

299. Synthesis and binding studies of anion-responsive pyridine-functionalized calixarenes

*Anthony L Possanza[1], Fang Liu[2], Gong Chen[3], K. N. Houk[2], **Nicola Y. Edwards**[1], nye1@psu.edu. (1) Department of Chemistry, The Pennsylvania State University, Worthington Scranton, Dunmore, Pennsylvania 18512, United States (2) Department of Chemistry, University of California, Los Angeles, Los Angeles, California 90095, United States (3) Department of Chemistry, The Pennsylvania State University, University Park, University Park, Pennsylvania 16802, United States*

This presentation will describe the synthesis and anion binding studies of pyridine-functionalized calixarenes. Calixarenes, appended at the lower rim with linkers containing amide and pyridine moieties, have been synthesized in four steps. The binding ability of these calixarenes for various anions was screened via molecular mechanics calculations and tested in organic media by monitoring the changes in their ^{1}H NMR spectra as a function of added anions.

300. Enantioselective copper-catalyzed alkynylation of chromene acetals

***Harathi D Srinivas**, hari@udel.edu, Prantik Maity, Mary P Watson.Department of Chemistry and Biochemistry, University of Delaware, Newark, DE 19716, United States*

Enantioselective additions to cyclic oxocarbenium ions would provide an efficient route to alpha-substituted oxygen heterocycles, important scaffolds in a number of biologically active molecules. However, controlling facial selectivity in additions to these electrophiles remains challenging, and such enantioselective additions are rare. Our group has recently developed enantioselective additions of terminal alkynes to racemic isochroman acetals. Here, we report an enantioselective, copper(I)-catalyzed addition of alkynes to racemic chromene acetals. This method delivers a wide range of substituted chromenes.

301. Suzuki cross couplings via nickel-catalyzed activation of benzylic C–N bonds

***Danielle M Shacklady-McAtee**, dmcatee@udel.edu, Prantik Maity, Mary P Watson.Department of Chemistry and Biochemistry, University of Delaware, Newark, DE 19716, United States*

Suzuki cross couplings have been achieved via selective activation of benzylic carbon–nitrogen (C–N) bonds using electron-rich nickel(0) catalysts. This reaction enables efficient transformation of readily available benzylammonium precursors into a wide variety of diarylmethylene products in high yields under very mild reaction conditions. The orthogonality of the benzylic C–N bond vs. other C–X bonds will also be demonstrated.

302. Enantioselective copper-catalyzed alkynylation of isochroman acetals

***Prantik Maity**, pmaity@udel.edu, Harathi D Srinivas, Mary P Watson.Department of Chemistry and Biochemistry, University of Delaware, Newark, DE 19716, United States*

Enantioselective additions to cyclic oxocarbenium ions would provide an efficient route to alpha-substituted oxygen heterocycles, important scaffolds in a number of biologically active molecules. However, controlling facial selectivity in additions to these electrophiles remains challenging, and such enantioselective additions are rare. We will present our development of a copper(I)-catalyzed addition of terminal alkynes to prochiral cyclic oxocarbenium ions, formed in situ from racemic isochroman acetals. This reaction enables preparation of a variety of substituted isochromans in good enantioselectivities. Our working model for enantioselectivity will also be presented.

303. Nickel-catalyzed Heck cross couplings via activation of strong C–O bonds

***Andrew R Ehle**, arehle@udel.edu, Qi Zhou, Mary P Watson.Department of Chemistry and Biochemistry, University of Delaware, Newark, DE 19716, United States*

The ubiquity of phenols makes them attractive starting materials for the preparation of elaborated aromatic targets. Although triflates have historically been used to enable aryl C–O activation, recent efforts have focused on use of less expensive, greener alternatives. We report the first Heck cross coupling of aryl pivalates with a variety of olefin partners. This method represents one of the first examples of a C–C cross coupling with a nonorganometallic coupling partner via activation of a strong C–O bond. It enables the transformation of phenol-based substrates into styrenyl products without generation of a halogenated byproduct or the use of expensive triflate groups.

304. Development of new, physiologically useful nitroxyl (HNO) donors

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Due to its inherent reactivity, nitroxyl (HNO), must be generated *in situ* through the use of donor compounds, but very few physiologically useful HNO donors exist. Novel *N*-substituted hydroxylamines with carbon-based leaving groups have been synthesized and their structures confirmed by X-ray crystallography. These compounds generate HNO under non-enzymatic, physiological conditions, with the rate and amount of HNO released being dependent mainly on the nature of the leaving group. A barbituric acid and a pyrazolone derivative have been developed as efficient HNO donors with half-lives at pH 7.4, 37 °C of 0.7 and 9.5 min, respectively.

305. Reaction of pyrroles with *N*-halo compounds: A theoretical study

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Reaction of an electrophilic *N*-halo compound with a nucleophilic pyrrole gave an ion-pair of a σ-complex and a nitrogen anion. Collapse of the ion-pair, followed by elimination of HX, gave an addition-elimination product; deprotonation of the σ-complex gave halogenation. Global electrophilicty(ω) has been used to study electrophile-nucleophile combinations. The ω values of the *N*-halo compounds (n=28) used were calculated (DFT/B3LYP method with 6-31g* basis set). No correlation was observed between ω and the pathway of reaction/non-reaction. A single parameter (ω) could not explain the results of the competing reactions that are taking place in this system — reactions that appear to depend on the *N*-halogen (F,Cl,Br,I) nucleophilicity/basicity and possibly hardness of the leaving group. Acknowledgement: This work was supported by grant number 0910668 from the National Science Foundation.

306. Selective functionalization of dibromobacteriochlorins leading to non-symmetrical derivatives

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Bacteriochlorins are attractive candidates for a wide range of photonic applications owing to their strong absorption in the near-infrared spectral region. In this communication we present a versatile route to non-symmetrical bacteriochlorin derivatives which relies on selective derivatization of 5-methoxy-3,13-dibromobacteriochlorin. The new route allowed us to obtain a series of variously substituted bacteriochlorins. In particular we were able to prepare a mono-functional, bioconjugatable bacteriochlorin derivatives, and push-pull bacteriochlorins, i.e. derivatives possessing electron-withdrawing and electron-donating substituents on the opposite sites of macrocycle. Taken together, method presented here enables synthesis of new bacteriochlorin architectures for fundamental studies and diverse applications.

307. Preparing allyl silanes via the silyl-Heck reaction

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A high-yielding protocol for the silylation of terminal alkenes has been developed using silyl halides using palladium catalysis. The key to this reaction is the use of (diphenyl*tert*-butyl)phosphine as the supporting ligand. This chemistry, which is analogous to the Heck reaction, allows for the conversion of styrenes to *E*-(β)-silyl styrenes, and the conversion of α-olefins containing an allylic-hydrogen to allyl silanes with good *E*:*Z* ratios. These transformations are performed under mild conditions and proceed in high yield. When in combined with known reactions of unsaturated organosilanes, this reaction provide a novel strategy for functionalizing alkenes at the terminal or allylic position. The scope and limitation of this process, as well as mechanistic studies, will be discussed.

308. Copper-catalyzed *C*-benzylation of nitroalkanes

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Nitroalkanes are important intermediates in organic synthesis for the introduction of nitrogen atoms into organic molecules. Despite undergoing a wide variety of useful transformations a highly desir-

able *C*-alkylation of nitronate-anions using simple alkyl electrophiles and readily available reagents has remained an open challenge in organic synthesis for more than seventy years.

Recently we have discovered a simple solution to this long-standing problem in copper-based catalysts that allow for the high-yielding alkylation of nitronate-anions using simple, commercially available benzyl bromide electrophiles. These operationally simple reactions proceed under mild conditions and tolerate a wide variety of functionality allowing access to complex nitroalkanes. Additionally, the current work provides facile access to phenethylamines, a common pharmacophore in many biologically active molecules. The scope and limitation of this method, as well as the future directions of this research program, will be discussed.

309. Preparation of carbocycles by intramolecular cyclizations of acyllithium equivalents

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The generation and utilization of acyllithium equivalents has been examined. The acyllithium equivalents were generated on compounds containing a remote carbon-carbon π-bond that were either activated or unactivated. The acyllithium equivalent was generated on both species, and it was found that cyclization of the acyllithium equivalent onto an activated olefin occurred in good conversion and modest yield.

310. Synthesis, characterization, and structural determination of a lower rim substituted calixarene by using a combination of 1D and 2D NMR experiments

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Calixarenes are of great interest because they form complexes with organic molecules and heavy metals. Some properties of calixarenes have been improved by rigidification of the skeleton. A new method for rigidification by bridging phenolic oxygens has been explored.

Treatment of *t*-butylcalix[4]arene with 1,5-dibromopentane (1:2 ratio) and K_2CO_3 in CH_3CN gave a 1,3-bis(5-bromopentoxy)calixarene as the major product together with a biscalixarene. Using the same reagents (1:3 ratio) with slightly different conditions gave a new calixarene as the major product together with small amounts of the (bromopentoxy)calixarene. The new compound was identified as a lower rim substituted calixarene with a cone conformation observed in which two of the phenolic oxygens are bridged by a $-(CH_2)_5-$ group and one of the other phenolic oxygens is attached to a bromopentyl group.

The structural assignment of the new calixarene was established using MALDI-TOF MS and a combination of 1D and 2D NMR spectral techniques.

311. Photochromic molecular switches

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In gated photochromism, a nonphotochromic system becomes activated to a photochromic system through a reaction with an external stimulus such as an ion. Since the color change of the molecule is strictly dependent on the presence of a specific ion, these types of systems have potential use as chemosensors. We are working towards the synthesis of a molecule containing a photochromic core bridged between an electron donor and an electron acceptor. This uncolored molecule undergoes a photochromic reaction to produce a highly colored molecule as a result of the charge transfer from the donor to the acceptor substituent. The stabilization from this charge transfer prevents the re-

verse photochromic reaction from occurring to produce the uncolored “open” isomer. However, the introduction of fluoride should disrupt this charge transfer, allowing the reverse photochromic reaction to occur. This gated photochromism will yield a new chemosensor for the fluoride anion.

312. New heterocycles for metal complexation

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1-Substituted benzimidazole and indazole derivatives have been synthesized for purposes of metal complexation. A novel compound, *N*-alkyl-1-(methylmercaptoacetone oxime)benzimidazole, has been confirmed by CI mass spectrometry. The preparation 2-(2,2-phenylethanone)benzimidazole was initially probed by CI-MS, but X-ray crystallography indicates that an analogous compound, 4-phenyl-1,3-dihydro-2*H*-1,5-benzodiazepin-2-one, results instead. *N*-methyl-2-(2’-[*N*’’-methylbenzimidazol-2’’-ylmethyl]phenyl)benzimidazole was synthesized and confirmed by CI-MS, NMR, and X-ray crystallography. An *N*-(2’-pyridylethyl)indazole was synthesized and investigated by CI-MS and NMR analysis.

313. Electrochemical characterization of Lewis acids in ionic liquids

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Electrochemical measurements have been used to characterize the interaction of Lewis acids such as aluminum chloride and hafnium(IV) chloride with the Lewis base 9-fluorenone in various ionic liquids. Most of the work has been carried out in 1-butyl-1-methylpyrrolidinium triflate and aluminum chloride : 1-ethyl-3-methylimidazolium chloride. The exent of potential shift for fluorenone reduction upon addition of a Lewis acid has been used to measure the extent of the acid / base interaction.

314. N-Glycan analysis on therapeutic antibodies

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Elucidating the structure of glycans present on glycoproteins is key to understanding glycoprotein function. Given the structural heterogeneity of N-glycosylation, an efficient method to characterize and quantify glycans is important for quality control and SAR analysis of therapeutic antibodies. We report here the development of a method for efficient analysis of antibody Fab and Fc glycans. Enzymatically released antibody glycans were labeled with 2-AB and analyzed using RP-HPLC, with fluorescence detection, and LC-MS. Site-specific trimming of N-linked glycans affords improved insight into the glycan topology of antibodies. Fc region glycans were efficiently released after treatment with Endo S. Analysis of the entire collection of antibody glycans was achieved through treatment with PNGase F. Glycans on the Fab regions were selectively trimmed by treating the antibody with papain, separating the two fragments by protein A affinity chromatography, and treating each fragment individually with PNGase F.

315. Using nano mechanical approach to study enzyme catalysis

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Cellulose is the skeleton structure of almost all plants, which makes it an unlimited source as nature polymers. Cellulose hydrolysis is of great importance in the conversion of plant biomass to fuel, and

has already attracted great interest from scientists in chemistry, biology and some other fields. Cellulase is a kind of enzyme which can break down the cellulose into simple sugars. Sugars can then be fermented into ethanol and many other products. Before hydrolytic cleavage, a process called enzymatic decrystallization will take place to break the aggregate of cellulose molecule and expose the cellulose molecule chains to active sites of cellulase. Although it has been speculated to be the rate-limiting step, the mechanism for decrystallization has not been elucidated. Using nano mechanical approach, such as micro-cantilever and AFM, we study this process by examining the bending of cantilever or morphology change of cellulose bilayer produced by the cellulose decrystallization.

316. Utilizing the vitamin B_{12} uptake pathway for oral delivery of peptides and proteins

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The non-invasive delivery of peptides/proteins continues to be a major goal in the treatment of diabetes mellitus (DM). The improved ease of administration associated with the oral-enteric pathway provides an attractive means for the delivery of peptide/protein based therapeutics since higher patient compliance and an improvement in glycemic control are likely. Considering the susceptibility of peptides/proteins to proteolytic degradation and inefficient enteric uptake, the oral-enteric pathway is an unlikely route. Here we show that a non-invasive oral delivery route *can* be achieved by utilizing the preexisting dietary uptake pathway of vitamin B_{12} (B_{12}). We have shown, in STZ-diabetic rat models, that insulin, conjugated to B_{12}, has the capacity to lower blood glucose levels when orally administered. Using the same technology we are now moving towards the delivery of the peptide GLP-1. We anticipate our findings to be a significant step toward developing orally active, non-invasive therapies for individuals with DM.

317. Computational study of substituted 5[H] - phenanthradin-6-ones as poly (ADP-ribose) polymerase-1 (PARP-1) inhibitors by analog and structure based methods

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The poly (ADP-ribose) polymerase-1 (PARP-1) is an abundant nuclear protein involved in DNA repair and programmed cell death. Substituted 5(H) phenanthradin-6-one analogs were found to be potent PARP-1 inhibitors. Semiempirical methods were used to estimate various physicochemical parameters. The hydration energy (HE), ionization potential (IP), electrophilic index (ω) and partition coefficient (LogP) were resulted as independent variables for inhibitory activity of the analogs. The overall increase of HE, IP, and EI and overall decrease of LogP enhance the efficacy of inhibitory nature of these analogs to PARP-1. Docking studies of 5(H) phenanthradin-6-one analogs with PARP-1 were also performed in support of the findings of QSAR studies. Analysis of results of both QSAR and docking studies suggested that remarkable inhibitory activity is exhibited by molecules 9b, 10b1 and 10b2. The hydrogen bond interactions along with hydrophobic and electrostatic interactions are mapped to confirm their potencies.

318. Conformational analysis of nucleosides: A systematic update of PSEUROT using quantum mechanical- and molecular mechanics-derived parameters

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Many nucleos(t)ides exist in solution as a mixture of 'north' (C2'-exo/C3'-endo) and 'south' (C2'-endo/C3'-exo) conformers. Rigorous identification of the N/S conformations and their relative populations is often performed by providing the program PSEUROT with ^{1}H-^{1}H coupling constant data

(^3J) obtained from high-resolution ^{1}H NMR spectra. PSUEROT then attempts to 'build' a pair of N/S conformers that best replicate in experimental *J*'s. The user must specify, from a limited selection within PSEUROT, the 'A' and 'B' parameters that allow PSEUROT to perform this building properly. This is a major limitation of the program, as A and B parameters for novel furanose rings not in the PSEUROT database must be derived from either from a large body of crystal structures or from high-level quantum mechanical structures. This talk will describe our recent success at deriving the A and B parameters for a variety of novel nucleosides using molecular mechanics (Amber) calculations.

319. Correlating reactivity to biological activity of halogenated pyrimidine analogues

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The presence of halogen has long been utilized in organic syntheses for functional group conversions. In context of pyrimidines, when comparing 4-Cl and 2-Cl analogues, the 4-Cl is very reactive towards soft nucleophiles like amines and thiolates. This difference in reactivity has rarely been exploited in drug design and enzyme inhibition however. Continuing our lab›s interest in sulfur-containing heterocycles and their corresponding nucleosides, a study of the thienopyrimidine scaffold was undertaken. The thienopyrimidine scaffold has been explored for antimicrobial and anticancer purposes and has been extensively studied for inhibition of variety of kinases. Chlorinated [3,2-*d*]pyrimidines were found to be very reactive towards soft nucleophiles and manifested good activity against cancer cell lines and fungal strains. A systematic structure activity relationship revealed the importance of the labile 4-Cl and the sulfur in manifesting biological activity. The synthesis and biological results of these investigations is discussed herein.

320. Structural and biological investigations of pyrophosphate coordination complexes

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Metal compounds have successfully transitioned from fundamental inorganic chemistry to applied medicinal chemistry, with metals used in the treatment of arthritis and cancer, as well as studied for diseases such as Alzheimer's. Herein a class of Co(II) and Cu(II) metal based complexes are described that feature the pyrophosphate ligand. The biological activity of monomeric and dimeric compounds has been assessed in a variety of cells with IC_{50} values in the range of picomolar to micromolar.

321. Synthesis and biological evaluation of 4,8-didesmethyl telithromycin(5) and 4,8,10-tridesmethyl cethromycin(6): An effort toward addressing antibiotic resistance

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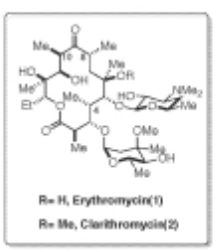
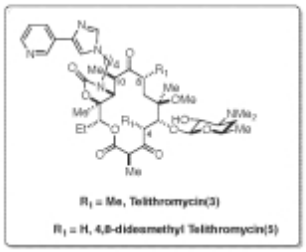
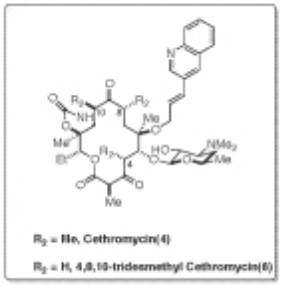
To address the issue of antibiotic resistance we have applied the paradigm of natural product structure simplification to the semisynthetic macrolide antibiotics Telithromycin (**3**) and Cethromycin (**4**). The rationale behind the desmethylation strategy is the study by Steitz, who successfully co-crystallized (**1**), (**2**) and (**3**) bound to ribosomal subunits of archaea. The *de novo* synthesis of

4,8-didesmethyl telithromycin (**5**) and 4, 8, 10-tridesmethyl cethromycin (**6**) and their biological evaluation would be presented.







Strain	Bacteria	wt/mutant	MIC(3)	MIC(5)	MIC(6)
SQ171/2058G	E.Coli	A2058G	>512	>256	>256
DK/pKK3535	E.Coli	w.t	**0.5**	**16**	**2**
DK/2058G	E.Coli	A2058G	**1**	**8**	**1**
UCN14	S. aureus	A2058T	>256	>256	>256
ATC33591	S. aureus	ermA	>128	>256	>128

322. Synthesis and characterization of fatty amide derivatives from gallic acid

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Fatty acid amides are endogenous substances that have been found to have antioxidant and neuroprotective properties. Evidence suggests that dopamine amides, such as N-arachidonoyl dopamine, interact with the proteins of the endocannabinoid system, which stimulates a self-protective response in the brain and counteracts oxidative stress. Another endocannabinoid, anandamide, has been shown to interact with lipoxygenase pathway that regulates inflammatory response. Other fatty amides such as those present in the Maca plant of Peru, have been shown to posses immunostimulation, memory improvement, antidepressant, and anticancer activity. In continuation of our chemical transformation of gallic acid, a naturally occurring antioxidant, we have designed the synthesis of fatty amide derivatives from gallic acid for biological evaluation. The synthesis and characterization of novel fatty amide analogs from gallic acid will be discussed.

323. Chemical analysis and monitoring of biological activities of different fractions of *Taraxacum officinale* in different stages of plant growth

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This paper describes the phytochemical study of *Taraxacum officinale* in two different stages of growth. The plant material was extracted sequentially with hot hexanes, then via percolation using chloroform, then a chloroform-methanol mixture (1:1), and finally methanol as solvents. The results obtained by biological activity tests show that the plant has a type of activity prior to maturity and another after development. The methanol extract of two month old leaves displayed an interesting

inhibitory activity to the system glucose-6-phosphatase: the percentage of inhibition in a system with histones and a system without histones was very similar. In contrast, the methanol extract from the five month old leaves showed a significant antibacterial activity. The Chicoric acid was from the two month old leaf extracts was found to cause a 57% inhibition of the enzyme glucose-6-phosphatase in a system without histones and a 33% inhibition in a system with histones.

324. Novel fluorescent antagonist as a molecular probe in A_3 adenosine receptor binding assays using flow cytometry

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The role of the A_3 adenosine receptor (AR) was explored in cardiac ischaemia, inflammatory diseases and cancer. We report a new fluorophore-conjugated human (h) A_3AR antagonist for application to cell-based assays. Fluorescent pyrazolo[4,3-e][1,2,4]triazolo[1,5-c]pyrimidin-5-ylamine (pyrazolo-triazolo-pyrimidine-PTP) and triazolo[1,5-c]quinazolin-5-yl)amine (triazolo-quinazoline-TQ) AR antagonists were compared. A chain-extended and click-conjugated AlexaFluor488 TQ derivative (MRS5449) displayed radioligand binding K_i value of 6.4 ± 2.5 nM (hA_3AR) and antagonized hA_3AR agonist-induced inhibition of cyclic AMP accumulation (K_B 4.8 nM). Using flow cytometry (FCM), MRS5449 saturated hA_3ARs with high specific-to-nonspecific binding ratio with an equilibrium binding constant 5.15 nM, comparable to the K_d value of 6.65 nM calculated from kinetic experiments. K_i values of known AR ligands in inhibition of MRS5449 binding in whole cell FCM were measured. Further binding analysis of MRS5449 suggested multiple agonist binding states of the A_3AR. Molecular docking predicted binding modes of these fluorescent antagonists. MRS5449 is a useful tool for hA_3AR characterization.

325. Inhibition of system x_c transporter-mediated cystine uptake by sulfasalazine analogs

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The system x_c^- antiporter is a sodium independent amino acid transporter that transports extracellular cystine in exchange for intracellular glutamate. The x_c^- transporter is a key determinant of both intracellular glutathione levels and extracellular glutamate concentrations. Therefore, blockade of system x_c^- may provide a new therapeutic opportunity for the treatment of glioma and neuroinflammatory diseases associated with excess extracellular glutamate. A series of sulfasalazine analogs were synthesized and tested for their ability to block system x_c^- using L-[^{14}C]cystine as a substrate. While the carboxylate group of sulfasalazine is essential for its inhibitory activity, the phenolic hydroxyl group is dispensable. Importantly, the replacement of sulfasalazine's diazo group with an alkyne or alkene group led to equally potent inhibitors. Given that sulfasalazine is rapidly metabolized through cleavage of the diazo bond, these analogs may serve as more valuable tool compounds to further understand the therapeutic utility of system x_c^- inhibition.

326. Design, synthesis, and pharmacological evaluation of glutamate carboxypeptidase II (GCPII) inhibitors based on thioalkyl benzoic acid scaffolds

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A series of thiol-based glutamate carboxypeptidase II (GCPII) inhibitors have been synthesized with either a 3-(mercaptomethyl)benzoic acid or 2-(2-mercaptoethyl)benzoic acid scaffold. Potent inhibitors were identified from each of the two scaffolds with IC_{50} values in the single-digit nanomolar range, including 2-(3-carboxybenzyloxy)-5-(mercaptomethyl)benzoic acid and 3-(2-mercaptoethyl) biphenyl-2,3'-dicarboxylic acid. The latter compound was found to be metabolically stable and selective over a number of targets related to glutamate-mediated neurotransmission. Furthermore, this compound was found to be orally available in rats and exhibited efficacy in an animal model of neuropathic pain following oral administration.

327. Antioxidant properties of novel NMDA receptor antagonists and radiosensitizers

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Our studies examined the antioxidant properties of two classes of compounds, N-methyl-D-Aspartate receptor (NMDAR) antagonists and radiosensitizers. Antioxidant properties can augment or attenuate desired functions of these compounds, which are their abilities to treat neurodegenerative diseases and cancers, respectively. We evaluated the capability of each compound to scavenge reactive oxygen species (ROS) using nitric oxide (NO) and 2,2-diphenyl-1-picrylhydrazyl (DPPH) free radical activity assays. The results showed insignificant decrease of free radical production in both assays. Hence, the findings support our hypothesis that the radiosensitizers do not show antioxidant properties. For the NMDAR antagonists, we still need to do more studies to affirm if they have a secondary mechanism of reducing ROS by acting as antioxidant species. We are now examining the abilities of these compounds to inhibit ROS production in a human neuroblastoma cell line (SK-N-SH). Such studies in cell culture could shed light on the antioxidant properties.

328. β-Lactam antibiotics: Chemical probes of the glutamate subtype 1 transporter

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Reduced uptake of glutamate via the glial transporter GLT-1 may play a role in withdrawal and relapse seen with substances of abuse (e.g., cocaine and heroin). Ceftriazone (CTX) has been shown to inhibit some of the behaviors associated with cocaine and opiate relapse in animal models. However, ceftriaxone does not penetrate the CNS well and its deleterious side effects make it an unlikely drug candidate for treating addiction.

Temple researchers recently showed that structural modification of CTX resulted in analogs with reduced antimicrobial activity. A series of novel analogs have been identified that enhance glutamate uptake in a cellular model and show significant selectivity for GLT-1 activity over antimicrobial activity. Initial analogs within this series suffered from poor permeability as a result of their physicochemi-

cal properties. Results pertaining to the structural elaboration aimed at identifying GLT-1 enhancers with improved physicochemical properties and permeability will be discussed.

329. *In vitro* anticonvulsant activity of 2,4-disubstituted phenyl enaminones

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Objective: The objective of the research project was to synthesize some 2,4-disubstituted phenyl enaminones and evaluate them for anticonvulsant activity *in-vitro*. Methods: Suitable intermediates were reacted with appropriate 2,4-dibromo anilines to obtain the corresponding enaminones. The enaminones were evaluated *in-vitro* in rat's hippocampus. Results and Discussion: The enaminones caused varying degrees of depression in the amplitude of population spikes that were recorded in the area CA1 of the hippocampus *in vitro*. The significant depression of amplitude of population spikes suggested anticonvulsant activity in the rat's brain. The most potent enaminone was methyl 4-(2',4'-dibromophenylamino)cyclohex-3-en-2-oxo-6-phenyl-1-oate. It was coded AK6, and it caused a maximum depression of the population spikes of 72% at 10 µM with an EC50 of 2.1 µM. Conclusion: Disubstituted phenyl enaminones were potent anticonvulsant compounds as they significantly decreased evoked population spike amplitudes in the rat hippocampus. This work was supported by KURA grant # PR01/08.

330. Removal of a ricin surrogate from water and reusable medical device surfaces

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Water and reusable medical device surfaces can be contaminated by natural toxins such as ricin and botulinum toxin (Bt). Previous work revealed a reverse osmosis (RO) system could remove Bt from water. We focused on ricin and used peanut lectin (PL) as a surrogate for ricin and an ELISA assay to determine if commercially available water filters could remove PL and if commercially available cleaning/disinfecting wipes could denature PL. Various medical devices and materials were tested to evaluate the removal of PL. The RO water system was effective in removing PL from water. Wipes containing sodium hypochlorite (0.9%) were most effective in denaturing PL within 2 minutes. The recovery of PL from the materials tested ranged from 76 to 100%. Recovery of PL from the surface of various medical devices ranged from approximately 71 to 89%. Confirmation with ricin will need to be conducted to verify these results.

331. Design, synthesis and biological evaluation of novel Mtb-specific Dxr inhibitors as potential anti-tubercular agents

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Tuberculosis (TB), a highly contagious disease caused by *Mycobacterium tuberculosis* (Mtb), represents one of the most threatening health problems globally. The emergence of drug-resistant strains is a serious threat to TB control and treatment. There is an urgent need for the discovery and development of novel anti-tubercular agents.

Mtb synthesizes isoprenoids, essential for mycobacterial survival, via the nonmevalonate pathway; the second step being mediated by the enzyme Dxr. Inhibitors of Dxr are potential anti-TB agents. The nonmevalonate pathway is absent in humans, therefore, Dxr can be specifically targeted without interfering with human metabolism.

The goal of this project is to design, synthesize and evaluate a unique class of analogues of fosmidomycin and FR900098, known inhibitors of Dxr, in order to study their structure-activity relationships and develop a new series of anti-TB drugs. Computational docking, synthetic results and biological evaluation will be presented.

332. Screening vorozole on a series of human liver cytochrome P450s

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Vorozole and letrozole are third generation aromatase (cytochrome P450 19A1) inhibitors. [^{11}C]-Vorozole can be used as a radiotracer for aromatase in the brain, however, when it is administered by IV to a baboon, some of it binds to the liver. Letrozole does not show specific binding to the liver. Since vorozole is an imidazole-based inhibitor of CYP19A1, it could be binding to another CYP found in the liver. We used fluorometric high-throughput screening assays to tested vorozole and letrozole on a series of CYPs found most abundantly in the human liver. We found that vorozole was a potent inhibitor of CYP1A1 and a moderate inhibitor of CYP2A6 and CYP3A4. Letrozole inhibited CYP3A4 less than 10% at 1 mM. CYP3A4 makes up the majority of the CYPs found in the human liver so it is a very good candidate for the protein that [^{11}C]-vorozole is binding to in the liver.

333. Antagonism of c-myc–max protein–protein interaction with small-molecules

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The basic helix-loop-helix-leucine zipper (bHLH-LZ) protein family is an extensive family of transcription factors that includes the c-Myc–Max heterodimeric protein complex, which regulates the transcription of genes involved in cell proliferation, cell cycle progression and apoptosis. Over-expression of c-Myc has been inextricably linked with multiple cancers. Since c-Myc becomes transcriptionally active only upon binding its obligate partner Max, the disruption of the c-Myc–Max protein–protein interaction is an attractive approach toward the development of c-Myc inhibitors. However, the identification of potent c-Myc inhibitors remains an elusive goal, which is largely attributed to the preference of monomeric c-Myc to exist in an intrinsically disordered state, and, hence, lacks any targetable binding sites. Building from a previously identified moderate inhibitor of c-Myc whose optimization was obstructed by poor solubility, we have enhanced the lead inhibitor's physicochemical properties, which has directly facilitated the development of more hydrophobic and more potent derivatives.

334. Synthesis and biological evaluation of novel tetracyclic indenoquinoline derivatives as anticancer agents

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Tetraheterocyclic backbones are important scaffolds for different biological targets and these types of compounds are widely used as anti-microbial/anti-cancer agents. This study describe the preparation of a series of novel tetracyclic indenoquinoline derivatives bearing aromatic and aliphatic ethers and their evaluation on human breast adenocarcinoma (MCF-7) and human alveolar adenocarcinoma basal epithelial cells (A-549) and human cervical cancer cells (HeLa) by MTT assay. Results show that most compounds have growth inhibition activities (GI50) at nM level. In addition, our studies show that aromatic derivatives display better inhibition of cell growth than aliphatic ethers. However, the simplest methyl ether indenoquinoline derivative demonstrated better growth inhibition (GI50 5 nM on A549 cells) or similar (2 nM on MCF-7 cells) activity when compared to camptothecin (GI50 of 7 nM on A-549 and 2 nM on MCF-7 cells respectively). Conversely in HeLa cells, aromatic ether derivatives showed approximately ten times better activity than Camptothecin.

335. Some limits of biocompatibility testing for lipohilic leachates

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Medical device standards recommend using both a polar and non-polar solvent to extract materials prior to in vitro testing. Testing lipophilic extracts in cell culture systems is limited by the toxicity of the lipophilic solvents used in extraction. This particular problem was approaced by 1) use of hydrotropes, and 2) by sealing the suspended cells in dialysis tubing and placing it directly in oil or media. The use of hydrotropes to eliminate micelle formation and increase the solubility of the lipophilic compounds was not useful as the hydrotropes themselves were toxic to the cells at concentrations that significantly increased analyte solubility. There were significant differences in toxicity for cells in dialysis tubing between devices extracted with peanut oil or media. This study illustrates the importance of examining if cell toxicity is due to micelle formation or if due to soluble chemicals for lipophilic extracts.

336. Insight into the hydroxylation of quinolone quorum sensing molecules across bacterial species

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The opportunistic pathogen *Pseudomonas aeruginosa* produces 4-hydroxy-2-alkylquinolines (HAQs) known to undergo hydroxylation. This generates the activated 3,4-dihydroxy-2-alkylquinolines (PQS) involved in quorum sensing. Our aim is to understand the role of hydroxylation across bacterial species through the use of *in vivo* enzymology and high-pressure liquid chromatography/mass spectrometry (LC/MS). Recent studies have shown that hydroxylation occurs on a multitude of structurally diverse quinolones such as methylated and *N*-oxide species present in *Burkholderia* and *P. aeruginosa*, respectively. Specifically, the *N*-oxide species are recycled by *P. aeruginosa* to form the activated 3,4-dihydroxy-2-alkylquinolines (PQS). Furthermore, the hydroxylation of the methylated species is potentially a form of sabotage implemented by *P. aeruginosa*. Isolation and characterization of the products will provide further insight into the hydroxylation pathway.

337. MD simulation studies to understand the role of active site residues in lesion processing by thymine DNA glycosylase

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DNA lesion caused by deamination of 5-methylcytosine to thymine give rise to mutagenic G-T mispairs, which contributes to cancer, genetic diseases, and aging. Thymine DNA Glycosylase (TDG) is a mammalian enzyme that initiates the base excision repair pathway by identifying these G-T lesions and removing the thymine. Molecular dynamics (MD) simulation studies were carried out to understand the role of selected conserved and catalytically critical active site residues (Ala145 and His151), which curtail repair activity and play an essential role to avoid aberrant action on undamaged DNA. We mutated these and some other important residues to observe their effect on flipping. Our simulation studies indicate the presence of steric hindrance between methyl group of thymine and the methyl of Ala145, which plays a role in destabilizing flipped dT. Results clarify the role of the A145G mutation in relieving the steric clash and stabilizing the flipped base in the active site.

338. Wetting properties of ionic liquids

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The wetting properties of 1,2,3-triazolium nitrate ([123tr][NO3]) on quartz surfaces were investigated using molecular dynamics simulations. The morphological transition from a spherical liquid drop in the vacuum to a hemispherical droplet of the liquid resting on top a quartz surface was simulated using a canonical ensemble. Hydrophobic and hydrophilic quartz surfaces were used. Once equilibrium was attained for the system, the liquid contact angles were determined along different crystallographic directions on the surfaces in order to examine the effect of the local structure on the liquid-surface interactions. Contact angles are lower for hydrophobic surfaces and there appear to not be an obvious correlation between their magnitude and the crystallographic directions in which they were determined. This work is part of a larger project to study properties of ionic liquids that can have immediate industrial applications. Wetting properties were examined to investigate the lubricating capabilities of these liquids.

339. Substrate binding and structure equilibration for the peptide hydrolysis catalyzed by human T-cell leukemia virus type 1 (HTLV-1) protease

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Human T-cell leukemia virus type I (HTLV-I) protease is a homodimeric aspartic acid protease that catalyzes the hydrolysis of peptide bonds by involving two active site aspartic acid residues. The function of this protein is critical for many HTLV-I associated diseases, our goal is to study the catalytic mechanism of HTLV-I protease. The first step of the catalytic study is substrate binding, a complex of HTLV-I protease and its substrate has been derived and the protein-substrate complex was then dissolved in a water box to explicitly treat the solvent environment. The solvated system was minimized using a molecular simulation program CHARMM and has been equilibrated for a combined quantum mechanical and molecular mechanical (QM/MM) simulation of the peptide hydrolysis reaction. In this presentation, the interactions between substrate and protein, thermodynamic properties of the equilibrated system, as well as the strategies to study the catalytic reaction will be discussed.

340. Computational simulation of laminaripentaose-producing β-1,3-glucanase (LPHase) catalytic reaction

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Laminaripentaose-producing β-1,3-glucanase (LPHase) is a member of glycoside hydrolase family 64; it cleaves a long chain polysaccharide β-1,3-glucan into specific pentasaccharide oligomers. Glycoside hydrolases play diverse roles during biomass degradation. To understand the role of LPHase during biomass degradation process, we plan to study the catalytic mechanism of this enzyme.

We have chosen laminarihexaose as the substrate of LPHase. One structure of laminarihexaose obtained from the Protein Data bank has been docked into the active site of LPHase using the Glide module of program Schrodinger. This LPHase-laminarihexaose complex structure was minimized and dissolved in a 90Å×70Å×70Å water box, and five chloride ions were added to neutralize the positive charge of the system. A combined quantum mechanical and molecular mechanical (QM/MM) method has been employed to study the hydrolysis of the glycosidic bond catalyzed by LPHase, some preliminary results will be presented.

341. Cyclic and linear homochiral decapeptides containing tryptophan and arginine/lysine residues as Src kinase inhibitors

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Src kinase is a key modulator of cancer cell invasion and metastasis. Src offers a promising molecular target for anticancer therapy. We previously reported cyclic and linear peptides containing tryptophan and arginine or lysine as drug delivery tools. Herein, we evaluated the inhibitory effect of four peptides including cyclic $[WR]_5$, cyclic $[WK]_5$, linear $(WR)_5$, and linear $(WK)_5$ on Src kinase activity. C-$[WR]_5$ was found to exhibit the highest Src Kinase inhibitory activity with IC_{50} value of 2.89 μM compared to L-$(WR)_5$, C-$[WK]_5$, and L-$(WK)_5$ with IC_{50} values of 7.1 μM, 46.9 μM, and 69.1 μM, respectively. Peptides containing tryptophan and lysine exhibited slightly higher antiproliferative activity than those containing tryptophan and arginine. C-$[WK]_5$ and L-$(WK)_5$ reduced the cell proliferation of human leukemia (32% and 28%) cells at a concentration of 100 μM after 24 h incubation. Peptides containing tryptophan and arginine residues represent a new scaffold as Src kinase inhibitors.

342. Polystyrene supported $AlCl_3$ as a highly chemoselective catalyst for Fries rearrangement of aryl esters

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Polystyrene supported aluminum chloride (Ps-$AlCl_3$) was prepared by addition of anhydrous $AlCl_3$ to polystyrene (8% divinylbenzene) in carbon disulfide under reflux condition with the loading value of 0.4 mmol $AlCl_3$/g. The Fries rearrangement of aryl esters was carried out by Ps-$AlCl_3$ in nitrobenzene at 90 ºC. The optimum molar ratio of aryl ester to catalyst was found to be 1:0.15. A general en-

hancement of *para* selectivity was observed for all products using Ps-$AlCl_3$ compared to homogeneous $AlCl_3$ catalyst.

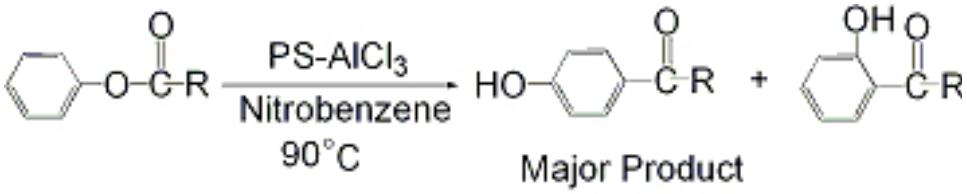

Figure 1

343. Amphiphilc cyclic peptide $[WR]_4$ as an efficient transporter of negatively charged phosphopeptides

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We previously reported a cyclic peptide containing alternative tryptophan and arginine $[WR]_4$ as a molecular transporter. Herein, the cellular uptake of several fluorescent-labeled phosphopeptides including, F-GpYLPQTV, F-NEpYTARQ, F-AEEEIYGEFEAKKKK, F-PEpYLGLD, F-pYVNVQN-NH_2, and F-GpYEEI, was evaluated in the presence or absence of $[WR]_4$ in human leukemia cells (CCRF-CEM) after 2 h incubation using flow cytometry (FACS). $[WR]_4$ improved the cellular uptake of all phosphopeptides. Among them, the cellular uptake of F-PEpYLGLD was enhanced dramatically (27-fold) in the presence of $[WR]_4$. PEpYLGLD is a sequence that mimics the $pTyr^{1246}$ of ErbB2 that is responsible binding to the chk SH2 domain. The cellular uptake of the F-PEpYLGLD was found to be time-dependent. TEM results showed that the mixture of PEpYLGLD and $[WR]_4$ formed nano-sized structures with range size of 10 to 30 nm. ITC results confirmed binding between $[WR]_4$ and PEpYLGLD. The binding isotherm curves, derived from sequential binding models, showed an exothermic interaction.

Contemporary Organic Materials

Presiding: J. Tovar

344. Organic materials research at Johns Hopkins University: Biomedicine, energy and nanoscience

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This presentation will highlight the many facets of current soft materials research at JHU focusing on efforts in the physical sciences and engineering fields.

345. Synthesis and characterization of functionalized graphite nanofibers

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Graphite nanofibers (GNFs) are novel nanoscale materials that can be prepared inexpensively, in gram quantities, via the catalytic decomposition of carbon monoxide or hydrocarbons over mono- or bi-metallic catalysts. GNFs have potential for applications across a diverse spectrum of research areas in chemistry, biology, medicine, and energy storage. Surface functionalization and characterization are both critical to the further development of GNFs. We have identified and quantified surface aldehyde/ketone, carboxyl, and hydroxyl groups on oxidized herringbone GNFs using a technique known as FLOSS (Fluorescent Labeling of Surface Species). Information that was obtained about the surface chemistry of GNFs can now be used to guide the covalent functionalization of the fiber surface with amino sugars, aminoglycoside antibiotics, and other molecules.

346. Comparison of polymer-fullerene heterojunction morphology to bimolecular recombination kinetics

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Organic photovoltaic (OPV) technology has the potential to lower the cost of solar power by enabling high-throughput fabrication. In bulk heterojunction (BHJ) OPV devices, the power conversion efficiency is thought to depend on the morphology of the blend, but correlations have been elusive. The first step toward correlation is the measurement of materials structure. This talk will cover measurement themes including interface composition, order and orientation, solubility and miscibility, and nanoscale morphology.

A particular focus will be our attempt to link bimolecular recombination and microstructure/morphology. Very few polymer-fullerene BHJ active layers exhibit slower-than-Langevin charge carrier recombination, which is a requirement for fabricating thick active layers (> 100 nm) while maintaining high fill factors. In collaboration with Mozer and Clarke at the University of Wollongong, we evaluate a variety of hypotheses related to nanoscale film structure in an attempt to determine why some special systems exhibit this unusual and desirable feature.

347. Electrochemical polymerization of conjugated polymers in living tissue

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We are investigating the direct electrochemical polymerization of conjugated polymers such as poly(3,4-ethylenedioxythiophene) (PEDOT) in living tissue. This method has been proposed as a means for improving the long-term performance of biomedical devices such as cortical microelectrodes. We monitor the extent of polymerization using optical and electron microscopy, and the electrical properties using cyclic voltammetry and impedance spectroscopy. We examine the response of the tissue using immunohistochemistry and fluoresence optical microscopy. The influence of the in-situ deposited PEDOT on animal behavior and memory is determined using a two-choice T-maze. We are currently investigating the importance of delay time from the initial surgery and the time of polymerization.

348. Poly(thiomethyl methacrylate): Sulfur's effect on polymerization and polymer properties

***Arthur Snow**, arthur.snow@nrl.navy.mil, Andrew Purdy, Michael Brindza, Guy Beadie.Naval Research Laboratory, Washington, DC 20375, United States*

The substitution of sulfur for oxygen in many simple compounds such as in H_2S for H_2O or CH_3SH for CH_3OH has rather dramatic effects. The same is true to a lesser extent in polymers. In this work we address the question of refining physical properties of a well-known polymer with a sulfur for oxygen substitution and focus on poly(methyl methacrylate). The incorporation of the thioester in place of the oxoester has interesting and potentially useful consequences for this well-known polymerization system whose optical clarity, stability, melt-processibility and rigidity have made it successful in many applications. The objective of this work is to quantify and understand the changes in polymerization reactivity and in polymer physical properties when the thioester structure is incorporated in place of the oxoester structure in the poly(methyl methacrylate) system.

349. Sorona® polytrimethylene terephthalate: A renewably-sourced polymer with enhanced performance

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Polytrimethylene terephthalate (PTT) is a polymer derived from the polymerization of 1,3 propane diol and terephthalic acid or dimethyl terephthalate. The 1,3 propane diol monomer used in the PTT sold under the trade name Sorona® is derived from corn sugar in a fermentation process, providing a polymer with 37% renewably-sourced content by weight. In addition to providing a renewably-sourced option in high performance polymer markets, the unique structure of PTT polymer impacts its performance in apparel fiber, carpet fiber and injection molded part applications. Several properties were identified that provided product attributes relative to other polyesters (namely polyethylene terephthalate and polybutylene terephthalate) including fiber softness, enhanced stretch recovery and dyeability. PTT composite work will be discussed towards viscosity modification at high temperatures.

350. Polypeptoids: Synthesis, characterization and materials properties

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Polypeptoids are a class of psudo-peptidic polymers featuring *N*-substituted polyglycine backbones with proteinogenic or synthetic side chains on the nitrogen atoms. This presentation will focus on our recent efforts in the development and mechanistic studies of *N*-heterocyclic carbene (NHC)-mediated living polymerization of *N*-substituted *N*-carboxyanhydrides (R-NCA) which yields cyclic or linear polypeptoids with diverse structures. Polypeptoids can be rendered hydrophobic/hydrophilic or semi-crystalline/amorphous by the introduction of appropriate side chain structures. Moreover, this structural control can be extended to induce the formation of random coil or helical conformations. The synthesis of polypeptoid copolymers and investigation of their solution properties (i.e., self-assembly and thermal responsive behavior) will also be presented.

351. Funtional hydrogel materials from self-assembling peptides

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Small molecules and proteins that exhibit systemic toxicity are typically disregarded as potential therapies. However, the ability to deliver these agents locally with spatial resolution can potentially circumvent this problem. We have designed a class of peptide-based hydrogels that enable the di-

rect three-dimensional encapsulation of small molecules, proteins, or even cells. Loaded gels exhibit shear-thinning/self-healing mechanical properties that enable their parenteral delivery via syringe/catheter to a site of interest. Once delivered, gels release their payload locally. Release rates can be controlled by predictably modulating the network properties of the hydrogel via *de novo* design of the peptides that comprise these self-assembled materials. Progress towards developing materials that impact cancer therapy will be discussed.

Mass Spectrometry of Biomolecules

352. Communicating concepts and methods in biological mass spectrometry: Development of an introductory tutorial series for the nonspecialist

James A. Kelley[1], *kelleyja@mail.nih.gov*, *Josip Blonder*[2], *Christopher C. Lai*[1], *Luke Stockwin*[3], *Timothy D. Veenstra*[2], *Lawrence R. Phillips*[4]. *(1) Chemical Biology Laboratory, CCR, National Cancer Institute, Frederick National Laboratory for Cancer Research, Frederick, MD 21702, United States (2) Laboratory of Proteomics and Analytical Technologies, ATP, SAIC-Frederick, Frederick National Laboratory for Cancer Research, Frederick, MD 21702, United States (3) Biological Testing Branch, DTP, SAIC-Frederick, Frederick National Laboratory for Cancer Research, Frederick, MD 21702, United States (4) Office of the Associate Director, Developmental Therapeutics Program, DCTD, National Cancer Institute, Frederick National Laboratory for Cancer Research, Frederick, MD 21702, United States*

The fields of biology and molecular science impacted by mass spectrometry are as diverse as they are extensive. It is in this context that the Mass Spectrometry Interest Group (MSIG) of the Frederick National Laboratory for Cancer Research exists to provide a forum for members to interact. An early result of this interaction was the realization that there was an absence of the fundamental chemical and analytical knowledge to allow non-mass spectrometry users to interface successfully with the mass spectrometry community. To address this need, a semiannual tutorial series was initiated in 2002. This MSIG educational project was designed to provide the nonspecialist with an introduction to and overview of the concepts, capabilities, current practices, and uses of mass spectrometry. The organization and conduct of this tutorial series mirrored that of a limited-enrollment, highly interactive short course. The development and evolution of this very successful tutorial series will be discussed.

353. Use of imaging mass spectrometry to find biomarkers and study time dependent lipid changes in brain trauma caused by controlled cortical impact

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We investigated molecular changes and their consequences in a rat model of controlled cortical impact (CCI) as over 350,000 soldiers have sustained battlefield brain trauma. Imaging Mass Spectrometry (IMS) was used to qualitatively characterize a range of brain lipid species. CCI causes localized area injury and brain parenchyma deformation resulting in apoptosis, and detectable lesion boundary effects.

A MALDI-Orbitrap (Thermo-Fisher) was used for imaging and provided accurate mass measurements coupled with precise localization of brain lipids. These images demonstrate anatomical changes that occur over time and implicate several lipid species involved in the dynamics of membrane disruption and signaling events following injury. Changes in the relative abundance and localization of lipids are readily observed in the injured tissue.

Ongoing studies include comparison of images between time points post trauma, to identify and target species responsible for disrupting cellular mechanisms after injury.

354. Major histoctocompatibility class II$^+$ invariant chain negative breast cancer cells present unique peptides that activate tumor-specific T cells from breast cancer patients

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We have generated cell-based MHC II vaccines to activate patients' CD4$^+$ T-cell to facilitate tumor immunity. This was based on the hypothesis that invariant chain (Ii) negative, MHC II and CD80 positive tumor cells present novel MHC II peptides and circumvent patients' tolerance to their cancer. We used LC-MS/MS to sequence MHC II-restricted peptides from Ii$^+$ and Ii$^-$ MCF10 human breast cancer cells transfected with MHC II in the presence or absence of Ii and determined that Ii$^-$ cells present novel peptides. Peptides from Ii$^-$ cells with the highest predicted MHC II binding affinity were synthesized, and activated tumor-specific human T cells from healthy donors and breast cancer patients, demonstrating that MS-identified peptides are bonafide tumor antigens. These results demonstrate that Ii regulates repertoire of tumor peptides presented by MHC class II$^+$ breast cancer cells and identify novel immunogenic MHC II-restricted peptides that are potential therapeutic reagents for cancer patients.

355. Middle out analysis in proteomic workflows

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Several state of the art mass spectrometers offer low or high resolution mass measurements. In proteomics the resolution and duty cycles of the analyzer are balanced to achieve the best analysis. Low resolution measurement is best suited for small peptides that are singly or doubly charged, since these peptides dissociate into singly or doubly charged fragment ions. Larger proteolytic products usually produce more highly charged fragment ions that require higher resolution for charge state assignment. We demonstrate a method that separates peptides by mass using molecular weight cutoff filters. High and low mass fractions are then analyzed using the appropriate analyzer to enhance analysis of both cohorts. The approach is illustrated with the whole cell lysate of MCF7 human cancer cells. Proteolysis was carried out by residue-selective microwave supported acid cleavage. PepArML was used for low mass peptide assignment, while ProSightPC was used for the high mass portion.

356. Small-volume sample analysis by mass spectrometry: From single cells to high-throughput product screening

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Recent advances in sample preparation and mass spectrometry (MS) have extended this powerful technique for the analysis of volume-limited samples. This presentation highlights two related MS-based developments for bioanalytical research and routine product quality screening. First, a single-cell capillary electrophoresis platform and data analysis methodology is presented for the metabolic differentiation of individual neurons in *A. californica* (sea hare); classical neurotransmitters and small compounds including amino acids are profiled among various neuron types as well as freshly isolated and cultured cells. Second, ambient MS via direct analysis in real time (DART) is visited for the analysis of chondroitin sulfate and heparin. These glycosaminoglycans, widely used in raw materials and medical device coatings, are here analyzed in small amounts and high throughput. Degradation of the polysaccharide chains in the ionization source is discussed as a means to rapidly distinguish safe and adulterated samples, potentially aiding product screening with on-site portability.

357. Validation of efficient LC-MS/MS calibration strategies

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The measurement of the standard curve for every batch of clinical samples comprises a major source of labor and materials costs and instrument time for LC-MS/MS quantitative analysis. It is also a significant consideration that influences clinical labs to favor multi-analyte to single-analyte LC-MS/MS assays. Multi-analyte assays are theoretically inferior because of their potential for chromatographic and isotopic carryover and the increased possibility of matrix effects leading to spurious over- or underestimation of analyte concentration. For all these reasons, a simple, efficient, and accurate calibration strategy for LC-MS/MS clinical assays is highly desired. This presentation will introduce such strategies and how they are implemented in a clinical setting for the therapeutic drug monitoring of tricyclic antidepressants.

358. MALDI ion mobility mass spectrometry of biomolecules and non covalent complexes

Damon Barbacci[1], *damon.barbacci@gmail.com, Shelley Jackson*[2], *Jeremy Post*[2], *Katie Baldwin*[2], *Ludovic Muller*[2], *J Albert Schultz*[1], *Amina Woods*[2], *Tom Egan*[1], *Kelley Waters*[1], *Steve Ulrich*[1], *Valerie Vaughn*[1], *Mike McCully*[1], *Ernest Lewis*[1]. *(1) Ionwerks, Houston, TX 77002, United States (2) Cellular Neurobiology, NIH-NIDA/IRP, Baltimore, MD 21224, United States*

Ion mobility coupled with mass spectrometry has become a power tool to separate and characterize three dimensional structures of all types of ions. In particular, MALDI ion mobility MS is a powerful tool for detecting, identifying and characterizing peptides, proteins, lipids, oligonucleotides and detailed structural information regarding the cross sectional area of an ion can be determined. MALDI is a soft ionization mechanism capable of keeping non-covalent complexes intact. MALDI coupled with IM-MS is a powerfool tool to explore relative binding affinity of NCXs of peptide-peptide, peptide-drug, drug-lipid interactions.

359. Unraveling the quagmire of oligonucleotides: Analysis by high resolution mass spectrometry

Joshua A. Wilhide, *Wilhide3@umbc.edu, William R. LaCourse.1000 Hilltop Circle, University of Maryland Baltimore County, Baltimore, Maryland 21250, United States*

It can be said that the study of oligonucleotides by mass spectrometry can be met with adversity mainly due to the rapid degradation of RNA/DNA products and the extremely low tolerances for salt concentrations allowed by the mass spectrometer. These two problems can be easily bypassed prior to analysis as well as during analysis to obtain publishable spectrum. The goal of this abstract will be to provide a clear road map from bench to instrument on how to properly prepare and analyze these samples on a Fourier Transform Ion Cyclotron Resonance Mass Spectrometer (FT-ICR-MS) using electro spray ionization (ESI). Furthermore, the presentation will also include tips and tricks on how to preserve the non-covalent complexes between DNA/DNA and protein/DNA which can then be used for alternative pathway for binding studies.

Active Learning in the Chemistry Classroom

Presiding: H. Perks

360. Comparing educational outcomes of a team-based learning approach and a traditional lecture approach to teaching genetics

***Steven Caruso**, scaruso@umbc.edu, Cynthia R. Wagner, David M. Eisenmann, Philip J. Farabaugh. Department of Biological Sciences, Univeristy of Maryland Baltimore County, Baltimore, Maryland 21250, United States*

Genetics is a course at UMBC that serves over 600 students a year. In the fall of 2011, a study investigating the effect of Team Based Learning (TBL) on educational outcomes was initiated. Students in the fall semester were divided into small teams and which sat together during class meetings and during their 30-person discussion sessions. Students were expected to complete assigned readings prior to class. Lecturing was avoided with the majority of class time spent having students complete concept applications and problem sets in their teams, followed by a class debriefing. In the Spring semester a more traditional lecture-based presentation was delivered. Both versions included interactive web-based material, use of an audience response system, and exams to assess student performance. A pre- and post-assessment is being administered to the class and repeated in the next course in the core curriculum to assess the effectiveness of the TBL approach.

361. Illustration of unreliability of calculated proton nmr spectra

***Donald D CLARKE**, clarke@fordham.edu.Department of Chemistry, Fordham University, New York, NY 10458, United States*

N-methyl-D-aspartic acid [NMDA] is an antagonist of a glutamate receptor in brain. [J Med Chem (1962) 5, 1187]. A supplier listed it in the 1970's but shipped the wrong isomer. I asked students: "how can you distinguish N-Methyl from C-methyl aspartic acid by proton NMR". They consulted a database, and got many wrong answers. As was known well before databases existed, an N-CH_3 group has a larger chemical shift than a C-CH_3. Calculated spectra show this. But students often selected differences for NH and COOH protons that were artifacts of calculated spectra. Amino acids, as zwitterions, are insoluble in $CDCl_3$. In real spectra run in D_2O, NH and COOH exchange with solvent. Thus calculated spectra unnecessarily confused students. This type of error appears often on websites of faculty currently teaching organic chemistry. Supported in part by an NSF grant for a 300 MHz nmr spectrometer.

362. Assessing the effect of active learning on student learning outcomes in the chemistry classroom

***Linda C Hodges**, lhodges@umbc.edu.Department of Faculty Development, UMBC, Baltimore, Maryland 21250, United States*

Active learning strategies in the classroom may seem to take time away from content coverage. How do we measure the value added of these approaches in a meaningful way either for ourselves, for accrediting agencies, or for grant funding? In this session we will talk about ways to assess the actual learning outcomes that result from class activities and how to use that data to design more effective, and efficient, classroom experiences. Examples include assessments embedded in normal assignments, pre- and post-concept tests, specifically designed criteria for grading (rubrics), and student interviews.

363. Organic chemistry and the 'structure-mechanism-reaction' paradigm: Structure knowledge is a powerful predictor of student performance

***Steven M. Graham**, grahams@stjohns.edu.Department of Chemistry, St. John's University, Queens, NY 11439, United States*

Much of organic chemistry presupposes knowledge of chemical structure; indeed structure is the foundation upon which mechanistic theory and chemical synthesis rest. For a number of years we have assessing which types of exam questions – those dealing with chemical structure, reaction mechanisms, and synthetic outcomes – students find most difficult, with the goal of designing an intervention that would address this difficulty. One such intervention was the use of personal response systems ('clickers') to create a numeric representation of organic chemistry mechanism arrows (Ruder and Straumanis, *J. Chem. Educ.*, **2009** , *86*, 1392-1396). Post-clicker introduction, we observed a significant improvement on mechanism-based exam questions. More dramatic, however, was the observation that a student's score on structure-based questions is tightly correlated to their overall exam score. This finding suggests that an increased emphasis in the classroom on the structure of organic molecules may be beneficial.

364. Development and analysis of course and program-level assessment tools and data from general education chemistry and physical chemistry courses

***Alfred T. D'Agostino**, adagostino@ndm.edu.Chemistry Department, Notre Dame of Maryland University, Baltimore, Maryland 21210, United States*

Assessment of student learning can provide information about learner preparation and progress, selection of course content, instruction effectiveness, and level of achievement of outcomes. A description of how assessment tools were developed and used to assess general education learning outcomes, student pre-course preparation, course-specific learning goals, and curriculum cohesiveness will be given. The following tools, data, and results will be discussed: "Student Self-Assessment of Course Outcomes" in a chemistry course for non-majors used to evaluate integration of knowledge, writing and communication; "Skills/ Concepts Competencies - Student Self-Assessment" in upper-level chemistry courses to assess pre- and post-course level of understanding; and "Prerequisite Concepts and Skills Inventory" to assess degree of preparation obtained in General Chemistry. Comments will be made regarding the correlation of assessment results to: validity of student self-assessment, course grade and evaluation, high school and undergraduate GPA, quantitative SAT score, and results of ACS and Major Field tests.

365. Mass, measurement, materials, and more mathematical modeling: The nuts and bolts of let's make an error

***Scott A. Sinex**[1], ssinex@pgcc.edu, Theodore L Chambers[1], Joshua B Halpern[2]. (1) Department of Physical Sciences & Engineering, Prince George's Community College, Largo, MD 20774-2199, United States (2) Department of Chemistry, Howard University, Washington, DC 20059, United States*

How can you get students into analyzing and understanding errors? Here we present a second semester general chemistry experiment that introduces students to error analysis via simple mass determinations using nuts, bolts, and washers. The laboratory consists of four parts: calibrating the balance; making errors to discover the behavior of constant and proportional systematic errors; analyzing the effects of an errant nut in a sequential addition of nuts to a bolt and sharing data in Google Docs for a collaborative online discussion by groups using the chat function; and verifying the errant nut problem by simulation in an interactive animated spreadsheet. Each group has a different set of results and must try to figure out what is possibly wrong with their results. Students must use some algebraic detective work to find the outlier and its influence on the regression line. We will discuss our experience with this experiment.

366. Implementing a classroom assessment technique in a large enrollment course

Daniel King, *daniel.king@drexel.edu.Department of Chemistry, Drexel University, Philadelphia, PA 19104, United States*

Large enrollment (more than 200 students) prohibits the implementation of some effective pedagogical techniques, such as muddiest point, where students are asked at the end of class to identify what topic is still unclear. Over the past two years, I have used personal response devices (or clickers) to collect muddiest point information in general chemistry courses. The clickers have provided a technological solution to the logistical challenge associated with collecting this information. Data will be presented on the topics that were most commonly chosen as the muddiest point. These topics will be compared to student responses to in-class clicker questions. Specifically, are students more likely to identify a topic as their muddiest point if they answered a related clicker question incorrectly? Student performance on exam questions related to muddiest point topics will be compared to student performance on exam questions related to topics that weren't chosen as a muddiest point.

Nanochemistry A

Presiding: M. Daniel

367. Characterization and evaluation of zein/chitosan nanocomplex for encapsulation and controlled release of hydrophilic and hydrophobic nutrients

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Current study is to develop nanoparticle complexes made with zein and chitosan for encapsulation of different nutrients. First part of the study focused on encapsulation of hydrophilic nutrient (selenite) in CS/TPP nanoparticles, which was then further coated by zein. The second part of the study investigated encapsulation of hydrophobic nutrient (α-tocopherol) in zein nanoparticles coated with CS. The physicochemical analysis showed that electrostatic interaction and hydrogen bonding were major forces responsible for nanocomplex formation. The scanning electron microscopy study revealed spherical nature with smooth surface of nanocomplex. The encapsulation of nutrients was also evidenced by differential scanning calorimetry. The encapsulation efficiency for coated nanocomplex was significantly higher than non-coated nanoparticles. Significant improvements of release profiles were observed in coated nanocomplex. The stabilities were also greatly enhanced in coated nanocomplex. Zein/CS complex is believed to be a promising delivery system for both hydrophilic and hydrophobic nutrients or drugs.

368. Use of a transferrin-functionalized gold nanoparticle-cored dendrimer for targeting advanced pancreatic cancer

Margaret E. Grow, *mgrow1@umbc.edu, Marie-Christine Daniel.Department of Chemistry and Biochemistry, University of Maryland, Baltimore County, Baltimore, MD 21250, United States*

Pancreatic cancer is currently the fourth leading cause of cancer-related deaths in the United States with a five-year survival rate of five percent, mainly due to late detection and low efficiency of current treatment. The transferrin protein has proved in the literature to be an effective targeting ligand, capable of enhancing chemotherapeutic drug delivery to the desired site. Specifically in the case of pancreatic cancer, while transferrin receptors are rarely produced on normal pancreatic cells, malignant pancreatic cells produce them in abundance. When these proteins are coupled with nanoparticles, they have the additional property of passively targeting tumor sites due to their enhanced permeation and retention (EPR) effect. Herein, transferrin derivatived poly(propylene imine) dendrons

were combined with gold nanoparticles to selectively target advanced pancreatic cancer in order to eventually assist in treatment.

369. Graphene oxide: A nano catalyst

Ganesh Rahul Bhimanapati[1,2], *gvb5099@psu.edu, Randy Vander Wal*[1,2,3,4], *Susana Carranza*[5]. *(1) John and Willie Leone Family Department of Energy and Mineral Engineering, The Pennsylvania State University, university park, Pennsylvania 16802, United States (2) The EMS Energy Institute, The Pennsylvania State University, university park, Pennsylvania 16802, United States (3) Department of Material Science and Engineering, The Pennsylvania State University, university park, Pennsylvania 16802, United States (4) Department of Mechanical and Nuclear Engineering, The Pennsylvania State University, university park, Pennsylvania 16802, United States (5) Makel Engineering, Chico, California 95973, United States*

Graphene Oxide (G.O.) can provide excellent stability and surface area as support material for catalysts. Three catalysts systems based on G.O. (synthesized by modified Hummer's process) and alumina nanopowder as support materials for ruthenium catalyst for the conversion of carbon monoxide to methane were made. A metal (Nickel) cation activation process modified the surface of the G.O. and G.O.-Al2O3 which facilitated the surface adsorption of ruthenium particles. The use of nickel as a nucleating center enhanced the ruthenium nanoparticle decoration on the G.O. SEM, TEM were used to verify the dispersion of the ruthenium nano particles on G.O. Elemental survey by XPS confirmed the ruthenium's presence.The mean diameter of the ruthenium nanoparticles was measured from TEM images as 2.7 nm. Porous aluminum foams supported the catalysts to create a hierarchical system with advantages of low pressure drop, excellent flow characteristic and heat transfer properties.

370. PtSn intermetallic nanoparticle electrocatalysts: Effects of graphene-based supports on electro-oxidation

Christopher M Sims, *cmsims@umd.edu, Audaldo A Ponce, Zhufang Liu, Bryan W Eichhorn.Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland 20742, United States*

Surfactant-free PtSn intermetallic nanoparticles (NPs) supported on functionalized graphene sheets (FGS) were synthesized by the co-reduction of platinum acetylacetonate and tin chloride in triglyme. Despite the lack of surfactants, most of the particles are small (<5 nm) and are well dispersed on the FGS support. To determine the effects of the carbon-based support material on the NPs' catalytic activity, the FGS-PtSn NP catalyst was evaluated for CO-tolerant H_2 electrooxidation against our previously reported PtSn catalyst, comprised of PtSn NPs supported on the standard Vulcan® XC-72 carbon black powder. While the FGS-PtSn catalyst shows higher activity for CO oxidation, the Vulcan-PtSn catalyst exhibits greater CO-tolerance. These observations show that the electrochemical properties and catalysis mechanisms of the two PtSn NP catalysts are remarkably different as a result of the support material.

371. Fabrication and characterization of UV-emitting defect-free 5-10 nm ZnO nanorings

Daniel C Micheroni, *daniel.micheroni@villanova.edu, Temer S Ahmadi.Department of Chemistry, Villanova University, villanova, PA 19085, United States*

Unprecedentedly small ZnO nanorings with near band edge ultraviolet photoluminescence and mitigated emission in the visible range were prepared by chemical synthesis using organic acids and butanol as surface modifiers in an in-situ procedure. Infrared spectroscopy (IR), transmission electron microscopy (TEM), uv-visible and photoluminescence spectroscopy, thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC) were employed in characterization, structure determination, analysis of optical properties, and investigation of the growth mechanism of the par-

ticles and their surfaces. Our results indicate that donut shaped nanorings can be fabricated with bound organic acids to the surface. No photoluminesce in our samples was observed in the visible region, which implies negligible defect formation in the ZnO nanoparticles. The effects of the surface groups, butanol, and reaction conditions on the size distribution and shape of the nanoparticles are presented here.

372. Solvent-free processing methods for formulation of dispersed multi wall carbon nanotube/epoxy composites

Murari L Gupta[1], *murari.gupta@howard.edu, Stefanie A Sydlik*[2], *Jan M Schnorr*[2], *Maraizu Ukaegbu*[1], *Charles Hosten*[1], *Timothy M Swager*[2], *Dharmaraj Raghavan*[1]. *(1) Department of Chemistry, Howard University, Washington, DC 20059, United States (2) Department of Chemistry, Institute of Soldier Nanotechnologies, Massachusetts Institute of Technology, Cambridge, MA 02139, United States*

For structural applications, typically 0.5 wt% loading of MWCNTs in epoxy resin is considered adequate so as to formulate high impact-resistant composite structures. For the translation of excellent mechanical properties of the MWCNTs into the MWCNT filled nanocomposites, good dispersion of MWCNTs in epoxy matrix is essential. The primary objective of this study is to evaluate the role of processing methods (microfluidics, planetary shear mixer, and ultrasonication) and nature of functional groups on MWCNTs (pristine, epoxy, hydroxy and amine) dispersion in cured epoxy resin matrix. Meso and microscale dispersion of CNTs in epoxy matrix was studied using optical microscopy, Raman Mapping and Field Emission SEM. The results have shown that a combination of microfluidics (MF) and planetary shear mixing (PSM) methods yielded best dispersion of CNTs. Evaluation of mechanical properties of solvent-free formulated MWCNTs/epoxy nanocomposites by various methods is underway.

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Renewable Energy C

373. Combined heat and power in automobiles: Utilization of waste engine heat to drive ethanol/water distillation

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Typical bioethanol processes use ~35% of the EtOH energy value to raise the ferment to 100% needed for USA fuel blending. This work shows a successful novel use of combined heat and power whereby the waste exhaust heat of a small gasoline fueled genset engine was used to power a still that readily raised 50% EtOH to burnable 90+%. A bioethanol product of ~50% EtOH is expected to use only ~10% of its ultimate fuel value to distill. Implementing this concept in a modified vehicle (Brazil flex fuel) or stationary engine has the potential to significantly improve the overall bioethanol energy balance. The limited scope of this promising initial work justifies further work to close the engine EtOH fuel loop, review bioethanol process economics, and evaluate energy infrastructure and regulatory changes needed to enable this energy savings concept to advance.

374. *In situ* studies of organic photovoltaic active layer formation and stability

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Organic photovoltaic devices are a promising route to lower costs via roll-to-roll manufacturing. The most promising device architecture involves a bulk heterojunction (BHJ) active layer in which nano-

scale phase separation into nominally bicontinuous donor and acceptor rich regions enables both exciton dissociation and charge extraction. The performance of BHJ based devices is a strong function of the active layer processing conditions and the optimized device structure is, in general, not the equilibrium structure. Optical techniques, such as spectroscopic ellipsometry, can provide detailed insights into film thickness, composition, and microstructure. We will discuss highlights from real-time studies of film formation where mechanisms by which small amounts of solution additives control final polymer crystallinity and nanostructure are revealed. Additionally we will discuss insights into the underlying diffusion dynamics and mixing characteristics of typical donor polymers and acceptor fullerenes by studies of the temperature dependent stability of model bilayer interfaces.

375. 3D Au–TiO_2 nanoarchitectures for plasmonic photovoltaic applications

*Paul A. DeSario, **Devyn E. DeVantier**, devyn.devantier@nrl.navy.mil, Jeremy J. Pietron, Lindsey C. Szymczak, Debra R. Rolison.Surface Chemistry Branch, Naval Research Laboratory, Washington, D.C. 20375, United States*

Titania (TiO_2) is an appealing material in applications related to solar energy conversion such as for photovoltaics and solar-generated fuels. We have chosen to design and fabricate photoanodes for solar cells in which the titania source is nanostructured in 3D as derived from aerogel synthesis. Titania in aerogel form features (1) high surface area and mesoporosity to facilitate mass transfer of electron-transfer mediators and (2) efficient response to visible light via plasmonic sensitization from nanoparticulate Au guests.

We synthesize Au–TiO_2 composite aerogels with highly dispersed ~6-nm Au nanoparticles incorporated into the nanoscale oxide network of the ultraporous nanoarchitecture. The Au–TiO_2 aerogels feature a broad surface plasmon resonance (SPR) feature centered at ~580 nm, and a visible light response with a wavelength-dependent photocurrent activity that tracks the shape of the SPR feature.

We will describe the synthesis and physical characterization of 3D Au–TiO_2 aerogel photocatalysts and present photocurrent results.

376. Fundamental insights to regeneration and recombination with the iodide/triiodide redox mediator relevant to dye-sensitized solar cells

***Byron H Farnum**, bfarnum1@jhu.edu, Gerald J Meyer.Department of Chemistry, Johns Hopkins University, Baltimore, Maryland 21218, United States*

Dye-sensitized solar cells provide an exciting molecular based opportunity in the field of solar energy conversion and renewable energy. Within these devices, a redox mediator is necessary to shuttle charge between a sensitized-TiO_2 photoanode and a counter electrode. By far the most common mediator is iodide/triiodide, where photon-to-current efficiencies in excess of 10% have been achieved. The success of this mediator has been attributed to rapid sensitizer regeneration by iodide and sluggish recombination of TiO_2 electrons with triiodide. This presentation will discuss fundamental studies in fluid solution aimed at understanding the reasons for this behavior. Specifically, driving force dependent iodide oxidation by Ru(II)-tris(diimine) excited-states suggests facile regeneration kinetics ($k > 10^9\ M^{-1}\ s^{-1}$) even for thermodynamically uphill reactions. In addition, flash-quench studies designed for one-electron triiodide reduction mimicked the recombination process, where it was found that the reduction potential for triiodide was surprisingly negative in energy.

377. Molecular level control for excited state electron injection and charge recombination at sensitized TiO_2 interfaces

Andrew Kopecky[1], *andrew.kopecky@gmail.com*, *Patrik G. Johansson*[2], *Gerald J. Meyer*[2], *Elena Galoppini*[1]. *(1) Department of Chemistry, Rutgers University - Newark, Newark, NJ 07102, United States (2) Departments of Chemistry and Materials Science and Engineering, Johns Hopkins University, Baltimore, MD, United States*

Some of the most promising dyes for dye-sensitized solar cells are the N3-type dyes, which consist of two dipyridyl ligands and two thiocyanate ligands coordinated to a ruthenium(II) center. Here we have studied a series of novel N3-type dyes modified to study distance/spacer length effects on injection and recombination dynamics in dye sensitized solar cells. Rigid oligophenyleneethynylene spacers have been employed to increase the distance of the isophthalic acid anchoring group (which is attached to the TiO_2) to the Ru sensitizer. The data acquired for this series of three compounds revealed that the bridge length imparts a strong influence on excited state injection and recombination kinetics. Larger spacer length led to inhibited charge recombination and decreased electron injection rates. Inhibited charge recombination was beneficial for solar energy conversion as larger open-circuit photovoltages were realized when the concentration of injected electrons was high, which manifests itself in an increased ideality factor.

378. New organometallic platforms for conversion of carbon dioxide to chemical fuels

John L. DiMeglio, *johnd@udel.edu, Joel Rosenthal.Department of Chemistry and Biochemistry, University of Delaware, Newark, DE 19716, United States*

A new platform for electrocatalytic CO_2 reduction has been developed. Compounds of the type $[PDC^RPd(CH_3CN)](PF_6)_2$, (R= methyl, ethyl, isopropyl, cyclohexyl, and mesityl) where PDC^R is a pyridine bridged N-heterocyclic carbene pincer ligand, were synthesized and studied by a suite of physical methods. These compounds have been characterized by ^1H, ^{13}C NMR, IR, and ESI mass spectrometry and molecular structures were determined by X-ray single-crystal diffraction experiments. Electrochemical experiments including bulk electrolysis and cyclic voltammetry clearly show that these compounds are effective catalysts for conversion of CO_2 to chemical fuels. The ability of these systems to serve as novel platforms for solar fuel production will be discussed.

379. New multielectron porphyrinoid platform for solar harvesting applications

Allen J Pistner, *apistner@udel.edu, Joel Rosenthal.Department of Chemistry and Biochemistry, University of Delaware, Newark, DE 19716, United States*

Dye-sensitized solar cells (DSSCs) are an attractive low cost alternative to costly silicon photovoltaics for solar harvesting applications. Porphyrin macrocycles have been employed as sensitizers in DSSC devices due to their intense absorbance profiles, however the absorption spectra for typical porphyrin-based chromophores is constrained to narrow bands of the solar power spectrum at ~ 400 nm and 550 nm. Accordingly, DSSC's that utilize porphryins are unable to effectively harvest photons at the low energy end of the visible spectrum. We have developed a new class of porphynoid (the phlorin) that displays photophysical properties tailored for light harvesting applications. Phlorins are tetrapyrrole macrocycles that display a much wider breadth in their absorption spectra and which display a multielectron reactivity. The synthesis, photophysical and unusual electrochemical properties of a suite of these novel porphyrinoids will be presented.

Carbohydrates in Drug Design A

Presiding: L. Wang

380. Advances in the synthesis and sequencing of glycosaminoglycans

Robert J. Linhardt, *linhar@rpi.edu.Department of Chemistry and Chemical Biology, Rensselaer Polytechnic Institute, Troy, New York 12180, United States*

Glycosaminoglycans (GAGs) are anionic polysaccharides of critical importance in human biology. Heparin, the most highly sulfated GAG has been used as an anticoagulant for over 75 years. Currently heparin and related low molecular weight heparins are prepared by extraction from porcine tissue. We have developed an efficient chemoenzymatic synthesis of heparin from a non-animal source. The varying sulfo group patterns make heparin chain an extremely challenging target. Efforts to synthesize heparin, low molecular weight heparin and ultra-low molecular weight heparins are described using a chemoenzymatic approach relying on biosynthetic enzymes, including heparosan synthases, sulfotransferases and epimerase. Once synthesized the structure of the GAG structure must be analyzed. New approaches utilizing Fourier transform mass spectrometry (FT-MS) for establishing the structure and sequence of intact GAGs, including the recent sequencing of the bikunin proteoglycan will be discussed.

381. Therapeutic potential of the tumor-associated Thomsen-Friedenreich carbohydrate antigen on nanoparticles

Joseph J Barchi[1], *barchi@helix.nih.gov, Susan K Keay*[2], *Kristie M Adams*[1], *Alexander Mackerell*[3], *Sairam S Mallajosyula*[3]. *(1) Chemical Biology, Frederick National Laboratory for Cancer Research, Frederick, MD 21702, United States (2) School of Medicine, University of Maryland, Baltimore, Baltimore, MD 21201, United States (3) Pharmacy, University of Maryland, Baltimore, Baltimore, MD 21201, United States*

Altered cell-surface glycans are hallmarks of tumorigenesis and these aberrant structres both 1) participate in tumor cell metastasis and 2) can be targets of the host antitumor immune response. One such glycan, the Thomsen Friedenreich diaccharide is expressed in a large percentage of carcinomas but rarely on normal tissue. This talk will highlight progress in developing gold nanoparticles coated with the TF antigen in various guises for use as anti adhesion agents or vaccine platforms for tumor immonotherapy.

382. Efficient chemoenzymatic glycosylation remodeling of therapeutic antibodies

Wei Huang, *whuang@ihv.umaryland.edu, John Giddens, Lai-Xi Wang.University of Maryland School of Medicine, Institute of Human Virology, Baltimore, MD 21201, United States*

Fc glycosylation is an important determinant of the bioligical activity and therapeutic efficacy of human IgG antibodies. Here, we describe an efficient chemoenzymatic method for site-specific glycosylation remodeling of Fc N-glycans of full-length therapeutic monoclonal antibodies (MAbs) and intravenuous immunoglobulin (IVIG) by an endoglycosidase from Streptococcus pyogenes (EndoS) for de-glycosylation and a novel glycosynthase mutant derived from EndoS for transglycosylation. Two clinical antibodies, rituximab and IVIG, were trasnformed from a mixture of G0F, G1F and G2F glycoforms to the pure G2 or S2G2F glycoform. Biological evaluation implicated the enhanced therapeutic efficacy of these remodeled antibodies.

383. Antivirals from nature: A decade with the cyanobacteria

***Carole A. Bewley**, caroleb@mail.nih.gov.Laboratory of Bioorganic Chemistry, NIDDK National Institutes of Health, Bethesda, Maryland 20892, United States*

The cyanobacteria, commonly known as blue green algae, are among the most abundant organisms on earth. Chemists have been studying these organisms for their wealth of secondary metabolites, otherwise known as natural products, many of which have therapeutic potential; as novel sources of biofuels; and more recently for the unusual carbohydrate binding proteins or lectins that many genera produce. The cyanobacterial lectins in particular are fascinating in that they exhibit novel 3-dimensional structures and carbohydrate-binding motifs, enabling some of these to bind and potently inhibit a number of enveloped virus families. Inspired by these properties, we have been studying all aspects of these proteins using an interdisciplinary approach including NMR and x-ray crystallography, biophysical characterizations, and virus neutralization assays. An overview of our research in this area will be presented, and descriptions of how these recognition processes have influenced our way of thinking about protein-carbohydrate recognition will be discussed.

Undergraduate Research Posters A

384. Cytochrome P450 functionalized electrodes for *in vitro* diclofenac metabolism

***Amos Mugweru**, mugweru@rowan.edu, **Elizabeth Cronin**, Cronin72@students.rowan.edu, **Monika Mihalenkova**, mihale95@students.rowan.edu.Department of Chemistry & Biochemistry, Rowan University, Glassboro, NJ 08028, United States*

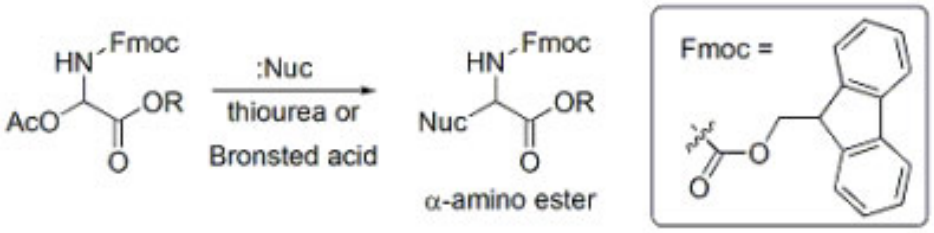
Cytochrome P450 enzymes mainly found in the liver have a heme cofactor which contains a porphyrin ring where both oxidation and reduction takes place. Cytochrome P450 enzymes were used to investigate the metabolic products of diclofenac. Diclofenac is a well-known representative of non-steroidal anti-inflammatory drugs (NSAIDs) with strong anti-pyretic, analgesic and anti-inflammatory properties. In this work the enzyme's drug metabolism capability was determined by immobilizing it on gold electrodes. Mercapto-undecanoic acid (MUA) and EDC /NHS chemistry was used to anchor the P450 enzyme onto the surface. This assembly was sampled using cyclic voltammetry to determine the oxidation and reduction of the P450 enzyme while the metabolic products of diclofenac were determined mass spectrometry. Mass spectrometer showed fragments at m/z of 214, 242, 277 and 295 with the specific peak at 277 correlating to a known metabolite formation. The detailed results of the experiment and the techniques will be discussed.

385. Organocatalyzed reactions of α-acetoxy glycine esters: Toward the asymmetric synthesis of unnatural amino acids

***Jeffery C. Zimmerman**, jcz001@lvc.edu, Alissa R Evenson, Timothy J. Peelen.Department of Chemistry, Lebanon Valley College, Annville, PA 17003, United States*

We have explored catalytic, asymmetric strategies for the synthesis of unnatural Fmoc-protected α-amino acids. We have synthesized Fmoc-protected glycine esters that are substituted with a leaving group at the α-carbon. We have explored substitution reactions at the α-position using nucleophiles in the presence of chiral thiourea and Brønsted acid catalysts. Our studies to date have focused

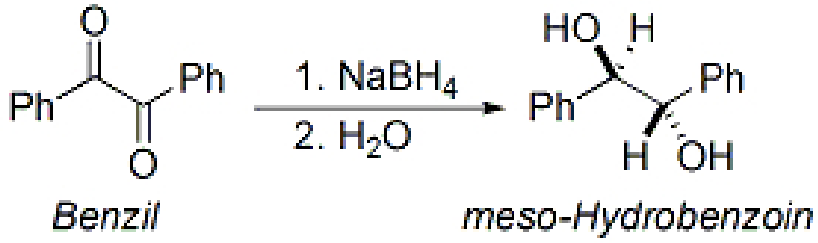
on examining reactivity of these catalysts in reactions involving additons of allyl silanes and silyl enol ethers.



386. Investigation of the mechanism of the sodium borohydride reduction of benzil

Rachel R Denny, *rrd001@lvc.edu,* ***Tai Nguyen***, *tn005@lvc.edu, Timothy J. Peelen.Department of Chemistry, Lebanon Valley College, Annville, PA 17003, United States*

We have developed a simple set of experiments for the undergraduate organic chemistry laboratory course that explore the mechansim of the reduction of benzil by sodium borohydride, a common undergraduate laboratory experiment that results in high selectivity for the *meso*-hydrobenzoin diastereomer. Most notably, we used a mixture of $NaBH_4$ and $NaBD_4$ to determine if the first and second carbonyl reductions are performed by the same borohydride.



387. Novel chemical methodologies for the preparation of betulin derivatives

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Betulin is abundantly available in nature and is found in the bark of yellow and white river birch trees (10-25 wt%). Betulinic acid, the more biologically active acid derivative of betulin, can be easily prepared from betulin, and possesses selective cytotoxicity against melanoma, and certain malignant brain tumor cell lines. However, it suffers from several major drawbacks for future clinical development. It has poor solubility in aqueous media and it also lacks broad spectrum activity against various important cancer cell lines. Hence, there is critical need for the design and structural modification of these molecules in order to increase their aqueous solubility as well as to increase their potency and broaden their biological activity against other cancers. In this poster, we present the preparation of exploratory betulin analogs employing several chemical methodologies such as the multi-component coupling reaction, chalcone formation, and reductive amination.

388. Morphology of soot aerosol particles by scanning electron microscopy

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Incomplete combustion of organic fuel releases carbonaceous aerosols (soot) into the atmosphere, with consequences for respiratory health, atmospheric chemistry, and absorption of solar radiation. Soot released by the combustion of some common fuels was deposited onto solid substrates to study its morphology via scanning electron microscopy (SEM). Particles of soot with fractal geometry were considered particularly interesting for their light-scattering properties. Changes in morphology of soot particles as they aged in the presence of oxygen were also examined by SEM. Fourier-Transform infrared spectroscopy (FTIR) and elemental analysis verified changes in the surface chemistry of soot during aging. Computational analysis of SEM images summarized changes in morphology of large numbers of soot particles. Future work will investigate the effects of moisture and other atmospheric components, such as acids and hygroscopic salts, on the aging, morphology, and interactions of organic soot with light.

389. Reversible damage and repair of hydrophobic self-assembled monolayers

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Well ordered hydrophobic self-assembled monolayers (SAMs) are easily generated from octadecyltricholorosilane (OTS) or analogous thiols on a variety of surfaces, including glass, silicon, and metallic thin films. Oxidative damage to SAMs by sulfuric peroxide (piranha etch) controllably reduced the hydrophobicity of the organic surfaces as measured by goniometry (contact angle of water). Fourier-Transform infrared spectroscopy (FTIR) provided information about the orientation of organic chains in the damaged layers and verified the presence of oxygen-containing functional groups. Subsequent treatment of oxidatively damaged SAMs with OTS restored hydrophobicity. FTIR was used to investigate the ordering and orientation of the repaired SAMs under various conditions. The repaired organic layers served as models for two-dimensional surfaces, and may be useful substrates for analytical work—including scanning probe microscopy in the presence of water or organic vapor—that requires surfaces with controllable hydrophobicity.

390. Mechanism of ring-contraction of 3H-1-benzazepine to quinoline

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Quinolines, like benzazepines, are pharmacologically active heterocycles that are potential antibacterial and antitumor agents. Attempted free-radical bromination of the allylic position of 3*H*-1-benzazepine with NBS led to an unusual ring-contraction reaction, giving rise to 2,4-diphenylquinoline in high yield. This is a convenient path for synthesis of quinoline in one step from the easily accessible 1-benzazepine. Similar reactions have been previously observed for conversion of 3*H*-azepines to pyridine derivatives, and 1*H*-benzazepines to isoquinoline derivatives. We describe here the intriguing mechanism of this transformation *via* a labeling experiment.

391. Ensuring New York City's water quality: The logistics and procedure learned from a DEP summer internship

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The Department of Environmental Protection (DEP) enforces New York›s environmental laws and regulations. Its purpose is to decrease air pollution and protect the river›s water quality by assisting in the waste removal, thus ensuring the safety of New York› drinking water. One of the DEP›s several divisions is the Monitoring Section that checks out sewer lines for water contamination and possible harmful industrial discharges. As an intern of the Industrial Pollution Prevention (or I.P.P) team I was involved with the logistics team evaluating the degree of contaminants› presence. A detailed insight into the I.P.P and the logistics team, the equipment and machines used, the protocol followed and the chemicals used to neutralize the contaminants will be presented.

392. Analysis of water samples at the Marine Science Department of New York's Division of the Environmental Protection Agency at Ward's Island

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As an intern at New York City›s Division of Environmental Protection (DEP) at Ward›s Island I was involved with several processes that dealt with the determination of water quality. Samples that were collected off the boat were analyzed for the amount of dissolved oxygen using the Winkler Method, in addition to determining the pH of different water levels and measuring the light penetration via the Secchi Disk Depth method. Another procedure measured the collected TSS (total suspended solids) from top and bottom levels of water and most importantly used the Membrane Filter Method to collect and analyze bacteria such as fecal coliform and enterococci.

393. Analysis of compositing samples of various sewage treatment plants at the Newtown Creek facility of New York's Department of Environmental Protection (DEP) Agency

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The Department of Environmental Protection of New York City, regulates the polluting factors that may affect the water quality. As an intern in the chemistry laboratory at the New Town Creek facility, I was involved with the compositing samples from several different sewage treatment plants, testing for the pH and conductivity of each sample, and measuring the effluent samples for chlorine residual. Part of my duties included helping in the analysis of fecal coliform in citywide samples in order to determine the appropriateness of minimal chlorine use and discharge into the receiving waters. The procedures and the difficulties encountered in every step will be presented.

394. Determination of gallic acid in various beverages using high pressure liquid chromatography (HPLC)

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Gallic acid, $C_6H_2(OH)_3COOH$, is an organic acid, that has many applications in the healthcare and pharmaceutical industry. It is also being used as a standard in the determination of the total phenol content in wines as determined by the UV-visible spetrophotometric Folin-Ciocalteau assay, where results are reported in “gallic acid equivalents”. A procedure has been developed that determines the amount of gallic acid present in various beverages using High Pressure Liquid Chromatography (HPLC). The preparation of the samples, treatment with sodium dihydrogen phosphate buffers as well as the identification and quantitative determination of the gallic acid content in these beverages will be described. Moreover similar studies on the same samples after left uncapped and exposed to air oxidation for a week were made, indicating a considerable decomposition of gallic acid with time.

395. Spectrophotometric determination of the total amount of antioxidants in juice beverages

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The Gallic Acid Equivalence method (GAE) measures the total amount of antioxidants in the wine industry (A.L Waterhouse. “Determination of Total Phenolics” *in* “Current Protocols in Food Analytical Chemistry”, I1.1.1-I1.1.8). The procedure uses the Folin’s phenol reagent to oxidize polyphenols into polyquinones, thus allowing the visible spectrophotometric determination of the polyphenols that are present in a beverage. The results are expressed as Gallic acid equivalents and the measurements are made using a Beer-Lambert plot. The procedure has been extended to several commercially available juice and fruit beverages and the semiquantitative measurement of the antiooxidants’ decomposition with time was determined.

396. Use of the Folin-Ciocalteau method to measure the total amount of antioxidants in tea samples

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The Folin-Ciocalteu reagent, also known as Folin’s phenol reagent or Folin-Denis reagent or Gallic Acid Equivalence method (GAE), is a mixture of phosphomolybdate and phosphotungstate ions. It is used in the colorimetric assay of phenolic and polyphenolic antioxidants in the wine industry. In this project the Beer-Lambert law was applied to measure the intensity of the blue color formed when the reagent is placed in contact with tea sample solutions to measure the total amount of the antioxidants present in the solution using Gallic acid as the standard. The study of tea samples included beverages as well as extracts of tea bags. A comparison of various brands of tea and the effect of air decomposition of the antioxidants with time was measured and compared.

397. Synthesis of oxyallyl silanes and their application as homoenolate equivalents

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Oxyallyl silanes are versatile substrates that contain three functional groups: a hydroxyl and silyl group and an alkene. New methodology is proposed in which the alkene will act as a homoenolate equivalent in the addition to electrophiles. Unlike the standard method using allyl silane to provide a vinyl group, oxyallyl silane addition furnishes the vinyl group at an increased oxidation state as the vinyl ether. This circumvents the need for an additional alkene oxidation step and will allow for quick conversions to more complex substrates. The synthesis of oxyallyl silane derivatives will be carried out using a coupling reaction of hydroxyallyl silane with a variety of substituted benzoic acids. In addition, initial work in converting the products to alkyl-protected oxyallyl silanes will also be discussed. Future work will involve adding the synthesized oxyallyl silanes to a variety of electrophiles.

398. Chemokine production in inflammatory bowel diseases

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Inflammatory bowel diseases (IBD) are a series of circumstance which lead to the inflammation of the colon and small intestine. IBD begin when the body initiates an abnormal immune response to normal bacteria flora. In many cases of IBD, a link has established that chemokines as one of the key factors regulating IBD pathogenesis. Chemokines are a family of small cytokines that facilitate the migration of circulating leukocytes to the inflamed site. Chemokines such as, monocyte chemotactic protein 1, macrophage protein 1-a, MIP-1b, RANTES, and interferon inducible protein 9 and 10 are reported to express in larger quantities during the active phase of the disease. Many of these chemokines are produced by immune cells. However, little is known about the role of colonic epithelial cells in immune cell recruitment. We evaluated these chemokine productions from isolated colonic epithelial cells using real time PCR in mouse model of inflammatory bowel diseases

399. Analysis of authentic versus imitation perfumes

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In the years since the Persian chemist Avicenna invented steam distillation in the early 11th century, perfume has become a multibillion dollar industry. Perfume is made of anywhere from 78-95% ethanol, with the rest as essential oils. Compared to toilet water and eau de cologne, perfume is the costliest fragrance, containing as much as 22% essential oils. Our investigation will focus on the number and amounts of essential oils present in the authentic and the imitation and the GC-MS profile of these oils. Our aim is to find out whether imitation perfumes are inexpensive because they contain less essential oil or perhaps different compounds, which may or may not faithfully recreate the fragrance of the original.

400. Effect of various compounds on the prevention and degradation of *Staphylococcus aureus* biofilms

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Methicillin-Resistant *Staphylococcus aureus* (MRSA) is responsible for up to 19,000 annual US deaths via this skin infection. MRSA is a strain of *Staphylococcus aureus,* a bacterium which produces a biofilm necessary for its survival and proliferation. Studies have shown that the serine protease ESP from *S. epidermidis* can destroy the formation of this biofilm. We examined the effectiveness of various compounds on both the prevention and destruction of the such as the supernatant from *S. epidermidis* and Biotene mouth wash. *S. aureus* was cultured and treated with Biotene PBF, Biokleen, Propolis and serine protease from *S. epidermidis compounds.* Our results indicate that Propolis did not show any impact on the biofilms. Results from *S. epidermis* serine protease treatment were not conclusive. However, the Biotene PBF mouthwash treatment was the most effective in the destruction of biofilm whereas Biokleen treatment had the most impact against preventing the formation of biofilm.

401. Effect of O-acetyl L-carnitine hydrochloride on MDA-MB 231 cells

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Many cancer cells rely on glycolysis for ATP production even in the presence of oxygen, a phenomenon known as the “Warburg Effect”. A number of studies have suggested that ATP production via aerobic glycolysis may alter the production of reactive oxygen species leading to evasion of apoptotic pathways. In our studies we investigated the ability of O-acetyl L- Carnitine Hydrochloride (a derivative of L-Carnitine) to induce cell death in MDA-MB 231 cells, a metastatic human cell line. L-Carnitine is a quaternary amine with important mitochondrial functions including the transport of lipids into mitochondria for oxidation and the export of toxic compounds from the mitochondria. Preliminary results show MDA-MB 231 cell death is increased at L-Carnitine concentration of 100μM The effect of O-acetyl L-Carnitine Hydrochloride on cell death was investigated. Further studies will determine if this metabolic pathway could be a target for cancer drug development.

402. Conjugating silver nanoparticle to the siloxane matrix

Sébastien Delva*,* ***Moni Chauhan****.Department of Chemistry, Queensborough Community College, Bayside,NY, New York 11364, United States*

Metal nanoparticles have great potential for application as catalyst, biosensor and nonlinear optical devices. For the construction of novel nanoporous architecture, bottom up approach has been the center of synthetic chemistry and advantageous functionalities can be introduced into the framework. In the past decade, hybrid materials with homogeneously distributed metal nanoparticles have been in great demand due to emerging applications in green catalysis, drug delivery, light harvesting material, gas storage and sensors. We have adopted the condensation of silanes and in situ reduction of metal salts to synthesize the polysiloxane with homogenous distribution of nanoparticle within the glass or polymer frame work. In our study Tris [3-trimethoxysilylpropyl] isocyanurate was the stabilizing agent for the nanoparticles and it was further cross linked with alkoxysilanes to generate a solid or gel like matrix. The synthesis, characterization and applications of these materials will be discussed.

403. Reactivity of tris(trimethylsilyl)phosphite (TMSP): Synthesis of a bisphosphonic derivative of bicine

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The synthesis of a potential inhibitor of the tyrosine phosphatase is presented. The compound, a bisphosphonic derivative of bicine, uses commercially available bicine as the starting reagent. The O-protected bicine is treated with thionyl chloride to form the corresponding acyl chloride and then reacted with tris(trimethylsilyl)phosphite (TMSP). After hydrolysis to regenerate the hydroxy group and spectroscopic identification, the compound will be tested as a potential inhibitor of the enzyme.

404. Synthesis and characterization of efficient Nek2 substrates employing solid phase synthesis procedures

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Nek2, a Serine/Threonine kinase present at the centrosome of the cell, is essential during mitosis and is greatly over-expressed in many forms of cancer. Nevertheless several of its biological functions remain unknown due to the lack of small molecule substrates and biosensors, which can serve in assaying its intracellular activity. C-Nap1, a known *in vivo* protein substrate of Nek2, has its phosphorylation sites identified by mass spectrometry, an information utilized to synthesize small peptide substrates of Nek2 and assess their catalytic efficiency via Michaelis-Menten kinetic parameters (high k_{cat} and low K_m values). In this project, FMOC-based solid phase peptide synthesis procedure is employed for the development of two potential peptide substrates of Nek2 (NAP-3 and NAP-4) which are purified using Reverse Phase-HPLC, and characterized by ESI-MS. The knowledge gained from these studies could be utilized in the development of Nek2 biosensors and small molecule inhibitors.

405. Reactivity of tris(trimethylsilyl)phosphite (TMSP): Synthesis of a bisphosphonic derivative of β-alanine

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The synthesis of a potential inbitor of the tyrosine phosphatase is presented. The compound, a bisphophonic derivative of β-alanine is synthesized using commercially available alanine. The protected β-alanine is reacted with thionyl chloride followed by reaction with tris(trimethylsilyl)phosphite (TMSP). After hydrolysis and spectroscopic identification the product will be tested as a potential inhibitor of the enzyme.

406. Expression of gamma-synuclein protein in cancer cells

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Gamma-synucleins (gamma-syn) belong to a small, soluble, highly conserved group of neuronal proteins implicated in both neurodegenerative diseases and cancer. They share sequence homologies and structural properties whose biological functions are still unclear. However their involvement in these diseasesmay provide insights into the pathological processes resulting from their effect, and present the possibility to serve as potential targets for early diagnosis and treatment. Recently, elevated levels of gamma-syn proteins were detected in advanced stages of cancer. Furthermore, studies to date indicate that overexpression of gamma-syn compromises normal mitotic checkpoint controls, resulting in multinucleation as well as faster cell growth. Gamma-syn has also been shown

to promote invasion and metastasis in animal models as well. These observations raise questions about the involvement of gamma-syn in the process of tumorigenesis and metastasis, and current efforts try to use them as markers in assessing breast cancer progression.

407. Partial sulfonation of polyaniline nanofibers by co-polymerization: Effects of monomer ratio and polymerization initiator

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We have observed enhanced deposition of positively charged gold nanoparticles (NPs) onto negatively charged sulfonated polyaniline nanofibers via electrostatic interaction. Such nanocomposites are of interest for catalysis, sensors, organic electronics, etc. However, since sulfonation increases water solubility, the nanofibers are typically degraded. To limit solubility, yet provide sufficient charge to attract Au-NPs, we have prepared partially sulfonated polyaniline nanofibers by co-polymerizing aniline and sulfonated aniline. SEM reveals similar morphology for nanofibers synthesized using 10% and 20% sulfonated monomer. However, as the quantity of the polymerization initiator is increased, fibers become increasingly fused and FTIR peaks related to the sulfonic acid group grow slightly in intensity. This suggests greater solubility due to increased sulfonation. The synthesis of pure polyaniline does not require an initiator, but in its presence, fused nanofibers are obtained. This is also consistent with increased solubility and may represent a simpler route towards sulfonation.

408. Preparation of poly(o-toluidine) as highly porous micron-scale spheres

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Nanofibers of substituted polyanilines have been widely reported, yet our own investigations of poly(o-toluidine), the methyl-substituted analog, have revealed additional and unexpected morphologies. The crude product is a thick precipitate produced in 1M HCl, and when exposed to ammonium hydroxide (1M and greater), it rapidly agglomerates into a sticky mass. By varying the concentrations of the monomer, oxidant, and base, we have obtained discrete, porous micron-scale spheres; clusters of highly fused, porous spheres; and low porosity slabs and “wrinkled” spheres. Notably, if excess acid is removed from the crude product prior to adding the base, only a granular material is obtained. This indicates that the unusual structures are formed after the polymerization is complete and specifically under the conditions of the acid-base neutralization. In general, more concentrated base favors the formation of discrete spheres. Their porosity may make them useful as encapsulants for other smaller particles to produce composite materials.

409. Reactivity of tris(trimethylsilyl)phosphite with chloroformates containing electron withdrawing groups

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Bisphosphonates are a class of drugs used, not only in the treatment of osteoporosis but also, to inhibit both in vivo and in vitro experimental angiogenesis. Studies have shown that nitrogen-containing bisphosphonates (N-BP) can focus on bone density and strength thanks to their antiresorptive properties and affinity to inhibit osteoclasts. Osteoclasts are tissue cells that control bone formation by breaking up mineralized matrix from the organic bone. The degenerative disease osteoporosis is caused by a combination of both decreased hormone levels and steady osteoclast activity. A novel approach in the synthesis of N-BP from 2-Nitrophenyl chloroformate using Tris(trimethylsilyl)Phosphite (TMSP) is discussed. TMSP is an alternative, highly nucleophilic reagent in place of the conventional trialkyl phosphites used in synthesizing bisphosphonic acids.

410. Reactivity of tris(trimethylsilyl)phosphite (TMSP): Synthesis of the bisphosphonic acid of 3-(trifluoromethyl) phenyl chloroformate

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A novel bisphosphonic derivative is proposed using an alternative reagent which increased the yield of our desired product – the bisphosphonic derivative of 3-(Trifluoromethyl) phenyl chloroformate. The degenerative disease osteoporosis is caused by a combination of both decreased hormone levels and steady osteoclast activity. Using 3-(Trifluoromethyl) phenyl chloroformate allows us to monitor and study the chloroformate group in the reactivity of Tris(trimethylsilyl) Phosphite. With this reaction, the corresponding bisphosphonate derivative of 3-(Trifluoromethyl) phenyl chloroformate is followed by spectroscopical analysis in hopes that this nucleophilic reagent will create the P-C-P bond that is characteristic in inhibiting the natural metabolic process of biological phosphates. Fosamax, a bisphosphonate drug that inhibits osteoclast-mediated bone resorption, has an amino group in which osteonecrosis of the jaw was strongly correlated with the use of aminophosphates. Thus we will test the reactivity of TMSP to synthesize new bisphosphonates that do not contain amino groups.

411. Synthesis of the fragrance Berryflor using only solid-supported reagents

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A synthesis of the common fragrance Berryflor® has been developed using only polymer-supported chemical reagents. Four synthetic operations transform commercially available adipic acid into ethyl 6-acetoxyhexanoate (Berryflor®). Each step (anhydride formation, reduction to lactone, transesterification and acetylation) uses polystyrene-bound reagents which are filtered from the reaction solvent at the completion of each operation. In addition, a polymer-bound scavenging reagent is used to eliminate the excess starting material and by-product. Solvent removal provides high yields of product with high chemical purity at each step. In addition, by employing a heterogeneous reaction medium shorter laboratory times are needed and significant reductions of hazardous waste materials are realized.

412. Preparation and biological activity of 4-allyl-2-methoxy-6-nitrophenol against four clinically relevant microbes

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Eugenol, 4-allyl-2-methoxyphenol, is a phytoconstituent isolated from an array of natural sources, such as cloves, cinnamon, basil, and nutmeg among other natural sources. It has been used for centuries in fragrances, preservatives, spices, and most notably, medicine. Eugenol has an array of documented medicinal properties including but not limited to bactericidal, virucidal, fungicidal, antiproliferative, and antioxidant activity. We carried out a nitration of eugenol utilizing potassium bisulfate, sodium nitrate, and wet silica in methylene chloride at room temperature. We collected a dark red oil which we purified by column chromatography and later characterized by GC-MS and NMR. We tested the biological activity of the product (4-allyl-2-methoxy-6-nitrophenol) by the disc-diffusion method against four clinically relevant microbes. Nitrated eugenol showed antimicrobial activity against *E. coli*, *P. vulgaris*, *B. cereus*, and most interestingly, *P. aeruginosa*.

413. Fluorescence based method for analyzing bacterial membrane permeability

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Small molecule permeability assays are an efficient way for detecting membrane disruption by antimicrobial agents. They often rely on the hydrolysis of a chromophoric enzyme substrate, which varies depending on the bacteria and membrane being studied. By utilizing a DNA binding fluorophore in these membrane permeability assays, presence of a specific cellular enzyme is not necessary. A broad-spectrum assay that utilizes the DNA binding fluorophore Diamidino-2-phenylindole (DAPI) was developed. Normally, DAPI does not efficiently cross the membrane or fluoresce strongly outside of the cell. When an antimicrobial agent disrupts the membrane, DAPI enters the cell and binds to DNA, resulting in a measurable increase in fluorescence emission intensity. This assay is more versatile and broadly applicable as it does not rely on the presence of specific cellular enzymes and is effective in both gram positive and gram negative species.

414. Understanding the mechanisms of copper induced, lipid peroxidation mediated cell death in *Saccharomyces cerevisiae*

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The long-term goal of this proposal is to understand the mechanisms of copper induced cell death by using *Saccharomyces cerevisiae*. Our working hypothesis, based on our preliminary results is that upon exposure to copper, toxicity is triggered by the increased lipid peroxidation of unsaturated fatty acids in the plasma membrane. In order to determine the relationship between exposure to copper alloy surfaces, lipid peroxidation, and cell death in *Saccharomyces cerevisiae* quantitative dilutions series were performed. Our results indicate a biphasic killing curve when *S. cerevisiae* is exposed to copper chips however this was not seen on steel chips. TBARS assay was used to measure the lipid peroxidation levels. In addition to looking at how copper effects the membrane we characterized the impact of exposure to copper alloy surface by using FM4-64, an amphiphilic styryl dye. Genomic DNA was analyzed in order to establish how the cell death was triggered.

415. Effect of copper surfaces on endospore-forming bacteria *Bacillus subtilis*

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The overall objective of this project is to determine the relationship between exposure to copper surfaces, lipid peroxidation, and cell death in different bacterial strains. In particular, this project explores the impact of copper exposure on the endospore-forming, gram-positive strain, *Bacillus subtilis.* Different time course trials were preformed to determine the correlation between copper exposure, amount of lipid peroxidation, and rate of cell death. A quantitative dilution series was used to determine bacterial cell death. The TBARS Assay was used to measure the amount of lipid peroxidation that occurs during exposure to copper. Genomic DNA was extracted to study the mode of death. Furthermore, fluorescent microscopy was done using a Live Dead Assay kit. Results indicate that cell death begins within five to ten minutes of copper exposure, except for the endospores. The increase in lipid peroxidation correlates with cell death as well as genomic DNA degradation.

416. Comparison of copper mediated toxicity in both *Staphylococcus aureus* and *Escherichia coli*

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The mechanism(s) by which copper alloy surfaces kill microorganisms is still largely unclear. The aim of our project is to determine the relationship between exposure to copper alloy surfaces or copper ions, lipid peroxidation, and killing of *Staphylococcus aureus and Escherichia coli.* Quantitative dilutions series were performed to test for bacterial cell death. Our results indicate a bisaphic killing curve when Gram positive and Gram negative bacteria are exposed to copper chips. TBARS assay was used to measure the lipid peroxidation levels. The bacterial killing rate upon exposure to copper surface also correlates with increased lipid peroxidation levels. There are some differences in the rate of cell death that correlates with the levels of lipid peroxidation between the two bacterial strains. Live/Dead assay with fluorescent microscopy was done and Genomic DNA was extracted to study the mode of cell death, apoptotic vs. necrotic. Results will be discussed.

417. Genomic toxicity of silver nano particles on *Escherichia coli*

***Kenya Joseph**[1], KJOSEPH09@tigermail.qcc.cuny.edu, Moni Chauhan[2], Mangala Tawde[1]. (1) Biological Sciences and Geology, Queensborough Community College, Bayside, NY 11364, United States (2) Chemistry, Queensborough Community College, Bayside, NY 11364, United States*

Silver (Ag) nano particles were synthesized in-house in one-step process by the reaction of silver nitrate, Tris [trimethoxysilylpropyl] isocyanourate and trioctyl amine. The nano Ag particles were then tested for antibacterial activity on *Escherichia coli* ATCC # 2374. Since one of the major causes of cell death by Nano materials is due to binding of nano particles to cellular DNA and organelles, thus interfering with normal cell function, we are interested in studying the effect of nano Silver on bacterial DNA. After treating the bacteria with nanosilver bacterial DNA is extracted, purified and subjected to DNA Gel Electrophoresis. By examining the pattern of genomic DNA gel electrophoresis in bacteria treated with Nano Silver compared to those not treated with nanomaterials, we could then assess whether binding of nano Silver to bacterial DNA is the cause for cell death. This data is correlated with cell death assayed by standard antimicrobial assays.

418. Structural and kinetic characterization of glycerolphosphodiesterase activity using a phosphatidylinositol-specific phospholipase C (PI-PLC) active site

***David M Strauss**, Thomas L Selby.Chemistry, Bucknell University, Lewisburg, Pennsylvania 17837, United States*

Glycerolphosphodiester phosphodiesterases are a family of enzymes that carry out metal-dependent hydrolysis of glycerophosphodiesters to form an alcohol and *sn*-glycerol 3-phosphate. The chemical reaction catalyzed by this enzyme is similar to that of PI-PLCs, which produce inositol phosphates and liberate glycerol during the reaction. *Streptomyces antibioticus* phosphatidylinositol-specific phospholipase C is a 38 KDa enzyme that utilizes calcium. The crystal structure was determined by our lab and shows a unique active site relative to other bacterial PI-PLC enzymes. A 3D structural search using the DALI program showed significant similarities between SaPLC and the GDPD from *E. coli* in terms of the protein fold as well as active site orientation of many amino acids. To test the hypothesis that SaPLC may have GDPD activity, we are investigating the kinetics using a coupled assay system and constructing site-specific mutants of SaPLC to create an active site that is more like GDPD.

419. Mechanistic characterization of a Ca^{+2} dependent phosphatidylinositol-specific phospholipase C (PI-PLC) from *Streptomyces antibioticus*

***Stefan Petrovic**, Thomas L. Selby.Chemistry, Bucknell University, Lewisburg, Pennsylvania 17837, United States*

Streptomyces antibioticus phosphatidylinositol-specific phospholipase C (*Sa*PLC) is a 38 KDa enzyme that catalyzes the hydrolysis of phophatidylinositol (PI) in a Ca^{+2} dependent manner. Due to active site similarities, this enzyme may represent an evolutionary link between Ca^{+2} dependent eukaryotic and prokaryotic calcium-independent phospholipases. Understanding the active site structure is key to determining the mechanism of this enzyme. X-ray structures of our enzyme and homologues from the database were computationally superimposed. This allowed the identification of the amino acids involved in the catalytic mechanism. Site-directed mutagenesis experiments were performed and these results will be discussed in this talk. As an example, the activity of mutant H236A (histidine to alanine) was observed to be lower than that of the wild type, but did not abolish activity, which rules out its role as the general base. Future work includes obtaining crystal structures of mutant versions of *Sa*PLC with bound inhibitors and/or substrates.

420. Ni content of the US nickel coin determined by X-ray fluorescence and visible spectroscopy

***Sharda Jagdeo**[1], jshin@qcc.cuny.edu, Esther J. Shin[2], Jun H. Shin[1]. (1) Department of Chemistry, Queensborough Community College, the City University of New York, Bayside, NY 11364, United States (2) Department of Chemistry, Roslyn High School, Roslyn Heights, NY 11577, United States*

We had successfully measured the copper content of the US penny using X-ray fluorescence, UV-Vis spectrophotometer, and gravimetric method. As a continuous study, nickel content of the US Nickels produced between 1962 and 2011 were determined by two methods: visible spectroscopy and X-ray fluorescence. Originally the five-cent coin was made of silver metal, but the shortage of silver during and after the American Civil War (1857-1864) resulted in the introduction of a new five-cent coin consisted of 12% nickel and 88% copper metals; it is called a ‹nickel› because of the nickel metal in the coin. From 1865 the nickel content in the US nickel increased to 25%, and the composition of the US nickel has remained unchanged with the exception during the World War II. The percent nickel in the US Nickels (1962-2011) was found to be 25±1% by visible spectroscopy, and 27±1% according to X-ray fluorescence analysis.

421. Application of the laser pointer method to determine the refractive index of solid compounds: Out-in method

***Suk Ju Ham**, jshin@qcc.cuny.edu, Rebecca Cho, Jun H. Shin.Department of Chemistry, Queensborough Community College, the City University of New York, Bayside, NY 11364, United States*

We have developed a simple, accurate, and inexpensive system for determining the refractive index of various compounds using a laser pointer and a chromatography column. We applied this system to measure the refractive index of a solid compound based on the observation that the refractive index of a liquid remains unchanged on addition of a solid if the refractive index of the solid is the same as the liquid. The refractive index of solid compounds including lauric acid, myristic acid, and *p*-dichlorobenzene has been determined using an out-in method. The refractive index determined by this new method was found to be close to the literature values for all three solids.

422. Determination of the refractive index of solid compounds by the laser pointer method: Extension method

***Jihyun Lee**, jshin@qcc.cuny.edu, Rebecca Cho, Jun H. Shin.Department of Chemistry, Queensborough Community College, the City University of New York, Bayside, NY 11364, United States*

A simple, accurate and inexpensive system using a laser pointer and a chromatography column has been developed to measure the refractive index of solid compounds. In the system, a good linear relationship, which was found between percent mass of solid-solvent mixture and its refractive index, was extended to 100% to determine the refractive index of a solid compound. A graph of refractive index vs percent mass was obtained in low concentration ranges (0 - 15%), and the line of the linear plot was extrapolated to 100% mass (*i.e.* pure solid) where the refractive index of the solid was calculated. The refractive index of solid compounds such as lauric acid, myristic acid, and *p*-dichlorobenzene has been investigated in several different solvents using this system.

423. Photonic crystal fiber bending loss sensitivity for design of fiber sensors

***Andrew Lee**, dkokkinos@qcc.cuny.edu, **Gilberto Constantinez**, dkokkinos@qcc.cuny.edu, **Leonardo Mora**, dkokkinos@qcc.cuny.edu, Dimitrios Kokkinos.Department of Physics, Queensborough Community College, Bayside, NY 11364, United States*

Fiber macro-bending loss is very important in telecommunications and the design of optical fiber sensors. Determining the bend loss sensitivity, would enable the design of optical fiber sensors with optimum bend conditions, including bend radii range and patterns, depending on the application. Reported results show that the bend loss sensitivity for standard Single Mode Fiber (SMF) is not uniform and increases as the bend radius decreases. SMF bend loss sensitivities reported are in the range of 0 to 15 dB/turn-mm bend radius, corresponding to a bend radius range of 3 to 15 mm. This study investigates the effects of optical fiber bend radius on bend loss sensitivity in Photonic Crystal Fibers (250mm coated) operating at 1550 nm, compared to SMF. The results show that the bend loss sensitivity is in the range of 0 to 3 dB/turn-mm bend radius, corresponding to a bend radius range of 3 to 7 mm.

424. Use of a microscale freezing point technique to determine the ionization constant of carboxylic acids

***Fathima Nazumudeen**, fthm.nazumudeen@gmail.com, Pedro Irigoyen Irigoyen, Paris Svoronos. Chemistry, Queensborough Community College, Bayside, NY 11364, United States*

The standard freshman General Chemistry laboratory uses freezing-point depression concept to determine the molar mass of a solute using the general equation

$\Delta T_F = (K_F) \times (m) \times (i)$ where

ΔT_F = freezing point depression (^oC),

K_F = the cryoscopic constant (^oC/ molal) of the solvent

m = molality of solution (mol solute/kg solvent) and

i = van 't Hoff factor, characteristic of the solute degree of ionization

We have developed a microscale procedure that uses a LabPro interface and aqueous solutions that are as low as 0.1g of solute in 3 mL water to determine the ionization constant of five carboxylic acids ($K_a = 10^{-1}$-10^{-2}) using the van 't Hoff factor at different concentrations.

The data are the first ones reported at the freezing point of water. Moreover our procedure uses much smaller quantities than the standard titration procedures which lead to potentially significant accumulations of waste chemicals.

425. Effects of resveratrol analogues on cell proliferation and migration of mouse melanoma cells

Fathima B. Nazumudeen[1], *fthm.nazumudeen@gmail.com, May Myat Moe*[1], *Valery Morris*[1], *Carmela Spatafora*[2], *Corrado Tringali*[2], *Susan A. Rotenberg*[3]. *(1) Department of Chemistry, Queensborough Community College, Bayside, NY 11364, United States (2) Dipartimento di Scienze Chimiche, Universita di Catania, Catania, Italy (3) Department of Chemistry and Biochemistry, Queens College, Flushing, NY 11367, United States*

Resveratrol (3, 5, 4'-trihydroxy-*trans*-stilbene), found in red wine and other foods, occurs naturally as both the *trans* and *cis* isomers and has both anti-oxidant and anti-cancer properties. This project examines the inhibitory effect of 50 µM resveratrol and analogues on proliferation and motility of metastatic mouse melanoma B16 cells using a fluorescence assay. Proliferation was inhibited substantially by of the trans isomer (A), while the *cis*-trimethoxy (B-OMe) analogue was similar to the parent compound (B) and more potent than (A). Motility was also substantially decreased by the (B-OMe), while (A) had no effect. While none of the analogues are more potent than the parent compound as inhibitors of proliferation, (B-OMe) shows novel and potent activity and therefore potential as an anti-metastatic agent. The phosphorylation of the PKC substrates, alpha-tubulin and MARCKS is associated with motility in these cells and is being analyzed by Western blots of lysates of resveratrol-treated cells.

426. Identification of mycotoxin and chemotherapeutics by FDA Northeast Region Laboratory

Fathima Nazumudeen[1], *fthm.nazumudeen@gmail.com, Shelema Cox*[2], *Hendri Chauca*[2], *Jose Obando*[2], *Paris Svoronos*[1]. *(1) Department of Chemistry, Queensborough Community College, Bayside, NY 11364, United States (2) 158-15 Liberty Avenue, Food and Drug Administration Northeast Region, Jamaica, NY 11433, United States*

One of the goals of The Food & Drug Administration is to test for drug residues, contamination of food and animal feed items and prevent the consumer and public from adverse effects. In Chemotherapeutic and mycotoxin lab, as a first step the collected samples as listed on current Fiscal Year ORA Field Work Plan by CFSAN (Center for Food Safety and Applied Nutrition) are composite. Then the composited sample is extracted for further analysis of drug residues. Chemotherapeutic is an antibiotic used in aquaculture and the analysis for chemotherapeutics include Fluoroquinolones, Quinolones, Ivermectin and Malachite Green. Mycotoxin is a fungal toxin and its analysis includes Alfatoxin, Patulin, Deoxynivalenol, Fumonisins and Ochratoxin.

Active Learning in the Chemistry Laboratory

Presiding: H. Perks

427. Active learning in the chemistry laboratory: The POGIL approach

Frank J. Creegan, *fcreegan2@washcoll.edu.Department of Chemistry, Washington College, Chestertown, MD 21620, United States*

In a POGIL laboratory, students, in advance of any classroom work on underlying principles, work in self-managed teams to conduct experiments rather than exercises that verify previously taught principles. In a pre-lab session, the instructor poses a focus question or Question of the Day *(How is the structure of a molecule related to its boiling point?),* and students propose a set of tentative answers. To test these hypotheses, students propose and run reactions and/or collect data, which are pooled

and then analyzed with the aid of in-lab and post-experiment or post-laboratory guided-inquiry questions. This Learning Cycle Approach (Exploration phase, Concept Invention phase, and Application phase) not only guides students to construct their own understanding of important chemical concepts but also helps them to develop valuable learning process skills. The application of the POGIL approach to courses in General and Organic chemistry will be described.

428. So you want to revise your laboratory course: What next?

***Scott E Van Bramer**, svanbram@science.widener.edu, Andrea Martin.Department of Chemistry, Widener University, Chester, PA 19013, United States*

Revision of a multi-section introductory laboratory course is a major undertaking. This talk will highlight some of the important steps to consider in the design and implementation of revisions to a multi-section laboratory course. The focus will be on: identifying an instructional philosophy, determining what students will do in lab, identifying student learning goals and outcomes, writing a lab manual, piloting changes, rolling out changes, and sustaining change. The objective is to provide a roadmap to help navigate systemic change.

429. Going off-recipe: Redesigning cookbook labs for greater pedagogical nutrition

***Meredith C Wesolowski**, mcw@udel.edu.Department of Chemistry & Biochemistry, University of Delaware, Newark, DE 19716, United States*

Research on laboratory science pedagogy strongly suggests that reordering student experiences around the Learning Cycle can significantly improve comprehension and concept retention. Therefore, improvement of laboratory activities need not require starting from scratch. This talk will discuss instructional laboratory models that have isolated key ingredients from 'cookbook' labs and complemented them with far more savory pedagogical scaffolds. A generalized, systematic framework for use during laboratory activity redesign efforts will then be described. Fusing chemistry laboratory cuisine with that of other disciplines for enhanced student interest will also be discussed.

430. Use of critical thinking skills in an undergraduate organic chemistry laboratory: The catalytic hydrogenation of *trans*-methyl cinnamate

***Kenneth J O'Connor**, oconnor9@marshall.edu.Department of Chemistry, Marshall University, Huntington, WV 25755, United States*

Catalytic hydrogenation is one of the most often employed methods for the conversion of alkenes to alkanes. These reactions are often conducted in an undergraduate organic chemistry lab using 5-10% Pd on carbon as the transition metal catalyst. At Marshall University, students hydrogenate *trans*-methyl cinnamate ($PhCH=CHCO_2CH_3$) in less than one hour in a lab using critical thinking skills. This hydrogenation experiment is unique in that students are not provided with the reaction time; by using a series of inquiry-based questions, students determine how to monitor this reaction by TLC. Students were videotaped during the pre-lab lecture and parts of the video will be played to illustrate the range of thought processes students exibit when implementing TLC to monitor this hydrogenation reaction. The value of recording parts of the pre-lab lecture for the purposes of understanding students' thought processes will be discussed.

431. Creating unique undergraduate research projects for nursing majors that investigate the antiproliferative effects of heavy metal compounds on MCF-7, A375, and HFF cells

***Amy J. Heston**, aheston@walsh.edu.Division of Math and Sciences, Walsh University, North Canton, Ohio 44720, United States*

Heavy metals, such as thallium and barium, are known for their toxicity. The focus of this project was to create research techniques for undergraduate nursing majors who had only two semesters of chemistry laboratory experience. This project investigated the antiproliferative effects of thallium and barium salts on breast cancer cells (MCF-7), skin cancer cells (A375), and normal Human Foreskin Fibroblasts (HFF). Thallium, barium, and potassium possess very similar atomic radii, resulting in the ability of Tl^+ and Ba^{2+} to easily enter the cell via the Na^+/K^+ pump. Cytotoxicity was monitored utilizing a Sulforhodomine B (SRB) assay. Results indicated cell death for MCF-7 (2 μM $TlCH_3COO$, 75 μM $TlNO_3$), A375 (100 μM $TlCH_3COO$, 75 μM $TlNO_3$), and HFF (100 μM $TlCH_3COO$, 100 μM $TlNO_3$). Remarkably, these cells tolerated 800 μM $Ba(NO_3)_2$. Techniques were designed to limit exposure to toxins and enhance the education of Walsh University's nursing majors.

Carbohydrates in Drug Design B

Presiding: L. Wang

432. Functionalized catanionic surfactant vesicles as "artificial pathogens": A new platform for the development of vaccines

***Philip DeShong**, deshong@umd.edu.Department of Chemistry & Biochemistry, University of Maryland, College Park, MD 20742, United States*

Catanionic surfactant vesicles are unilamellar vesicles that form spontaneously from mixtures of cationic and anionic surfactants. The size of the vesicle and its surface charge can be controlled by choice of surfactants, and the external leaflet of the vesicle can be decorated with non-ionic surfactants in concentrations as high as 20 mole percent without affecting the stability of the vesicle in biologically relevant media. Unlike liposomes, catanionic vesicles are extraordinarily stable at high ionic strength (2M NaCl buffer), have a wide pH latitude (pH 2-12), can be autoclaved and lyophilized without damage. Accordingly, these vesicles are an ideal platform for vaccine development.

Functionalization of the bilayer leaflet with pathogenic bacterial antigens can be accomplished readily by a variety of techniques. The resulting "artificial pathogens" can be employed as candidates for vaccines. Progress in the development of vaccines against infections by *Neisseria meningitidis*, *Francisella turlensis*, and *Mycobacterium tuberculosis* will be discussed.

433. Selective control of N-glycan sialylation via metabolic flux

***Kevin J. Yarema**.Department of Biomedical Engineering, The Johns Hopkins University, Baltimore, MD 21231, United States*

A global proteomic analysis of SW1990 pancreatic cancer cells established that flux through the sialic acid biosynthetic pathway selectively modulates a subset of N-glycosylation sites providing evidence that sialoglycoprotein patterns are not determined exclusively by the transcription of biosynthetic enzymes or the availability of N-glycan sequons. Instead, bulk metabolic flux showed a remarkable ability to increase the abundance of certain sialoglycoproteins while having a minimal impact on others. Specifically, of 82 glycoproteins identified through a mass spectrometry and bioinformatics approach, 31% showed no change in sialylation, 29% exhibited a modest increase, whereas 40% experienced an increase of greater than twofold. These changes altered the adhesive properties of the cells indicating that cancer cells can become more aggressively malignant by controlling the sialylation of proteins implicated in metastatic transformation exclusively via metabolic flux.

434. Personalizing cancer treatment with the aid of glycan array technology

***Jeffrey Gildersleeve**, gildersj@mail.nih.gov.National Cancer Institute, United States*

Cancer cells undergo major changes in carbohydrate expression during the onset and progression of the disease. Aberrantly expressed glycans on cancer cells can serve as important targets for natural immune surveillance and as cancer vaccine antigens. However, immune responses to glycans have been largerly understudied. Our group uses chemical synthesis to obtain a diverse collection of carbohydrates, which are then printed onto glass microscope slides to produce glyan arrays. We have used this technology to evaluate immune responses induced by a poxvirus-based prostate cancer vaccine, PROSTVAC-VF, that is currently in Phase III clinical trials. We have profiles over 140 patients from two phase II trials and have identified serum antibodies with statistically significant correlations with overall survival. Theses antibodies are new biomarkers for predicting which patients will respond favorably to PROSTVAC-VF and highlight the utility of anti-glycan antibodies as biomarkers for personalized medicine.

435. How NMR spectroscopy reveals the function of the genes for pneumococcal capsular polysaccharide biosynthesis

***C. Allen Bush**, bush@umbc.edu.Chemistry and Biochemistry, University of Maryland UMBC, Baltimore, MD 21250, United States*

The oral cavity is the normal home for *Streptococcus oralis*, a commensal species that is an important member of the oral microbiome which has cell wall polysaccharides involved in formation of biofilms on the teeth. The related micrombial pathogen, *S. pneumoniae* expresses capsular polysaccharides that are closely related both in carbohydrate structure and in the genes responsiblefor their biosynthesis. I will describethe technology of high resolution heteronuclear NMR spectroscopy used to determine the structures of a large number of these complex polysaccharides. Correlation of the resulting collection of accurate structural data with the rapidly expanding genetic database for these microbes makes possible assignment of the function of the gene products such as glycosyl transferases and polymerases responsible for biosynthesis of these polysaccharides. I will discuss how the results can contribute to the important new field of polysaccharide conjugate vaccines in clinical use against pneumococcal disease.

436. Glycoconjugate vaccine manufacturing: Lattices and hairy balls

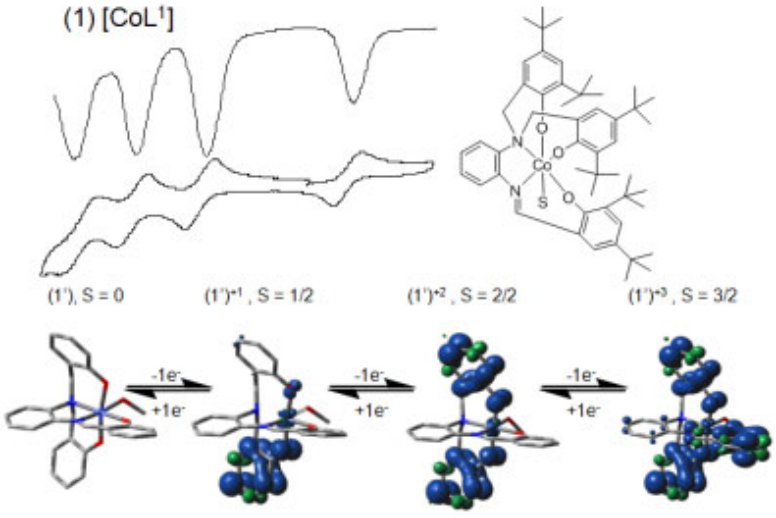
***Willie F Vann**, wvann@helix.nih.gov.Laboratory of Bacterial Polysaccharides, Food and Drug Administration/CBER, Bethesda, Maryland 20892, United States*

Glycoconjugate vaccines based on the capsular polysaccharides of encapsulated pathogens are very effective at preventing infectious disease caused by these bacteria. Several vaccines against diseases caused by *Haemophilus influenza*, *Neisseria meningitidis*, and *Streptococcus pneumoniae* are licensed in the United States. These vaccines are glycoconjugates of saccharide covalently coupled to a carrier protein by a defined but random chemistry. While the strategies used to prepare these vaccines result in very effective products, characterization of the glycoconjugate products and control of their consistency is complex. This presentation reviews the commonly used approaches to the characterization of glycoconjugate vaccines and the goals of these approaches.

437. Sequential phenolate oxidation in octahedral cobalt(III) complexes with $[N_2O_3]$ ligands

Marco M. Allard, *mallard@chem.wayne.edu, Claudio N Verani, Debashis Basu, Fernando R. Xavier. Department of Chemistry, Wayne State University, Detroit, MI 48202, United States*

A series of six-coordinate cobalt(III) complexes containing electron-rich phenolato pentadentate ligands were synthesized and characterized consistent with hexacoordinated cobalt(III) metal centers with a sixth position occupied by a methanol molecule. These complexes exhibited similar electronic behavior resulting in four redox accessible states involving three distinct phenolato/phenoxyl radical couples and a fourth process thought to be associated with a Co(II)/Co(III) couple. Electronic structure DFT calculations favor localized phenoxyl radicals and suggest distinct oxidation sequences which are directed by the local environment.



438. Enhanced water stability of carboxylate containing metal organic frameworks via plasma enhanced chemical vapor deposition of perfluorocarbons

Jared B DeCoste[1], *jared.b.decoste2.ctr@mail.mil, Gregory W Peterson*[1], *Martin W. Smith*[2], *Corinne A. Stone*[2], *Colin R. Willis*[2]. *(1) Edgewood Chemical Biological Center, Aberdeen Proving Ground, MD 21010, United States (2) Defence Science and Technology Laboratory, United Kingdom*

Metal organic frameworks (MOFs) have become a leading class of porous materials for applications such as gas storage, catalysis, and toxic gas removal. However, the pitfall of many of these materials has been their instability in the presence of moisture. Through perfluoroalkane plasma enhanced chemical vapor deposition (PECVD), we have shown a dramatic increase in the water stability of carboxylate containing MOFs under a variety of humidity conditions. The MOFs explored include those containing either Zn or Cu secondary building units. PECVD treated MOFs were characterized with 19-F MAS NMR, ATR-FTIR, XRD, and SEM. Breakthrough studies performed under dry (0% RH) and humid (80% RH) conditions show an enhancement in the ammonia adsorption capacities of plasma treated MOFs over the parent material. The increase in water stability of carboxylate containing MOFs opens the door to a wide array of applications that were previously inaccessible under ambient conditions.

439. Synthesis of novel low coordinate manganese-nitrogen clusters in quest of water oxidation catalysts

***Sandeep K Kondaveeti**, tua45335@temple.edu, Shivaiah Vaddypally, Michael J Zdilla.Department of chemistry, Temple University, Philadelphia, PA 19122, United States*

Most of the existing synthetic manganese-oxo clusters contain 6- coordinate, multidentate ligation modes, which stabilize these systems, and disfavor geometric rearrangement[1]. Furthermore, due to lack of chemical control, metalloclusters traditionally do not lend themselves well to mechanistic studies. The low-coordinate manganese-nitrogen clusters prepared in our laboratory exhibit well-controlled reactivity and offer an exciting and rare opportunity to explore bio-inspired cluster chemistry. In the present work, we have prepared High-valent, 4-coordinate manganese-imido- and -nitrido-bridged hetero-dicubane and cubane motif type of clusters. These clusters have been characterized by single crystal X-ray diffraction, mass spectroscopy, FT-IR, electronic absorption, ^{1}H NMR spectroscopies. Currently, we are focused on understanding the chemical behavior of these low-coordinate manganese clusters, and explore their potential as a new class of chemical mediators in the development of novel water-oxidation catalysts.

Reference:

1. Mukhapadhyay, S.; Mandal, S. K.; Bhaduri, S.; Armstrong, W. H. *Chem. Rev.* **2004** , *104*, 3981.

440. Iron-based hydrogen evolution catalysts

***Charles A Mebi**, cmebi@atu.edu, Derek Karr, Ruixiao Gao.Physical Sciences, Arkansas Tech University, Russellville, Arkansas 72801, United States*

Hydrogen is considered a clean and primary energy carrier of the future. Currently, the production of hydrogen from water by electrolysis requires expensive platinum catalysts. Hence, the development of cheaper alternatives to platinum catalysts has gained a lot of attention. Our research and this presentation is focused on preparation and characterization of iron-based catalysts designed to model the structure and function of the active site of the efficient hydrogen producing [Fe-Fe] hydrogenase enzyme. We have prepared and characterized a series of diiron-carbonyl clusters coupled to polyaromatic thiolate ligands. The aryl groups are used to tune the proton reduction overpotentials of the clusters. These compounds have been structurally (X-ray crystallography) and spectroscopically (IR, UV-visible and NMR) characterized, and examined as catalysts for the electrochemical reduction of proton to hydrogen. Our catalysts generate hydrogen from acidic water at milder reduction potentials than similar complexes reported in the literature.

441. Pseudorotational rearrangement of ligands at a rhenium(V) pentahydride complex as opposed to simple rotation about a single Re-N bond

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Attempts to prepare a compound which contained two rhenium polyhydride centers bridged by a single aromatic amine ligand led to the observation of rotational isomers for complexes of the form $ReH_5(PPh_3)_2L$ (where L = 4-phenylpyrimidine, 2-aminopyridine, or 2-aminopyrimidine). Previous work by Crabtree et al. suggested that rotational isomers such as those described above could convert via a pseudorotational mechanism. An alternative mechanism for the interconversion of the above rotational isomers would be a simple rotation about the single Re-N bond in such complexes. Investigations of a new chiral rhenium(V) pentahydride complex demonstrate that the ligand inter-

conversion in such complexes occurs via a psudorotational mechanism rather than by rotation about the Re-N bond.

442. Some chiral copper(II) complexes of piperazine derivatives

Molly A. O'Connor[1], *maoconnor83@drexel.edu, Anthony W. Addison*[1], *Matthias Zeller*[2], *Allen D. Hunter*[2]. *(1) Department of Chemistry, Drexel University, Philadelphia, PA 19104, United States (2) The STaRBURSTT CyberDiffraction Consortium, Youngstown State University, Youngstown, OH 44555, United States*

Tetradentate branched cyclic ligands with N4 donor sets were synthesized using vinylpyridine and chiral piperazine derivatives, and complexed with Cu(II) to form both enantiomers of the chiral complexes. Similar non-chiral complexes were also prepared from achiral derivatives of piperazine and homopiperazine. Crystal structures show that the complexes are square-pyramidal with an anion ligated in the axial position. Optical absorption results will be presented as well as ECD spectra for the chiral complexes. Complexes were also characterized using electrochemistry and ESR.

443. Ligand odyssey: Synthesis and structural characterization of redox-active second and third generation tris(pyrazolyl)borate ligands

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Tris(pyrazolyl)borate (Tp) ligands have enjoyed a long and rich history in inorganic and coordination chemistry due to their ease of steric and electronic modification. We have observed that the oxygen chemistry of first-row transition metal complexes, several of which were isolated, structurally characterized and reported by us, is often plagued by ligand decomposition via ligand C-H bond activation. This has led us to synthesize Tp ligands using ferrocenyl substituted pyrazoles both for its C-H bond strength and steric bulk. We shall discuss the synthesis and characterization of these new Tp ligands and their representative metal complexes

Nanochemistry B

Presiding: C. Geddes

444. Metal-enhanced fluorescence: Progress towards a unified plasmon-fluorophore description

Chris D Geddes, *geddes@umbc.edu.Department of Chemistry and Biochemistry, Institute of Fluorescence, Baltimore, Maryland 21202, United States*

In recent years we have described in over 150 peer-reviewed publications the favorable interactions of both plasmon supporting particles with electronically excited states, i.e. Fluorophores. These favorable effects have included significantly enhanced fluorescence from singlet states, as well as enhanced phosphorescence from triplet states. As a result of enhanced triplet yields, we have also observed both enhanced singlet oxygen and superoxide anion yields.

Current thinking, describes Metal-Enhanced Fluorescence as the near-field coupling of electronic excited states to surface plasmons, the particle subsequently radiating the photophysical characteristics of the coupled excited state quanta. In this lecture, we communicate our recent findings for metal-fluorophore interactions and our current thinking towards developing a unified metal-fluorophore description.

445. Quantitative measurement of enzyme activity loss on biofunctionalized gold nanoparticles

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Biofunctionalized gold nanoparticles (AuNP) are being investigated as a next-generation drug carrier used to target cancer cells due to the unique properties of nanoparticles. Before the biofunctionalized nanoparticles can be used as effective drug carriers, a method needs to be determined to ensure the efficacy and quality of the attached therapeutic enzymes. In this work, horseradish peroxidase (HRP) was functionalized to AuNPs via peptide coupling chemistry. Immunolabeling creates raspberry-like structures, which can be imaged and counted, here by atomic force microscopy (AFM). The quantitative model for interpreting AFM results will also be discussed. UV-Vis enzyme kinetic measurements showed the activity of the HRP both by itself and functionalized to a AuNP, thereby determining the loss in enzyme activity due to attachment to the AuNP. These enzyme attachment yields were compared to those calculated from the enzyme kinetics loss measurements.

446. Nanosized semiconductors and metals formed from PMMA ionomers

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Semiconductor (CdS) and metal (Pd and Ag) nanoparticles are produced in a polymer matrix. Poly(methylmehtacrylate) (PMMA) ionomer is used as a starting material, since nano-sized ionic aggregates formed in the ionomer can be used as precursors for semiconductor and metal nanocrystallites. Compared with nanoparticles formed in nonionic polymers (PMMA), the CdS nanoparticles made from PMMA ionomers are smaller due to the constraining effect provided by the ionomer chains. Wide-angle X-ray scattering (WAXS) experiments have been used as a major tool to study the formation and structure of nanoparticles.

447. Synthesis of asymmetric polymer/metal hybrid nanoparticles by interfacial reactions

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We present the facile synthesis of a new class of asymmetric conjugated polymer/metal hybrid nanoparticles via water/oil interfacial reactions. The synthesis relies on the simultaneous reduction of metal precursors and polymerization of monomer that are spatially separated in the immiscible organic and aqueous solution at the liquid-liquid interface. Under the balance of the diffusion and polymerization rate, the polymer/metal hybrid nanoparticles can be readily generated in a single step. By varying the concentration of each regents and reaction conditions, the high quality asymmetric nanoparticles with fine-tuned morphologies (i.e. lollipop, dumbbell, frog-egg and patchy particles) and dimensions of polymer/metal domains (10 to 200 nm) can be obtained. We have also identified this new interfacial reaction mechanism by the time-dependent reactions. Such asymmetric nanoparticles with multiple controllable domains can be applied as the novel building blocks for the self-assembly of new functional devices.

448. Self assembled nanopillars

***Hai-Feng JI**, hj56@drexel.edu, Noah Johnson, Xiaohe Xu, Arben Kojtari, Dayne Swearer.Chemistry, Drexel University, Philadelphia, PA 19104, United States*

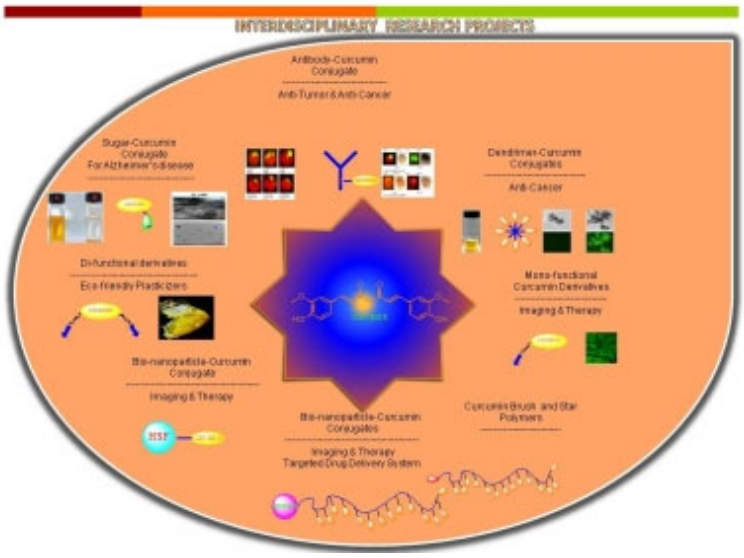
With the ultimate objective of the miniaturization of electronic device components, various methods for the fabrication of well-defined nanostructures have been extensively studied, not only to improve device performance, but also to take advantage of the remarkable properties of nanostructures that raise new possibilities at the nanoscale. Significant progress has been made in the area of 'supramolecular electronics' that has opened up potential applications in nanoelectronics, sensors, catalysts, etc. However, work demonstrating the formation of three-dimensional (3D) nanostructures from supramolecular systems is rare.

In this work, we will report the formation of nanostructures arrays from a library of molecular building through a self-assembled process. The nanoassemblies prepared by this method could be made in large quantities at a low cost due to the facile CAMS method, which makes them competitive for preparing nanostructure-based devices or coatings.

449. Bionanoparticle polymer hybrids and curcumin conjugates for biomedical applications

***Krishnaswami Raja**, Krishnaswami.Raja@csi.cuny.edu, Wei Shi, Sukanta Dolai, Chong Sun, Rema Balambika.Chemistry, College of Staten Island, Staten Island, New York 10314, United States*

A general synthetic methodology to produce a range of living copolymer protein conjugates with an amplified loading of dyes/drug will be presented. Over 18 clinical trials support the potential of Curcumin (the active ingredient in the spice Turmeric) to treat a range of pathological conditions. Curcumin is poorly absorbed by the body thereby severely limiting its potential as a drug candidate. A comprehensive strategy towards drug candidates with enhanced bioactivity based on curcumin conjugates will also be presented.



450. Silicon agents for large scale synthesis of active noble metal nanoparticles

***Bhanu P. S. Chauhan**, chauhanbps@wpunj.edu, Swetha Matam, Ramani Thekkathu, Hardika Shukla.Engineered Nanomaterials Laboratory, Department of Chemistry, William Paterson University, Wayne, NJ 07470, United States*

Synthetic methods to produce surface active nanoparticles in near quantitative yields under mild reaction conditions are very desirable and can open new avenues for green and inexpensive industrial processes. In this context, we have been investigating the possibility of using various types of silicon agents to accomplish the dual task of reducing and stabilizing agents.

In this presentation, we will describe our new one pot strategy, in which Si-H bonds are used to produce and stabilize nanoparticles by reduction of corresponding metal salts. New type of functional nanoparticles of Ag, Pd, Pt and Rh were produced at room temperature and their characterization was accomplished by UV-VIS, IR, AFM and EM techniques. In addition, the kinetic studies of the silane induced reduction process and its compatibility with external stabilizing agent were also undertaken.

NMR Spectroscopy of Biomolecules

Presiding: A. Drohat

451. Effects of deuteration on NMR parameters of proteins

***Vitali Tugarinov**, vitali@umd.edu.Department of Chemistry and Biochemistry, University of Maryland, College Park, MD 20742, United States*

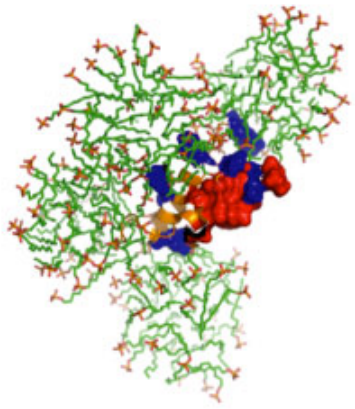
Deuteration of aliphatic sites in protein molecules is commonly used to reduce inter-proton dipolar interactions in large proteins, and has profound effects on the quality of solution NMR spectra of macromolecular systems. The effects of proton-to-deuterium substitution at aliphatic carbon positions (alpha, beta and methyl) on a number of important NMR parameters (chemical shifts, scalar couplings and relaxation times) are rigourously quantified in small partially deuterated model systems as well as the methyl sites of high-molecular-weight proteins.

452. Tales of two detergents in solubilizing and stabilizing protein for NMR studies

***Michael A Massiah**, massiah@gwu.edu.Chemistry, The George Washington University, Washington, DC 20052, United States*

The talk will focus on the solubilizing effects of commonly used detergents for NMR studies. Recently, we showed that inclusion bodies from bacterial extracts can be solubilized by sarkosyl. I will provide evidence that sarkosyl-solubilized proteins are almost native their structure and this provide an alternatives to chaotropic agents. Conversely, protein denaturing SDS was used to stabilized the structure

of an intrinsically unstructured peptide. NMR data revealed that the mechanism of peptide stability was via charge stabilization.



453. Proteins that switch folds

John Orban, *jorban@umd.edu.Institute for Bioscience & Biotechnology Research, University of Maryland, Rockville, MD 20850, United States*

Two wild-type domains of streptococcal protein G, the albumin binding domain (G_A) and the IgG-binding domain (G_B), were used as starting points for designing high sequence identity proteins with different folds. G_A is a 3-helix bundle while G_B has a 4beta+alpha structure. Both proteins are 56 amino acids in length and have 16% sequence identity in the parent sequences. Using a combination of phage display and site-directed mutagenesis, these proteins were co-evolved to 98% sequence identity while maintaining their distinct wild-type folds. Structures of high identity mutants were characterized using NMR spectroscopy.

The results show that alternative fold space can be accessed with just a single amino acid mutation in a small protein. Moreover, the data are consistent with accepted principles of protein folding and suggest that large-scale conformational switching through relatively short mutational pathways may be a more facile process for evolving new folds and functions than previously thought.

454. NMR detection of an RNA structural switch in the HIV-1 leader that regulates genome dimerization and packaging

Xiao Heng, *hxiao1@umbc.edu.Department of Chemistry and Biochemistry, University of Maryland, Baltimore County, Baltimore, MD 21250, United States*

HIV-1 genome dimerization and packaging is mediated by interactions between the 5'-leader of genome RNA and the nucleocapsid (NC) domain of the viral Gag polyproteins. The 5'-leader RNA contains conserved residues spanning the *gag* start codon (AUG), which are critical for RNA dimerization and packaging, and have been proposed to function as a regulatory element. Here, using a new approach for *long-range Adenosine Interaction Detection* (lr-AID), we show by NMR that the dimerization initiation site (DIS) is sequestered in base pairing with the Unique-5´ region (U5) in the monomeric leader, and is exposed by formation of U5:AUG long-range interaction in the dimer (230 kDa). U5:AUG formation promotes dimerization and enhances binding by the NC. Our findings are consistent with a novel nucleotide displacement RNA switch mechanism, in which U5:AUG formation triggers simultaneous exposure of dimer-promoting and NC-binding elements.

455. Carbon detected NMR methods probe folding-upon-binding events involving intrinsically disordered proteins

***Scott A Showalter**, sas76@psu.edu.Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802, United States*

Rather than being rare exceptions to the rule, intrinsically disordered proteins (IDPs) have been found to function in important signalling processes. These proteins tend to have poor ^{1}H-amide chemical shift dispersion, making heteronuclear ^{13}C-detected NMR spectroscopy an attractive method for structure characterization. The intrinsically disordered C-terminus of FCP1 forms an alpha helix when bound to RAP74 and we observe a partial helical character to the unbound ensemble. Furthermore, carbon-detected ^{15}N-spin relaxation experiments developed in our laboratory support a model in which very few residues of FCP1 experience an increase in backbone order upon complex formation. Multiple microsecond simulations calculated using ANTON assist in quantifying persistent disorder in the complex and are able to qualitatively capture the ensemble properties of unbound FCP1 established by our carbon-detected NMR strategy. Taken together, our data suggest that the moderation of binding affinity associated with folding-upon-binding mechanisms may be generally less severe than previously indicated.

456. Molecular recognition by carrier proteins in non-ribosomal peptide synthetases

***Dominique P Frueh**, dfrueh1@jhmi.edu, Andrew Goodrich, Subrata Mishra, Scott Nichols, Bradley Harden.Department of Biophysics and Biophysical Chemistry, Johns Hopkins School of Medicine, Baltimore, MD 21205, United States*

Non-ribosomal peptide synthetases (NRPSs) are multi-module, multi-domain enzymes, that synthetize important natural products in bacteria and fungi, many of which with pharmaceutical applications (e.g. antibiotics, antitumor agents, immunosuppressants). NRPSs use an assembly line organization to covalently load substrates onto so-called Carrier Proteins in each module and catalyze peptide bond formation between substrates loaded on adjacent modules. These multiple catalytic steps require a series of sequential domain/domain and domain/substrate interactions, which are currently poorly understood. We have used NMR to study the interaction between Carrier Proteins and either substrates or cognate catalytic domains. We show that carrier proteins recognize both chemical and protein substrates and we discuss structural and dynamics effects during molecular interactions. Understanding the dynamic mechanism of NRPS domain communication may open the venue to efficient NRPS assembly line reprogramming and the production of novel pharmaceuticals.

Photochemistry

457. Examing the effects of laser ablation on gold nanoparticles

***Douglas C Meier**, dmeier@nist.gov, Richard E Cavicchi.National Institute of Standards and Technology, Gaithersburg, MD 20899-8371, United States*

Examining the processes that occur on the nano- and microscale during laser ablation of metal nanoparticles will inform practical applications of the technique, such as targeted thermal therapy. Herein we characterize the physical and chemical effects of laser ablation on gold nanoparticles using transmission electron microscopy (TEM), dynamic light scattering (DLS), UV-visible absorption spectroscopy, and reflection electron energy loss spectroscopy (REELS).

Monodisperse suspensions of gold nanoparticles of various sizes were exposed to 532 nm laser pulses at a range of power settings prior to deposition on a thiol-terminated SiN TEM window. The particles form a bimodal size distribution upon ablation, e.g. 30 nm particles are transformed into a dispersion of 25 nm particles along with many particles in the 5 nm range. Particles are not only reduced

in size, but also exhibit surface morphologies with smaller facets and larger numbers of defects than their parent particles.

458. Standoff laser-induced fluorescence-backscattered amplified stimulated emission (LIF-BASE) detection of explosive vapors

Jeffrey B Oleske, *oleskej1@gmail.com.Department of Chemistry and Biochemistry, University of Maryland Baltimore County, Baltimore, MD 21250, United States*

A method for the stand-off detection of vapors with laser-induced fluorescence–backscattered amplified stimulated emission (LIF-BASE) has been developed. LIF-BASE generates uniaxial intensity distributions of the observed fluorescence with the majority of intensity propagating along the excitation axis in both the forward and backward directions. It was determined in this study that a high powered pumped laser system can generate and detect ASE of low concentration vapors from stand-off distances in the backscattered direction. LIF-BASE been shown to selectively detect organic vapors, nitric oxide (NO), and NO photofragmentation products of NO_2 and explosive vapors with sensitivity in the ppm to ppb range. Intrinsically low vapor pressure of most primary explosives under ambient conditions is a significant challenge to standoff detection, but this new strategy allows for the identification of several nitroaromatic vapors.

459. Probing thermodynamics of pseudo-polymorph conversion in peptides using terahertz spectroscopy

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The far-infrared Terahertz radiation spanning the region 0.1 to 1 mm is exquisitely sensitive to coupled motions of protein and water.[1] Coupling of water to protein global modes can enhance dipole moments and yield strong THz signals. It is therefore possible to selectively study biological water using THz spectroscopy. In our on-going THz studies of model peptide-water systems we have used THz spectroscopy and density functional calculations to understand the thermodynamics of water loss for the case of bound and channel waters.[2] Our results indicate that DFT calcuations when optimized to reproduce THz spectra correctly predict the overall sign of ΔG but overestimate the ΔH of water loss by a factor of 4.

1. Zhang et al *Methods in Nano Cell Biology,* Elsevier, Amsterdam, 2008
2. Ahmed et al *Faraday Discuss*., 2011, **150** , 1-18

460. Design and construction strategies for assembling artificial redox and light-activatable and light-harvesting proteins

Goutham kodali[1], *kodalig@mail.med.upenn.edu, Lee A Solomon*[1], *Tammer A Farid*[1], *Olga A Mass*[2], *Aravindu Kunche*[2], *Nicholas Roach*[3], *Tatiana V Esipova*[1], *Sergei A Vinogradov*[1], *Jonathan S Lindsey*[2], *David Officer*[3], *Christopher C Moser*[1], *P Leslie Dutton*[1]. *(1) Department of Biochemistry and Biophysics, University of Pennsylvania, Philadelphia, Pennsylvania 19104, United States (2) Department of Chemistry, North Carolina state university, Raleigh, NC 27695, United States (3) The Intelligent Polymer Research Institute, University of Wollogong, Wollongong, Australia*

We demonstrate the design and construction strategies for artificial proteins capable of redox catalysis, light-harvesting and light-activated electron transfer using natural, synthetic phorphyrins and chlorins. A multiple-a-helical single chain protein platform is developed from scratch avoiding mimicry and complexity of natural proteins. These protein maquettes are expressed in *e.coli* in high yields and strategies are being developed for simple assembly of natural and synthetic cofactors both in vitro and in vivo. Binding of several Fe,Zn tetrapyrroles with different substituents to the hydrophilic single chain maquettes were explored. Based on this binding data we have hypothesized an amphiphillic character of a tetrapyrrole as an essential requirement for efficient and fast binding. We also

demonstrate binding of different synthetic heme analogues with redox potentials varied over 300mV. This simple amphiphillic model will enable us to design new tetrapyrrole cofactors, for engineering and assembling maquettes capable of diverse functions.

461. Multiple photochemical transformations of organic molecules: Juggling with atom connectivity

***David J Aitken**, david.aitken@u-psud.fr, Hendrik Eijsberg, Jean Ollivier.Department of Chemistry, University Paris-Sud, Orsay, France*

Photochemically induced transformations represent a valuable yet sometimes underestimated tool for the synthetic chemist. With the objective of preparing high-added-value small molecules from simple starting materials, we have examined the photochemical reaction of cyclopentenones with alkenes. Depending on the reaction conditions, a single, tandem, or triple photochemical process is privileged, leading to bicyclic ketones, cyclobutene aldehydes or tricyclic oxetanes respectively. These molecular skeletons represent a remarkable molecular diversity accessible from the same starting materials, with 100% atom economy in each case.

462. Synthesis and polarity sensing with benzo[ghi]perylene monoimides

***Steven J Manning**, smanning130@yahoo.com, John A Arthur, Lisa A Kelly.Department of Chemistry and Biochemistry, University of Maryland, Baltimore County, Baltimore, Maryland 21250, United States*

In this work we describe the synthesis and photophysics of a set of benzo[ghi]perylene monoimides (BPIs) that show promise as local polarity sensors in complex polymer and biological microenvironments. The compounds exhibit strong absorbance, high quantum yields and solubility in a range of common solvents. Most importantly, BPIs show solvatochromic fluorescence ($\lambda_{nonpolar}$=469nm, λ_{polar}=550nm) as a function of local polarity. The solvent dependencies of eight BPI derivatives were evaluated according to the Lippert-Mataga approach and excited-state dipole moment changes of 4.2±0.6 D were determined.

Incorporation of the dyes into thermo-responsive N-isopropylacrylamide nanogels shows the ability to dynamically report breaching of temperature thresholds within 0.5°C. A temperature induced coil-to-globule phase change was observed at 30.5±0.5°C via dynamic light scattering concurrent with a six-fold increase in fluorescence emission. Modification of the BPI or acrylamide host allows for smart polymers with user-defined temperature ranges which are promising for smart packaging and quality control applications.

463. Photochemical degradation kinetics of 2- and 3-nitrofluoranthene in organic solvent

***Salvador Gavalda**, salvi_prl@yahoo.com, Rafael Arce.Department of Chemistry, University of Puerto Rico - Rio Piedras Campus, San Juan, Puerto Rico 00979, Puerto Rico*

Nitrated polycyclic aromatic hydrocarbons, especially 4-ring compounds such as nitrofluoranthenes, have been shown to have cancerous and mutagenic properties. The mechanisms responsible for the phototransformation of these compounds are not well understood. The photochemistry of 3-nitrofluoranthene (3NF) was studied in solvents simulating the organic liquid portion of aerosols. When irradiated under anaerobic conditions, a decrease was observed in the characteristic absorption band for the compound (382nm) and new bands were observed, depending on the solvent. 3NF phototransformation was found to occur at a faster rate in 2-propanol and other alcohols. This is in agreement with previously done flash photolysis of transient species, where triplet states were observed to produce stable complexes with alcohols which could possibly later on undergo hydrogen abstraction. Various photoproducts were observed though HPLC, including 3-aminofluorathene and fluoranthene.

Aminofluoranthene production was not detected in solutions where the stable complex mentioned above was not observed.

Undergraduate Research Posters B

464. Synthesis of curcumin incorporated copolymers via ATRP

Frantz Pierre Toussaint, *ptoussaint.frantz@cix.csi.cuny.edu,* ***Oluwatobi Ajayi***, *icefire10314@hotmail.com, Krishnaswami Raja, Sukanta Dolai.Department of Chemistry, College of Staten Island-CUNY, Staten Island, New York 10314, United States*

The chemical synthesis of therapeutically relevant, well-defined high molecular weight polyphenols is very rare. We propose to employ the following strategy: synthesizing livingpolymers in which the side chain pendant groups and the polymer chain end possess orthogonal reactivity, followed by the attachment of a number of water soluble, biocompatible moieties and appropriately designed curcumin derivatives to the reactive polymer side chains. In one embodiment embodiment glycidyl methacrylate will be polymerized via Atom Transfer Radical Polymerization (ATRP) using an azide incorporated initiator. The resulting polymer will be further reacted with varying ratios of mono-carboxylic acid derivatives of curcumin followed by commercially available Glucuronic acid in two sequential ring-opening esterification steps to produce libraries of polymers with varying loadings of curcumin. The glucose component of the polymers serves to improve the water solubility of the polymers.

465. Synthetic lethal screen to identify genes related to MAM33 in *S. cerevisiae*

Gabrielle A Roloff[1], *mazam@wcupa.edu, Emily Luvison*[1], *Michael F. Henry*[2], ***Mahrukh Azam***[1], *mazam@wcupa.edu. (1) Department of Chemistry, West Chester University of Pennsylvania, West Chester, Pennsylvania, United States (2) Department of Molecular Biology, University of Medicine and Dentistry of New Jersey, Stratford, NJ, United States*

The cellular role of Mam33p, a highly conserved, non-essential mitochondrial protein, is still unclear. With the exception of an N-terminal mitochondrial targeting sequence, MAM33 doesn't have any identifiable motifs that suggest its function. Mam33p has been proposed to be involved with interactions between the nucleus and mitochondria. The human homolog of Mam33p, p32, has been localized to the nucleus, cytosol, and mitochondria in human cell lines. In order to further our understanding of the cellular role of Mam33p we have performed a synthetic lethal screen. The objective of this screen is to identify functionally related genes that if mutated, will cause death in Δ*MAM33* cells. Since Mam33p is a mitochondrial protein, it may play a role in cellular aerobic respiration. Therefore, the phenotypes of the synthetic lethal mutants were also examined on both fermentable and non-fermentable carbon sources. We have identified *two genes* as the final two candidates.

466. Which hydroxyl groups of epigallocatechin gallate (EGCG) are needed for binding to DNA g-quadruplexes?

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The therapeutic effects of green tea have been studied extensively over the past three decades. Of particular interest are the anti-carcinogenic characteristics of green tea, which have been attributed to the catechin compound epigallocatechin gallate (EGCG). EGCG has been studied as an anti-oxidizing agent and free radical destroyer, but more recent studies have focused on its interactions with DNA. Our recent experimental results suggest EGCG preferentially binds to DNA G-quadruplexes, which are promising drug-targets for cancer treatment. We hypothesize that the many hydroxyl

groups of EGCG play an important role in the binding to G-quadruplex DNA. This will be tested by methylating various EGCG hydroxyl groups and measuring the resulting effect on binding to G-quadruplexes. Results will help establish the significance of the hydroxyl groups in the binding of EGCG to G-quadruplexes, and provide potential background for future studies aimed at the better design of G-quadruplex ligands for cancer treatment.

467. Oxidation of alcohols to esters using *N*-bromosuccinimide in aqueous media

Mitchell C. Stadler, *mcstadler@centurylink.net, Justin Fair.Department of Chemistry, Indiana University of Pennsylvania, Indiana, Pennsylvania 15701, United States*

The usefulness of esters in fragrances, flavorings, and polymer chemistry makes the green synthesis of esters appealing. Thus, this research proposes a new synthetic method for the oxidation of primary alcohols to the corresponding ester products. The synthesis will be carried out in aqueous media using the oxidative agent *N*-bromosuccinimide. The project will investigate what types of primary alcohols, aliphatic or aromatic, can be oxidized to the corresponding ester. The research also investigates the potential of this same reaction to oxidize a primary alcohol and an aldehyde to yield an asymmetric ester. Although current methods for these types of oxidations use hazardous bromine, heavy metals, expensive catalysts, acids and bases, as well as other hazardous chemicals and solvents, this new method promises to be a cheap, efficient, and environmentally benign pathway to synthesizing both symmetric and asymmetric esters.

468. Construction of a coronal discharge ozone generator

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We report on the construction of a coronal discharge ozone generator and the quantitation of ozone formed. Feeding compressed air into ozone generator produced the highest concentration of ozone in air (1% v/v) at a flow rate of 170 mL/min corresponding to 3.3 mmol of ozone per hour. The production of ozone using the inexpensive instrument shows promise for milligram scale reactions for research or education.

469. Environmentally friendly synthesis of novel mono-azo and bis-azo dyes using a polymer resin

Annie R Pulcini, *arpulcini@cedarcrest.edu, Jeanne R Berk.Department of Chemical and Physical Sciences, Cedar Crest College, Allentown, PA 08848, United States*

Due to their vivid colors, azo dyes are among the most popular synthetic dyes in the fashion industry. Original synthesis of azo dyes involves using a coupling reaction which produces a copious amount of environmentally harmful waste. A more efficient and cleaner method using a polymer support resin by means of combinatorial methods to generate a large number of novel azo compounds was found. [i] Only a few specific coupling components and diazonium compounds were considered. Therefore, the aim of this study was to consider different diazonium and coupling components to extend the library of mono-azo compounds and to determine if the method could be used to synthesize bis-azo compounds. Data representing 16 new mono-azo and 4 bis-azo compounds successfully synthesized will be presented, with spectral characterization.

[i] Caldarelli, M.; Baxendale, I.R.; Ley, S.V. Clean and Efficient Synthesis of Azo Dyes Using Polymer-Supported Reagents. *Green Chem.* **2000,** *2*, 43-46.

470. Bromine radical ring closure of α-tethered sulfonyl ene-allenes

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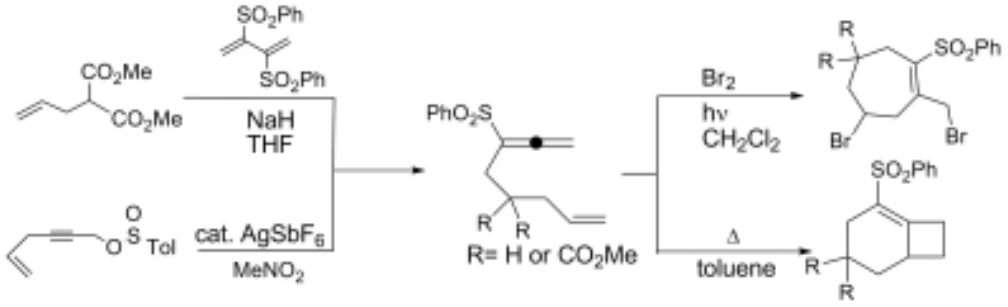
In an effort to expand the established scope of sulfonyl ene-allene chemistry, a variety of α-tethered sulfonyl ene-allenes were produced from either substituted malonates using 2,3-bisulfonyl-1,3-diene or the silver hexafloroantimonate catalyzed rearrangement of sulfinate esters. The versatility of these substrates was demonstrated through an unprecedented and mechanisitcally novel bromine radical ring closure, which is an interesting compliment to the known [2+2] thermal cycloaddition reactivity of sulfonyl ene-allenes.



471. Studying the displacement of the chloride leaving group in chloroformate esters

***Gabriel Fernandez-Bueno**[1], Gabriel.Fernandez@email.wesley.edu, Malcolm J. D'Souza[1], Dennis N. Kevill[2]. (1) Department of Chemistry, Wesley College, Dover, DE 19901, United States (2) Department of Chemistry & Biochemistry, Northern Ilinois University, DeKalb, IL 60115, United States*

Linear Free Energy relationships (LFERs) such as the Grunwald-Winstein equation are useful tools to analyze solvolytic mechanisms of a variety of chloroformate esters. The purpose of this project is to carefully examine the kinetic data previously obtained for 9-fluorenylmethyl chloroformate and compare its regression analysis results to those obtained for the substituted phenyl chloroformates. A thorough understanding of the solvent mechanisms is important as these esters are frequently used precursors in agricultural products and pharmaceutical formulations.

This research is funded in part, by a National Institute of General Medical Sciences (8 P20 GM103446-12) grant from the National Institutes of Health; a National Science Foundation (NSF) EPSCoR grant (EPS-0814251); a NSF ARI-R2 grant (0960503), and a DESGC NASA Undergraduate Tuition Award.

472. Metal cluster formation in a designed protein scaffold

***Eugene J Palovcak**, tuc68010@temple.edu, Sandeep Kondaveeti, Michael J. Zdilla.Department of Chemisty, Temple University, Philadelphia, Pennsylvania 19122, United States*

Biological metal clusters enable living systems to catalyze difficult and indispensable biochemical reactions, such as long-distance electron transfer, water oxidation, and nitrogen fixation. The study of these clusters can be assisted by the growing field of de novo protein design, in which a small model or "maquette" of a protein-bound cofactor can be studied in an environment that approximates and simplifies the natural state. A trimeric bundle protein has been rationally designed to scaffold the formation of an iron-sulfur cluster. Results from UV spectroscopy, cyclic voltammetry and circular dichroism studies suggest that an iron-sulfur cluster has formed within a tricarboxylate binding site on the synthesized, assembled protein. This research offers a means of investigating biological iron-

sulfur cluster formation, structure and reactivity. Also, it demonstrates the feasibility of functionalizing a designed protein with a metal cluster, potentially relevant to the development of man-made protein catalysts with novel activities.

473. Unprecedented azine formation via proton tautomerismof isoquinolyl-1-hydrazones

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Previously reported structures of isoquinolyl-1-hydrazones were subjected to electronic structure calculations using density functional theory (DFT). For six targeted compounds, calculations were applied to multiple conformations for both azine and hydrazone tautomers in order to determine the relative energies of the possible conformations. Then calculations were performed using the hybrid functional B3LYP and a 6-31G**++ basis set using the program Jaguar. The lowest gas phase Gibbs free energy conformation was a function of substitution. In some instances, an azine tautomer was the lowest energy conformation,and in others it was a hydrazone. Compounds which showed a significant calculated preference for either the azine or hydrazone tautomer was synthesized and characterized by x-ray crystallography. Compounds characterized thus far possess solid state structures which agree with those based on the lowest energy conformations.

474. Engineering enzyme therapeutics for gluten degradation

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Gluten intolerance currently has no treatment. Enzyme therapeutics can mitigate symptoms by breaking down gluten peptides before they reach the intestine. The enzymes in clinical trials lack ideal therapeutic properties, therefore our goal was to find a novel enzyme with better activity and stability in the stomach. We identified Kumamolisin-As, and computationally redesigned its active site to enhance hydrolysis of the repetitive PQ motif in gluten. One characterized design demonstrates 2400-fold greater activity than an enzyme in clinical trials.

475. Convenient strategies to force difficult lactamisations

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A new method to form cyclic dipeptides is reported based on the Staudinger reaction. The methodology developed an efficient and mild approach for the preparation for the synthesis of cyclodipeptides and their conformational preferences were investigated by empirical force-field calculations and X-ray crystallography.

476. Investigation into the thermoreversible gelation of polycaprolactone

Joseph Monaghan, *isaacvonrue@kings.edu, Isaac VonRue.Department of Chemistry and Physics, King's College, Wilkes-Barre, Pennsylvania 18711, United States*

It was recently discovered that polycaprolactone (PCL) homopolymer samples in dimethylformamide form thermoreversible gels. Three PCL samples of varying molecular weight were synthesized via ring opening polymerization. The transition temperature from gel to solution was measured by DSC as a function of PCL molecular weight and concentration. The transition temperature increases with both concentration and molecular weight.

477. Synthesis of four spermidide derivatives using long chain alcohol solvents and coupling of these derivatives to manganese as possible anti-cancer drugs

***Brett Begovich**, francis.mayville@desales.edu, Clayton Litchmore, Francis C. Mayville, Sara E. N. Hayik.Natural Science, DeSales University, Center Valley, Pennsylvania 18034, United States*

Past research has found spermidine to inhibit the growth of breast cancer cells. Using spermidine as a lead compound, new spermidine derivatives were synthesized to study any possible increased effect on breast cancer inhibition. The different analogues that were developed were chosen because of their similar structure to spermidine. The following analogues were synthesized: N^1,N^8 bis(ethyl) spermidine HBr, N^1,N^8 bis(propyl)spermidine HBr, N^1,N^8 bis(butyl)spermidine HBr, N^1,N^8 bis(acetyl) spermidine HCl, and N^1,N^8 bis(propionyl)spermidine HCl. Previous research indicated low yield with methanol as a solvent for this system. An increase in alcohol chain length (ethanol, 1-butanol, 1-pentanol, 1-hexanol, and 1-octanol) was seen to improve the yield of the synthesis. The analogues were coupled to manganese using air sensitive techniques.

478. Spectroscopic properties of tetracyclines

***Mariya Rozov**, mr99316n@pace.edu.Department of Chemistry and Physical Sciences, Pace University, NY, NY 10038, United States*

Tetracyclines (TCs) are an important family of low molecular weight and broad spectrum antibiotics. They have been widely used in the prevention and treatment of infectious diseases and as food additives for growth promotion, as well, in fish farming. Tetracyclines are amphoteric molecules containing several ionizable functional groups that exist predominantly as zwitterions at a given pH value. TCs are reported to undergo a wide variety of reactions at different pH values. As an example, TCs undergo reversible epimerization at position C-4 to form 4-epi-TCs between pH 3 and 6. The formation of anhydrotetracyclines at low pH and isotetracyclines at high pH values are also known. In this presentation, we report on the pH-dependent absorbance and emission properties of several tetracyclines. We also report on the absorbance and emission of the tetracycline in various alcoholic solvents.

479. Novel synthesis of high-valent and low-coordinate manganese clusters

***Sean F. McWilliams**, sfmcwilliams@temple.edu, Sandeep Kondaveeti, Shivaiah Vaddypally, Michael J. Zdilla.Department of Chemistry, Temple University, Philadelphia, Pennsylvania 19122, United States*

Photosynthetic organisms catalytically oxidize water to dioxygen using an oxo-bridged Mn_4-Ca cluster called the Oxygen Evolving Complex (OEC) located within the Photosystem II protein. The manganese atoms are high-valent Mn(IV & V) when water oxidation occurs. Our goal is to oxidize manganese clusters prepared by the Zdilla group with initial focus on $Mn(\mu\text{-}OPhPh_2)_2(Et_2O)_2$ and $Mn_3(\mu\text{-}OPhPh_2)_4(NR_2)_2(THF)_2$ (R = Me_3Si). The starting clusters have low-valent Mn(II), but biologically active manganese like those in the OEC require higher oxidation states. Oxidation of these clusters was explored using techniques of ligand exchange and oxygen transfer with focus on labile, non-chelating ligands in order to promote reactivity. Oxidized ligand byproducts were observed when oxidizing the monomer. Reactions of the trimer have led to strongly colored products that will be characterized and presented. Creation of new high valent clusters will lead to new novel approaches to catalysis of organic reactions and ultimately water oxidation.

480. Synthesis and characteristic study of artificial anthocyanidine

Anthony Pagan[1], *apagan@sjcny.student.edu, Jeonghee Kang*[1], *Jong I. Lee*[2]. *(1) Department of Chemistry, St. Joseph's College, Brooklyn, NY 11205, United States (2) Department of Chemistry, York College of CUNY, Jamaica, NY 11451, United States*

Anthocyandin is a natural pigment which can be used as a dye in Dye-Sensitized Solar Cell (DSSC). It absorbs visible range light and shows efficient electron transfer from LUMO to a conduction band of titanium dioxide in DSSC device. In order to improve the efficiency of the device, artificial anthocyanidins with various functional groups on the flavylium ring were synthesized. The design of artificial anthocyanidins was focused on the effect of functional groups depending on number of groups and their positions on the flavylium ring for investigating LUMO energy levels and binding onto TiO_2 surface. The products were confirmed and characterized by UV/Vis, IR and NMR spectroscopies.

481. Spectroscopic study of metal complexed anthocyanins from plants for dye-sensitized solar cells

Carmen M. Lorenzo[1], *clorenzo@sjcny.student.edu, Pamela Djan*[1], *Jeonghee Kang*[1], *Jong I. Lee*[2]. *(1) Department of Chemistry, St. Joseph's College, Brooklyn, NY 11205, United States (2) Department of Chemistry, York College of CUNY, Jamaica, NY 11451, United States*

Despite of many advantages Dye-sensitized Solar Cells (DSSC); cheap and easy fabrication, its low energy conversion is still a constant barrier. Anthocyanin is a natural pigment with various colors. The structure of anthocyanin adjusts to the pH of the solution as a natural pH indicator. This property renders tuning of HOMO/LUMO energy levels in order to improve light harvesting efficiency and energy transfer rate between various forms of anthocyanin dyes in the cell.

The energy conversion efficiency varies with the position of functional groups on each anthocyanin due to the interaction between the dye compound and titanium dioxide. Transition metals were also used to enhance the light harvesting efficiency through coordination with anthocyanins and (or) titanium dioxide in the system. UV/Vis absorption spectra, IR spectroscopy, and electrochemical data of anthocyanins will be presented.

482. Microwave synthesis: Sulfoindocyanine dyes

Rachael Matthews, *ramat1@morgan.edu.Department of Chemistry, Morgan State University, Baltimore,, MD 21251, United States*

Sulfoindocyanine dyes are water soluble cyanine compounds that luminescence in the near infrared (NIR) region, 650-900 nm; are not obstructed by background interference from tissue used in vivo detection; and maintain their natural existing properties in solution.[1,2] Traditional methodologies utilize too much solvent, involve long reaction times (16 - 18h), and contain impurities in the products.[2] This study applies microwave assisted organic synthesis (MAOS) as an eco-friendly, faster, and cleaner approach to synthesizing sulfoindole dyes. The specific aims to this approach are the synthesis of the: 1) potassium indolenine starting material, 2) sulfoindole heterocyclic salt derivatives 3) water soluble dye derivatives; with regard to high yields and purity.

The various salt derivatives were successfully synthesized using a Biotage and CEM microwave as well as the water soluble symmetrical dyes. Concisely, the sulfoindocyanine dyes and salts can by successfully synthesized using MAOS with a reduced reaction time and less waste.

483. Analysis of caffeine in energy drinks using liquid-liquid extraction and gas chromatography-mass spectrometry

***Kaitlyn A Snyder**, wendlingk@chc.edu, Karen S Wendling.Department of Chemistry, Chestnut Hill College, Philadelphia, PA 19118, United States*

The goal of this study is to develop a method to extract caffeine from various energy drinks (NOS, Monster, AMP Energy, Red Bull, and Rock Star) and quantify the caffeine concentration using gas chromatography-mass spectrometry (GC-MS). A calibration curve was created using non-caffeinated soda, spiked with known amounts of caffeine, to account for a similar matrix as is present in the energy drinks. To extract the caffeine, a liquid-liquid extraction with n-butyl chloride was used. The extracts were dried under nitrogen, reconstituted in ethyl acetate, and then analyzed using GC-MS. An internal standard (phenytoin) was used to account for variations in injection efficiency. A preliminary calibration curve showed excellent linearity in the 0.15 to 0.75 mg/mL caffeine concentration range, having an R^2 value of 0.9977. Additional studies are currently being performed to improve the calibration method and determine the method's extraction efficiency/percent recovery.

484. Calculating partial atomic charges from quantum mechanics: A theoretical study of substituted thiazolidinones and the prediction of their NMR spectra

***Kaitlyn J. Kober**, kjk5062@psu.edu, Kurt A. Kistler.Department of Chemistry, Pennsylvania State University, Brandywine Campus, Media, PA 19063, United States*

Partial atomic charges, which give rise to molecular polarity and help explain reactivities, are not singularly defined in quantum mechanics (QM). Several methods for calculating these charges exist, with sometimes conflicting, even erroneous, results. A good experimental gauge for judging partial charge methods is nuclear magnetic resonance (NMR), where the spectral frequencies of atoms in molecules are directly affected by the electron density surrounding their nuclei. We present results of four QM partial charge methods, Mulliken Population Analysis, Löwdin Population Analysis, Natural Population Analysis, and Charges from an Electrostatic Potential on a Grid, used to investigate series of substituted 2,3-diphenyl-1,3-thiazolidin-4-ones, with phenyls having substituents that affect the density of the thiazolidinone ring atoms, and their NMR spectra are known, as well as the experimentally-derived Hammett parameter σ, known to be predictive of NMR shifts for these systems. The roles different density methods and basis sets play will also be presented.

485. Impact of plasma membrane unsaturated fatty acid levels on copper surface mediated cell death in *Escherichia coli*

***Robert Hong**, bhong65@tigermail.qcc.cuny.edu, Tae Y. Kang, Nidhi Gadura.Department of Biology, Queensborough Community College, Bayside, NY 11364, United States*

The broad goal of our study is to understand the mechanism(s) by which copper alloy surfaces kill microorganisms. Our results indicate that copper surface mediated cell death of *Escherichia coli* correlates with increased levels of lipid peroxidation at the plasma membrane. We also determined the relationship between membrane lipid peroxidation levels and cell death in *Escherichia coli* on both copper and steel surfaces. Quantitative dilutions series were performed to test for bacterial cell death. Our results indicate a biphasic killing curve when *E. coli* is exposed to copper chips however this was not seen on steel chips. TBARS assay was used to measure the lipid peroxidation levels. Genetically altered bacterial strains show that when exposed to copper surfaces, increased levels of unsaturated fatty acids in the plasma membrane results in faster cell death rates in *E. coli*. Genomic DNA analysis show a necrotic cell death pattern.

486. Microwave assisted synthesis of cyanine dyes for fluorescence resonance energy transfer

***Grace Nyambura**, grnya1@morgan.edu.Department of Chemistry, Morgan State University, Baltimore, Maryland 21251, United States*

Real Time Polymerase Chain Reaction has been used to detect pathogens using pentamethine cyanine dyes as the fluorophore. The effect of heptamethine cyanine dyes as fluorophore based on the selectivity and sensitivity are of interest. The 5' nuclease assay was developed to allow the real-time monitoring of the reaction. Fluorescence resonance energy transfer is utilized in the 5' nuclease assay. The principle is that when a donor molecule is in close proximity to an acceptor molecule there will be a transfer of energy from high to low through dipole-dipole interactions. In this study, the microwave synthesis and characterization of various near-infrared cyanine dye donor and acceptor molecules have been investigated. The acceptor dyes are produced by reacting the synthesized benzo salt, bisimine, sodium acetate and ethanol in a microwave. The donor dyes have been synthesized using a similar technique. The donor and acceptor molecules were characterized using spectrophotometer, and fluorimeter.

487. Molecular docking simulations of indoles/ β-cyclodextrin inclusion complexes

***LaRhonda Brown**, iposey@udc.edu, Isadora Posey.Department of Biology and Chemistry, University of the District of Columbia, Washington, DC, United States*

β-Cyclodextrin (BCD) is a cyclic seven-membered oligosaccharide composed of alpha- 1,4-linked D-glucose monomers. BCD has a hydrophobic internal cavity and a hydrophilic external surface. BCD is widely used in pharmaceuticals because of its ability to alter solubility properties of molecules. Melatonin (MLT) and diindolylmethane (DIM) are indoles that have therapeutic properties but are poorly soluble in water. Inclusion complex formation of the indoles with BCD could greatly increase their bioavailabilty. The molecular modeling program Molecular Operating Environment (MOE) was used to study these complexes. The indole structures were built in MOE, and the BCD structure was obtained from the Cambridge Structural Database. Docking simulations were performed using a docking module in MOE. The lowest energy conformations were determined using the MMFF94x force field for geometry optimization. Interaction energies of the complexes were determined. Structural aspects of the BCD/MLT complex are similar to results from NMR data found in the literature.

488. Strongly conjugated hydroporphyrin arrays: Synthesis and optical properties

***Chirag Pancholi**, mptaszek@umbc.edu, Jamie Nguyen, Zhanqian Yu, Shannon Zik, Marcin Ptaszek. Department of Chemistry and Biochemistry, University of Maryland Baltimore County, Baltimore, MD 21250, United States*

Development of the near-IR fluorescent molecules with tunable optical properties has a great importance for various areas of biological sensing and medicinal imaging. Hydroporphyrins (chlorins and bacteriochlorins) posses strong absorption and fluorescence in red and near-IR spectral windows. To further improve and tune their optical properties we proposed to assemble hydroporphyrins into strongly-coupled dyads. We hypothesized that strongly conjugated hydroporphyrin arrays would exhibit absorption and emission at longer wavelengths, improved fluorescence quantum yields, and their optical properties can be more extensively tuned. We prepared series of chlorin and bacteriochlorin strongly coupled dyads, where hydroporphyrin subunits are connected by conjugated linkers at their respective 13,13' positions. Their synthesis, absorption and emission spectra, as well as results of DFT calculations of their electronic structure will be presented.

489. Novel water-soluble tetrapyrrolic derivatives via “click” reaction

*Melanie Ehudin, **Dalia Akkad**, mptaszek@umbc.edu, Rafael Arias, Christian Toonstra, Marcin Ptaszek.Department of Chemistry and Biochemistry, University of Maryland Baltimore County, Baltimore, MD 21250, United States*

Tetrapyrrolic macrocycles posses a set of optical properties making them attractive candidates for various applications in photomedicine. 1,3-Dipolar cycloaddition of azides to terminal acetylene (“click” reaction) potentially represents a convenient method for elaboration of tetrapyrrolic macrocycles. Here we present new PEG-ylated tetrapyrrolic compounds, where PEG-chains were conveniently attached to macrocycle via microwave-assisted “click” chemistry. Azide-derivatized PEG has been reacted with tetrapyrrolic macrocycles, equipped with 2,4,6-tripropargyloxyphenyl substituent, to provide non-aggregating, water-soluble derivatives. We examined this motif for boron-dipyrromethanes, porphyrins and chlorins, and we have found that chlorins derivatives exhibit highest fluorescence quantum yield. The influence of 1,2,3-triazol ring (formed upon “click” reaction) on the optical properties of chlorins has been also examined.

490. G6PDiagnostic: Point-of-care diagnostic to detect glucose-6-phosphate-dehydrogenase deficiency

***Rohit Dasgupta**, rdasgup1@jhu.edu.Department of Biomedical Engineering, Johns Hopkins University, Baltimore, MD 21218, United States*

We have developed a simple point-of-care diagnostic for detection of Glucose-6-phosphate-dehydrogenase (G6PD) deficiency based on a color change proportional to the activity of G6PD in red blood cells. The chemical reaction for our diagnostic test is based on a previously published enzymatic reaction that produces an orange color dye derived from WST-8, one of the reagents in the reaction. We have designed an unique filter device used to transform the measurement reading of the WST-8 test from a qualitative color gradient to a binary measurement. Our current prototype also uses a stamp device to apply reagents to the testing material before the application of blood. This test can be used on whole blood and the result can be read in under 30 minutes. Our methods demonstrate a path for the development of simple and inexpensive diagnostic assays that may be useful for detecting G6PD deficiency in remote settings.

491. Comprehensive catalase enzyme activity mechanism: Conformer multiplicity and kinetic deviations explained

***Jared Rosenblum**[1], jaredrosenblum@gmail.com, James P Mack[1], William Schreiber[1], Dora Schnur[2]. (1) Department of Biology and Department of Chemistry, Monmouth University, West Long Branch, NJ 07764, United States (2) Department of Chemistry, Drexel University, Philadelphia, PA 19104, United States*

Atypical function of catalase, responsible for maintaining the redox state of the cell, is implicated in the regulation of neurodegeneration, immunology, and mitochondrial disorders.

The differential regulation of catalase in enzyme kinetics was previously suggested (Rosenblum et al. NJAS 2012) to fit under the Morpheein Hypothesis.

A more complete mechanism is suggested accounting for deviations from prototypic kinetics related to conformer multiplicity explored in computational modeling. Combination of inactive and active structurally determined and hypothesized forms of catalase suggest a rationale for distinct conformer multiplicities.

(1) Fe(III)-Por (Resting) + $H_2O_2 \rightleftharpoons$ Fe(III)-Por-H_2O_2 (Compound O)

(2) Fe(III)-Por-$H_2O_2 \rightarrow$ O=Fe(IV)-Por($\bullet$+) (Compound I) + H_2O

(3) O=Fe(IV)-Por(•+) + Phenol → O=Fe(IV)-Por (Compound II) + Phenol(•)+ H^+

(4) O=Fe(IV)-Por + H_2O_2 ⇌ O=Fe(IV)-Por-H_2O_2 (Compound O—Conformer Shift)

(5) O=Fe(IV)-Por-H_2O_2 → O=Fe(IV)-Por(•+) + H_2O

(6) O=Fe(IV)-Por(•+) + H_2O_2→ Fe(IV)-Por(•+)-H_2O_2 (Ogura Complex)

(7) O=Fe(IV)-Por(•+)-H_2O_2→ Fe(III)-Por + H_2O + O_2

492. Construction of an inexpensive in-house Raman spectrometer

Benjamin Eagleton, *chemistryfullerene@gmail.com, Jiangyue Zhang.Department of Chemistry, Immaculata University, Immaculata, PA 19345, United States*

Raman technique has its wide applications in pharmaceutical, materials science and life science. But in the current market, the price of the instrument ranges from $20,000 to 200,000. This project is working on to build an in-house Raman Spectrometer within the budget of $6000. Improvements were made from the original schematic including adding a prism and improving the sensitivity of the monochromator. The in-house Raman Spectrometer can be serving as a new tool for the chemistry department for research as well as teaching. It can be used in many fields of chemistry with applications in classes such as instrumental analysis, physical, inorganic, and organic chemistry as well as forensics science.

493. Clicked sweet-curcumin: Modulator of amyloid-β aggregation at ultra-low concentrations

Dinali Obeysekera, *dinali.obeysekera@cix.csi.cuny.edu.Department of Chemistry and Neuroscience, College of Staten Island (CUNY), Staten Island, New York 10314, United States*

: We have developed a general strategy towards mono-functional derivatives of curcumin, the active ingredient in turmeric (the dried rhizomes of *Curcuma longa*).The synthesis of a water/plasma soluble , non-toxic, bio-compatible derivative of curcumin with amplified bio-efficiency in modulating amyloid-β aggregation is presented. Curcumin mono-alkyne was 'Clicked' with commercially available acetal-protected galactose azide. The deprotected curcumin Clicked galactose (sweet curcumin) is freely soluble in water. Sweet-curcumin inhibits Aβ aggregation at significantly lower concentrations compared to curcumin. Where curcumin barely inhibits Aβ aggregation at a concentration of 8 mM, sweet-curcumin inhibits aggregation at concentrations as low as 8nM. It was found to be a more powerful antioxident than curcumin. A MTT assay on cultured hippocampal slices of mouse-brain indicated that the sweet-curcumin is potentially neuroprotective and non-cytotoxic. Thus Sweet-curcumin is a promising Green-drug candidate against Alzheimer's Disease.

List of Authors

CAMPUS DIRECTORY

FREQUENT DESTINATIONS

Bookstore, The Commons E6
bwtech@UMBC North - Research Park I5
bwtech@UMBC South - Incubator and Accelerator J2
Center for Art, Design and Visual Culture,
105 Fine Arts Building F4
The Commons E6
Graduate Admissions,
2nd Floor Administration Building E5
Library & Gallery, Albin O. Kuhn D5
Parking Services, 100 Facilities Management Building I10
Recital Hall, 118 Fine Arts Building F4
Retriever Activities Center (RAC) G6
Theatre, 131 Theatre/Academic Services Building F6
Undergraduate Admissions, Ground Floor facing Pond
Albin O. Kuhn Library & Gallery E5
University Center Ballroom, 301 University Center F5

BUILDINGS

Academic IV Building G5
Administration Building G5
Alumni House D3
Biological Sciences Building F5
Central Plant D4
Child Care Center C7
The Commons E6
Engineering Building F4
Facilities Management Building I10
Fine Arts Building F4
Greenhouse D4
Information Technology/Engineering Building (ITE) G4
Library & Gallery, Albin O. Kuhn D5
Mathematics & Psychology Building F5
Meyerhoff Chemistry Building F5
Performing Arts and Humanities Building F4
Physics Building F7
Public Policy Building E7
Recreation House D2
Retriever Activities Center (RAC) G6
ROTC House D2
Satellite Utility Plant C7,8
Sondheim Hall G5
Student Development & Success Center (SDSC) D7
Surge Facility 1 F1
Technology Research Center (TRC) C10
Tech 2 Building C10
Theatre/Academic Services Building F6
True Grit's D7
University Center F5
Warehouse E9

LECTURE HALLS

LH 1 Adjacent to Biological Sciences Bldg F5
LH 2 030 Meyerhoff Chemistry Bldg F5
LH 3 101 Administration Bldg G5
LH 4 003 Academic IV Bldg G5
LH 5 027 Engineering Bldg F4
LH 6 101 Physics Bldg E7
LH 7 104 ITE Bldg G4
LH 8 102 ITE Bldg G4
LH 9 105 Public Policy Bldg E7

STUDENT HOUSING

Chesapeake Hall D7
Erickson Hall D6
Harbor Hall D7
Patapsco Hall D8
Potomac Hall D8
Susquehanna Hall D7
Walker Avenue Apartments C3

Hillside Apartments
Sideling (SDL) I6
Pocomoke (POC) B6
Manokin (MAN) B6
Patuxent (PTX) C6
Elk (ELK) C6
Deep Creek (DPC) C6
Casselman (CAS) C6
Breton (BRE) C6

West Hill Apartments
Severn (SEV) C5
Chester (CHS) C4
Wye (WYE) C4
Magothy (MAG) C4
Tangier (TAN) C4
Choptank (CHO) C4

Terrace Apartments
Nanticoke (NAN) C5
Gunpowder (GUN) C5
Monocacy (MON) C5
Sassafras (SAS) C5
Wicomico (WIC) C6
Antietam (ANT) C6
Chincoteague (CHI) C5
Tuckahoe (TUC) C5

VISITOR PARKING

Administration Drive Garage H5
Commons Drive Garage F7
Walker Avenue Garage D5
Lot 7 D6

LEGEND

- Visitor Parking
- Accessible Parking
- Information Desk/Vehicular Kiosk
- Dining Locations
- ATM
- University Health Services
- MTA and UMBC Shuttle Bus Stop
- UMBC Shuttle Bus Stop Only
- Taxi Pickup Area
- Bike Rack
- Emergency Phone

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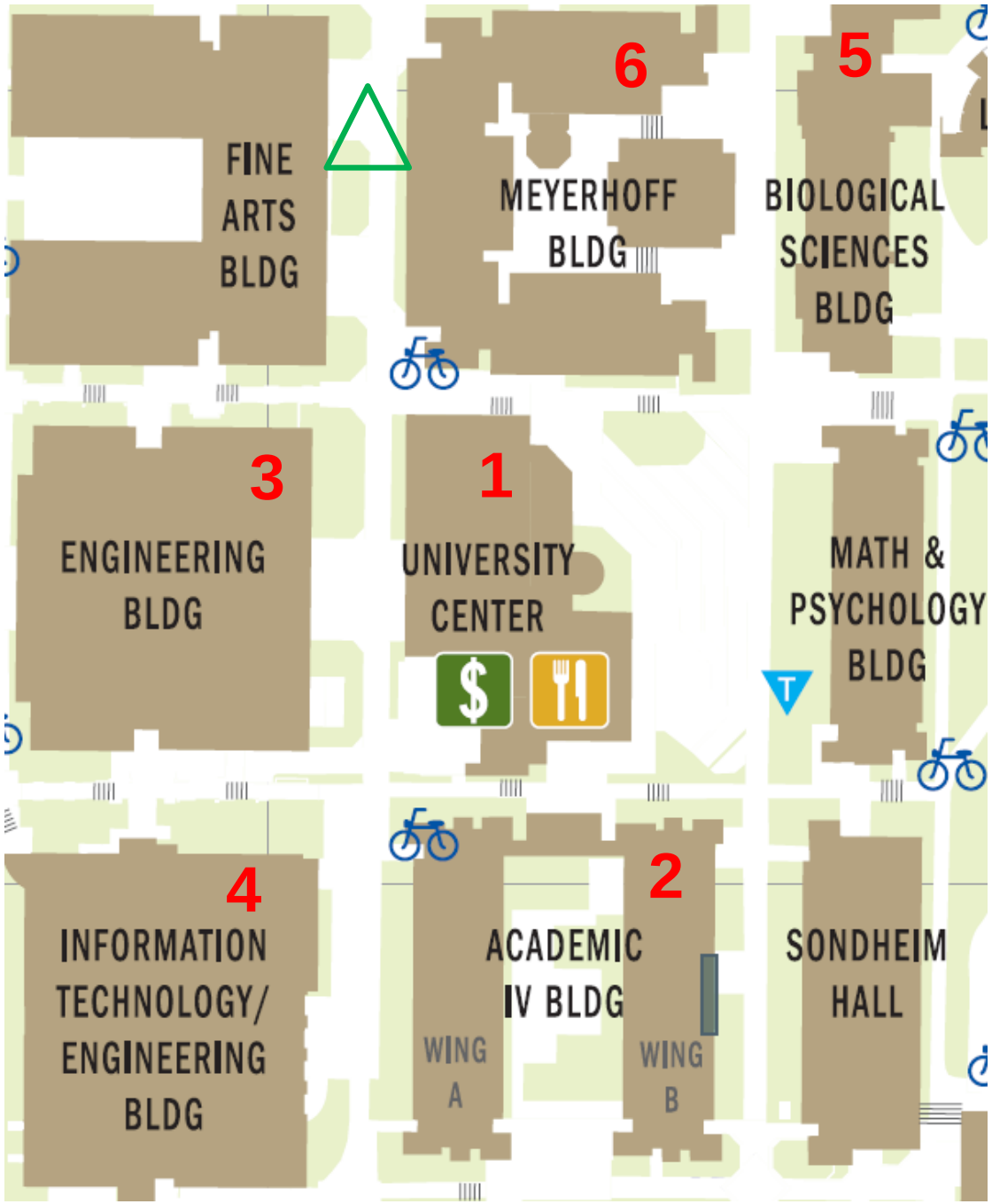
For more information call 410-455-1000

For Campus Police, located at the Central Plant, call 410-455-5555

September 9, 2011
PEDESTRIAN VISITOR STATION CAMPUS PLAN1



General

1. Registration (UC 310)
Dinner Events (UC 312)
Exhibits/Poster Session (UC Ballroom)

Symposium and General Sessions

2. Lecture Hall 4 (LH4)

3. Lecture Hall 5 (LH5)

4. Lecture Hall 7 (LH7)
Lecture Hall 8 (LH8)

5. Biological Sciences 120 (BS 120)

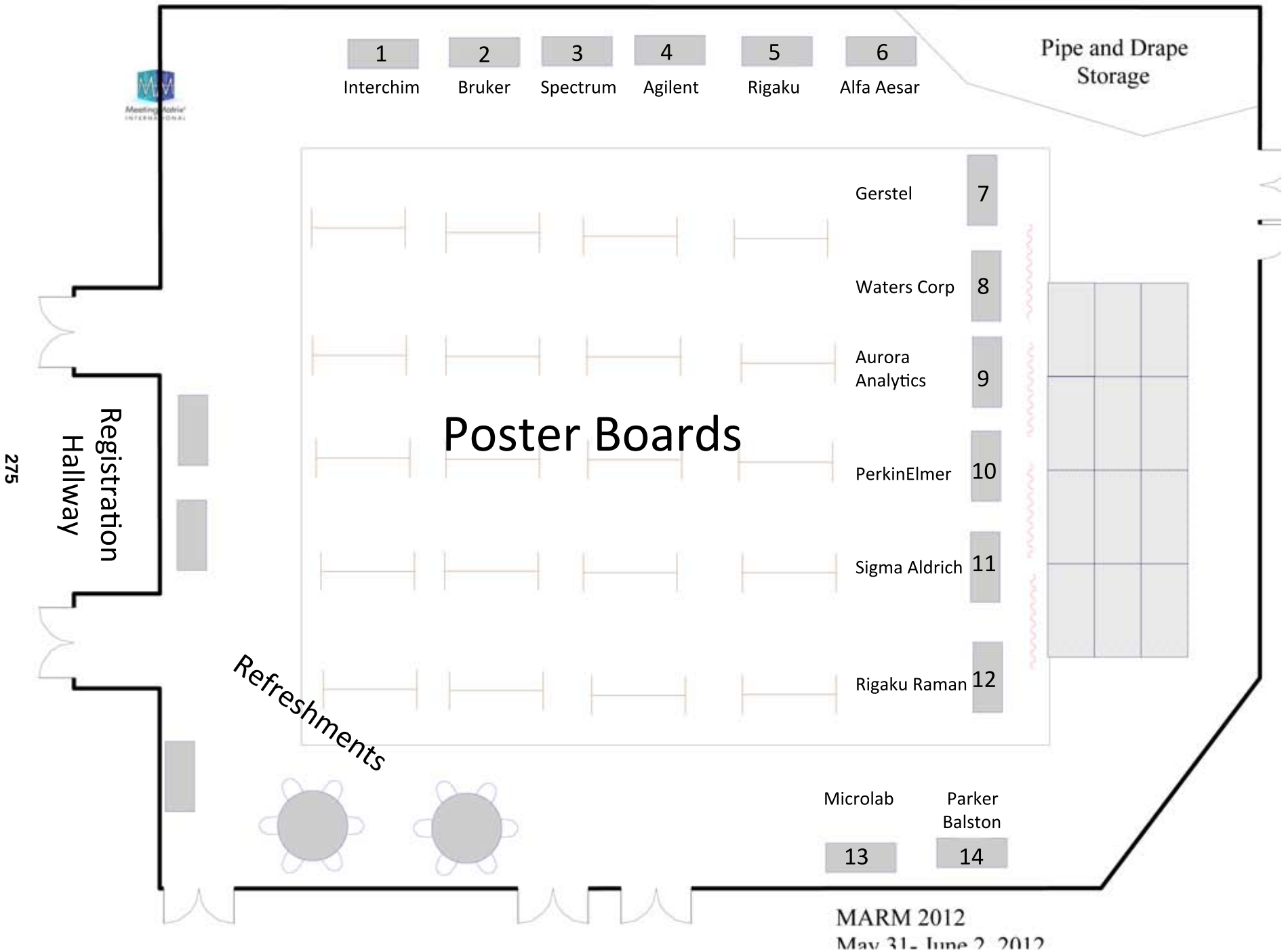
Workshops

1. University Center 115 (UC115)
University Center 220 (UC220)

6. Meyerhoff 120 (MEYR120)
Meyerhoff 272 (MEYR272)
Meyerhoff 256 (MEYR256)

Cookouts/Outdoor Seating

△ Tent


1
Interchim
2
Bruker
3
Spectrum
4
Agilent
5
Rigaku
6
Alfa Aesar
Pipe and Drape Storage
Gerstel
7
Waters Corp
8
Aurora Analytics
9
Poster Boards
PerkinElmer
10
Sigma Aldrich
11
Rigaku Raman
12
Registration Hallway
Refreshments
Microlab
13
Parker Balston
14
MARM 2012
May 31- June 2, 2012

Save the date:

Thursday, May 16th, 2013

The ACS - Philadelphia Section
in conjunction with
The ACS's Middle Atlantic Regional Board
will be hosting the awards ceremony for:

- **Philadelphia Region's Award for Excellence in Pre-College Teaching**
- **Philadelphia Region's Award for Excellence in Undergraduate Education**
- **E. Emmet Reid Award in Chemistry Teaching at Small Colleges in the ACS Mid-Atlantic Region**
- **ACS Division of Chemical Education Middle Atlantic Region Award for Excellence in High School Teaching**
- **E. Ann Nalley Regional Award for Volunteer Service to the American Chemical Society**
- **Chromatography Forum of Delaware Valley Student Award Symposium**

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