Co-hosted by the **University of Delaware** *and the* **Delaware American Chemical Society**

American Chemical Society
49th Middle Atlantic Regional Meeting
VIRTUAL

MARM 2021

Driving Innovation

University of Delaware

ACS Delaware Section

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49th Middle Atlantic Regional Meeting

Welcome to the first *virtual* MARM!

On behalf of the organizing committee, the University of Delaware, and the Delaware Section of the American Chemical Society, we are pleased to welcome you to the 49th Middle Atlantic Regional Meeting, MARM 2021. As the first *virtual* MARM, we're thrilled you are joining us from wherever you are.

The theme of this meeting is "Driving Innovation," originally inspired by Delawareans' love of our license plates and motivated by the creativity of the chemistry community in the Mid-Atlantic region and beyond. Although we would have loved to welcome you in person to the beautiful University of Delaware campus, we are thankful to be able to hold this meeting virtually. We are especially aware of the ingenuity and determination of the scientific community as we continue to battle the coronavirus pandemic. We celebrate the victories of science in the discovery of vaccines, and we celebrate the fortitude of our scientific community as we've continued to do research, collaborate, teach, meet, and move forward despite the unexpected obstacles and tragedies of the pandemic. We hope this meeting will be a celebration of all your hard work and your passion for chemistry. We also hope this meeting will provide opportunities for you to reconnect with old friends, make new contacts, and expand your professional networks.

Our program provides opportunities for deep scientific discussion, casual networking conversations, and valuable workshops. The technical program includes analytical, biological, computational, inorganic, organic, materials, medicinal, physical, and polymer chemistry. Daily plenary lectures, as well as the BMGT-sponsored BILL® Talk and the Carothers Award Lecture, will broaden your perspective and appreciation for science. Workshops focus on career discovery, increasing diversity and inclusion in science, and grant writing. Networking events give opportunities to connect with other attendees, and the virtual platform allows you to connect and chat with other attendees via both text and video platforms. We are especially excited to see you "have a cup of coffee" or "grab lunch" with other attendees, just as you might if you bumped into each other at an in-person meeting.

We are grateful to our generous sponsors and exhibitors for their support of this meeting, and encourage you to connect with them throughout the meeting. We also regcognize the tireless efforts of the organizing committee and all the volunteers who are working hard to make this meeting a success.

Again, welcome to MARM! We are so glad you're here.

Best regards,

Mary P. Watson

Mary P. Watson
2021 MARM General Chair

Welcome to MARM 2021!

As one of the ACS Regional Meetings, MARM 2021 is honorably co-hosted by the University of Delaware and the Delaware ACS. We aim to present the richness of chemistry in the Middle Atlantic and beyond. It is a pity that we won't be able to meet you in person this year, but through the virtual format, MARM 2021 will make the participation of scientific discussions and networking more effortless.

We hope you share your passion for chemistry, connect with people with the same passion, and celebrate your hard work together here. We believe innovation will be inspired by the great work presented in this meeting.

On behalf of the Delaware Section of the American Chemical Society, and the University of Delaware, I would like to acknowledge Mary Watson for serving as the General Chair of MARM 2021, Joel Rosenthal and Nora Radu as the Program Co-Chairs, Martha Hollomon as the Awards Chair, Anthony Tomaine as the Treasurer, Shara Compton and Louise Lawter as Chemagination Chairs, and all the other volunteers for their hard work. This wonderful event wouldn't come true without their dedications and great work.

Hope you enjoy the MARM 2021. We are looking forward to virtually meeting you this summer!

Best regards,

Jing Qu
Chair, ACS Delaware Section

Middle Atlantic Region Local Sections

Central Pennsylvania
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Maryland
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North Jersey
Ocean County
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Princeton
South Jersey
Southeastern Pennsylvania
Susquehanna Valley
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ACS Board of Directors

The following members of the ACS Board of Directors are expected to be at MARM 2021. Join us for the ACS Governance Social on Thursday evening, 6:30–7:00pm, just before the Carothers and Regional Award Ceremony.

H.N. Cheng, President

H. N. Cheng is a Research Chemist at U.S. Department of Agriculture. Previously he worked for many years at Hercules Incorporated, where he held various R&D and managerial positions. He received his BS (summa cum laude) in Chemistry from UCLA and his PhD in physical chemistry from the University of Illinois, Urbana-Champaign. He did his postdoctoral work at Bell Telephone Laboratories in Murray Hill, NJ. He has been a member of the American Chemical Society since 1982.

Tom Connelly Jr., Executive Director & Chief Executive Officer

Thomas M. Connelly, Jr. is the Executive Director and CEO of the American Chemical Society. Dr. Connelly retired from DuPont in December 2014, where he was Executive Vice President, Chief Innovation Officer. At DuPont, Dr. Connelly led businesses and R&D organizations, while based in the U.S., Europe, and Asia. Dr. Connelly graduated with highest honors from Princeton University with degrees in Chemical Engineering and Economics. As a Winston Churchill Scholar, he received his doctorate in chemical engineering from the University of Cambridge. He has served in advisory roles to the U.S. Government and the Republic of Singapore.

Katherine L. Lee, Director, District I

Katherine L. Lee is the Senior Director and Head of Project Planning and Operations in the Inflammation and Immunology Research Unit at Pfizer, Inc. She earned a Bachelor of Science degree, *summa cum laude*, with Distinction in Chemistry, from Yale University in 1991 and her Ph.D. in organic chemistry from the Massachusetts Institute of Technology in 1996. Katherine was a postdoctoral fellow at the University of Texas at Austin before joining Mitotix, Inc. (now Agennix) in 1998. She moved to Wyeth (now Pfizer) in 2000 and joined Pfizer in 2009. She has been a member of the American Chemical Society since 1991.

Teri Quinn Gray, Director, District III

Teri Quinn Gray is Global R&D Operations Leader for DuPont Transportation & Industrial. She is co-chair of the Delaware STEM Council, serves on executive committee of the Delaware Foundation for Science & Math Education and advisory board for Delaware Campaign for Action Now. Teri holds a B.S. in chemistry from Jackson State University in Mississippi and doctorate in analytical chemistry from University of Maryland, College Park. She has been a member of the American Chemical Society since 1989.

Bryan Balazs, Director-At-Large

Bryan Balazs is a recent retiree from Lawrence Livermore National Laboratory where he held numerous positions in research and management. He received his bachelor's degree in chemistry in 1985 from Washington and Lee University, was an ITT-Fulbright Scholar in Germany from 1985 to 1986 at the University of Erlangen-Nuremberg, and received his Ph.D. in chemistry in 1992 from the California Institute of Technology. He has been an active member of the ACS since 1987.

Lee H. Latimer, Director-At-Large

Lee H. Latimer is a Consultant in drug development with LHLatimer Consulting, formerly with Elan Pharmaceuticals. He earned his B.S. degree in chemistry at Tulane University in 1971, and his Ph.D. in organic chemistry from the University of Wisconsin-Madison in 1976. He has been a member of the American Chemical Society since 1972.

Ingrid Montes, Director-At-Large

Ingrid Montes is the Assistant Dean of Graduate Studies and Research Program, University of Puerto Rico, Río Piedras Campus. She earned her Bachelor's degree at the University of Puerto Rico in 1980, and her Ph.D. in 1985. She has been a member of the American Chemical Society since 1980.

Carolyn Ribes, Director-At-Large

Carolyn Ribes is the Business Analytical Leader for Industrial Intermediates & Infrastructure at Dow Chemical. She received her B.S. in Chemistry in 1983 from University at Buffalo, SUNY, and her Ph.D. in Chemistry in 1989 from State University of New York at Buffalo. She joined Dow in 1989 and has worked in Louisiana, Texas, and Argentina and is currently located in Terneuzen, Netherlands. She has been a member of the American Chemical Society since 1982.

MARM 2021 Organizing Committee

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Program Chairs	**Nora Radu, DuPont** **Joel Rosenthal, University of Delaware**
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Office of Regional Meetings	**Shantesse Dortch, ACS**

MARM 2021 Volunteers

This regional meeting would not have been possible without the invaluable efforts of the volunteers – session chairs and moderators, workshop leaders, career panelists, event organizers, networking hosts and everyone else who lent a helping hand along the way.

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This regional meeting would not occur without the generous financial contributions from individuals, corporations, universities, and ACS divisions listed on the following pages. Thank you to all our sponsors!

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BILL TALK

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Dr. Barbara Morgan
Sr. Global Business Director Pharma Sector
Lubrizol Life Science – Health

The Transition from Chemist to Business Director: Leadership Lessons
Friday, June 9, 2021, 6:00 – 8:30 PM EDT
[insert link to event]

This inspiring BILL Talk provides perspectives on career opportunities on the business and corporate side of chemistry.
Networking reception immediately following:
Career Opportunities on the Corporate Side of Chemistry

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Exhibitors at MARM 2021

Adesis, a chemistry contract research organization, solves clients' complex chemistry problems and accelerates their research and manufacturing goals. Based 100% in Delaware, the U.S., the combination of state-of-the-art laboratories (72,000 sq. ft.), responsive project teams and highly qualified and experienced chemists (over 80% PhD chemists) makes Adesis the trusted choice for pharma, biotech and specialty chemical industries. The chemistry team delivers deep expertise in discovery, medicinal, analytical and process chemistry.

Delaware Prosperity Partnership (DPP) leads Delaware's economic development efforts to attract, grow and retain businesses; to build a stronger entrepreneurial and innovation ecosystem; and to support private employers in identifying, recruiting and developing talent. The DPP Innovation team works to advance a culture of innovation in Delaware, working with innovators and startups to spotlight and celebrate successes and connect them with the resources they need to succeed. DPP and its partnerships throughout Delaware support and advance the missions of companies of all sizes and sectors. For more information, visit choosedelaware.com.

PharmaBlock established its business by rationally designed building blocks and has expanded into CDMO space in recent years with well-established manufacturing facilities and GMP compliance system. PharmaBlock is a leading provider of chemical products and services throughout pharmaceutical R&D and commercialization, and strives to bring greener, safer, and cost-efficient solutions to pharmaceutical industry with innovative chemistry and technologies.

TA Instruments provides innovative material characterization instruments that are widely used for research, analytical, and quality control in the evaluation of physical properties. We are the world's leading supplier of thermal analysis, rheology, and microcalorimetry instruments, and our product areas have expanded to include thermal conductivity & diffusivity, dilatometry, rubber testing, and dynamic mechanical characterization. With direct operations in 24 countries, we are uniquely positioned to support all of our customers with an extensive local support network. We are committed to providing high reliability and high-performance products to meet the needs of our customers.

Sharing a customer-focused, workflow-enhanced vision, Advion X Interchim offers a single source for sample preparation, high-performance integrated systems for purification and mass spectrometry, novel media, and consumables solutions. Advion X Interchim led the market by being the first to develop integrated Flash-MS by seamlessly coupling Advion's expression® CMS with Interchim's puriFlash® chromatography systems. Visit advion.com and flash-chromatography.com to learn more.

Agilent is a global leader in life science, diagnostics and analytical laboratory technologies. Leveraging more than 50 years of expertise, we create instruments, software, services and solutions that provide trusted answers to our customers' most critical questions. We are passionate about helping them solve their most ambitious scientific challenges, increase laboratory performance, and advance the quality of life.

Biotage is a Global Impact Tech Company committed to solving society's problems. We offer workflow solutions and products to customers in drug discovery and development, analytical testing and water and environmental testing.

Given the wealth of chemical industry talent and opportunities around green chemistry and renewable products, DESCA was formed in 2010 as the Delaware Sustainable Chemistry Alliance—a non- profit, public-private partnership with the support of Ashland Chemicals and Governor Jack Markell. DESCA's mission was to enable Delaware to become a globally recognized center of excellence in Sustainable Chemistry by building upon its strong existing foundation of chemistry and materials science within the region. Between 2010 and 2019 DESCA began to drive its mission and prove its premise through the Innovation 2 Invoice (I2I) Programming. DESCA gradually evolved along the way as it uncovered regional needs – each time testing and proving a premise and fulfilling a gap.

Academic Program Exhibitors at MARM 2021

The University of Delaware is situated less than an hour from Philadelphia, PA, and is within easy driving distance of New York City and Washington, D.C. Our graduate programs in Chemistry and Biochemistry, Chemical Engineering, and Materials Science combine a rich historic legacy with a strong commitment to education and innovation. Students at UD benefit from a highly supportive and collaborative environment that supports a wide array of cutting-edge Core Facilities, and dynamic initiatives focused on driving advancements across all areas of chemistry, biochemistry and related fields.

The University of Pennsylvania's Master of Chemical Sciences prepares you for diverse career and academic possibilities in the chemistry fields. We feature PhD-level courses, individualized advising, six chemistry concentrations, and Ivy League facilities and resources. Complete your research with local and national industry partners or at Penn's stellar facilities. www.upenn.edu/chemistry

The Department of Chemistry and Biochemistry at UMBC offers a world-class Ph.D. program in Chemistry.. Faculty research interests consist of traditional and emerging areas of chemistry and biochemistry and include inorganic and organic synthesis, drug design and delivery, quantum dot fabrication, nanomaterial reactivity, fluorescence and photoacoustic imaging probes and sensors, single-molecule spectroscopy, photochemistry and ultrafast spectroscopy, bioinorganic chemistry, computational chemistry, structural biology, cell biochemistry, microfluidics, 3D bio-printing, and solar energy conversion. We are large enough to have cutting-edge internationally recognized research programs as well as outstanding facilities, yet we are sufficiently small so that faculty and students know each other well.

Temple University's Department of Chemistry, within the College of Science and Technology, offers a wide range of educational and research opportunities, from traditional disciplines in chemistry to cross-cutting interdisciplinary programs. The Department offers PhD and MS degree programs in Analytical, Biochemistry, Inorganic, Organic, Physical, and Theoretical Chemistry, as well as a Professional Science Master's (PSM) in Forensic Chemistry.

The Graduate Program in Chemistry at Villanova is designed to accommodate both the working professional and the full-time student. Graduate classes are taught by both full-time Villanova faculty and adjunct faculty from local industries who are expert in their field. The Master's program provides an excellent classroom and research experience to the full-time student who is looking for extensive research training. Students complete a thesis project under the direction of a research faculty member in the Chemistry Department.

General Meeting Information for MARM 2021

Registration

You may register on-line at any point during the meeting at this link: https://cvent.me/4x0oxl. We will do our best to upload new registrations into the virtual platform, but please allow a few hours delay between your registration and receiving your log-in credentials via email from no-reply@showcare.com.

Virtual Platform

MARM 2021 will be held virtually with Showcare as our virtual platform provider. Once registered, you will receive your log-in credentials from no-reply@showcare.com. Please log in to the MARM 2021 platform before the meeting to explore the virtual event platform, complete your profile set-up, and start building your network with connections. You can also access the complete meeting schedule and set a personalized schedule in the platform. It is recommended that you be hardwired or at least have a strong reliable internet connection to view the conference. It is also recommended that you disconnect from any VPN, as this can block your access to the platform. Finally, please note that the Virtual Platform only supports Chrome, Firefox, or Safari. Microsoft Edge is not supported. All times are EDT.

In addition to attending the technical sessions, workshops, and networking events, we encourage you to connect to other attendees in the Virtual Platform. In "Attendee Connections," you can send invitations to other attendees to connect. Once connected, you can chat via text or set up a live video meeting with any attendees (up to 16 people) at any time. Use this feature to enjoy a coffee break, meal, or just a quick conversation with other attendees.

Program

Symposia, workshops, and plenary sessions are listed on subsequent pages. Each day features a plenary lecture at 1:00pm, as well as excellent technical content and knowledge-building workshops. The undergraduate poster session (Wed, June 9, 2:30–4:30pm) and general poster session (Thurs, June 10, 5:30–7:30pm) will also be highlights.

All components of MARM 2021 will be available in the virtual platform from the Home Lobby.

Networking Events

We hope MARM 2021 will allow you to connect with old friends and make new professional contacts! There will be a Topical Networking Event on Wednesday, June 9, 7:00–8:30pm, where attendees can visit breakout rooms of their choosing (topics are listed on subsequent pages). On Thursday, June 10, meet members of the ACS Board of Directors at the ACS Governance Social (6:30–7:00pm), before celebrating the achievements of the Carothers Lecturer and Regional Awardees at the Awards Symposium. On Friday, June 11, join us for a fast-paced Speed Networking Event from 5:45–7:00pm.

Plenary Lectures are Wed, Thurs, and Fri at 1:00pm.

MARM 2021 Schedule Overview

All components of MARM 2021 will be available in the virtual platform from the Home Lobby.

Wednesday, June 9, 2021	Time (EDT)
High-Throughput Experimentation to Advance Discoveries in Academia and Industry	8:30–10:25 am
Innovations in Chemistry Education	8:30–11:45 am
Innovations in Inorganic and Organometallic Chemistry	8:30–11:40 am
Innovations in Physical Chemistry	8:30–11:45 am
Workshop: Career Panel: Choosing Your Own Path	12:00–12:50 pm
Plenary: Donna Huryn	**1:00–2:00 pm**
Undergraduate Poster Sessions	2:30–4:30 pm
BILL Talk: Barbara Morgan	**6:00–6:35 pm**
BMGT: Bench to Business Discussion	6:35–8:30 pm
Topical Networking Sessions	7:00–8:30 pm

Thursday, June 10, 2021	Time (EDT)
Advances in Chemistry in Pharmaceutical and Agriculture Industry	8:30–11:45 am
Empowering Chemists with Disabilities	8:30–10:50 am
Inorganic and Organometallic Young Investigator Symposium	8:30–11:45 am
Protein Quality Control	8:30–10:20 am
Spectroscopy: From Molecules to Macrostructures (Part 1)	8:30–11:45 am
Workshop: Careers in Industrial Chemistry: Identifying Your Role in the Industrial Value Chain (ACS Career Pathway Workshop)	12:00–12:50 pm
Workshop: The ACS Bridge Program: Enhancing diversity, equity, inclusion, and respect in graduate education in the chemical sciences	12:00–12:50 pm
Workshop: Funding for STEM Graduate Studies: The National Science Foundation (NSF) Graduate Research Fellowship Program (GRFP)	12:00–12:50 pm
Plenary: Dan Nocera	**1:00–2:00 pm**
Energy Catalysis	2:00–5:15 pm

Thursday, June 10, 2021 (continued)	Time (EDT)
Biophysical Chemistry	2:00–4:55 pm
Frontiers in New Methods for Organic Synthesis	2:00–5:15 pm
Innovations in Chemical Biology	2:00–5:15 pm
Spectroscopy: From Molecules to Macrostructures (Part 2)	2:00–4:15 pm
General Poster Sessions	5:30–7:30 pm
ACS Governance Social	6:30–7:00 pm
Carothers & Regional Award Symposium	**7:00–8:30 pm**

Friday, June 11, 2021	Time (EDT)
Alternative Grading in the Chemistry Curriculum	8:30–11:45 am
Frontiers in Chemical Biology	8:30–11:40 am
Innovations in Organic Chemistry	8:30–11:45 am
Nanoparticles: Characterization & Applications (Part 1)	8:30–11:45 am
Porous Materials	8:30–11:45 am
Workshop: Opportunities for Chemists in the Federal Government (ACS Career Pathway Workshop)	12:00–12:50 pm
Workshop: Leveraging our diversity to create equity, inclusion, and respect in our chemistry communities	12:00–12:50 pm
Plenary: LaShanda Korley	**1:00–2:00 pm**
Diversity in Polymer Chemistry and Engineering	2:00–5:15 pm
Dimensionality in Nanoscale Materials	2:00–5:15 pm
Excellence in Organic Chemistry and Chemical Biology Research with Undergraduates	2:00–5:15 pm
Nanoparticles: Characterization & Applications (Part 2)	2:00–5:15 pm

Speed Networking	5:45–7:00 pm
Saturday, June 12, 2021	**Time (EDT)**
Chemagination	1:00–4:00 pm
Workshop: Climate Science Concepts Fit Your Classroom	1:00–3:00 pm

Awards

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

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

2020 Awardee

Dr. Jean M. Mihelcic

Conestoga High School

2021 Awardee

Laura Trout

Lancaster Country Day School

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

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

2020 Awardee

Enju Wang

St. John's University

2021 Awardee

Dr. Marsha R. Baar

Muhlenberg College

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

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

2020 Awardee

Brian Gibbney

Brooklyn College

2021 Awardee

Patricia Redden

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

To recognize individuals and/or institutions that have advanced diversity in the chemical sciences and significantly stimulated or fostered activities that promote inclusiveness within the region. Sponsored by the Committee on Minority Affairs of the American Chemical Society

2020 Awardee

Bob Hoyte

SUNY-Old Westbury

WE STAND AGAINST HATE

Enhancing Understanding and Compassion at Brooklyn College

2021 Awardee

Brooklyn College, Department of Chemistry

2020 Wallace H. Carothers Award

To recognize outstanding contributions and advances in industrial applications of chemistry.

Dr. Allison Campbell

Former ACS President & Associate Laboratory Director at Pacific Northwest National Laboratory

Lessons Learned from Nature: From Biomineralization to Biomaterials

In 2020, Dr. Allison Campbell retired from the Associate Laboratory Director for Earth and Biological Sciences at PNNL. In this role, she set the vision and strategy for PNNL's research in support of the U.S. Department of Energy's Office of Biological and Environmental Research and National Institutes of Health. Her organization was comprised of more than 530 staff.

Prior, she served for more than 10 years as director of the Environmental Molecular Sciences Laboratory (EMSL), a DOE Office of Science User Facility, located at PNNL. EMSL provides experimental and computational resources for discovery and technological innovation in the environmental molecular sciences to support the needs of DOE and the nation. More than 700 scientists from around the world access EMSL's capabilities each year. Campbell revitalized EMSL's scientific resources with the16-month implementation of a strategy to build and/or purchase 32 instruments with $60 million in Recovery Act funds. Also, during her tenure, EMSL expanded with 4,000-square-foot raised floor for computing, an office wing to house 100 staff, a $7 million Quiet Wing for advanced microscopy, and a recently opened RadEMSL.

Dr. Campbell is nationally recognized for her contributions in chemistry through her research in the field of biomaterials and biomineralization. She is credited with co-inventing a bio-inspired process to "grow" a bioactive calcium phosphate layer, from the molecular level, onto the surfaces of artificial joint implants (total hip and knee) to extend implant life and reduce rejection. This lead to a joint effort with the US Army's Medical Research and Materiel Command (USAMRMC) to develop bioactive anti-microbial coatings for external fixation pins. The technology was licensed to Bactrin, Inc. (http://xtantmedical.com/) in 2004. She also co-invented "radiogel," a novel polymeric hydrogel that allows for the targeted delivery of radiotherapy to solid tumors. This technology was licensed to Vivos (https://www.radiogel.com/).

Her research led to securing five U.S. patents, an R&D 100 award, a Federal Laboratory Consortium Award for Technology Transfer, an ACS Regional Innovation Award and over 30 peer reviewed publications including *Science* and the *Proceedings of the National Academy of Science*.

Dr. Campbell received her Ph.D. in Physical Chemistry from State University of New York at Buffalo. She is a Fellow of the American Association for the Advancement of Science, a member of the Washington Academy of Sciences and a member of the National Academies Chemical Sciences Roundtable.

Workshops

Wednesday, June 9, 2021

Career Panel: Choosing Your Own Path 12:00–12:50 pm

Moderators: Mary P. Watson and Joel Rosenthal

As a student or postdoc, it can be hard to know that various career paths really look like. This career panel will pull back the curtain on multiple career trajectories with the panelists discussing scientific, professional, and personal accomplishments and challenges that they have faced along the way. Participants will come away with a deeper understanding of what various careers entail and how to maximize your success in getting and thriving in their career choice.

Thursday, June 10, 2021

Careers in Industrial Chemistry: Identifying Your Role in the Industrial Value Chain (ACS Career Pathway Workshop) 12:00–12:50 pm

Moderator: Moji Bonakdar

This workshop offers an overview of the job market and job types for industrial chemistry. Participants will also learn how the industrial value chain can be used as a tool to help refine your job search in alignment with your strengths and values. The course will also help uncover key components of job descriptions and participants will learn how to break down job descriptions to best match job opportunities with their experience, strengths, and values.

The ACS Bridge Program: Enhancing diversity, equity, inclusion, and respect in graduate education in the chemical sciences 12:00–12:50pm

Moderator: Joerg Schlatterer

The ACS Bridge Program is an effort to increase the number of doctoral degrees in the chemical sciences awarded to students from underrepresented groups including Black, Latinx, and Indigenous students, to match the fraction of bachelor's degrees in the chemical sciences granted to these groups. Since 2019, more than 30

students have been placed in bridge programs leading to a doctoral program or placed directly in a doctoral program. Successful bridge programs share key components and exist within a supportive institutional context. These contextual and programmatic components build on one another to provide students with a complete educational experience, from admissions and induction to research and mentoring. The ACS Bridge Program has partnered with over 29 graduate programs to place students who did not get accepted through the traditional graduate admissions process. The ACS Bridge program collaborates more than 30 organizations to achieve collective impact in physical science graduate education as the NSF INDLUDES Alliance: Inclusive Graduate Education Network.

Funding for STEM Graduate Studies: The National Science Foundation (NSF) Graduate Research Fellowship Program (GRFP) 12:00–12:50 pm

Moderators: Chris Hill, Narcrishna Norman, LaNysha Adams

The Graduate Research Fellowship Program (GRFP) at the National Science Foundation (NSF) provides up to three years of funding to individuals pursuing full-time research-based master's and doctoral degrees who have demonstrated the potential for significant achievements in science, technology, engineering, and mathematics (STEM) or STEM education. NSF Program Officers will provide an overview and description of GRFP, including information on eligibility (and ineligibility), the application package, and review criteria. There will be an opportunity to ask questions about the application process.

Friday, June 11, 2021

Opportunities for Chemists in the Federal Government (ACS Career Pathway Workshop) 12:00–12:50 pm

Moderator: Allison Aldridge

An overview of the demographics of employment for the federal government. Participants will also learn about the General Schedule (GS) as well as the three types of positions in the federal government. The course will also determine federal coding for chemists and chemical engineers as well provide data about employment by geography, discipline, department, and agency to help participants match job opportunities with their experience, strengths, and values.

Leveraging our diversity to create equity, inclusion, and respect in our chemistry communities 12:00–12:50 pm

Moderator: Benny Chan

Join this open discussion of how we can make our chemistry community more diverse, equitable, and inclusive, with a specific focus on steps we can take in the Mid-Atlantic region.

Saturday, June 12, 2021

Climate Science Concepts Fit Your Classroom 1:00–3:00 pm

Moderators: Bassam Shakhashiri, Jerry Bell

This workshop is designed for instructors at the middle school, high school, and college levels, including teaching assistants. It is also suitable for people doing public engagement and outreach.

The Earth's climate is changing, and we are responsible.

It is important to understand the changes—how our activities cause them, and the responsibility each of us has to consider ways we might act to help lessen the disruption. This understanding can start with your students, in your classroom. Climate disruption and basic climate science are complicated but based on fundamental concepts from our more familiar sciences. You can use climate science concepts as a context for the topics already in your courses. You can use the concepts in your curriculum as a context for climate science topics. The examples chosen to illustrate this approach for this on-line workshop include the classroom topics of density,

buoyancy, acid-base chemistry, and precipitation, partnered with climate concepts of global warming, sea level rise, ocean acidification, and increasing anthropogenic atmospheric carbon dioxide. These examples are developed by analysis of demonstrations adapted from hands-on activities included in the Climate Science Workbook available at the www.scifun.org website. The workshop will also explore how incorporating climate science in your classroom extends to community effects, and to your vital role as an exemplar empowered by understanding.

Networking Sessions

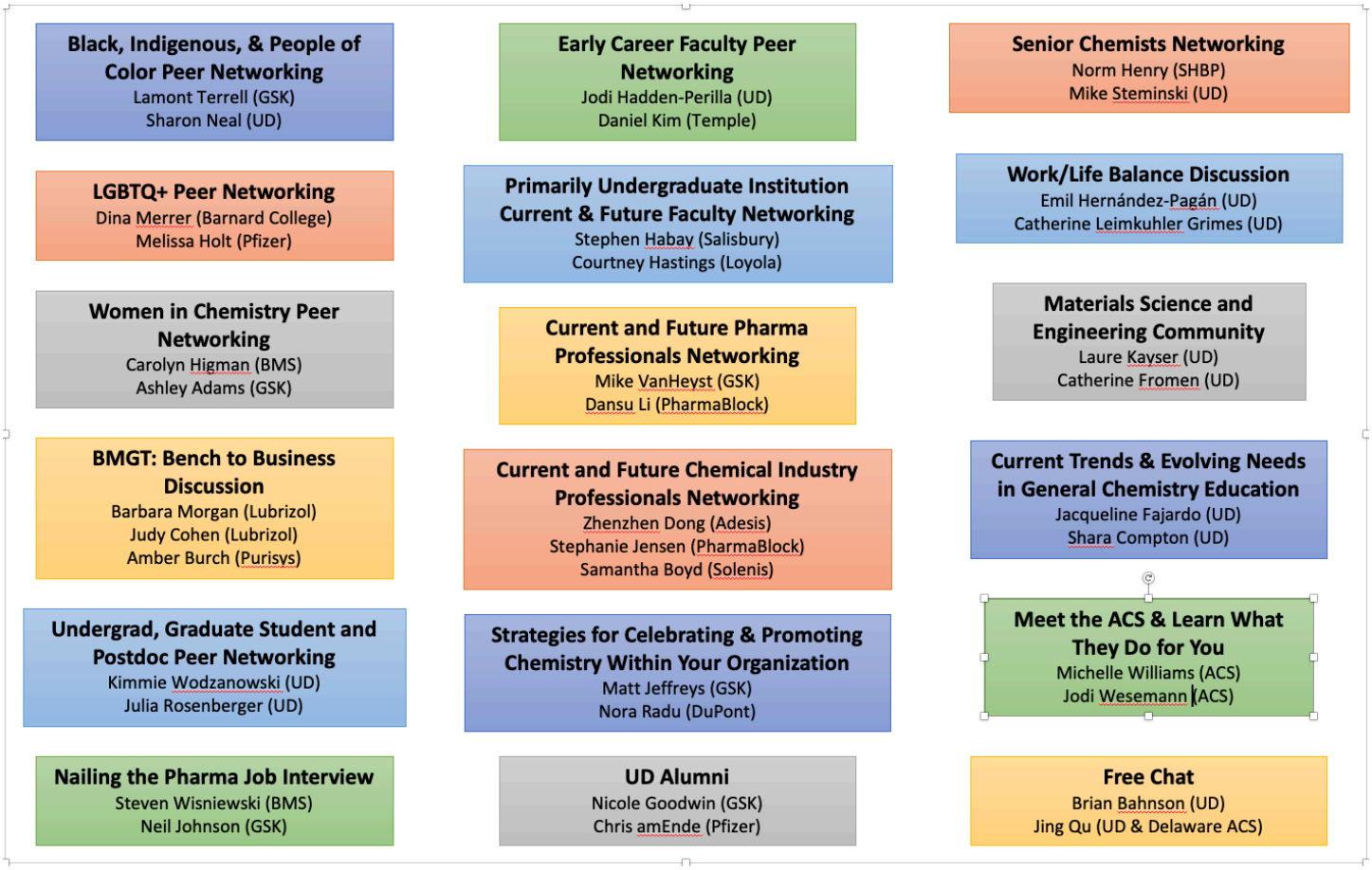
Wednesday, June 9, 2021

BMGT: Bench to Business Discussion 6:40–8:30pm

Connect with Barbara Morgan, representatives from the ACS Division of Business Development and Management, and others on the business side of chemistry at this networking event.

Topical Networking Sessions 7:00–8:30 pm

Connect with chemists and biochemists in breakout rooms focused on a variety of topics. Feel free to visit multiple rooms throughout the evening.



Thursday, June 10, 2021

ACS Governance Social 6:30–7:00 pm

Come meet members of the ACS Board of Directors at this networking event.

Friday, June 11, 2021

Speed Networking 5:45–7:00 pm

Expand your nework in this fast-paced and fun networking event.

MARM 2021
Chemagination Contest

"Chemagination" is a contest in which 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."* The article is written to fit in one of four categories (Alternative Energy, Environment, Medicine/Health, or New Materials). 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 2046, looking back at innovations that have occurred since 2021.

The Regional Chemagination Competition will take place on Saturday, June 12, 2021, via Zoom.

First place category winners from Local ACS section competitions are eligible to participate. If a first place winner cannot participate for any reason, sections can elect to send an alternate team. If your section did not hold a local competition, interested students could participate directly at the regional level (contact the Chemagination coordinators for more details).

Contest coordinators: Louise Lawter, Councilor, Princeton ACS Section (louise.lawter@gmail.com) and Shara Compton, University of Delaware (scompton@udel.edu). Event sponsored by the MARM Board.

MARM 2021

Program & Abstracts

MARM 2021 Program

All components of MARM 2021 will be available in the virtual platform from the Home Lobby.

Wednesday, June 9, 2021 – Morning

High-Throughput Experimentation to Advance Discoveries in Academia and Industry

Virtual Room
Financially supported by GlaxoSmithKline
A. Kelly, *Organizer, Presiding*

8:30 1. High-throughput chemistry: An asset to the modern academic chemist. **M.C. Nicastri**

8:50 2. HTE in medicinal chemistry. **S. Dreher**

9:10 3. Bigger isn't always better: Efficiency gains through smaller reactions in Discovery High-Throughput Chemistry at GSK. **N.C. Goodwin**

9:30 Intermission.

9:45 4. Development of the High Throughput Experimentation (HTE) core facility at the University of Delaware: Design, implementation, applications, and innovations. **D.A. Watson**

10:05 5. Enabling medicinal chemistry through high-throughput experimentation. **S. Berritt**

Innovations in Chemistry Education

Virtual Room
S. A. Habay, *Organizer*
S. Compton, *Organizer, Presiding*

8:30 6. Multiple ways to virtually engage students in chemistry labs. **A.S. Smeltzer Schwab**

8:50 7. PubChem and its application for cheminformatics education. **S. Kim**, E. Bolton

9:10 8. Secondary chemistry teaching: Do you know the facts?. T.M. Chambers, **J. Breakall**, **E.C. Gravely**, **W. Hunter**, **J.B. Nielson**, E.J. Yezierski

9:30 9. Changing the sequence kinetics material for general chemistry: Introducing mechanisms first to help students develop a conceptual understanding of reactions. **C.R. Pulliam**, **D. Rieck**

9:50 Intermission.

10:05 10. Cookie challenge: A unique way to encourage office visits. **D.B. King**

10:25 11. Toward equitable assessment of English Language Learners in chemistry: Identifying helpful features in assessment items. **E. Lee**

10:45 12. Teaching single crystal x-ray crystallography in the undergraduate classroom with common household chemicals. **A. Beauparlant**, **C.T. Eagle**, R. Mohseni

11:05 13. Video introduction to single crystal x-ray crystallography starring pyrite (fool's gold). **A. Beauparlant**, C.T. Eagle

11:25 14. Efficiently visualizing implicit hydrogens with the prime method. **D.L. Silverio**, A. Sam, M. Mistretta, S. Buzzolani

Innovations in Inorganic and Organometallic Chemistry

Virtual Room
W. Farrell, *Organizer, Presiding*

8:30 15. Activity studies of pentamethylcyclopentadienyl chromium complexes in N_2 activation. **F. Ahmadi Darani**, K.H. Theopold

8:50 16. Optical properties of cesium bismuth bromide perovskites. **M.N. Tran**, I. Cleveland, E.S. Aydil

9:10 17. Palladium biladiene complexes bearing alkynyl-aryl groups for sensitization of $^1O_2$ and photodynamic therapy. **A. Rice**

9:30 18. High near-infrared photoluminescence quantum yield in Yb-doped cesium lead halide perovskites. **I. Cleveland**, M.N. Tran, E.S. Aydil

9:50 Intermission.

10:00 19. Improvement of electron transport in cathodes via integration of nanostructured carbons with layered oxides for high power Li-ion batteries. **T. Averianov**, E. Pomerantseva

10:20 20. Improving electrochemical behavior of layered oxides through the intercalation and heat treatment of carbon precursors for next generation cathodes. **R. Andris**, E. Pomerantseva

10:40 21. Why is the product of the reaction (first done by Dr Frankenstein) of green vitriol with the lye of blood one of the ingredients in the table salt that I brought at Wegman's last month. **S.A. Koch**

11:00 22. Bifunctional nickel and copper electrocatalysts for CO_2 reduction and the oxygen evolution reaction. **H. Pan**, C. Barile

11:20 23. Reactivity of zinc oxide clusters supported on mesoporous silica sieve (SBA-15) towards thiophene hydrodesulfurization. A. Chakradhar, **C. Wagner**, R.T. Koodali, B. Selvaratnam

Innovations in Physical Chemistry

Virtual Room
A. V. Teplyakov, *Organizer, Presiding*

8:30 24. Unveiling the genetic fragility of HIV-1 through deep learning. **J.S. Rey**, W. Li, H. Beatson, C. Lantz, A. Bryer, A.N. Engelman, J.R. Perilla

8:50 25. Combining time-resolved spectroscopy and computer simulations to reexamine our picture of bimolecular electron transfer. **C. Rumble**, E. Vauthey

9:10 26. Understanding the charge transfer mechanism in protic ionic liquids. **C. Arntsen**

9:30 27. Fabrication of thermoresponsive bilayer hydrogels through vat photopolymerization additive manufacturing. **F. Klincewicz**, J. Thomas, C.B. Thompson, S. Alfieri, L. Korley

9:50 Intermission.

10:05 28. Withdrawn

10:25 29. Enhanced light scattering and absorption by soot aerosols with different coating distributions. **E. Demidov**, A. Khalizov

10:45 30. Mercury cycle: Oxidation, deposition, reduction and diffusion in the arctic. **A. Asaduzzaman**

11:05 31. Atomic-resolution structure of CA_{CTD}-SP1 crystalline arrays in complex with maturation inhibitors by solid state MAS NMR. **S. Sarkar**, K. Zadrozny, R. Zadorozhnyi, R. Russell, C. Quinn, C. Xu, C. Wild, T.J. Nitz, J.R. Perilla, E. Freed, B. Ganser-Pornillos, O. Pornillos, A.M. Gronenborn, T.E. Polenova

11:25 32. Atomic-resolution structures of protein assemblies by integrating magic-angle-spinning NMR distance restraints and low-to-medium resolution cryo-EM density maps. **R.W. Russell**, C. Zhang, C. Guo, M. Lu, C. Quinn, A.M. Gronenborn, T.E. Polenova

Wednesday, June 9, 2021 – Afternoon

Workshop: Career Panel: Choosing Your Own Path

Virtual Room
Moderators: M. P. Watson and J. Rosenthal
12:00 – 12:50

Plenary: Donna Huryn

Virtual Room
Financially supported by Amgen
M. P. Watson, *Organizer, Presiding*

1:00 Introductory Remarks.

1:05 33. Academic drug discovery: Playing to the strengths to address challenging targets and unmet medical needs. **D.M. Huryn**

1:50 Discussion.

Undergraduate Poster Session: Chemical Biology

Virtual Room
Financially supported by J-Star Research
J. Fox, *Organizer*
2:30 - 4:30

34. Adsorptive removal of hair dye BB99 from solution using agricultural waste. **G. Mascagni**, M. Nassar, S.A. Shahrear, A. Ulay, A.E. Navarro

35. Optimization of drug-like quinoline based pharmacophore for irreversible inhibition of Nek2 kinase. **L.K. Hauter**, A.I. Bhuiyan, R. Musayev, C. Sweeney, A. Dickson, S. Tabassum, D. Hernandez, A.J. Finkelstein, D. Dana, T.T. Talele, T.K. Das, S.K. Pathak

36. Synthesis of isatin-thiazolidine-2-thione hybrids for acetylcholinesterase inhibition. **S. Davis**, T.J. Eckroat

37. How do lipids bind to the vanilloid site of TRPV1? Insights from molecular docking. **A. Wilson**, V. Carnevale, E. Gianti

38. Thermodynamic measurements of the oxidation-reduction (Fe3+/Fe2+) reactions of heme-fluoride complexes of hemoglobin and myoglobin: Insights into oxygen binding. **K.G. Flanders**, S.M. Klumpp, J. Cerda

39. Synthesis of m-DAP crosslinked muramyl dimers. **J.R. Ramsey**, S. Mashayekh, C.L. Grimes

40. Importance of MAS-R in inflammation, inflammatory disease, and COVID-19 therapeutics. **Z. Sessions**

41. Using bioinformatic approaches to investigate neisseria meningitidis serogroup W enzyme. **M. Balogun**, N. Johnson, P.C. McCarthy

42. Optimizing conditions to maximize algae growth for biodiesel production. **W.T. Jacoby**, D.D. Zhogina, L.H. Saggese, P. Ananev, S. Ross

43. Identifying small organic molecules that induce an alternative structure in precursor miRNA-92b. **S. Hurwitz**, C.M. Connelly

44. Optimization and characterization of novel formulations for hydrophilic biological drug encapsulation. A. Sanders, J.T. Zangaro, N.K. Webber, S. Ricci, H. Work, **A. Rajan**, K. Casey, B. Carone, N.V. Nucci

45. Green chemistry/bioremediation: Converting SmFixL from an oxygen sensor into a dye-decolorizing peroxidase. **S. Pogash**, M. Reynolds, D. Barry

46. Encapsulation in reverse micelles reveals the thermodynamic impacts of confinement versus interfacial interactions in the unfolding of myoglobin. **C. Stackhouse**, **L. Staman**, **C. Mejia**, N.V. Nucci

47. Fatty Acid Amide Hydrolase (FAAH) inhibitors designed for reduced permeability Bailey Mims, Julianna Young, So Jung Kim, Grace Roe, Dr. Lazenka, Dr. Fulp*. **B.J. Mims**, J. Young, S. Kim, G. Roe, A. Fulp, M. Lazenka

48. Catalysis by sol-gel encapsulated enzymes: Hb/Mb and H_2O_2 dismutation. **N. Shohet**, J. Haidery, H. Ariel, J. Ramos, U. Samuni

49. Investigating the effects of DNA base substitution on DNA structure and dynamics with high-affinity Fis-DNA complex. S. Hancock, **H.E. Little**

50. Separating the effects of confinement and interfacial interactions for the model protein cytochrome c using reverse micelle encapsulation. **B. Berry-White**, **K. Fennimore**, N.V. Nucci

51. Overexpression and purification of alexphander gp94: A predicted MerR-like transcriptional regulator. **e. Chong Qui**, S. Hancock

52. Harnessing green chemistry in the search for agricultural sustainability. **A.B. Saul**, U. Rao

53. In vitro effect of Bee Propolis on Human Tongue Cancer cell death. **E. Asani**

54. Elimination of organosulfur compounds from model fuels with biological wastes: Tackling the acid rain. **A.O. Efunnuga**, A.E. Navarro

55. Uptake of Co(II) ions from aqueous solutions by low-cost biopolymers and their hybrid. **S. Cime**, M. Nassar, A.E. Navarro

56. Effects of annona muricata on a breast cancer cell line. **J. Leon**

57. Triticain-α: An enzymatic approach to managing celiac disease. **J.S. Clem**, S. Grau, H.N. Currie, D. Puthoff

58. Adsorption of heavy metals using chemically-modified tea leaves. **R.A. Ulay**

59. Milk stretches the non-toxic range for curcumin-induced NRF2-activation. **G. Fardella**, E. Chang, I. Gazaryan

Undergraduate Poster Session: Inorganic and Organometallic Chemistry

Virtual Room
N. S. Radu, *Organizer*
2:30 - 4:30

60. Synthesis of mixed bi-icosahedron nanoclusters with increased fluorescence. **S. Topka**, N. Stevens, N. Hondrogiannis, **M. Devadas**

61. Solar degradation of toxic colorants in polluted water by thermally tuned ceria nanocrystal-based nanofibers. **w. wei**, E. Rooney, C. Beck, K. Xu, P. Lu

62. Growth mechanism study and emulsion-templated self-assembly of semiconducting cadmium selenide nanoplatelets. **Z. Jiang**, E. Marino, S. Yang, C.B. Murray

63. Profiling trace element contaminants of toxicological interest in commercially available hemp derived CBD tincture oils. **M.Z. Walton**, T. Gluodenis, R. Thomas

64. Crystallographic effects of doping early transition metals (V, Nb, Mo) into MnO_2 (2x2 tunnel, OMS-2). **T. Praisner**, A.C. Mirich, M. Pickett, S.L. Suib

65. Design and characterization of a novel enzymatic immobilization structure. **M. Pickett**, A. Mirich, S. Pierce, S. March, A.M. Angeles Boza, J.L. Rouge, S.L. Suib

66. Systematic analysis of nanoparticle synthesis in reverse micelles using CdS quantum dots as a model system. C.L. Johnson, A.V. Scorzo, N.K. Webber, **A.R. Calabrese**, A. Weyhmiller, T.V. Douglas, N.V. Nucci

67. Heme model compound peripheral group interactions in low dielectric medium. **K.A. Moulton**, J. Cerda

68. Thin layer chromatography and column chromatography in the advanced inorganic laboratory. **A. Chandra**, L. My, M. Chernys, M. Kim, G. Paniconi

69. Ruthenium(II) based water-oxidation catalyst supported on graphene oxide composites. **C. Amaya**, Y.M. Badiei, W. Li

70. *In vitro* evaluation of a potential Ruthenium-based chemotherapeutic agent for triple negative breast cancer. **A. Yeasmin**, **N. Nayeem**, **M. Contel**

71. Organometallic MRI contrast agents. **M. Izykowicz**, **M. Staszewski**

72. Development of a colorimetric assay for the carcinoembryonic antigen. **B. Berger**, J. Smith

73. Synthesis of meso-Tetraphenylporphin (H_2TPP): A quest for better yield and purification. **M. Chernys**, A. Chandra, M. Kim, L. My, G. Paniconi

Undergraduate Poster Session: Measurement and Data Science

Virtual Room
K. S. Booksh, S. L. Neal, *Organizers*
2:30 - 4:30

74. Random forest model prediction of compound oral exposure in the mouse. **H. Mughal**, H. Wang, M. Zimmerman, M. Paradis, J.S. Freundlich

75. Mechanistic investigation of fragmentation of protonated of nitroanisoles by mass spectrometry. **D. Ju**, A.B. Attygalle

76. Evaluate the effectiveness of washing strategies on pesticide removal from skin and flesh of strawberries, apples, and grapes using QuEChERS and LC-MS/MS analysis. **V. Tran**, J.A. Palkendo

77. Development of a method for the quantitation of carbohydrates in aquatic systems. **M.H. Schuch**, W.R. Lacourse

78. Analysis of benzodiazepines used in drug facilitated crimes. **M. Gysbers**, **T. Maslin**, S. Haddadi, V. Niri

79. Tongue cancer viability in organic tea tree and alma treatments. **R. Gonzalez**

Undergraduate Poster Session: Organic Chemistry

Virtual Room
Financially supported by PharmaBlock
M. P. Watson, *Organizer*
2:30 - 4:30

80. Synthesis of phenyl pyridines, pyridazines and pyrimidines to test for their inhibition on the enzyme Uridine Nucleoside Ribohydrolase (UNH). **E. Ajmal**

81. Investigation of pyridine-based bis-benzimidazoles as potential chemotherapeutic lead compounds. **A. Alagaratnam**, L. Barasa, S. Yoganathan

82. Greener synthesis of pterostilbene derivatives as drug candidates for the treatment of Alzheimer's. **V. You**, K. Bhat

83. Ni-catalyzed oxidative esterification of allylic sp^3-carbon. **I. Hicks**, **E. Sehovic**, P. Kaur

84. Novel conversion of 1,3-thiaza-4-ones to dimeric thioacetals. **M.W. Russell**, L.J. Silverberg

85. Synthesis of 2-(2-methylpyridin-3-yl)phenol derivatives as uridine nucleoside ribohydrolase inhibitors. **D. Vanegas**

86. Synthesis of phenyl pyzaroles for the inhibition of unh in trichomonas vaginalis. **K. Nelson**

87. C-glycosides synthesis by coupling C-linked glycosyl crotylboronates with simple aldehyde. **A. Anous**

88. Use of heme proteins in bioremediation efforts: Turning heme green. **D. Barry**, M. Reynolds, S. Pogash

89. Desolvation pathways of four niclosamide solvates. **R. Gao**, J.E. Werner, J.A. Swift

90. Non-precious metal-based MOFs as catalysts for decarboxylative coupling reactions. **C.B. Aristil**

91. From natural to synthetic: Photophysical improved cyanine dyes and their bright future. **Y. Liang**, Z. Zhou

92. Synthesis of sulfoxides from 2,3-diphenyl-2,3-dihydro-1,3-thiaza-4-ones. **G. Muench**

93. Synthesis of 1(benzotriazolyl)ethyl ferrocene: A potential cancer growth inhibitor. **A. Aryal**, M. Squires, D. Aucoin

94. Benzylic functionalization electrochemical oxidation. **K. Lee**, Y. Xing

Undergraduate Poster Session: Physical Chemistry

Virtual Room
M. P. Watson, *Organizer*
2:30 - 4:30

95. Using NMR titrations to assess halogen-bonding strength as a function of molecular structure towards sensor development. **Q. Dang**, L.B. Hughes, M.C. Leopold

96. Design of ionic liquids bearing thioether side chains. **M. Mughal**, J.F. Wishart, E.W. Castner, Jr., S.I. Lall-Ramnarine

97. Preparation and characterization of ionic liquid–polymer gels. **S. Nembhard**, N. Zmich, J.D. Ramdihal, J.F. Wishart, E.W. Castner, Jr., S.I. Lall-Ramnarine

98. Determination of asymmetrical viral capsid morphology through computational modelling of cryo-EM data. **T. Nesterova**

99. Enhanced ionic liquid- single-walled carbon nanotubes mixtures for energy storage applications. **Z. Piao**, T. Hemraj-Benny

100. Assessing the long-term effects of the cellular environment on HIV-1 pNL4-3 capsid. **C.A. Sheopurkar**

101. Antibacterial activity of sulfur-doped carbon/g-C_3 N_4 composite under visible light. **M. Mirza**, A. Daoud, W. Li

102. Single-particle tracking measurements in poly(ethylene glycol) hydrogels: Does size matter?. **K. Foreman**, K. Tran-Ba

103. Absorption IR spectroscopy tracks the effect of gold nanoparticles on the ordering of phospholipids. **K. Kalloo**, S. Finn, N. Escoffery, Q. Lu, **R. Helburn**

Undergraduate Poster Session: Polymers & Soft Materials

Virtual Room
M. P. Watson, *Organizer*
2:30 - 4:30

104. Solvent-assisted nanochannel encapsulation of a natural phase change material in polystyrene hollow fibers for high-performance thermal energy storage. **D.K. Patel**, H.S. Singh, P. Lu

105. In-air polymerization and crosslinking of monomers during electrospray deposition. **C. Nachtigal**, J. Singer

Wednesday, June 9, 2021 – Afternoon (continued)

106. Study of nanocomposites of PolyRhodanine/Palladium/Cobalt: Synthesis and application. **M. Chauhan**, A. Sharma, S. Jaser, S. Nieves, Q.R. Johnson, G.K. Longia

107. G3-G5 PAMAM dendrimer demulsification studies of known oil compositions in water emulsions. **M.A. Salah**

108. Interactions of CO_2 with polymer surfaces for sequestration: A computational study. **R.B. Komma**, L. Tribe

109. Polyaniline nanofiber-metal nanoparticle composites for the catalytic degradation of congo red and other targets: A mini-review. **D. Mahabir**, D.M. Sarno

110. Porous microspheres of polyaniline and its derivatives as a material for cargo loading and delivery: A mini-review. **M. Chen Weng**, D.M. Sarno

Wednesday, June 9, 2021 – Evening

BILL Talk: Barbara Morgan

Virtual Room
Sponsored by BMGT
M. P. Watson, *Organizer*
J. Cohen, *Presiding*

6:00 Introductory Remarks.

6:05 111. Transition from chemist to business director: Leadership lessons. **B. Morgan**

6:25 Discussion.

BMGT: Bench to Business Discussion

Virtual Room
Sponsored by BMGT
J. Cohen, B. Morgan, A. Burch, *Presiding*
6:40 – 8:30

Topical Networking Sessions

Virtual Room
M. P. Watson, *Organizer*
7:00 – 8:30pm

Thursday, June 10, 2021 – Morning

Advances in Chemistry in Pharmaceutical and Agriculture Industry

Virtual Room
Financially supported by Adesis Inc.
Z. Dong, *Organizer, Presiding*

8:30 Introductory Remarks.

8:35 112. Recent success stories from the women of Merck small molecule process research and development. **J. McCabe Dunn**

9:05 113. Chemical process development innovations to expand patient access to transformative medicines: Recent examples from the Janssen pipeline. **J. Balsells**, S. Wagschall, D. Broggini, R. Panish, S.L. Plunkett

9:35 114. Flavonids revisit. **V.J. Lee**

10:05 Intermission.

10:15 115. Withdrawn

10:45 116. Development of a scalable process for insecticide Tyclopyrazoflor. **X. Li**, Q. Yang, B.A. Lorsbach, K. Gray

11:15 117. Overview of agricultural discovery at FMC. **T. McMahon**

11:45 Concluding Remarks.

Empowering Chemists with Disabilities

Virtual Room
K. S. Booksh, *Organizer, Presiding*

8:30 118. Communicating chemistry content effectively to the blind. **C.A. Supalo**

8:50 119. Computational biophysical chemistry for researchers who are visually-impaired. O.R. Shaw, **J.A. Hadden-Perilla**

9:10 120. Voice control of a raman microscope with Commercial Off the Shelf (COTS) software. **K.S. Booksh**, R. McCormick, D. Greco

9:30 121. Well succeed experience in teaching chemistry to deaf students in Brazil. **H.V. Silva**

9:50 122. Panel discussion: Making career decisions during the pandemic. **K.S. Booksh**

Inorganic and Organometallic Young Investigator Symposium

Virtual Room
Cosponsored by INOR
Financially supported by DuPont
W. Farrell, *Organizer, Presiding*

8:30 Introductory Remarks.

8:35 123. Design and synthesis of highly porous coordination cages. **E.D. Bloch**

9:10 124. Molecular strategies to modulate the electrode-electrolyte interface in heterogeneous electrocatalysis. **V. Thoi**

9:45 125. Photoswitchable extended network materials. **K.M. Waldie**

10:20 Intermission.

10:35 126. Developing hydrolytic mini-metalloenzymes using *de novo* proteins. **K. Buettner**

11:10 127. Olefin metathesis with vanadium(V) alkylidenes: Current possibilities and limitations. **W. Farrell**

Protein Quality Control

Virtual Room
Financially supported by Purisys
K. R. Schmitz, *Organizer*
K. R. Schmitz, *Presiding*

8:30 128. Systematic discovery of terminal sequences that mark proteins for proteolysis in *E. coli*. P.C. Beardslee, **K.R. Schmitz**

8:55 129. Co-translational protein quality control is a target for new antibiotics. **K. Keiler**, J.N. Alumasa, M. Cabrera, Z. Aron, C. Dunham

9:20 Intermission.

9:30 130. Proteasomal conformation controls unfolding ability. J. Cresti, A. Manfredonia, C. Bragança, J. Boscia IV, C. Hurley, M. Cundiff, **D. Kraut**

9:55 131. Countering deleterious phase transitions in ALS/FTD. **J. Shorter**

Thursday, June 10, 2021 – Morning (continued)

Spectroscopy: From Molecules to Macrostructures

Virtual Room
Cosponsored by COLL
A. V. Teplyakov, *Organizer, Presiding*

8:30 132. Properties of solar energy and spintronic materials from DFT. **L. Bendavid**, O.T. Fauth, A.O. Atsango, R.W. Smith

9:00 133. Surface supportive metal-organic framework as a drug delivery system. S.G. Guillen, A. Bui, **F. Tian**

9:30 134. Time-resolved X-ray spectroscopy studies of long lived photoinduced charge separation in redox active metal organic frameworks. **J.V. Lockard**, L. Hanna

10:00 Intermission.

10:15 135. Imaging partially ordered molecular materials through vibrational nano-spectroscopy. **E.A. Muller**, B.T. O'Callahan, J. Joseph, T. Cigeroglu

10:45 136. High-resolution, rotationally-resolved spectroscopy of the 3300 cm^{-1} band of astrochemically-relevant HCN. J. Palko, T. Howard, **L.G. Dodson**

11:15 137. Gas-surface interactions of Hg(II) compounds probed by mass spectrometry. **A. Khalizov**, N. Mao

Thursday, June 10, 2021 – Afternoon

Workshop: Careers in Industrial Chemistry: Identifying Your Role in the Industrial Value Chain (ACS Career Pathway Workshop)

Virtual Room
Moderator: M. Bonakdar
12:00 – 12:50

Workshop: The ACS Bridge Program: Enhancing diversity, equity, inclusion, and respect in graduate education in the chemical sciences

Virtual Room
Moderator:J. Schlatterer
12:00 – 12:50

Workshop: Funding for STEM Graduate Studies: The National Science Foundation (NSF) Graduate Research Fellowship Program (GRFP)

Virtual Room
Moderators: C. Hill, N. Norman, L. Adams
12:00 – 12:50

Plenary: Dan Nocera

Virtual Room
Financially supported by Chemours
J. Rosenthal, *Organizer, Presiding*

1:00 Introductory Remarks.

1:05 138. Complete artificial photosynthesis: Sustainable and renewable carbon, nitrogen and phosphorus cycles for fuel and crop production. **D.G. Nocera**

1:50 Discussion.

Biophysical Chemistry

Virtual Room
Cosponsored by COMP and PHYS
J. R. Perilla, *Organizer*
G. Brannigan, E. R. May, *Presiding*

2:00 139. Atomistic dynamics of a viral infection process: Release of membrane lytic peptides from a non-enveloped virus. **E.R. May**

2:20 140. Differential thermodynamics and kinetics of prefusion spike proteins of SARS-CoV-1 and 2. V. Govind Kumar, D. Ogden, U. Isu, A. Polasa, J. Losey, **M. Moradi**

2:40 141. Protein interface flexibility in pleomorphic viral assemblies via solid-state NMR spectroscopy. G. Michel, J. Gonzalez-Roman, C.A. Figueroa Morales, N. Rodriguez-Marino, **M.J. Bayro**

3:00 142. All-Atom MD simulations of the HBV capsid: Revealing mechanisms of function and disruption. **J.A. Hadden-Perilla**

3:20 Intermission.

3:40 143. Updating the CHARMM lipid force field and modeling membrane leaflet composition asymmetry. Y. Yu, M. Hsieh, **J.B. Klauda**

4:00 144. Identifying structurally-resolved lipid fragments through molecular simulation. T.T. Joseph, M. Arcario, J. Petroff, W. Cheng, J. Henin, **G. Brannigan**

4:20 145. Plasma membranes are asymmetric in lipid unsaturation, packing and protein shape. **I. Levental**

4:40 Concluding Remarks.

Energy Catalysis

Virtual Room
Financially supported by Strem
J. Rosenthal, *Organizer, Presiding*
H. Shirly, *Presiding*

2:00 Introductory Remarks.

2:05 146. Coordination chemistry flow battery. **S. Reece**

2:35 147. Anti-catalysis: Applications of the kinetic inhibition of water splitting. **M.P. Marshak**

3:00 148. Sustainable and efficient energy storage using a flow battery assembly based on iron, air, and water. **L. Tran**, J. Rosenthal

3:20 Intermission.

3:30 149. Insights into electrocatalytic oxidation reactions using first-row transition metal complexes. **K.M. Waldie**

3:55 150. Recent developments in the application of oxazoline-containing ligands in CO_2 reduction catalysis. **A.M. Angeles Boza**, J.K. Nganga, K.A. Grice, M.Z. Ertem

4:20 151. Anion induced surface structuring of copper cathodes as a means to control the selectivity and activity of electrochemical CO_2 reduction. **L. Xiong**, T. Kunene, J. Rosenthal

4:40 152. Approaches to the catalytic synthesis of weak bonds. **P.J. Chirik**

5:10 Concluding Remarks.

Frontiers in New Methods for Organic Synthesis

Virtual Room
Cosponsored by ORGN
M. P. Watson, *Organizer, Presiding*

2:00 Introductory Remarks.

2:05 153. Umpolung approaches to aryl ether synthesis via electrophilic oxygen species. **S. Wengryniuk**

2:35 154. Fe-catalyzed multicomponent Radical cascades/cross-coupling accelated by a computational and experimental approach. **O. Gutierrez**

3:05 155. New methods for the development of novel ingredients. **K. Steward**

3:35 Intermission.

3:45 156. New reactions for installing heteroatoms in complex molecules. **D.A. Watson**

4:15 157. Oxygen driven fragment coupling for the synthesis of natural products and antibacterials. **M. Kozlowski**

4:45 158. Innovation in the synthesis of complex pharmaceutical agents. **M.D. Eastgate**

Innovations in Chemical Biology

Virtual Room
Financially supported by Merck Sharpe Dohme
J. Fox, *Organizer, Presiding*

2:00 159. Salt bridge between a conserved arginine and a heme propionate plays a key role in the oxygen sensing mechanism of the FixL protein from *Sinorhizobium meliloti*. **M. Reynolds**

2:20 160. PubChem for drug discovery in the age of big data and artificial intelligence. **S. Kim**, E. Bolton

2:40 161. Theranosis of liver fibrosis in non-alcoholic fatty liver disease (NAFLD) with collagen-targeted thermoresponsive assembled protein. **A. Wang**, E. Fisher, J.K. Montclare

2:55 162. Engineering fluorinated thermo-responsive assembled protein (F-TRAP) for theranostic applications in glioblastoma multiforme. **A. Bhattacharya**, Y.Z. Wadghiri, D. Placantanokis, J.K. Montclare

3:10 163. Potential muscarinic antagonist antidepressants that lack cognitive deficits in rodents. **C.R. Johnson**, B. Kangas, E. Jutkiewicz, G. Winger, J. Bergman, A. Coop, J. Woods

3:25 164. Chemical approaches for understanding the landscape of RNA modifications. **E. Arguello**, R. Kleiner

3:40 Intermission.

3:50 165. Fluorescent probe design for targeting and imaging carbonylation in live cells. H. Erkan, D. Telci, **O. Dilek**

4:10 166. Sponge Mimetic Tubules (SMT) to explore biomorph templated evolution of animal life. **K.S. Raja**

4:30 167. Visible light promoted tryptophan photoconjugation using donor-acceptor pyridinium salts. **C. Hoopes**, A. Sarkar, N. Kuehl, N. Collins, M. Taylor

4:45 168. Post-polymerization modification of hydrogel microfibers synthesized via interfacial tetrazine ligation. **P. Ramaraj**

5:00 169. Electrogenetic control and regulation of a synthetic *Escherichia coli* consortia. **E. VanArsdale**, J. Pitzer, S. Wang, K. Stephens, G.F. Payne, W.E. Bentley

Spectroscopy: From Molecules to Macrostructures

Virtual Room
Cosponsored by COLL
A. V. Teplyakov, *Organizer,*
F. Tian, *Presiding*

2:00 170. Oxidation of $Cu_2O(111)$ by NO_2 : An ambient pressure x-ray photoelectron spectroscopy study. **B. Karagoz**, M. Blum, A.R. Head

2:20 171. Investigating plasmonic resonances in metal-semiconductor heterostructures. **J.P. Avenoso**, M. Jia, O.E. Babawale, L. Gundlach

2:40 172. Reactions of boric acid and 4-fluorophenylboronic acid with H- and Cl-terminated Si(100) surfaces. **D. Silva Quiñones**, A.V. Teplyakov

3:00 Intermission.

3:15 173. Pump-degenerate four wave mixing spectroscopy of the interfacial electron transfer on perylene-sensitized TiO_2 surfaces. **H. Yan**, J.P. Avenoso, S. Doble, L. Gundlach, E. Glaoppini, L. Rego

3:35 174. Comparison of spectral unmixing algorithms applied to simulated and measured frequency domain dynamic fluorescence reaction monitoring of semiconductor quantum dot surface passivation. **D.B. Sanap**, M. Murray, S.L. Neal

3:55 175. Mapping preferential adsorbate interactions at electrodeposited Cu interfaces via shell-isolated nanoparticle enhanced raman spectroscopy. **D. Raciti**, A.R. Hight Walker, T.P. Moffat

Poster Session: Innovations in Chemical Biology

Virtual Room
J. Fox, *Organizer*
5:30 - 7:30

176. Toward a mechanistic understanding of ferrous iron transport: Deciphering the function of FeoA. **A. Sestok**, J. Brown, J. Obi, S. O'Sullivan, D. Deredge, A.T. Smith

177. Withdrawn

178. Study of dopamine-induced functional adaptations in astrocytes. **S.P. Aryal**, C.I. Richards

179. Aptamer based label-free and sensitive detection of miRNA. **M. ISLAM**

180. Epigenetic modifications of histones in a yeast amyloid-beta overexpression model. **M. Hugais**, S. Cobos, S. Bennett, G. Foran, J. Paredes, M. Torrente

181. Indirect downregulation of MCL-1 via targeted PROTACs. **A. Chan**, S. Fletcher

182. PROTAC strategy to rescue venetoclax sensitivity in AML-resistant cells. **C.C. Goodis**, I.L. Conlon, A. Cottingham, S. Fletcher

183. Structure-activity relationship studies of ketamine. **A. Abelian**, M. Dybek, J. Wallach, A. Adejare

184. Identification of diverse targets of arginine phosphorylation in *Mycolicibacterium smegmatis* by shotgun proteomics. **E.C. Ogbonna**, K.R. Schmitz

185. Mapping out histone post-translational modifications in a yeast prion model. **S. Cobos**, E. Son, J. Paredes, N. Rana, A. Olivera, H. Ibrahim, B. Salib, S. Bennett, M. Torrente

186. Functional characterization of undenatured type II collagen supplements : Are they interchangeable?. R.B. Harris, F. Fonseca, C. Ottinger, **M. Sharp**

Thursday, June 10, 2021 – Evening

187. Development and application of methods to classify Clp protease protein paralogs in actinobacteria. **J. Jiang**, K.R. Schmitz

188. Targeted, catalytic, near-IR light-triggered release from dihydrotetrazine precursors. **J. Rosenberger**, Y. Xie, Y. Fang, A. Tallon, J. Fox

189. Exploring the relationship between temperature activated hydrogen-deuterium exchange and protein stability with SANS. **R. Donnelly**, Y. Liu, N.J. Wagner

190. Blood-brain barrier permeability and AChE inhibition of ionophoric polyphenols. **A. Martinez**, M. Zahran, M. Gomez, J. Guevara, R. Pichardo-Bueno

191. High-throughput discovery of sequences that promote proteolysis in bacteria. **P. Beardslee**

192. Activation of tetrazines by a genetically encodable catalyst for intracellular spatially controlled bioorthogonal chemistry. **A. Tallon**, Y. Xie, J. Fox

193. Application of Fundator's multidimensional time model to finding trace of fractional multidimensional Fokker-Plank equation dynamics in DNA replication in formation of CpG islands, analog bases, and repeats of G-quadruplexes. **M. Fundator**

194. Novel application of qPCR melt analysis following BRED. S. Hancock, **F. Habtehyimer**

195. Identification of a secondary binding site for acyldepsipeptide fragments within the bacterial Clp protease. **M. Prorok**, J. Husdon, K.R. Schmitz

196. Nipamovir: Synthesis and preclinical evaluation of an anti-HIV thiobenzamide prodrug. **M. Robello**, H. Nikolayevskiy, M.T. Scerba, R. Nahui Palomino, V. Mercurio, T.L. Hartman, R.W. Buckheit, L. Margolis, D.H. Appella

197. New electron transport and biomedical applications for peptide amphipile materials. **L.A. Solomon**

Poster Session: Innovations in Chemistry Education

Virtual Room
S. Compton, S. A. Habay, *Organizers*
5:30 - 7:30

198. Case for case studies when teaching biochemistry. **D. Bassolino**, D.A. Barr, K. Schroeder

199. Sustainability and safety in chemistry: An upper level undergraduate elective. **C.A. Dougherty**, K.E. Kristian

200. Impact of recitation timing on student performance in undergraduate general chemistry. **A. Howcroft**, D. King

201. Hybridization of C-H bonds is directly related to electronegativity of substituents. **D.D. Clarke**

202. Teaching hands on chemistry labs to the visually impaired. **T. Ladogana**

Poster Session: Innovations in Inorganic and Organometallic Chemistry

Virtual Room
E. A. Hernandez-Pagan, *Organizer*
5:30 - 7:30

203. Strategies for the photoreduction of Tc-99 pertechnetate to low valent Tc by Keggin polyoxometalates. **I. Radivojevic Jovanovic**, C.M. Gallagher, R. Salcedo, W.W. Lukens, B.P. Burton-Pye, D.M. McGregor, L.C. Francesconi

204. Mathematical aspects of application of fractional multidimensional Fokker-Plank equation to the theory of rate of chemical reactions based on spectroscopy experiments with examples. **M. Fundator**

205. Optimizing the properties of sol-gel based silica nanoparticles. A. Fried, H. Ariel, J. Ramos, J. Lam, **U. Samuni**

206. Electron microscopy of platinum-based anti-cancer drugs: Cisplatin, oxaliplatin, and carboplatin. **V. Galemba**, G. Paniconi

207. Development of heterometallic platinum(IV)-gold(I) compounds as potential chemotherapeutics against specific genitourinary cancers. **J. Lopez-Hernandez**, H. Karim, R. DeGregorio, M. Contel

208. Two-dimensional materials based photocatalysts for light-induced H_2 production. **J. Ran**

209. Designing silicon substrates for area-selective deposition of TiO2. **T. Parke**, A.V. Teplyakov

210. Interplay between mesoscale architecture and catalytic output in CO_2 gas-diffusion electrolyzers. **D. Raciti**, T. Braun, B. Tackett, H. Xu, M. Cruz, B.J. Wiley, T.P. Moffat

211. Immobilization of water-oxidation catalysts on plasma grafted poly(acrylic) acid modified anodes. **Y.M. Badiei**, C. Traba, C. Amaya

212. Mechanism and kinetics of the MAX etching reaction for MXene synthesis. **M. Anayee**, A. Goad, D. Dogias, Y. Gogotsi

213. Flexible approach to fabricate a well-ordered array of Metal/Semiconductor hemispherical nano-heterostructures. **O.E. Babawale**, J.P. Avenoso

214. *In situ* adsorption studies of anisole on NiMo oxide catalysts under hydrodeoxygenation reaction conditions. **T. Hu**, S. Blomberg, A.R. Head

215. C-N bond formation by nitride migratory insertion into Cr-C bond. **L. Zhang**, K.H. Theopold

Poster Session: Innovations in Measurement and Data Science

Virtual Room
L. Gundlach, S. L. Neal, *Organizers*
5:30 - 7:30

216. Fluorescence reaction progress monitoring of solid-phase asymmetric ionic nanoscale probe synthesis. **C. Von Suskil**, S.L. Neal

217. Photodegradation of semiconductor quantum dots in microheterogeneous media using wavelength- and frequency-resolved fluorescence decay measurements. **M.J. Murray**, S.L. Neal

Poster Session: Innovations in Organic Chemistry

Virtual Room
M. P. Watson, *Organizer*
5:30 - 7:30

218. Deaminative reductive methylation of alkylpyridinium salts. **O. Bercher**, S.L. Plunkett, T. Mortimer, M.P. Watson

219. Synthesis and evaluation of biaryl compounds as inhibitors of nucleoside hydrolases to treat trichomoniasis. **M.A. Vanalstine-Parris**, V. Abrego, E. Ajmal, A. Gil, K. Nelson, R. Shin, D. Vanegas, E. Saljanin, C. Ventura, B.J. Stockman

220. Reactions of isocyanates and isothiocyanates with 2-bromoallylamines: Investigations into the synthesis of 1,3-dihydro-2*H*-imidazol-2-ones and 4-imidazoline-2-thiones. **T.J. Eckroat**

221. One-pot chemoenzymatic reactions in water enabled by micellar encapsulation. **C. Hastings**

222. Photochemical and photophysical study of *bis*-alkylated lumazine and pterin photosensitizers. M. Sosa, M. Vignoni, M. Urrutia, M.I. Quindt, S. Bonesi, D. Denburg, A. Greer, A.H. Thomas, **E. Greer**

223. Adjuvant compound analysis for mechanistic insight to promote photodynamic action. **S. Jabeen**, **L. Lapoot**, R.M. O'Connor, M. Zatoulovski, A. Greer

224. Superhydrophobic antimicrobial photodynamic inactivation of bacterial biofilm with airborne singlet oxygen. **C. Tonon**, S. Ashraf, A. Rastelli, G. Ghosh, T. Hasan, Q. Xu, **A. Greer**, A.M. Lyons

225. Deaminative nickel-catalyzed one-carbon homologation of alkyl amines. **C. Twitty**, J. Xu, M.P. Watson

226. Development of a hiyama cross-coupling of highly substituted vinylsilanes. D.A. Watson, S.B. Krause, H. Omar, **A. Conner**

Poster Session: Innovations in Physical Chemistry

Virtual Room
J. R. Perilla, *Organizer*
5:30 - 7:30

227. Computational design of foldamer based water channels. **S. Houshyar Azar**, Z. Liu, V. Pophristic

228. Development of ^{19}F fast magic-angle-spinning NMR spectroscopy for structural characterization of protein assemblies. **B.R. Runge**, C. Quinn, R. Zadorozhnyi, M. Fritz, J. Struppe, I.L. Byeon, A.M. Gronenborn, T.E. Polenova

229. ^{19}F magic angle spinning NMR spectroscopy to probe protein-ligand interactions. **R. Kalabekova**, C. Quinn, M. Akke, A.M. Gronenborn, T.E. Polenova

230. Determination of histidine protonation states in proteins by fast magic angle spinning NMR. **R. Zadorozhnyi**, B.R. Runge, S. Sarkar, C. Quinn, K. Zadrozny, B. Ganser-Pornillos, A.M. Gronenborn, T.E. Polenova

231. Towards the atomic resolution structure of a novel disulfide-rich biomaterial. **S. Zeinalilathori**, C. Zhang, T.E. Polenova, C. Thorpe

232. Thermal dry etching of CoFeB alloy thin films using chlorine and acetylacetone (acacH). **M. Konh**, A.V. Teplyakov

233. Realistic SARS-CoV-2 liposomes via *VesGen*: an efficient tool for modeling large and complex lipid membranes. **A.J. Bryer**, J.R. Perilla

234. Molecular determinants of Ebola nucleocapsid stability from molecular dynamics simulations. **C. Xu**, N. Katyal, T. Nesterova, J.R. Perilla

235. Impact of cavity losses on nonadiabatic couplings and dynamics for many molecules coupled to a single photon in polaritonic chemistry. **F. Suchanek**, J. Foley

236. All-atom MD simulations of CpAM-bound HBV capsids reveal allosteric mechanisms relevant to assembly regulation and inhibitor binding. **C. Perez Segura**, B.C. Goh, J.A. Hadden-Perilla

237. Development of novel xanthate-modified and unmodified exchangers for remediation of effluent in contaminated water within Enugu State metropolis. **E. Agboeze**, J.C. Attah

238. Three conformationally distinct models of the full-length SARS-CoV-2 spike protein with representative post-translational modifications. **P. Jones**, J.A. Hadden-Perilla

Poster Session: Innovations in Polymers & Soft Materials

Virtual Room
L. Kayser, *Organizer*
5:30 - 7:30

239. Conductive hydrogels based on a water-soluble EDOT derivative. **D. Nguyen**, L. Kayser

240. Degradable multiblock copolymers as scaffolds for conductive polymers. **E. Awuyah**, L. Kayser

241. Synthesis of stimuli-responsive and conducting polyelectrolyte complexes. **V. Damani**, L. Kayser

242. Tunable microfibers via interfacial tetrazine ligation. **O.J. George**, H. Zhang, A. Ravikrishnan, S. Liu, H. Zhang, J. Fox, X. Jia

243. 3-D cytocompatible network construction mediated by long wavelength photocatalytic activatable bioorthogonal reactions. **H. Zhang**, C. Wang, J. Fox, X. Jia

244. Impact of the molecular structure of poly(styrene sulfonate) on the mixed ionic-electronic conduction of PEDOT:PSS. **C. Lo**

245. Celebrating the 100th Anniversary of the Delaware ACS Section. **N.W. Henry**

246. Electrochemical behaviour of polymer nanocomposite on differents electrode substrates. **F. SALIH**, A. OUARZANE, K. Lafdi, M. EL RHAZI

Thursday, June 10, 2021 – Evening (continued)

ACS Governance Social

Virtual Room
S. Dortch, *Organizer*
6:30 – 7:00pm

Carothers & Regional Award Symposium

Virtual Room
Financially supported by Incyte
M. P. Watson, *Organizer*
J. Qu, N. Radu, *Presiding*

7:00 Introductory Remarks.

7:30 247. Lessons learned from nature: From biomineralization to biomaterials. **A. Campbell**

8:15 Discussion.

Friday, June 11, 2021 – Morning

Alternative Grading in the Chemistry Curriculum

Virtual Room
S. A. Habay, *Organizer, Presiding*

8:30 Introductory Remarks.

8:35 248. Getting started with mastery grading. **A. Deckert**

9:05 249. Implementation and outcomes of mastery-based grading in general chemistry. **E.E. Wilson**

9:35 250. Student-centered grading practices and the journey to (mostly) gradeless chemistry labs/lectures. **C.J. Sobers**

10:05 Intermission.

10:15 251. Bundle up! Using bundled grading in a remote organic chemistry course. **S.A. Habay**

10:45 252. Techniques for getting students to meet the "specification" in specifications grading. **W. Hollinsed**

11:15 253. Five year study using specifications grading in an undergraduate chemistry curriculum. **H.J. Fletcher**

Friday, June 11, 2021 – Morning (continued)

Frontiers in Chemical Biology

Virtual Room
Financially supported by Bristol Myers Squibb
J. Fox, C. L. Grimes, *Organizers, Presiding*

8:30 Introductory Remarks.

8:35 254. Mapping glycoconjugate interactions in native cellular environments. E. Joeh, W. Li, C. Parker, **M. Huang**

9:15 255. Catalytic activation of bioorthogonal chemistry with light (CABL) enables rapid, spatiotemporially-controlled labeling and no-wash, subcellular 3D-patterning in live cells using long wavelength light. **A.W. Jemas**

9:30 256. Modified *N*-acetyl muramic acid probes for improved bacterial peptidoglycan metabolic incorporation. **A.R. Brown**, K. Wodzanowski, C.C. Santiago, S.N. Hyland, J.L. Follmar, C.L. Grimes

9:45 257. Development of chemical biology probes for applications in drug discovery. **C. Am Ende**

10:25 258. Programmable technologies to retune gene expression at the RNA level. **K. Jones**, Y. Cao, S. Rauch, B.C. Dickinson

10:55 259. Activity-based proteomics: Target and ligand discovery on a global scale. **B.F. Cravatt**

11:35 Concluding Remarks.

Innovations in Organic Chemistry

Virtual Room
Financially supported by Organic Reactions
M. P. Watson, *Organizer, Presiding*

8:30 260. New methods for the synthesis of tetraarylmethanes. **A.J. Catino**, J.D. Selingo, M.J. Fadelici

8:50 261. Deaminative alkyl–alkyl cross-couplings of alkylpyridinium salts and alkenes. **K. Baker**, D. Lucas Baca, S.L. Plunkett, M.E. Daneker, M.P. Watson

9:05 262. Rapid synthesis of diverse imidazoles through microwave-assisted multicomponent reaction. **J.A. Smith**, M. Rotella, M. Osunsanya, I. Nwadike, B. Tankeu, O. Gutierrez

9:25 263. Diastereoselective alkynylations of β-(Bromo)iminium ions via Copper(I) catalysis. **S.O. Santana**, W. Guan, M.P. Watson

9:40 264. Study of the solubility of hypervalent iodine reagents and synthesis of hypervalent iodine reagents with increased solubility in non-polar solvents. **D.L. Silverio**, I.D. Hyatt, V. Seecharan, L. Armand, J. Noorollah, N. Singh, A. Zhang, K. Freddo, N. Spatola, S. Prasad, A. Chaudhry, S. War

10:00 Intermission.

10:10 265. Withdrawn

10:30 266. Cyclic sulfones from double conjugate addition of Rongalite. **M. Bebbington**

10:50 267. Practical implementation of predictive retrosynthesis in ReaxysCchemistry database. **I. Samkurashvili**, S.E. Dueball

11:10 268. Photoredox catalysis for the synthesis of ambiphilic polymers via decarboxylative fluorination. **M. Talley**, C. Machado, W. Guan, T.H. Epps, M.P. Watson

11:25 269. T3P promoted synthesis of 2,3-diaryl-2,3-dihydro-1,3-thiaza-4-ones. **L.J. Silverberg**

Nanoparticles: Characterization & Applications

Virtual Room
Financially supported by Waters Corp.
L. Gundlach, *Organizer*
S. L. Neal, *Organizer, Presiding*

8:30 270. Plasmonic electricity: Fluorophore-induced plasmonic current. **C.D. Geddes**

9:10 271. Visualizing dynamic changes in metal nanoparticle surface chemistry. **K.A. Willets**

9:40 272. Terahertz camera-less imaging of semiconductors overcoming the Abbe diffraction limit. **A. Rahman**

10:10 Intermission.

10:25 273. Synthesis and characterization of carbon dots and their application in dye sensitized solar cell (DSSC). **J. Uddin**

10:55 274. Enhanced catalytic activity of nickel nanoparticles explained by bimetallic effect on carbon nanotube formation. **C. Byron**, M.S. Ferrandon, G. Celik, R. McCormick, J. Sloppy, K.S. Booksh, M. Delferro, C. Ni, A.V. Teplyakov

11:25 275. Algorithm for soot aggregate restructuring. **D. Singh**, O. Enekwizu, A. Khalizov

Porous Materials

Virtual Room
Financially supported by TA Instruments
E. D. Bloch, *Organizer, Presiding*
C. M. Brown, T. J. Kempa, *Presiding*

8:30 276. Design of functional sites in porous framework materials for energy storage. **V. Thoi**

8:50 277. Adsorption of small molecules in metal-organic frameworks. **C.M. Brown**

9:10 278. Perspective on novel porous materials scale-up: Practical challenges in manufacturing and commercialization. **M. Kapelewski**

9:30 279. Tunable Metal-Organic Framework (MOF) nanoparticles as inhaled drug delivery vehicles. Z. Stillman, B. Jarai, G. Decker, L. Attia, E.D. Bloch, **C. Fromen**

9:50 280. Microporous nanocomposite emulsion thermosets for multi-material, multifunctional porous composites. **Y.K. Patel**, J. Singer

10:10 Intermission.

10:25 281. Kinetic and deactivation mechanisms of isostructural MIL-101 for organic small-molecule oxidations. R. Yang, **M.L. Sarazen**

10:45 282. Stimuli-responsive 2D metal-organic frameworks prepared by chemical vapor deposition. **T.J. Kempa**

11:05 283. Beyond nanostructured supports: Maximizing catalytic centers in metal-organic frameworks. **A.J. Morris**

11:25 284. Metal-organic frameworks at the interface of medicinal and materials chemistry. M. Zick, R. Mandel, F. Chen, J. Woods, J. Lee, M. Gonzalez, E. Velasquez, A. Uliana, J. Hsu, J. Fuentes-Rivera, J.R. Long, J.J. Wilson, **P.J. Milner**

Friday, June 11, 2021 – Afternoon

Workshop: Opportunities for Chemists in the Federal Government (ACS Career Pathway Workshop)

Virtual Room
Moderator: A. Aldridge
12:00 – 12:50

Workshop: Leveraging our diversity to create equity, inclusion, and respect in our chemistry communities

Virtual Room
Moderator: B. Chan
12:00 – 12:50

Plenary: LaShanda Korley

Virtual Room
Financially supported by University of Delaware
M. P. Watson, *Organizer*
L. Kayser, *Presiding*

1:00 Introductory Remarks.

1:05 285. Manipulating hierarchy, mechanics, and function in polyurea-peptide hybrids. **L. Korley**

1:50 Discussion.

Dimensionality in Nanoscale Materials

Virtual Room
Financially supported by Solenis
E. A. Hernandez-Pagan, *Organizer*
E. Hernandez-Pagan, *Presiding*

2:00 Introductory Remarks.

2:05 286. Insights into reaction intermediates to predict synthetic pathways for shape-controlled copper nanocrystals. **R. Buonsanti**

2:35 287. Chemically reversible isomerization in magic-sized clusters. **R.D. Robinson**

3:05 288. Laser-made nanocatalysts with controlled properties. **A.M. Müller**

3:35 Intermission.

3:45 289. Chelating agents in tandem with minimal concentrations of HF as an alternative method to produce highly crystalline MXene $Ti_3C_2T_x$ nanostructures. **L.R. De Jesus**, T.E. Mallouk

4:15 290. Design and synthesis of colloidal quantum dot nanostructures for photon upconversion. **T. Welsch**, J. Cleveland, M. Doty

4:45 291. Energy-based applications of multi-functional nanoscale systems. **S.S. Wong**

Diversity in Polymer Chemistry and Engineering

Virtual Room
Cosponsored by PMSE
Financially supported by Covestro
C. Fromen, L. Kayser, *Organizers, Presiding*

2:00 Introductory Remarks.

2:05 292. Merging organic synthetic and polymer chemistry: Toward accelerated catalysis and architecturally-diverse Sp^3-enriched polymers. **E. Elacqua**

2:35 293. Two-dimensional perovskites with bifunctional ligands yield efficient and stable solar cells. **M. Ball**, X. Zhao, A. Kakekhani, T. Liu, A.M. Rappe, Y. Loo

3:05 294. Polymeric nanofiber scaffolds as an ex-vivo method for CD34+ Hematopoietic Progenitor Stem Ccell (HPSC) growth and expansion. **C. Winstead Casson**, L. Lott

3:35 Intermission.

3:45 295. Responsive polymer nanocomposites. **S. Yang**

4:15 296. Precision polyolefins and the circular economy. **K. Beers**

4:45 297. New family of guanidine based n-type dopants and the structural effects on doping efficiency. **J.A. Schneider**, H. Nakayama, H. Wang, J. Read de Alaniz, M.L. Chabinyc

Excellence in Organic Chemistry and Chemical Biology Research with Undergraduates

Virtual Room
Cosponsored by ORGN
S. A. Habay, *Organizer*
J. Fox, *Organizer, Presiding*

2:00 Introductory Remarks.

2:05 298. Observing and reversing the cysteine-perfluoroarene S_NAr reaction: towards a traceless tag for isolating expressed peptides. **J. Gavenonis**

2:35 299. Good things come in small packages: Cyclic peptide inhibitors to a protein-protein interaction initiating thrombosis and novel short peptide helices and turns. **D. Guarracino**

3:05 300. Designing 'intelligent' MRI contrast agents. **A.J. Rojas**

3:35 Intermission.

3:45 301. Untangling the mechanisms of chlorocarbene additions to strained bonds. **D.C. Merrer**

4:15 302. Bacterial capsule polymerases as tools for carbohydrate synthesis. **P.C. McCarthy**

4:45 303. From heterocycles to carbacycles: How to exploit nitrogen in small rings. **G. Moura-Letts**

Nanoparticles: Characterization & Applications

Virtual Room
S. L. Neal, *Organizer*
L. Gundlach, *Organizer, Presiding*

2:00 304. Manipulation of dimensionality, edge state, and strain in transition metal dichalcogenide nanocrystals. **T.J. Kempa**

2:40 305. Photo-induced charge transfer dynamics and mechanisms in thin-films of Sb_2S_3. **E.R. Young**

3:10 306. Bidirectional excited-state charge-transfer and extended charge separation within covalently-tethered type-II CdSe/CdTe quantum dot heterostructures: Colloidal and multilayered systems. **C. McGranahan**, G. Wolfe II, D. Watson

3:40 Intermission.

3:55 307. Fibrous phosphorus quantum dots for cell imaging. P. Amaral, D.C. Hall, J. Krol, G. Ehrlich, **H. Ji**

4:25 308. Lipoic acid decorated gold nanoparticles and their application in the detection of lead ions. **W. GHANN**, T. Harris, J. Uddin

4:55 309. Long chain hydrosilanes as phase transfer agents. B.P. Chauhan, **E. Cook**, Q.R. Johnson

Friday, June 11, 2021 – Evening

Speed Networking

Virtual Room
M. P. Watson, *Organizer*
5:45 – 7:00

Saturday, June 12, 2021 – Afternoon

Workshop: Climate Science Concepts Fit Your Classroom
Virtual Room
Moderators: B. Shakhashiri, J. Bell
1:00 – 3:00

Chemagination
Virtual Room
Organizers: L. Lawter, S. Compton
1:00 – 4:00

MARM 2021 Abstracts

High-Throughput Experimentation to Advance Discoveries in Academia and Industry

1. High-throughput chemistry: An asset to the modern academic chemist

***Michael C. Nicastri**, nicastri@sas.upenn.edu. Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania, United States*

High-throughput experimentation (HTE) has become common place for chemists at the University of Pennsylvania. Techniques in HTE enable academic chemists to study reaction discovery and optimization in greater depth, in less time, and more cost effectively. Academic workflows for HTE are tailored to support bespoke experimental arrays rather than preset experimental designs. The capability to setup custom experiments has been crucial for HTE to facilitate the successful exploration of hypothetical chemical transformations. The HTE laboratory is maintained as a core facility within in the chemistry department, providing resources, training, and expertise to academic researchers. Over the past ten years, the services provide by the HTE laboratory have had a positive impact on the quality and efficiency of published chemistry research at the University of Pennsylvania.

2. HTE in medicinal chemistry

***Spencer Dreher**, spencer_dreher@merck.com. Process Chemistry, Merck, Metuchen, New Jersey, United States*

High throughput experimentation (HTE) chemistry has been evolving in leaps and bounds. In industry and academic labs, reactions are run in increasingly miniaturized and parallelized format changing the very nature of what we can make and the overall cost-structure of synthesis. At Merck, HTE was initiated in Process Chemistry to rapidly solve difficult problems and has more recently become pervasive in Medicinal Chemistry labs for problem-solving and library synthesis. In Med-chem, nanomole-scale screening can uncover unique conditions for micromole scale parallel synthesis libraries to greatly increase hit rates. In addition, increasingly, direct-to-biology approaches allow for nanomole-scale reaction arrays wherein parallel conditions are applied to parallel reactions and successful reactions are tested directly in biology, without chromatographic purification. In the very near future, the data that is generated in these experiments will be used to create models to help predict successful conditions to minimize the need for screening. Massively parallel, integrated chemistry/ biology with data-driven conditions prediction is on the horizon for discovering new drugs rapidly, and cheaply.

3. Bigger isn’t always better: Efficiency gains through smaller reactions in Discovery High-Throughput Chemistry at GSK

***Nicole C. Goodwin**, nicole.c.goodwin@gsk.com. Medicinal Chemistry, Pharma R&D, GlaxoSmithKline USA, Collegeville, Pennsylvania, United States*

High throughput experimentation (HTE) has had a revolutionary impact on the pharmaceutical industry. While HTE is more often associated with in vitro screening of large compound libraries or reaction screening for the optimization of single chemical transformations, the application of HTE principles to medicinal chemistry lays an important foundation on how we prosecute our chemistries to deliver on programs to ultimately provide high quality drug candidates to patients. Automation and miniaturization of chemistry activities have allowed for increased efficiencies in reaction development, parallel synthesis, and other enabling technologies that innovate and drive success in GSK's discovery chemistry groups. Selected applications of these technologies will be presented in this talk.

4. Development of the High Throughput Experimentation (HTE) core facility at the University of Delaware: Design, implementation, applications, and innovations

***Donald A. Watson**, dawatson@udel.edu. Chemistry/Biochemsitry, University of Delaware, Newark, Delaware, United States*

For the past decade or more, the use of High Throughput Experimentation (HTE) modalities has been commonplace in industrial labs and is widely used to speed the identification and development of new chemical reactions. At the same time, the use of HTE methods has been more limited in academic settings, in part due to the cost and complexity of establishing an HTE Core Facility. In this talk, I will discuss our successful efforts to design and build the HTE Core at the University of Delaware. I will discuss both the equipment and cost considerations that have guided our design and implementation. I will also highlight some of the reaction discovery that the UD HTE Core has enabled in my lab’s research. Finally, I will discuss our innovations in analytical methods for asymmetric catalysis discovery using HTE.

5. Enabling medicinal chemistry through high-throughput experimentation

***Simon Berritt**, simon.berritt@pfizer.com. WWRD, Pfizer Global Research and Development, Groton, Connecticut, United States*

High-throughput experimentation plays a pivotal role in drug discovery and development, and as the synthesis of medicinal chemistry targets and libraries expand beyond amidations and SnAr reactions to more challenging chemo- and biocatalyzed transformations, the need to quickly identify best conditions covering a broad range of sterically & electronically diverse monomers and templates becomes paramount. Herein, we present ongoing efforts to rapidly test multivariate reactions crossing both monomers and templates, detailing successes, failures, and the applicability of this workflow to Big-Data generation.

Innovations in Chemistry Education

6. Multiple ways to virtually engage students in chemistry labs

***Audrey S. Smeltzer Schwab**, bluetiger313@yahoo.com. Science, Muhlenberg High School and Penn State University, Temple, Pennsylvania, United States*

Because of the coronavirus, the format for experimentation in chemistry had to change. However, the skills and knowledge gained from experimentation is still important. Therefore, this presentation will show many ways to engage students virtually in chemistry Furthermore, this presentation will also explain how to adapt labs to incorporate the necessary objectives or skills while engaging students at home. Additionally, this presentation will allow participants to ask questions and ways to modify their current experiments into the virtual world.

7. PubChem and its application for cheminformatics education

***Sunghwan Kim**, kimsungh@ncbi.nlm.nih.gov, Evan Bolton. National Library of Medicine, National Institutes of Health, Bethesda, Maryland, United States*

PubChem (https://pubchem.ncbi.nlm.nih.gov) is a chemical information resource, developed and maintained by the U.S. National Institutes of Health. It contains a large corpus of publicly chemical data collected from more than 700 data sources. Visited by millions of users every month, it serves a wide range of audiences, from scientific communities to the general public. Considering that many PubChem users are undergraduate and graduate students at academic institutions, it has great potential as a cheminformatics education resource. In this presentation, we will give a brief overview of PubChem's data content, tools, and services. Important aspects of PubChem as cheminformatics education will be discussed, including data quality and accuracy, data provenance and governance, and structure standardization. Besides, we will discuss PubChem's education and outreach efforts, including the PubChem Laboratory Chemical Safety Summary (LCSS) and the Cheminformatics On-Line Chemistry Course (OLCC).

8. Secondary chemistry teaching: Do you know the facts?

*Terri M. Chambers[1], **Jared Breakall**[6], jbreakall@mines.edu, **Etta C. Gravely**[3], gravely@ncat.edu, **William Hunter**[5], wjhunte@ilstu.edu, **Jennifer B. Nielson**[4], jnielson@chem.byu.edu, Ellen J. Yezierski[2]. (1) American Chemical Society, Washington, District of Columbia, United States (2) Chemistry & Biochemistry, Miami University, Oxford, Ohio, United States (3) North Carolina AT Univ, Greensboro, North Carolina, United States (4) BYU Dept of Chem and Biochem, Provo, Utah, United States (5) Department of Chemistry & School of Teaching & Learning, Illinois State University, Normal, Illinois, United States (6) Department of Physics, Colorado School of Mines, Golden, Colorado, United States*

The U.S. is currently facing a shortage of secondary chemistry teachers. Earlier survey research has demonstrated that negative and inaccurate perceptions of teaching are substantive reasons that faculty may not encourage and students may avoid teaching careers. Understanding the facts about teaching is essential and can advance respect for the profession and help us to overcome the national chemistry teacher shortage. Get the Facts Out, an NSF-funded advocacy and research project, is changing the conversation around STEM teacher recruitment and offers genuine support to those who are considering teaching as a career. This interactive session will not only help chemistry faculty learn the facts about secondary chemistry teaching, but it will also furnish strategies and networks to enrich how faculty support students' career exploration. We invite MARM colleagues to lend their valuable influence to solving this national problem.

9. Changing the sequence kinetics material for general chemistry: Introducing mechanisms first to help students develop a conceptual understanding of reactions

Curtis R. Pulliam[1]*, cpulliam@utica.edu,* ***David Rieck***[2]*, dfrieck@salisbury.edu. (1) Utica College, Utica, New York, United States (2) Salisbury University, Salisbury, Maryland, United States*

We propose teaching Collision Theory and reaction mechanisms before introducing the concept of overall rate laws in general chemistry courses. Textbooks, and we assume most chemistry instructors, briefly mention Collision Theory early in the discussion of kinetics. However, they follow this superficial presentation by quickly moving along to the overall reaction rate law with particular focus on the determination of rate laws from experimental data. Students are generally confused by the lack of relationship between a reaction’s balanced chemical equation and its rate law. Nonetheless, they generally accept, usually without understanding, that the exponents of the rate law do not necessarily derive from the coefficients of the overall equation. They also learn to use data algorithmically in order to determine the overall rate law for a reaction. It is only after their acceptance of this process that elementary reactions and the concept of a reaction mechanism are introduced. The idea of a reaction proceeding through a series of steps is challenging for students who are used to viewing reactions in terms of reactants and products and never worrying about how the change occurs. Additionally, after determining rate laws from experimental data for so long, students are frequently baffled by the fact that the exponents for elementary reactions *are* taken from the coefficients of its equation. We believe that by introducing elementary reactions and their rate laws first and then developing the overall rate law from the mechanism, the confusion about the relationship between the coefficients of an equation and the exponents of a rate law is lessened. Additionally, by emphasizing reaction mechanisms first, student can see how studying rate laws sheds light on how reactions occur. While one of us teaches a modified atoms first presentation and the other teaches a traditional order of topics, we will share our experiences with focusing on reactions mechanisms first when introducing kinetics in general chemistry.

10. Cookie challenge: A unique way to encourage office visits

***Daniel B. King**, daniel.king@drexel.edu. Chemistry, Drexel University, Philadelphia, Pennsylvania, United States*

One of the challenges faced by faculty who teach large-enrollment courses is how to connect with the students. In addition, many students are reluctant to seek help when they struggle in courses. Most faculty provide office hours as a way for students to ask questions in a less stressful environment; however, few students take advantage of that resource. Despite multiple office hours scheduled at various times, it is typical to have less than 5% of the students visit a faculty member's office. This is particularly true in large enrollment courses, such as general chemistry, where faculty are not able to individually connect with each student. Attendees will learn about a technique that has been used in a 200+-student freshman chemistry course to encourage students to attend office hours. During the first class of the term, the instructor issues a challenge to the class. The challenge is for 50% of the students visit the instructor's office at some point during the term. If the students meet the challenge, the instructor promises to bake cookies for the entire class. Over the course of 5 years only a few sections have reached 50%; however, the percentage of students visiting the instructor's office has increased dramatically. Data will be presented that demonstrates a correlation between office visits and student performance. Student scores in a variety of course components (e.g., exams, lab and online homework) were generally higher for students who visited than for students who didn't visit.

11. Toward equitable assessment of English Language Learners in chemistry: Identifying helpful features in assessment items

***Eshani Lee**, egl51@psu.edu. The Pennsylvania State University, University Park, Pennsylvania, United States*

Many students experience a language barrier in chemistry which may keep them from fully understanding and engaging in the complex chemistry content. In fact, some argue that language is a greater barrier to learning science than the content itself. Scientific language is cognitively demanding and consists of technical terminology and discourse structures specific to the context. Students struggle with understanding words in the chemical context and fail to make intended meanings. For example, words such as *volatile* and *state* are well understood in everyday life, but poorly understood in the context of chemistry. Decoding these types of terms within the context of chemistry is notably a challenging task for most students; however, for English language learner (ELL) students, the task of learning chemistry is particularly arduous. This study examined a method for mitigating the language barrier in written assessments in ways which make the questions linguistically accessible without reducing the content difficulty. The Equitable Framework for Classroom Assessment (EFCA) was implemented to modify three general chemistry assessment items on the topics of limiting reactant and percent yield. These three original items were revised for linguistic simplification and accessibility. In this presentation, ELL students' perceptions of original and modified versions of each assessment item will be discussed. Specifically, the features of the items that students

found to be *helpful* will be reported. Results suggest that ELL students were better able to comprehend the modified versions of assessment items and use features that are less language-dependent to solve the problems.

12. Teaching single crystal x-ray crystallography in the undergraduate classroom with common household chemicals

***Alain Beauparlant**, abeauparlant@gmail.com, **Cassandra T. Eagle**, eaglec@etsu.edu, Reza Mohseni. Chemistry, East Tennessee State University, Johnson City, Tennessee, United States*

We adapted both a live, on ground experiment and a virtual, asynchronous experiment designed to teach the basics of crystallography though the crystal structure of sugar. We also developed a more challenging live experiment using Epsom Salt suitable for upper level undergraduate students. The live experiments were used in the Fall of 2019 at the Junior and the Senior level. In the Summer of 2020, we developed and implemented an asynchronous lab in the General Chemistry laboratory curriculum which has been used in both the Fall 2020 semester and the Spring 2021 semester. During the Fall 2020 semester, 74 students completed the virtual, asynchronous lab, and during the Spring 2021 semester, over 200 students completed the virtual, asynchronous lab.

The sugar experiment is designed with a pedagogical emphasis on VSEPR theory and intermolecular forces. Sugar works well for teaching VSEPR because students get exposed to identifying what an atom is based on its environment. To determine the structure of sugar from crystallographic data, students must use their knowledge of how valence electrons determine bonding, and their knowledge of molecular geometry, to predict whether an atom is a carbon, an oxygen, or a hydrogen. Sugar also provides a visual example of intermolecular forces because it contains two internal hydrogen bonds. The Epsom salt experiment requires greater skill in selecting a suitable crystal for analysis, and introduces students to coordination chemistry.

None of our experiments require any expertise in X-ray crystallography or related software. No expertise in crystallography is necessary to implement these experiments (the live, on ground one, or the asynchronous one). Both table sugar and Epsom salt are inexpensive and readily available in X-ray quality crystalline form. For our live experiments, we used a Rigaku XtaLAB Mini diffractometer (built 2011) and analyzed the data and generated a model using CrysAlis Pro Online and Reduction, Olex2, and ShelX. All aspects of these experiments use user friendly free software.

13. Video introduction to single crystal x-ray crystallography starring pyrite (fool's gold)

***Alain Beauparlant**, abeauparlant@gmail.com, Cassandra T. Eagle. Chemistry, East Tennessee State University, Johnson City, Tennessee, United States*

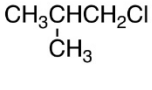
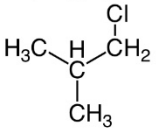
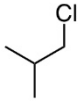
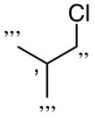
We wrote a script and filmed a twenty-minute video that teaches students how to run a single crystal X-ray crystallography experiment using pyrite (iron sulfide). The purpose of the video is to assist in teaching practical crystallography to undergraduate and graduate students. The video guides students in selecting a suitable crystal, mounting it on a fiber, centering it inside the diffractometer, running the experiment, reducing the data, solving the structure and preparing an ORTEP. The video may be used either as a stand-alone background material for a virtual lab, or as preparation for a live experiment. This video builds on ongoing work since 2019 in developing live single crystal X-ray crystallography experiments for the undergraduate curriculum using table sugar and Epsom salt. This video will be used in General Chemistry II laboratory, Senior Advanced Analytical Laboratory, Graduate level X-ray Crystallography, and as an Introduction to Research to Single Crystal x-ray Crystallography.

14. Efficiently visualizing implicit hydrogens with the prime method

Daniel L. Silverio[2]*, dsilverio@adelphi.edu, Arun Sam*[1]*, Matthew Mistretta*[1]*, Scott Buzzolani*[1]*. (1) Chemistry, Adelphi University, Floral Park, New York, United States (2) Chemistry, Adelphi University, Garden City, New York, United States*

The ability to interpret and provide arrow-pushing mechanisms is crucial for students to obtain a deep understanding of organic chemistry. A classic way to teach students how to work out mechanisms is to have them determine what bonds are broken and what bonds are formed. In practice, the most difficult part of the process is mapping the atoms in the starting material(s) to those in the product(s). One aspect that makes mapping atoms challenging is novice students often miss the presence of hydrogens that are implicit in line-angle formula (Figure 1).
Using the "prime method", students explicitly represent the amount of hydrogens on the carbon atoms (o = 0H, '= 1 H, " = 2H, ''' = 3H) in a way that takes far less time than other methods for explicitly drawing hydrogens (Figure 1). With this method, decisions students need to make regarding mapping atoms are simplified. Data showing the impact of the prime method on mapping atoms in starting materials to their correct location in the products will be discussed.

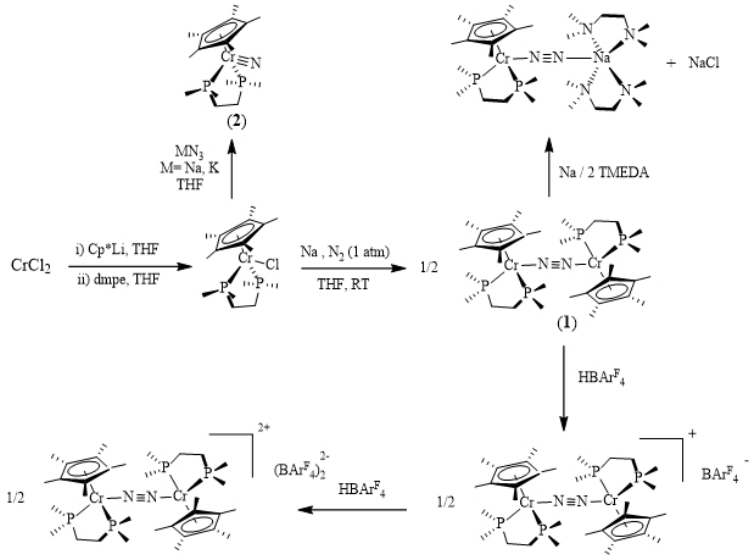
Figure 1. Common Organic Structure Types vs. Prime Method

Examples of Types of Structure Drawing in Organic Chemistry				
	I Condensed	**II Hybrid Condensed/ Line-Angle**	**III Line-Angle**	**IV Prime Method**
Are Hydrogens Shown?	Yes	Yes	No	Yes
Easy to Interpret?	No	Yes	Yes	Yes
Quick to Draw?	No	No	Yes	Yes

15. Activity studies of pentamethylcyclopentadienyl chromium complexes in N_2 activation

***Farzaneh Ahmadi Darani**, fdarani@udel.edu, Klaus H. Theopold. University of Delaware, Newark, Delaware, United States*

Designing transition metal complexes that can coordinate to the free dinitrogen ligand, elongate the dinitrogen bond length and finally cleave its triple bonds with a low barrier, is of great importance.
This presentation will describe the synthesis and structural characterization of a new chromium dinitrogen complex, namely $[Cp^*Cr(dmpe)]_2(\mu\text{-}N)_2$ (**1**), and its desired cleavage product, i.e. $[Cp^*(dmpe)Cr{\equiv}N]$ (**2**), which was prepared by an independent method. **1** can be reduced and oxidized and the effect of these transformations on the N_2 ligand was monitored by structural studies.
DFT calculations were performed on the neutral and cationic complexes of dinitrogen and nitride to find the thermodynamic product of the interconversion reaction. Based on the calculations, the dinitrogen complex is the thermodynamic product of the interconversion reaction and the free energy of activation for the interconversion was calculated to be 56.4 kcal/mol. This number is very large, suggesting an insurmountable intrinsic activation barrier for the formation of the N_2 molecule.



Activity studies of chromium complexes in dinitrogen activation.

16. Optical properties of cesium bismuth bromide perovskites

***Minh N. Tran**, mnt267@nyu.edu, Iver Cleveland, Eray S. Aydil. Chemical and Biomolecular Engineering, New York University, New York, New York, United States*

In the search for lead-free perovskites for solar cells, cesium bismuth halides are emerging as potential photovoltaic materials. Cs^+, Bi^{3+}, and Br^- form multiple compounds with different stoichiometries and crystal structures. Among these, $Cs_3Bi_2Br_9$ and Cs_3BiBr_6 are stable with respect to decomposition into CsBr and $BiBr_3$, at room temperature: when these salts are mixed in appropriate proportions, the phase with the expected stoichiometry forms and is stable in air, as determined by X-ray diffraction (XRD). Published optical absorption and photoluminescence of $Cs_3Bi_2Br_9$ and their interpretations vary significantly from paper to paper, while there are only a few articles where synthesis and properties of Cs_3BiBr_6 were reported. There are almost as many optical absorption and emission spectra published for $Cs_3Bi_2Br_9$ as there are articles on this material. Much of this research focused on thin films and nanocrystals synthesized from solutions comprising metal halide salt precursors. We address these discrepancies in the literature by depositing phase pure $Cs_3Bi_2Br_9$ and Cs_3BiBr_6 thin films via co-evaporation of CsBr and $BiBr_3$ and studying the effects of CsBr:$BiBr_3$ ratio and the film stoichiometry on their optical properties. In addition to optical properties, the films are characterized by a battery of techniques, including XRD and Raman spectroscopy. We found that $Cs_3Bi_2Br_9$ and Cs_3BiBr_6 thin films show absorption peaks centered at 435 and 383 nm, respectively. These peaks are associated with excitations localized on $[BiBr_6]^{3-}$ octahedral in the solid phase. These octahedra share corners in $Cs_3Bi_2Br_9$ but are completely isolated from each other in Cs_3BiBr_6. Visible emission from $Cs_3Bi_2Br_9$ is centered at 470 nm with a long tail up to 600 nm. We show that the discrepancies in the literature have two reasons, phase impurities and the inevitable absorption and emission by dissolved $[BiBr_6]^{3-}$ in colloidal dispersions, which may be easily misinterpreted as originating from the solid product.

17. Palladium biladiene complexes bearing alkynyl-aryl groups for sensitization of $^1O_2$ and photodynamic therapy

***Anthony Rice**, atrice@udel.edu. Chemistry, University of Delaware, Newark, Delaware, United States*

Photodynamic therapy (PDT), which involves the photoinduced sensitization of singlet oxygen is an attractive treatment for certain types of cancer. The development of new photochemotherapeutic agents remains an important area of research. Macrocyclic tetrapyrrole compounds including porphyrins, phthalocyanines, chlorins, and bacteriochlorins have been pursued as sensitizers of singlet oxygen for PDT applications but historically are difficult to prepare/purify and can also suffer from high non-specific dark toxicity, poor solubility in biological media and/or slow clearance from biological tissues. In response to these shortcomings, we have developed a series of novel linear tetrapyrrole architectures complexed to late transition metals as potential PDT agents. We find that these dimethylbiladiene (**DMBil1**) tetrapyrrole complexes can efficiently photosensitize generation of $^1O_2$ oxygen upon irradiation with visible light. To extend the

absorption profile of the **DMBil1** platform, alkynyl-aryl groups have been conjugated to the periphery of the tetrapyrrole using Sonogashira methods. Derivatives of this type containing ancillary phenyl (**DMBil1–Ph**), naphthyl (**DMBil1–Nap**) and anthracenyl (**DMBil1–An**) groups have been prepared and characterized. Extension of the tetrapyrroles conjugation successfully redshifts the absorption of the **DMBil1–Ar** family of biladienes further into the phototherapeutic window (*i.e.,* 650–850 nm). Photochemical sensitization studies demonstrate that our series of new palladium biladiene complexes (**Pd[DMBil1–Ar]**) can sensitize the formation of $^1O_2$ with quantum yields of approximately F_D = 0.60 upon irradiation with light of l > 600 nm. The improved absorption properties of the **Pd[DMBil1–Ar]** complexes in the phototherapeutic window, together with their high $^1O_2$ quantum yields highlight the promise of these compounds as potential agents for PDT and other photomedicine applications.

18. High near-infrared photoluminescence quantum yield in Yb-doped cesium lead halide perovskites

Iver Cleveland[1]*, ijc263@nyu.edu, Minh N. Tran*[1]*, Eray S. Aydil*[2]*. (1) Chemical and Biological Engineering, New York University, Brooklyn, New York, United States (2) Chemical Eng Mat Sci Dept, University of Minnesota, Minneapolis, Minnesota, United States*

Inorganic halide perovskites have attracted attention with potential applications in high-efficiency solar cells. Recently, ytterbium-doped $CsPbCl_{3-x}Br_x$ (x<1) perovskite showed efficient quantum cutting, a process wherein photons absorbed at high energies (*e.g.*, > 2.5 eV) generate two photons with energies ~ 1.25 eV close to the silicon bandgap energy (1.1 eV). A thin layer of this material on a silicon solar cell can convert blue photons to two near-infrared (NIR) photons, decreasing energy losses due to the relaxation of the high-energy charge carriers to the band edges. In this way, silicon solar cell efficiencies can surpass the Shockley-Quessier limit. Towards this end, we deposited Yb-doped $CsPbCl_{3-x}Br_x$ films using reactive physical vapor deposition by co-evaporating CsCl, $PbCl_2$, and $YbBr_3$ and controlling the flux of each using quartz crystal microbalances. We investigated the effects of film stoichiometry, Yb concentration, and post-deposition annealing conditions on film composition, microstructure, and photoluminescence quantum yield (PLQY). After annealing at 350 ^oC for 2 hours, the films emitted NIR photoluminescence at ~990 nm (Yb^{3+} $^2F_{5/2} \rightarrow {}^2F_{7/2}$ *f-f* transition, 1.25 eV) with quantum yields (PLQY) exceeding 60%, when excited with photons with energies above the $CsPbCl_{3-x}Br_x$ bandgap (*e.g.*, > 2.5 eV). The PLQY depended strongly on the annealing environment. Surprisingly, films annealed in nitrogen-filled glove box had the lowest PLQY, while films annealed in glove box first and then in air had the highest. We hypothesize that grain growth in the glove box followed by oxygen passivation of remaining defects in the air is responsible for high PLQYs. The transient NIR PL shows a rise time of ~0.7-1.5 ms followed by decay with a time constant of ~30 ms. On the other hand, the visible PL lifetime is < 1 ns indicating ultrafast trapping of excitons followed by energy flow into longer-lived intermediate states likely associated with Yb-related defects.

19. Improvement of electron transport in cathodes via integration of nanostructured carbons with layered oxides for high power Li-ion batteries

***Timofey Averianov**, tka33@drexel.edu, Ekaterina Pomerantseva. Materials Science, Drexel University, Philadelphia, Pennsylvania, United States*

Bilayered vanadium oxide, δ-V_2O_5●nH_2O, is an attractive cathode material in rechargeable batteries. Its large interlayer spacing of produces a high theoretical capacity as a result of the denser intercalation of charge-carrying ions. This bilayered phase has been previously explored in Li-, Na-, and K-batteries, and it was shown that the specific capacity and the stability of the cathode can be improved by processes such as chemical preintercalation, hydrothermal treatment, and vacuum annealing. However, rate performance is limited as a result of the oxide's low electronic conductivity, even when a carbon black additive is used in electrode preparation. As a result, other avenues must be explored for improving rate capability of δ-V_2O_5●nH_2O.
Due to its compatibility with sol-gel processes, bilayered vanadium oxides can be integrated with electronically conductive nanostructured carbons, such as carbon nanotubes and graphene, where the oxide crystals grow on the carbon surface. The sp^2 hybridization of these carbon species provides a pathway for electrons to easily move during operation, and the heterointerface provides dense and intimate contact between the two components. In this study, we report, for the first time, synthesis of nanocomposite based on bilayered vanadium oxide and identify the role of the heterointerface on the rate performance of V_2O_5/C electrodes. We demonstrate not only an improved rate performance, but also an improved stability of the electrode structure even at high discharge currents as compared to the bilayered vanadium oxide electrode prepared using the same synthesis technique but without addition of nanostructured carbons. We also discuss the effect of the nanostructured carbon dimensionality on electrochemical properties of the produced nanocomposites. Our results illustrate the potential of sol-gel synthesis approaches to produce intimate heterointerface between dissimilar materials in nanocomposite architecture leading to advanced functional properties.

20. Improving electrochemical behavior of layered oxides through the intercalation and heat treatment of carbon precursors for next generation cathodes

***Ryan Andris**, rga25@drexel.edu, Ekaterina Pomerantseva. Materials Science and Engineering, Drexel University, Philadelphia, Pennsylvania, United States*

Next generation cathode materials require new synthetic strategies to achieve increased capacities, improved rate capability, and high stability. Two dimensional heterostructures that combine a transition metal oxide with highly conductive carbon promise improvement on today's cathodes. Here, we report a method to create alternating layers of redox active material and carbon based on a chemical preintercalation synthesis approach. This approach is a versatile, low temperature technique, that uses sol-gel chemistry to intercalate polar organic molecules between transition metal oxide layers. The sol-gel synthesis step is followed by extended aging and hydrothermal treatment to improve

crystallinity and heat treat the carbon precursor. In this work, we used chemical preintercalation of dopamine molecules between bilayers of vanadium oxide to form a layered 2D δ-$C_xV_2O_5$-*n*H_2O heterostructure after hydrothermal treatment.

The carbon layers within the bilayered structure are confirmed via X-ray diffraction, thermogravimetric analysis, Raman spectroscopy, X-ray photoelectron spectroscopy, electrochemical impedance spectroscopy, four-probe conductivity measurements, and scanning transmission electron microscopy characterization. In addition, scanning electron microscopy is used to highlight the morphological differences between bilayered vanadium oxide and the heterostructure. Notably, 2D δ-$C_xV_2O_5$-*n*H_2O cathodes demonstrated significantly improved electrochemical performance in Li-ion cells at higher current densities compared to the reference electrode. The heterostructure retained 75% of its initial capacity when the current density was increased from 20 mA g^{-1} to 300 mA g^{-1} compared to 10% retention shown by the pure bilayered material. Further, 2D δ-CxV2O5-nH2O heterostructure electrodes retained 94% of their initial capacity after 30 cycles with a 20 mA g^{-1} current density. The electrochemical results indicate that the dopamine derived carbon layers enhance electronic conductivity and structural stability that improves rate capability and capacity retention.

21. Why is the product of the reaction (first done by Dr Frankenstein) of green vitriol with the lye of blood one of the ingredients in the table salt that I brought at Wegman's last month

***Stephen A. Koch**, koch.stephen@gmail.com. Chemistry Department, SUNY Stony Brook, Stony Brook, New York, United States*

The history of the reaction of Fe2+ with CN- will be reviewed from the synthesis of Prussian Blue in 1704 to current research in the Koch group.

22. Bifunctional nickel and copper electrocatalysts for CO_2 reduction and the oxygen evolution reaction

***Hanqing Pan**, schizokangaroo@hotmail.com, Christopher Barile. Chemistry, University of Nevada Reno, Reno, Nevada, United States*

In this study, a bifunctional electrocatalyst for CO_2 reduction and the O_2 evolution reaction (OER) was constructed from the electrodeposition of cuprous oxide (Cu_2O) and Ni on a carbon substrate. Different Ni thicknesses on Cu_2O were achieved by varying the time of chronopotentiometric deposition of Ni. Electrochemical CO_2 reduction was carried out at -0.89 V and -1.89 V vs. RHE, and it was found that formate and CO were the two major products. Cu_2O modified with a Ni overlayer with a thickness of ~700 nm resulted in the highest formate Faradaic efficiency of 18%, and Cu_2O resulted in highest CO Faradaic efficiency of 7.9%. The enhanced Faradaic efficiency for formate is attributed to the synergistic effect between Ni and Cu_2O due to maximized amounts of exposed bimetallic sites that facilitate CO_2 reduction. The electrocatalyst also produces ~9 times more current density than previous studies using Ni-Cu_2O electrocatalysts for the OER. The ability of

the Ni-Cu_2O thin films to catalyze both the OER and CO_2 reduction allows them to be incorporated in the first demonstration of a two-electrode CO_2 conversion device with a bifunctional catalyst.

23. Reactivity of zinc oxide clusters supported on mesoporous silica sieve (SBA-15) towards thiophene hydrodesulfurization

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The morphology, chemical composition, and reactivity of mesoporous materials impregnated with ZnO (SBA-15) towards hydrodesulfurization (HDS) of thiophene were studied. This research helps in the current need for cleaner fuels with a new generation of catalysts with higher reactivity. Morphology and chemical composition were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), and energy dispersive X-ray spectroscopy **(**EDX). The reactivity was studied in a gas-chromatograph based mini flow reactor using thiophene as a probe molecule. Thiophene is part of natural petroleum and it is a simple enough probe molecule to obtain mechanistic molecular-level information. This is ongoing research and hydrocarbons are the expected products from the reaction between hydrogen and thiophene in the presence of a ZnO catalyst.

Innovations in Physical Chemistry

24. Unveiling the genetic fragility of HIV-1 through deep learning

***Juan S. Rey**[1], jsreyl@udel.edu, Wen Li[2], Hagan Beatson[1], Christian Lantz[1], Alexander Bryer[1], Alan N. Engelman[2,3], Juan R. Perilla[1]. (1) Department of Chemistry and Biochemistry, University of Delaware, Newark, Delaware, United States (2) Department of Medicine, Harvard Medical School, Boston, Massachusetts, United States (3) Department of Cancer Immunology and Virology, Dana-Farber Cancer Institute, Boston, Massachusetts, United States*

The use of Transmission Electron Microscopy (TEM) in medical imaging has become of extreme importance due to its ability to visualize particles at the nanometer scale. For instance, tracking the HIV-1 virion during its maturation, a fundamental process for identifying non infective or genetically vulnerable particles. However both the preparation and analysis of TEM micrographs requires time consuming manual labor. Through the dedicated use of computer vision frameworks and machine learning techniques we have developed a convolutional neural network backbone of a two-stage Region Based Convolutional Neural Network (RCNN) capable of identifying, segmenting and classifying HIV-1 virions at different stages of its life cycle. Our results outperform common RCNN backbones achieving a 77.13% mean Average Precision (mAP) on a diverse set of micrographs comprising different mutations and magnifications.

25. Combining time-resolved spectroscopy and computer simulations to reexamine our picture of bimolecular electron transfer

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Spectroscopic experiments have provided exquisite insight into the dynamics of photoinduced charge transfer processes. Interpretation of these experiments has been aided by Marcus theory, a linear-response description based primarily on a picture of spherical reactants immersed in a continuum solvent. Although this model has found much practical success, most analyses disregard the molecular nature of the system and many of the parameters underlying the theory are not directly accessible by experiment. We must therefore combine detailed computer simulations with insight from experiments in order to answer the fundamental question: how good are sphere/continuum models when the system's molecularity is accounted for?

The first system we will examine are electron donor/acceptor complexes (EDACs), donor/acceptor pairs whose electronic structure allows for direct excitation from the neutral to ion pair states. Using a unique combination of ultrafast spectroscopy and mixed quantum/classical simulations, we are able to unravel the complex conformational dynamics of EDACs. Given the sensitivity of charge-transfer processes to donor/acceptor orientation, future descriptions of EDAC dynamics must take into account the molecularity and structural evolution of the excited state in order to properly model the reaction.

Additionally, we will use classical molecular dynamics simulations to explore electron donor/acceptor systems in ways that are impossible with experimental techniques alone. We are able to demonstrate with umbrella sampling molecular dynamics simulations that the hard-sphere model and continuum electrostatics are poor descriptors of the reactant and product potentials of mean force, functions that describe the spatial distribution of donor/acceptor pairs and factor into predictions for the reaction driving force using the Weller equation. We will also show that simulated solvent reorganization energies deviate strongly from the predictions of continuum electrostatics, and that the linear-response approximation can break down in weakly polar solvents. Our experiments and simulations demonstrate that the real dynamics underlying photoinduced electron transfer are significantly more complex than traditional theories would predict.

26. Understanding the charge transfer mechanism in protic ionic liquids

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Ionic liquids (ILs) possess a number of desirable properties, such as high stability and low volatility. Due to their high concentration of charged species, they also have high ionic

conductivity. Protic ILs, i.e. those in which the cations contain an acidic proton, also have the unique property of being able to undergo charge transfer via proton hopping. The high concentration of hydrogen ions makes these materials an appealing option for the electrolyte layer of fuel cells. In this work, the results of *ab initio* molecular dynamics (AIMD) simulations of protic ILs consisting of 1-methylimidazolium with several anions are presented. AIMD explicitly treats electronic degrees of freedom and can thus treat bond breaking and formation, making it an ideal method for studying proton hopping in liquid systems. We present insights into the proton transfer mechanism, as well on the influence of additional solvent molecules on proton diffusion.

27. Fabrication of thermoresponsive bilayer hydrogels through vat photopolymerization additive manufacturing

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Soft actuators are structures made from stimuli-responsive materials which exhibit motion, making them useful in applications such as soft robotics and sensing devices. One element of designing stimuli-responsive soft materials is control of polymer topology; for example, a bilayer structure exhibits a bending response. Additive manufacturing via vat photopolymerization allows for rapid fabrication of complex, three-dimensional polymer network architectures, making it an ideal method for achieving the precise geometrical control needed to design bilayer actuators. However, photopolymerizable soft material resin systems often suffer from having many components or requiring many monomer functionalization steps.
In this work, we use a set of commercial monomers for the rapid fabrication of thermally responsive bilayers through Digital Light Processing (DLP) additive manufacturing. These multi-material structures show progressive actuation when heated in water. We show that the degree of actuation of bilayers and of one-component controls are directly related to processing parameters, such as photopolymerization time and swelling equilibration time. The thermal response of bilayer actuators is directly related to the thermal response of individual layers and the geometric composition of the bilayers, as shown by experimental measurements. We demonstrate the use of our bilayer actuators in the design of complex, printed objects illustrating the customizability of additive manufactured stimuli-responsive parts. Through this work, we illustrate the ability to engineer stimuli-responsive materials using precise control of additive manufacturing process parameters.

28. Withdrawn

29. Enhanced light scattering and absorption by soot aerosols with different coating distributions

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Carbon soot is released into the atmosphere upon incomplete combustion of fossil fuels and is a major contributor to climate change through light absorption and scattering. In the atmosphere, soot particles, which are structurally fractal carbon aggregates, interact with other chemicals, to acquire coatings and undergo changes in their composition, size, and morphology. Particles with different sizes, morphologies, and coating distributions affect the climate differently. In order to accurately model behavior of soot aerosols in the atmosphere we need to determine the relationship between different coating distributions and optical properties of soot. Theoretical studies had been conducted in this area and experimental data are needed to verify the predictions. We studied the dependence of optical properties on mixing with intermediate and low volatility chemicals relevant to those encountered in the atmosphere. To simulate interactions that occur in the atmosphere, soot aerosol was passed through a temperature-controlled chamber, containing organic compounds. Evaporated compounds condensed on soot aggregates and formed coatings of various thickness and distributions, which depended on volatility of the compounds and chamber temperature. Mass, size, and optical properties of bare and coated soot were measured. Optical properties included absorption, scattering, extinction, and single-scattering albedo. Aerosols with different coating distributions were compared. Presence of liquid coatings on soot aggregates alters their morphology and optical properties. Our results suggest that increasing coating thickness leads to a significant (up to 1000%) increase in light scattering. Absorption is also enhanced (up to 50%). Coated particles' mobility diameter first decreases due to prevalent restructuring of the soot core, reaches a minimum, and then starts increasing again due to increase in the volume of coating material. Removal of the coating material by thermal denuding allows quantifying the degree of compaction of soot aggregates. Scattering of light by coated soot is increased from both restructuring and coating material addition, while absorption enhancement is only due to coating material. Climate impact of coated soot is a combination of cooling due to light scattering and heating due to light absorption, with scattering contribution dominating over absorption contribution for thicker coatings.

30. Mercury cycle: Oxidation, deposition, reduction and diffusion in the arctic

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Mercury is known to be a toxic element. One of the striking features in the mercury toxicity is that its levels found in the blood of Indigenous Peoples living in the Arctic are higher than those in individuals living in temperate, and industrialize regions, where most mercury is emitted. The long-range transport ability of mercury is linked to the elevated level of mercury in the Arctic. Geoscientific numerical models determine where, when, and how much mercury deposition occurs onto different surfaces. The elemental mercury has a low water solubility and is less reactive, whereas the oxidized form of mercury, Hg^{II}, is water-soluble, more reactive and is primarily responsible for mercury's neurotoxicity. The

oxidation of mercury occurs in the atmosphere by halogens, ozone or nitro species under ultraviolet rays. The oxidized mercury then deposits in the surface environment or reduces back to elemental mercury via various processes. The inorganic Hg^{II} in the aquatic environment can be converted to methylmercury, which is then readily taken up by and is biomagnified in the food web. A rapid mercury oxidation in the atmosphere, deposition of oxidized mercury into the surface snow/ice and traverses into the ocean water is evident in the Arctic region owing to unusual seasonal variations and higher mercury content in the blood of fishes and Arctic mammals. Using the first-principle Density Functional Theory, the oxidation of Hg^0 in the atmosphere, and deposition on the snow and ice surface, reduction of Hg^{II} on the ice surface and diffusion of Hg^0/Hg^{II} into the ice will be presented and discussed.

31. Atomic-resolution structure of CA_{CTD}-SP1 crystalline arrays in complex with maturation inhibitors by solid state MAS NMR

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HIV-1 contains an assembly and maturation switch, which spans the C-terminal domain (CTD) of the capsid (CA) region and the first spacer peptide (SP1) of the Gag polyprotein. HIV maturation inhibitors, which have emerged as an attractive alternative to the current anti-HIV treatments, disrupt the final step of the viral protease activity by binding to the CA_{CTD}-SP1 junction. Maturation inhibitors, such as Bevirimat (BVM), PF-46396, and their analogs are known to inhibit the maturation by binding to the CA_{CTD}-SP1 junction in the immature lattice and stabilizing its helical conformation. This stabilization of helical conformation interferes with the access of the viral protease to its substrate cleavage site and prevents the formation of mature conical capsid core. We analyzed the crystalline CA_{CTD}-SP1 free and bound to BVM, using solid-state magic angle spinning (MAS) NMR (spectroscopy. We obtained a large number of distance restraints and calculated the structure of CA_{CTD}-SP1/BVM/IP_6 and CA_{CTD}-SP1/IP_6 crystalline arrays to the precision backbone RMSD of 0.6 Å. Simultaneous binding of BVM and IP_6 and orientation of BVM inside the 6-helix bundle were discerned based on MAS NMR drug-protein correlations. Taken together, our results reveal a novel allosteric mechanism by which BVM blocks the pore and arrests the maturation and will be important to guide the new generation of maturation inhibitors.

32. Atomic-resolution structures of protein assemblies by integrating magic-angle-spinning NMR distance restraints and low-to-medium resolution cryo-EM density maps

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Atomic-resolution protein structures determined by nuclear magnetic resonance (NMR) spectroscopy in solution and in the solid state rely on experimental distance restraints obtained through dipolar correlation experiments and dihedral restraints derived from NMR chemical shifts. While in smaller proteins NMR experimental restraints alone are sufficient for deriving the structures, for systems of increasing complexity/size as well as those possessing multiple domains, integration of several techniques is necessary. One example of such integration is combining experimental restraints from magic angle spinning (MAS) NMR experiments with medium- and low-resolution electron density maps obtained through cryoelectron microscopy (cryo-EM). We have undertaken this approach to devise a general protocol for atomic-resolution structure determination of large protein assemblies. We discuss the technical requirements of our integrated approach as well as its application to derive atomic-resolution structures of HIV-1 capsid assemblies and kinesin assemblies with polymerized microtubules.

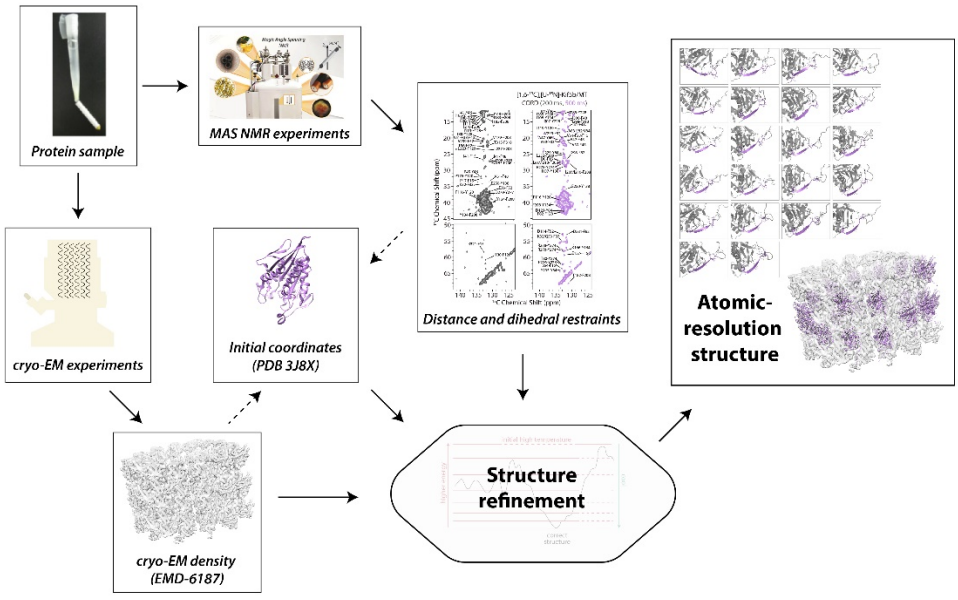

Figure 1. An integrative protocol for atomic-resolution structure determination of large protein assemblies. Experimental MAS NMR restraints and medium- to low-resolution cryo-EM density

maps are jointly refined.

Plenary: Donna Huryn

33. Academic drug discovery: Playing to the strengths to address challenging targets and unmet medical needs

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Over the past twenty years, scientists in academia have placed an increased focus on translational science, with chemists contributing novel biologically active molecules, new efficient synthetic methodologies and innovative technologies that have brought important medicines to patients. Rather than competing with drug discovery organizations in pharma or biotech companies, efforts in academic laboratories can complement those endeavors by playing to the strengths inherent in a university setting including working on high risk projects, taking advantage of unique expertise in specific areas, and pausing to pursue basic science questions. This talk will describe two projects, one targeting acute kidney injury (AKI) and the other cancer, that exemplify the unique opportunities as well as challenges in academic drug discovery.

Undergraduate Poster Session: Chemical Biology

34. Adsorptive removal of hair dye BB99 from solution using agricultural waste

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Hair coloring is a growing industry, as a demand for cosmetics and personal care increases. Dyes are not considered toxic in aquatics systems but they do have consequences in the environment such as a sun light availability, aesthetics of water resources and bioaccumulation in living organisms. Some dyes are biodegradable, but the degradation products have not been evaluated yet for harmful effects. Different agricultural wastes and hydrogels were used as adsorbents for BB99 dye from solutions. Alginate hydrogel spheres (AB), Chai tea leaves (CT), decaffeinated green tea (DGT), green tea (GT) and peppermint (PM) spent tea leaves were tested for the removal of BB99 in batch assays at room temperature. Equilibrium parameters such as pH and adsorbent dose were studied to maximize the uptake of BB99. Results indicate that the adsorption of BB99 is strongly affected by the pH, showing its highest adsorption values at pH range 4-8 (95%) for PM and CT. Adsorption of BB99 followed the trend: PM>CT>AB>DGT>GT and was strongly affected by the presence of salts. The adsorption was modeled according to the Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherm theories to provide equilibrium parameters. Instrumental analyses in

thermogravimetry, and morphology indicate these materials have appropriate textural and mechanical properties for adsorption. According to the results, solid wastes such as spent tea leaves and hydrogel spheres have not only proven to be potential BB99 adsorbents, but also inexpensive and biodegradable materials.

35. Optimization of drug-like quinoline based pharmacophore for irreversible inhibition of Nek2 kinase

Lamia K. Hauter[1]*, lamia.hauter33@qmail.cuny.edu, Ashif I. Bhuiyan*[1]*, Rafael Musayev*[1]*, Chloe Sweeney*[1]*, Anna Dickson*[1]*, Syeda Tabassum*[1]*, Dianne Hernandez*[1]*, Alan J. Finkelstein*[1]*, Dibyendu Dana*[2]*, Tanaji T. Talele*[3]*, Tirtha K. Das*[4]*, Sanjai K. Pathak*[5]*. (1) Chemistry & Biochemistry, Queens College Division of Mathematics and the Natural Sciences, Flushing, New York, United States (2) dept. of chemistry biochemistry remsen 206, queens college, cuny, Woburn, Massachusetts, United States (3) St Johns University, Jamaica, New York, United States (4) Icahn School of Medicine at Mount Sinai, New York, New York, United States (5) Chemistry & Biochemistry, Queens College of the City University of New York, Queens, New York, United States*

Nek2, a serine/ threonine protein kinase is a core component of the human centrosome. It plays critical roles in regulating cell division, controlling kinetochore–microtubule attachment, and promoting spindle checkpoint assembly. Aberrant activity of Nek2 kinase has been associated with highly invasive behavior of metastatic tumors. Furthermore, the overexpression of Nek2 has also been correlated with chemotherapeutic drug resistance. Novel inhibitory agents of Nek2 kinase are thus urgently needed for development of targeted therapeutics. Using the first whole-animal Nek2 overexpression fly model developed in our laboratory, we have identified a novel drug-like quinoline-based pharmacophore that inhibited Nek2 function *in-vivo* and reduced metastasis. The current work involves developing structure-activity relationship (SAR) on this newly discovered pharmacophore so that a time-dependent covalent Nek2 inhibitor with high selectivity profile is emerged. It is anticipated that that developed inhibitory molecule will possess desirable anti-cancer activities with superior toxicity profile.

36. Synthesis of isatin-thiazolidine-2-thione hybrids for acetylcholinesterase inhibition

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Alzheimer's disease (AD) is the leading neurodegenerative disease, with over twenty million cases worldwide. While there is no cure for AD, certain treatments have been used clinically to help alleviate symptoms. One of the main ways this is done is by inhibiting acetylcholinesterase (AChE), the enzyme that breaks down the neurotransmitter acetylcholine. The current AChE inhibitors (AChEi) are both incapable of halting or reversing disease progression and potentially damaging to other organs, such as liver toxicity from tacrine. New AChEi that could simultaneously target another aspect of AD would be an important advancement, and a promising contender is isatin. In the literature,

isatin has proved to be a better AChEi than tacrine, while also showing diverse additional biological activity. The current research will focus on the synthesis of isatin-thiazolidine-2-thione hybrid molecules as AChEi. The thiazolidine-2-thione heterocycle has yet to be investigated in this capacity, but it is anticipated to interact favorably with the aromatic amino acids at the peripheral and catalytic sites of AChE. The results of a synthetic sequence to access these hybrids with varying length carbon chains linking the two molecules and varying bromo-substituents will be presented. An in vitro AChE assay will be used to determine inhibitory activity. In addition, molecular modeling images of selected hybrids docked with AChE will show the predicted binding energies and conformations. Isatin-based inhibitors could be the key in discovering new treatments to slow AD progression.

37. How do lipids bind to the vanilloid site of TRPV1? Insights from molecular docking

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The Transient Receptor Potential Vanilloid 1 (TRPV1) is a nonselective cation channel with the greatest permeability to Ca^{2+}. TRPV1 is activated by low pH, noxious heat, and the binding of certain lipids and vanilloid molecules, among which is the exogenous agonist capsaicin. Activation of TRPV1 leads to nociceptive pain and is implicated in a number of physiological roles, such as body temperature regulation, inflammation, increase in the blood brain barrier's permeability, etc. Recent experimental structures revealed that vanilloid ligands, toxins and, importantly, lipids can bind to the vanilloid site of TRPV1, the latter resulting in either a capsaicin-agonist or -antagonist effects. Despite being largely investigated, the molecular determinants of binding and the precise mechanisms of regulation exerted by different lipids on TRPV1 remain to be elucidated. To investigate lipid binding to TRPV1, we examined a cryo-EM structure of the apo channel captured with a lipid bound to the vanilloid site. We then performed molecular docking of several classes of lipids (https://www.lipidmaps.org/) against TPV1 using Glide (www.schrodinger.com). The top scoring lipids were also evaluated using AutoDock Vina (http://vina.scripps.edu/), to compare binding modes and predicted affinities, as well as to identify and further characterize TRPV1 residues responsible for lipid binding. Results obtained from this investigation can be used as a basis for characterizing the role of biologically relevant lipids in TRPV1 activation, and as a starting point for the design of TRPV1 modulators.

38. Thermodynamic measurements of the oxidation-reduction (Fe3+/Fe2+) reactions of heme-fluoride complexes of hemoglobin and myoglobin: Insights into oxygen binding

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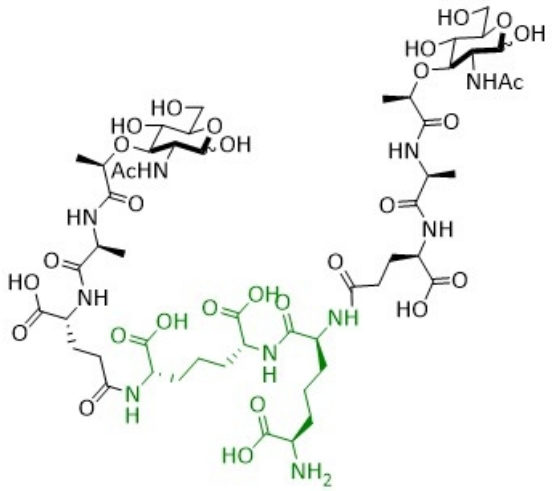
Oxygen binding equilibrium in myoglobin (Mb) is proposed to occur via the formation of a heme (ferric-superoxide) complex, $Mb(Fe^{2+}) + O_2 \rightarrow Mb(Fe^{3+}\text{-}O_2^-)$ [1]. The ferric-superoxy heme complex is electrostatically stabilized by the distal histidine E7his. In our most recent study, we utilized fluoride binding in hemoglobin (Hb) and myoglobin (Mb) and measured the enthalpy (D*H*) and entropy (D*S*) for the Fe^{3+}/Fe^{2+} redox change in hemoglobin-fluoride (Hb-F) and myoglobin-fluoride (Mb-F) complexes at pH 5 and pH 7. We then used the determined thermodynamic values to obtain the D*H* and D*S* for the oxidation of Hb and Mb in the presence of the fluoride ion: $Hb(Fe^{2+}) \rightarrow Hb(Fe^{3+}\text{-}F^-)$ [2] and $Mb(Fe^{2+}) \rightarrow Mb(Fe^{3+}\text{-}F)$ [3]. The oxidation of Hb and Mb in the presence of fluoride ion is similar to the oxygen binding equilibrium shown in [1]. Our results show that the oxidation of Mb-F complex, reaction 3, at pH 5, is the most favorable process at physiological temperature. The measured D*S* and D*H* for reaction 3 were -97.5 J K^{-1} mol^{-1} and -33.0 kJ mol^{-1}, respectively. The measured Gibbs energy for reaction 3 at pH 5 and at 37°C was -3.0 kJ mol^{-1}. Regarding the measured Gibbs energy for the Hb-F complex at 37°C, reaction 2, the process was more favorable at pH 5 with a value of 6.1 kJ mol^{-1}, while the same reaction at pH 7 was 6.5 kJ mol^{-1}. These results show that stabilization of the heme-fluoride complex by the distal E7his plays a role in the fluoride-binding equilibrium in Mb and Hb: at low pH, the positively charged histidine stabilizes the heme-fluoride complex. Such role of E7his has also been proposed in the regulation of oxygen binding in Mb and Hb.

39. Synthesis of m-DAP crosslinked muramyl dimers

***Jared R. Ramsey**, jaredramsey6@gmail.com, Siavash Mashayekh, Catherine L. Grimes. University of Delaware, Newark, Delaware, United States*

The bacterial cell wall, peptidoglycan (PG), is a key tool for the identification of bacteria by the innate immune system. For the body to function properly, this system needs to be able to accurately dispose of pathogenic threats while retaining commensal bacteria. To accomplish this, immune receptors can recognize PG from a variety of bacterial species and differentiate between them. Unfortunately, errors are known to occur in this recognition, leading to false inflammatory responses. For many people, this occurs in the gut, resulting in inflammatory bowel diseases (IBD's). The immune proteins NOD1 and NOD2 (nucleotide oligomerization binding proteins) have been found to bind PG fragments known as muramyl dipeptide (MDP), and iE-DAP respectively. Both are PG derived ligands which have been studied frequently. However, when bacteria are digested in the body, PG can fragment into structures with much greater diversity. Our synthesis focuses on obtaining a library of muramyl dimers linked through their peptide chain, a class of compounds whose properties have been scarcely studied. The synthesis of lysine crosslinked dimers was previously displayed in our lab using solid phase techniques. This work expands on the aforementioned synthesis by implementing *meso*-diaminopimelic acid (m-DAP) crosslinking patterns which are characteristic to gram-negative bacteria. Furthermore, a solution phase approach has been devised. The completed synthesis of these compounds will open the doors to an array of applications for muramyl dimers such as RT-PCR for analysis of gene activation, or surface plasmon resonance (SPR) protein binding assays.



m-DAP crosslinked muramyl dimer

40. Importance of MAS-R in inflammation, inflammatory disease, and COVID-19 therapeutics

***Zoe Sessions**, zoe1117@live.unc.edu. Chemistry, The University of North Carolina at Chapel Hill, Chapel Hill, North Carolina, United States*

The infection caused by SARS-CoV-2, COVID-19, is highly contagious and presents many outcomes in varying individuals, including those that are fatal. ACE2 is the primary cell entry point for SARS-CoV-2 and serves a key enzyme in the RAAS. The RAAS is a master regulator and therapeutic focus for pulmonary, immune, renal, or lung disease. ACE2 deficiency has been associated with increased ANG II levels, cardiac dysfunction, fibrosis, heart failure, hypertension, renal damage, diabetes, and severe acute lung failure (which was attenuated by intervention with soluble recombinant ACE2). ACE2 converts ANG II to Ang 1-7 which in turn activates the MAS-R. Assuming ACE2's enzymatic abilities are inhibited by SARS-CoV-2 binding, this process would also be inhibited. MAS-R activation leads to anti-inflammatory and anti-fibrotic effects, as well as nitric oxide production and vasorelaxation. This pathway is a crucial regulator of the body's inflammatory response. We attempted homology modeling of MAS-R but failed due to the insufficiency of homologous crystal structures/proteins. Further research should be done into MAS-R as its therapeutic potential is expansive and goes well beyond COVID-19.

41. Using bioinformatic approaches to investigate neisseria meningitidis serogroup W enzyme

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Neisseria meningitidis serogroup W (NmW) capsule polymerase and other serogroups of Neisseria are leading causes of bacterial meningitis. The NmW capsule polymerase enzyme is responsible for creating the galactose-sialic acid-containing capsular polysaccharide of this serogroup. This enzyme contains 1037 amino acids and has three domains: an N-terminal galactosyltransferase, an intervening sequence, and a C-terminal sialyltransferase domain. Currently, there is no three-dimensional structure of this protein. We hypothesize that using bioinformatics will save time and effort by allowing us to predict key amino acids important to substrate specificity. This project uses the known amino acid sequence of the enzyme combined with open-source bioinformatics tools (ExPasy's ProtParam tool, the Protein Data Bank (PDB), NCBI BLAST, I-TASSER) and protein visualization software (Swiss PDB Viewer) to obtain three-dimensional models of the sialyltransferase domain (original and newly reclassified). The NmW enzyme amino acid sequence was entered into ProtParam to aid in the identification of domain sequences. The sequences of the original and revised sialyltransferase domains were put into I-TASSER. Five predicted three-dimensional structures were obtained for each. The best model for the original and revised sialyltransferase domains had C scores of -0.71 and -1.03, respectively. Ten proteins from the PDB were used to create each homology model. Escherichia coli MurG was predicted to be the most similar to the original model with a TM

score of 0.897. V-ATPase in bacteria was predicted to be the most similar to the revised model with a TM score of 0.912. In conclusion, through the use of the described bioinformatics tools, we obtained homology models that can be used as a foundation to study the potential activity of the serogroup W enzyme with modified substrates.

42. Optimizing conditions to maximize algae growth for biodiesel production

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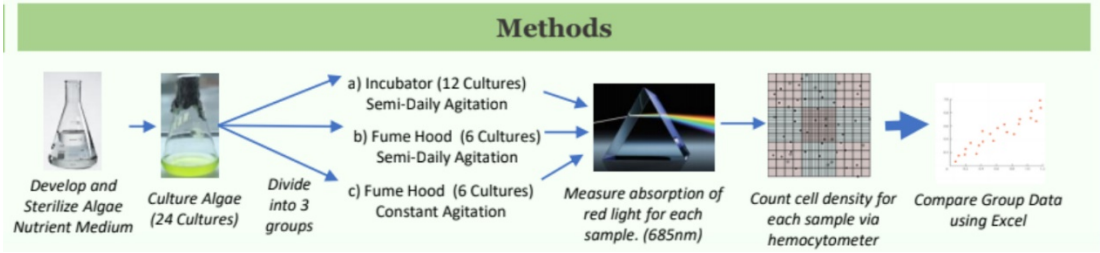
Select subspecies of microalgae are considered to be the most promising candidates for third generation renewable resources of biodiesel. Algae not only ingest excess carbon emissions from the atmosphere, they also convert it into energy-dense lipids which can be harvested, and then transformed into biodiesel. However, before the fuel industry can adopt algae farming as a realistic alternative to fossil fuels, the process of harvesting algal lipids must be optimized further. Our research aims to make algal lipid extraction more realistic by determining the ideal growing conditions of the algae species Chlorella Vulgaris. Our research this semester focused on two objectives: The first objective was to generate a standard plot which relates Absorbances of algae cultures to their cell densities. A standard plot would then replace cell-counting and hemocytometer usage, saving us many hours per semester. The second objective was to determine the highest algae growth rates between three groups: a) incubation with semi-daily agitation, b) fume hood with semi-daily agitation, and c) fume hood with constant agitation. Our resulting standard plot shows a direct linear relationship between absorbance and cell density with a R squared value of 0.8629. Group c had the slowest growth rate, while groups a and b had similar growth rates which were nearly double that of group c. Our data suggests that constant agitation is not an ideal condition for algal growth.



Research Methods

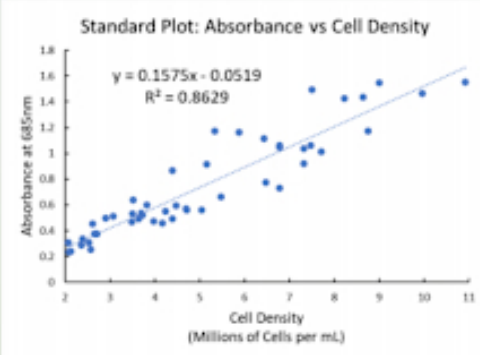


Figure 1 (left): Standard Plot Relating Absorbance of Culture to Cell Density. One goal of our study was to determine whether a standard plot may serve as a future tool to quickly determine the cell density of any given culture by simply measuring the culture's absorbance, rather than spending hours counting cells with a hemocytometer. Absorbance values were measured using 1.00cm polystyrene cuvettes in a Varian Cary 50 UV-Vis Spectrophotometer. Cell Density values were determined by taking microscope photographs of a Bright-Line hemocytometer, and then counting the individual cells in the photo. Data was acquired from the even numbered algae cultures (6, 3, and 3 from groups a, b and c respectively).

43. Identifying small organic molecules that induce an alternative structure in precursor miRNA-92b

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Translational regulation of protein synthesis is partially controlled by small non-coding RNAs called microRNAs (miRNAs). A miRNA downregulates protein translation by acting as a guide for the RNA-Induced Silencing Complex (RISC), which binds to a target mRNA and inhibits its translation. MiRNAs have a multiple step biogenesis that relies on two cleavage events, first by the enzyme Drosha and then by a second enzyme Dicer. The canonical stem-loop structure of precursor miRNAs (pre-miRNAs) has been found to be necessary for Dicer cleavage, as Dicer recognizes the pre-miRNA's two nucleotide 3' overhang, among other features, prior to cleavage. Recently however, it has been shown that some pre-miRNAs exist in an equilibrium between the stem-loop structure and a non-canonical guanine quadraplex (G4) structure. One of the identified G4 containing pre-miRNAs is miRNA-92b, which is a clinically important miRNA as its upregulation as been correlated with multiple types of cancer and chemotherapy resistance. We used a small molecule microarray screen to identify compounds that selectively bind to the G4 forming pre-miR-92b. Additionally, we performed dose-dependent fluorescence-based titrations to assess the concentration in which these compounds bind to the RNA and to investigate their selectivity for the G4. We are currently working to analyze the compounds' ability to stabilize the G4 structure through both biochemical and biophysical means. Lastly, we are exploring the effects that these compounds and the induced G4 structure have on pre-miR-92b maturation through Dicer cleavage.

44. Optimization and characterization of novel formulations for hydrophilic biological drug encapsulation

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Despite considerable advances in recent years, challenges in delivery and storage of biological drugs persist and often delay or prohibit their clinical application. Nanoparticle-based approaches for drug encapsulation have become highly sophisticated, yet application of these methods to biologics is often limited by negative effects of the encapsulation approach on the structure or stability of the drug. A reverse micelle encapsulation approach using mixtures of decylmonoacyl glycerol (10MAG) and

lauryldimethylamino-*N*-oxide (LDAO) in low-viscosity alkanes has been shown to preserve the structure and stability of a wide range of biological macromolecules. Here, a comprehensive screen of the 10MAG/LDAO system using two preparation methods across seven biocompatible solvents is presented with analysis of toxicity and encapsulation efficiency for each solvent. The findings of this study indicate strong potential for modification of the 10MAG/LDAO system for encapsulation of proteins in fully biocompatible formulations. The insight gained lays the foundation for further development of this system toward long-term room-temperature storage of biologics or toward water-in-oil-in-water biologic delivery systems.

45. Green chemistry/bioremediation: Converting SmFixL from an oxygen sensor into a dye-decolorizing peroxidase

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Pollution in the environment is a widespread issue, specifically from industrial sources polluting water systems with textile dyes. Techniques in place today to remove the dyes from our environment are costly and cause additional harm to our environment. A new technique involving heme based proteins that is environmentally friendly may replace the old techniques in a push for bioremediation. Heme proteins that are able to remove harmful dyes from the environment are classified as dye-decolorizing peroxidases (DyPs). A key feature to dye-decolorizing peroxidases is the presence of arginine and aspartic acid residues that are said to help with the catalytic mechanism of the enzyme. These enzymes are able to degrade dyes slowly and in a narrow pH range. With the use of mutations, other heme type proteins may be converted to dye-decolorizing peroxidases. In fact, the heme based oxygen sensor SmFixL may be able to be converted to a dye-decolorizing peroxidase. Prior research suggests that an arginine residue at position 214 in the amino acid chain is important for its catalytic function, which suggests that mutation of a nearby residue that interacts with it to aspartic acid may convert it to a peroxidase. The variant proposed to convert SmFixL into a dye-decolorizing peroxidase is mutation of the leucine residue at position 230 to aspartic acid. If this mutation is successful and SmFixL expresses the catalytic function of a dye-colorizing peroxidase, then it may be used to remove harmful dyes from the Earth’s environment.

46. Encapsulation in reverse micelles reveals the thermodynamic impacts of confinement versus interfacial interactions in the unfolding of myoglobin

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Studies of protein folding thermodynamics are often performed in bulk aqueous solutions that do not model the biological environment of the macromolecular crowded cell. The effects of cellular confinement on protein stability are poorly understood. One solution to better account for and understand this problem is the introduction of proteins to reverse micelles. Reverse micelles are nanoscale water droplets encapsulated by surfactants dissolved in a bulk nonpolar solvent. Under optimized conditions, proteins can be encapsulated with maintenance of the native conformation seen in bulk aqueous solution. In this study, the effects of confinement were studied in bulk solution and in reverse micelles by chemically inducing myoglobin unfolding with guanidinium hydrochloride. The Soret band was monitored by UV/Vis absorbance spectroscopy to determine the protein structural state. The composition of the reverse micelle was varied to manipulate the degree of confinement and the surfactant interfacial charge in an effort to separate these effects and determine their impact on the stability of the protein.

47. Fatty Acid Amide Hydrolase (FAAH) inhibitors designed for reduced permeability Bailey Mims, Julianna Young, So Jung Kim, Grace Roe, Dr. Lazenka, Dr. Fulp*

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Peripherally selective compounds have been shown to offer advantages in some indication such as eye wound healing and modulation of gastrointestinal pain. Cannabinoid receptor 1 (CB1), an endocannabinoid receptor located ubiquitously in the human body, is activated by the endocannabinoids anandamide (AEA) and 2-arachyidonoylglycerol (2-AG). AEA is rapidly hydrolyzed by the fatty acyl amide hydrolase (FAAH) enzyme. To enhance CB1 activation, FAAH was targeted for therapeutic inhibition. Peripherally selective inhibitors were designed and synthesized as sulfonamide derivatives to increase topological polar surface area (TPSA). This modification was done to prevent compounds from crossing the blood-brain barrier in order to avoid adverse effects on the central nervous system. The compounds were purified through the use of radial preparative layer chromatography (RPLC), and identity as the desired products was confirmed via nuclear magnetic resonance (NMR). Cayman's FAAH inhibitor screening assay kit was used to assess the percent inhibition exerted on FAAH. JZL 195, a well-studied inhibitor of endocannabinoid receptors, was used as a control. Compound permeability was assessed in a PAMPA assay.

48. Catalysis by sol-gel encapsulated enzymes: Hb/Mb and H_2O_2 dismutation

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Heme proteins play important roles in biological systems often through enzymatic function. Interestingly, even Hemoglobin (Hb) and Myoglobin (Mb) that are traditionally categorized as oxygen binding and transport proteins can also act as catalysts - a function that may play an important role under conditions of inflammation. The method of silica based sol-gel encapsulation of proteins is a powerful approach for studying and characterizing proteins function under conditions of high viscosity. Moreover, encapsulated protein in sol-gel matrices were shown to have enhanced stability under high temperature or extreme pH. This can lead to better utilization of enzymes for a variety of applications. We performed a range of kinetic experiments to explore the catalytic function of heme proteins in solution vs. when they are encapsulated within the silica based sol-gel matrices. A relatively well defined system that lends itself to such studies is the catalytic role of heme proteins in the catalysis of hydrogen peroxide dismutation reaction. This system provides several reliable markers for kinetic studies of this reaction enabling the evaluation of the catalytic function of the enzymes. Moreover, in this reaction, overtime, the heme protein can undergo inactivation losing it's catalytic activity. This is a good test case for exploring the role of the sol-gel environment in modulating both the catalytic activity of heme proteins as well as the enzymatic inactivation processes. We present our ongoing studies and contrast the results in solution and when the heme proteins are in the sol-gel matrix.

49. Investigating the effects of DNA base substitution on DNA structure and dynamics with high-affinity Fis-DNA complex

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Fis is a highly expressed nucleoid-associated protein that co-regulates a variety of DNA transactions in bacteria. High-affinity Fis-DNA binding requires specifically-recognized G-C base pairs spaced 13 base pairs apart, an intrinsically narrow central minor groove, and Fis-stabilized DNA kinks. Fis establishes critical contact between backbone phosphates between ±7 and ±10. The most extensive phosphate interactions occur at the 5' phosphate of the ±8 nucleotide where peptide amides from two residues (Gln74 and Thr75) and side-chain groups from two residues (Asn73 and Thr75) hydrogen bond to the non-esterified oxygens. The base at the ±8 position can have a large effect on Fis binding with a G being strongly inhibitory, with 150-fold worse binding than the high-affinity F1 (8T) site. Purines, especially guanines at the ±8 position inhibit the formation of critical backbone contact. Our research investigates why the 8G substitution results in such a large reduction in binding affinity and the effects of the 8G substitution on the structure and dynamics of the protein residues contracting the flanking DNA. We propose that the 8G substitution will result in alterations to DNA structure and dynamics, which could include variations in groove widths, DNA bending, and DNA roll angles critical to Fis-DNA complex stability. To investigate the effects of the 8G substitution on DNA structure and dynamics, we performed 500 ns molecular dynamics simulations on the high-affinity Fis-F1 complex and 8G substitution using the AMBER suite of programs. The relative

distances and dynamics of key phosphate interacting residues in the Fis-F1 and Fis-8G complexes will be reported in addition to relative differences in global and local variations in DNA structure and dynamics as analyzed by cpptraj and Curves+. Together these analyses will provide insight into the structural and dynamic origins associated with the dramatic reduction in Fis-DNA binding affinity for sites containing a +/-8G flanking the core Fis binding site.

50. Separating the effects of confinement and interfacial interactions for the model protein cytochrome c using reverse micelle encapsulation

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Bulk aqueous solution has been the standard conditions for studying protein stability. Inside the cell, however, large molecules are packed tightly, resulting in a highly crowded environment with limited space that may cause changes in protein thermodynamics. This crowded condition presents a wide range of spatial restriction, but it also presents opportunities for nonspecific interactions between proteins and their environment that may further alter stability. We are using reverse micelles to mimic the confinement presented by intracellular confinement. Reverse micelles are spontaneously organizing complexes with an aqueous core surrounded by a layer of surfactant dissolved in a nonpolar solvent. By encapsulating cytochrome c in the reverse micelle interior, we are using this system to examine the effects on protein stability. The folded state of cytochrome c is easily monitored by observing the absorbance of the Soret Band. By varying the amount of water in the system and the composition of the surfactants in the reverse micelle shell, we can compare the effects of confinement to the effects of nonspecific interactions with the interface on the thermodynamic stability of the protein. The results of our analysis will be presented and will show the differential effects of these important aspects of the protein's environment.

51. Overexpression and purification of alexphander gp94: A predicted MerR-like transcriptional regulator

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Bacteriophages are viruses that infect and kill a specific bacterial host by hi-jacking the bacterial machinery to replicate within and lyse bacterial cells. With the rise of antibiotic resistant strains of bacteria, use of phages has been proposed as an alternative to antibiotics. One potential benefit of using phages as therapy is that they can evolve with the bacterial host, reducing the probability of phage resistant bacterial strain. our research group studies phages that infect *M. Smegmatis*, a close relative the pathogenic

bacteria *M. tuberculosis* and *M. leprae*, the causal agents of tuberculosis and leprosy respectively. Specifically, we are interested in understanding the role of the mycobacteriophage Alexphander gp94 in mycobacteriophage infections. Gp94 is predicted to encode a MerR-like transcriptional regulator that may regulate phage gene expression in response to stress such as DNA damage. To further characterize the DNA binding properties and atomic structure of gp94, it must first be purified from an E. coli expression system. Immobilized metal affinity chromatography (IMAC) has been performed on the 6-His tagged, full length, gp94 expressed from *E. coli*. This process yielded large quantities of 90 to 95% pure gp94. Our purest fractions of gp94 eluted at 75 mM and 100mM imidazole. Interestingly, addition of dithiothreitol to SDS PAGE samples results in a shift of gp 94 to a higher molecular weight species suggesting that intrachain disulfide bonds may stabilize some aspects of gp94 structure. This work provides an efficient method to obtain pure gp94 and sufficient quantities to embark upon biochemical and structural characterization of gp94. These future studies will include elucidating gp94 DNA-binding properties and crystallization trials on full length and truncated gp94 constructs.

52. Harnessing green chemistry in the search for agricultural sustainability

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Agriculture, the largest industry on the planet employing one in three humans, is faced with the daunting challenge of feeding an ever-increasing population while also reducing its untenable ecological impacts. Farming must also evolve to respond to the increasing impacts of climate change, water shortages, and pesticide resistance worldwide. We examine how the design framework of green chemistry can help bring about a paradigm shift in how humans farm. Emerging trends and challenges in green chemistry-compatible advances in agriculture, such as the use of semiochemicals and biologically derived pesticides, the genetic modification of crops, the application of chemical and biological enhancers for fertilizer nutrient uptake, and nanotechnology in agriculture, will be assessed through a biogeochemical and ecosystem lens.
The goal of our project will be to explore the theory and applications of Green Chemistry in achieving agricultural sustainability, which is becoming an urgent need due to our ever-increasing population, resource depletion, and widespread pollution and climate change related to current agriculture practices. The United Nations' 2030 Agenda for Sustainable Development which was adopted by 115 nations, has 17 stated sustainable goals, most of which deal either directly or indirectly with agriculture, reflecting the urgent need for new and interdisciplinary research in this area.

53. In vitro effect of Bee Propolis on Human Tongue Cancer cell death

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There are an estimated 52,000 Americans who will be diagnosed with oropharyngeal or oral cancer over the next year. Of those 52,000 individuals diagnosed, only 57% are expected to be alive in five years. Treatment methods for oral cancers currently include surgery, chemotherapy, radiation, and immunotherapy. However, these treatments do not guarantee recovery, and may cause adverse effects. Bee propolis is a natural substance which is well known for its anti-inflammatory, antibacterial, antifungal, and anticancer properties. The goal of this research project was to evaluate the effects of ethanol-extracted propolis on tongue cancer cell death. A human tongue cancer cell line of metastatic squamous cell carcinoma (SCC154) was cultured at 37^{o}C with 5% CO_2 in an Eagle's Minimum Essential medium supplemented with fetal bovine serum (10%), L-Glutamine (2 mM), Amphotericin B (2.5 µg/mL), and Gentamycin (50 µg/mL). In our tests, we replaced 10% of the medium with various concentrations of ethanol-extracted bee propolis (0.01% and 0.1%; V/V) in culture flasks containing 90-95% cell confluency. The same was done using ethanol as a negative control. The cultures were evaluated over seven days for confluency. At the end of the treatment, the cells were digested and treated with trypan blue to determine the amount of dead and live cancer cells using a hemocytometer and microscopy. The propolis dose dependently reduced the total cell count and stimulated cell death. The 0.01% caused a 6.7 times increase in cell death, while slightly effecting the total cell count and the 0.1% resulted in an 18 times increase in cell death and a 5.7 times decrease in the total cell count. These results suggest that the ethanol-extracted propolis has anticancer properties against tongue cancer, and therefore has the potential to aid individuals suffering from this disease.

54. Elimination of organosulfur compounds from model fuels with biological wastes: Tackling the acid rain

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The prevalence of organosulfur compounds compounds in fuels has been an important concern since the XIX century as an environmental risk due to the increase of greenhouse gases in the atmosphere and accentuation of acid rain. This project evaluates the potential of solid waste such as fruit peels as adsorbents for the removal dibenzothiophene (DBT). The adsorption on the fruit peels of orange (OG), lime (LM) and pineapple (PN) was investigated in a batch and continuous- flow systems with synthetic fuels (gasoline and diesel) as a function of type of adsorbent, adsorbent dosage, initial concentration of DBT and column experiments. DBT adsorption follows this trend in gasoline: LM (12.3%) > PN (8.8%) > OG (6.9%) with 50mg, 125mg, and 50mg, respectively. On the other hand, the adsorption of DBT in diesel followed the trend: LM (14.6%) > OG (4.2%) > PN (3.5%) with 50mg, 75mg, and 75mg, respectively. Instrumental analyses propose a polar-drive mechanism by the interaction of carboxyl and hydroxyl groups of the adsorbent and the sulfur atom of DBT. Thermal analysis also suggest that these materials have good thermal and mechanical properties. Column experiments indicate that this approach can be used in continuous-flow system for the treatment of

larger volumes of fuels. This work highlights the potential use of fruit peels for the elimination of organosulfur compounds from model fuels as a low-cost and environmentally friendly purification technique.

55. Uptake of Co(II) ions from aqueous solutions by low-cost biopolymers and their hybrid

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Alginate hydrogel beads (AB), spent peppermint leaf (PM) and a hybrid adsorbent of these two materials (ABPM) were studied as potential biosorbents of Cobalt (II) ions from aqueous solutions. Cobalt ion is a commonly underestimated pollutant that is responsible for several health problems. Discontinuous batch experiments were conducted at room temperature to evaluate the effect of solution acidity and mass of adsorbent on the adsorption of Co(II) ions. The interfering effect of salinity, presence of surfactants, an organic dye, and Pb(II) ions were also studied to resemble the application of these adsorbents in real wastewater. Equilibrium results indicate that Co(II) uptake is maximized at pH values higher than 5, with adsorbent doses of 200 mg, 200 mg, and 120 mg for AB, PM and ABPM, respectively. Co(II) adsorption followed the trend AB > ABPM > PM with adsorption percentages of 77%, 71% and 64%, respectively. Salts had a strong negative effect on the adsorption due to the increase of the ionic strength and the competition for adsorption sites. Presence of Pb(II) ions, surfactant and dye BY57 had a slightly negative effect on the adsorption, apparently due to their interaction with different adsorption sites that do not interfere with the removal of Co(II). A polar-electrostatic adsorption mechanism is proposed based on the experimental results. Scanning electron microscopy indicates that adsorbent have appropriate morphological and textural properties, and that ABPM encapsulated most of the PM inside of the hydrogel beads. These experimental results revealed that AB, PM and ABPM are promising adsorbents for the elimination of Co(II) ions from aqueous solutions under different experimental conditions. These biopolymers are proposed as eco-friendly alternatives for the removal of heavy metal ions at lower costs than conventional techniques.

56. Effects of annona muricata on a breast cancer cell line

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Cancer has become a pressing issue around the world and according to the National Cancer Institute, breast cancer was the most frequently diagnosed type in 2020. While there are several treatment options available such as chemotherapy, surgery, and radiation; these invasive methods have side effects. Several natural remedies have been indicated as alternative treatment options including *Annona muricata* (soursop), which is rich in alkaloids, acetogenins, and quinolones with anticancer potential. Since the anticancer property of *Annona muricata* has never been evaluated on cancer, we tested its effects on a breast cancer cell line (MD-kb2). The cells were maintained in Leibovitz's L-15 Medium supplemented with 10% Fetal Bovine, Amphotericin B (2.5 µg/ml), and Gentamicin (50 µg/ml), and grown in a 37 degrees Celcius incubator. A powdered drink

form of *Annona muricata* was dissolved and added to the cultures by replacing 10% of the medium, resulting in 2.5 mg/ml, 5 mg/ml and 10 mg/ml concentrations. The control flasks received 10% sterile distilled water. The confluency was monitored for two weeks using the inverted microscope. On day 14 the cells were treated with Trypan blue and counted using a hemocytometer to obtain the number of viable and dead cells. The treatments dose dependently inhibited the growth in confluency, and increased the cell death count. The study demonstrated that *Annona muricata* can be an effective alternative preventative treatment for breast cancer.

57. Triticain-α: An enzymatic approach to managing celiac disease

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Celiac Disease (CD) is an autoimmune disorder characterized by the inability to digest gluten proteins in genetically susceptible individuals, resulting in chronic inflammation of the small intestine and mucosal damage. Genetic determinants of the condition are the presence of human leukocyte antigen (HLA) DQ2 and HLA-DQ8 encoding genes. The global prevalence of CD is around 1%. Currently, the only known treatment for CD is a gluten-free diet. Triticain-α is a wheat cysteine protease demonstrated in prior research to elicit glutenase activities in the immunodominant 33-mer α-gliadin-derived peptide in conditions simulating the gastric environment of the stomach. RNA was isolated from germinating *Triticum aestivum*, cDNA was polymerized, and the Triticain-α coding sequence was amplified with polymerase chain reaction (PCR). The obtained coding sequence was inserted into the expression plasmid aLICator Ligation Independent Cloning and Expression System. Triticain-α was expressed by isopropyl β-d-1-thiogalactopyranoside (IPTG) induction of the *lac* operon promoter in *E. coli* (BL2-DE3). Further analysis of enzymatic potentiality of Triticain-α will include the purification and incubation of the protein with gluten in gastric conditions. Gluten hydrolysis products will be identified to confirm glutenase activities of Triticain-α.

58. Adsorption of heavy metals using chemically-modified tea leaves

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Copper is perhaps the most prevalent heavy metal used in the manufacturing industries, from food additives to metal-mechanic factories. Common methodologies to remove copper are expensive and produce undesired substances that need to be taken care of. A good decontaminating candidate should be environment-friendly, inexpensive, and capable of eliminate low concentration of the metal. This can be achieved by chemically-modifying known adsorbents to enhance their adsorption properties. This work suggests the use of a chemically-modified spent tea leaves of chamomile, peppermint and green tea under their thiolated, sulfonated and carboxylated forms as candidates for the removal of copper from solutions. Batch experiments were carried out to maximize the adsorption

of copper (II) ions. Effects such as acidity, salinity, adsorbent dose, metal concentration, and presence of surfactant were explored. Experimental data shows that the maximum adsorption is reached at neutral pH. The results indicate that Cu(II) can be removed up to 53%, 22% and 19% with the thiolated, carboxylated and sulfonated adsorbents, respectively. The maximum adsorption of copper on TPM (53%) is achieved with 150mg and decreases with the presence of salts, and surfactants. Conversely, sulfonated and carboxylated adsorbent show a better adsorption in the presence of surfactants. Time dependent experiments show that adsorption is reached in less than 25 min for TCM and 5 min for SCM. Instrumental analyses were used to determine the presence of active functional groups, thermal resistance, and scanning electron microscopy; indicating that both adsorbents are promising cost-efficient materials for the selective recovery and treatment of metal ions from wastewaters. Finally, columns were prepared with these adsorbents to explore their application in scaled-up processes, with very positive results. A long-term goal involves the recycling of the exhausted adsorbent and/or their use in the preparation of biofuels due to changes in materials' structures.

59. Milk stretches the non-toxic range for curcumin-induced NRF2-activation

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Nuclear factor erythroid2-related factor 2 (Nrf2) is a leucine zipper transcription factor whose activation restores redox homeostasis. Activators of Nrf2 have gained popularity due to their implication in slowed aging and neurodegeneration. Currently, there is only one FDA-approved Nrf2 activator, dimethyl fumarate (Tecfidera), which is used as a treatment for multiple sclerosis. The remainder of marketed supplements are sold over the counter with claims not verified by the FDA. We tested five popular turmeric-based supplements in a cell-based Neh2-luc fusion reporter assay designed to screen for Nrf2 activators working via disruption protein-protein interaction between Neh2-domain of Nrf2 protein and its inhibitor, a ubiquitin ligase adaptor protein Keap1. The potency of supplements was quantified with respect to pure curcumin. Poor solubility in water makes curcumin bioavailability low. Yet, an appreciable degree of activation was seen in DMSO solubilized samples, with some solubility in alkaline solutions. Additionally, we found that milk is an effective solubilizer of curcumin from turmeric powder, and it is milk protein, not milk fat, which increases curcumin bioavailability. Milk is also known to contain stoichiometric antioxidants, which may lower the toxicity of curcumin in the high concentration range. In fact, we did observe that milk also stretched the range of non-toxic curcumin concentrations without compromising its maximum potency.

60. Synthesis of mixed bi-icosahedron nanoclusters with increased fluorescence

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This study aims to use the unique properties of gold bi-icosahedron nanoclusters and synthesize mixed metal alloys in order to increase fluorescence. Alloys are useful and important to nanoscience as they improve the properties of the homogeneous gold clusters. Creating alloys modifies the electronic structure as well as the surface composition of the parent cluster. However, the quenching or enhancement of the fluorescence caused by interaction with metal ions is not yet understood. The goal of this research is to establish the interaction of Ag and Cd with bi-icosahedron gold nanoclusters and observe the impact the metals have on the properties of the parent cluster for the first time.
Mixed metal clusters can be synthesized by first making the gold nanoclusters and then reacting them with metal salts or metal thiolate complexes or by altering the synthesis process for the clusters to include the metal ions. The parent clusters will be bi-icosahedron gold nanoclusters. Gold nanoclusters are used as a fluorescence probes in the biomedical field due to their unique properties. In addition, they also serve in the field of nanoengineering for light harvesting applications. Increasing the fluorescence of the clusters can improve this function for the field, which is my goal using Ag and Cd atoms for the first time. So far, previous work has provided a 200-fold increase with the icosahedral structure and I am looking to push this improvement further with my research on the bi-icosahedral structure.

61. Solar degradation of toxic colorants in polluted water by thermally tuned ceria nanocrystal-based nanofibers

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In our work, we demonstrated a facile method for synthesizing a sustainable photocatalyst, which is CeO2 nanofiber crystals for efficient solar degradation of toxic colorants in polluted water. To fabricate CeO2 nanofiber crystals, we used electrospinning and thermal tuning technique at 500−1000 °C. According to our results, the photocatalytic performance of the CeO2 has been improved by this simple thermal tuning. Under the simulated solar irradiation condition, the pure CeO2 nanofiber crystals which do not corporate any potentially harmful impurities degraded up to 97.6% methylene blue (MB) over 180 min. Further, the CeO2 nanofiber crystals demonstrated excellent long-term recycling stability with less than 1% activity fluctuations in 10 cycles. The improved photocatalytic performance was attributed to the small crystal size, clean crystal surface, and plenty of oxygen vacancies of CeO2. SEM and TEM observations showed that the

average fiber diameter decreased while the particle size increased with tuning temperature. FTIR revealed that the surface-adsorbed organic moieties decreased with the increase of temperature, making active sites more accessible for photocatalysis. The presence of oxygen vacancies was confirmed by both Raman and XPS, which were critical for the activation of oxygen in photocatalysis. The CeO2 photocatalyst obtained from electrospinning and thermal tuning is eco-friendly and inexpensive for large-scale application in removing toxic colorants in water.

62. Growth mechanism study and emulsion-templated self-assembly of semiconducting cadmium selenide nanoplatelets

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Colloidal semiconductor nanoplatelets (NPLs) are rectangular-shaped, quasi-two-dimensional nanoparticles with bandgaps discretely tunable by the number of atomic layers. Anisotropic NPLs have much narrower photoluminescence peaks compared with more conventional spherical quantum dots (QDs), generating intense interest, but the NPL growth kinetics has not yet been fully explained. The first half of this study focuses on understanding the growth mechanism of zincblende CdSe NPLs using aliquots isolated periodically from the growth solutions. Optical spectroscopy and electron microscopy are used to characterize the samples. At an early stage of the reaction, QD-like nucleates of different sizes are observed to grow into anisotropic NPLs with uniform thickness through island-nucleation. At a later growth stage, Ostwald ripening is observed when smaller NPLs laterally dissolved to form larger NPLs. The growth mechanism study allows a deeper understanding of the NPL synthesis and thus obtaining more monodisperse NPL samples for better assembly.

Supraparticles are ordered assemblies of colloidal nanoparticles and therefore enable electronic coupling for better device applications. Using a wide range of highly tunable nanoparticles as building blocks, supraparticles can generate new properties from the interaction between different components. In the second half of this presentation, binary CdSe NPL-Au nanocrystal superstructure obtained using emulsion-templated assembly is described. Surfactant concentration and particle molar ratios are both explored to optimize the assembly conditions. With these self-assembled semiconductor-plasmonic superstructures, we hope to utilize the photon-plasmon interaction to achieve temperature-dependent switching between the photoluminescence quenching and plasmonic enhancement modes of the system.

63. Profiling trace element contaminants of toxicological interest in commercially available hemp derived CBD tincture oils

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CBD or cannabidiol is a phytocannabinoid found in hemp plants and is often extracted for use in supplements, oil, lotions and more. CBD oil in particular is a combination of extracted CBD and various oils such as medium chain triglycerides (MCT), hemp and olive oil. Hemp is also known for its bioaccumulation properties that allow for the extraction of metals from the soil in which the hemp plants grow. Due to the bioaccumulation properties hemp plants have been used to decontaminate soils. This ability to accumulate metals raises questions about the levels of metals in CBD based products and how safe they are for consumers. Pharmaceutical products are regulated for over twenty types of metals, while states typically regulate only four metals (Pb,Cd,As,Hg) in CBD derived products.

The goals of this research are 1) to determine if CBD derived products are safe for consumption, 2) to determine the effectiveness of regulatory standards for CBD products and 3) to assess if there are key metals present in CBD oils that pose a threat to consumers health. This research is part of a more comprehensive study funded by the Forensic Science Foundations and was conducted with 3 CBD samples obtained from local smoke shops. Acid Digestions and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) were used to prepare and analyze samples. Acid Digestions were performed with a hot plate, water bath, hot block and microwave digestion system. Microwave digestion was considered to be most effective; Digested samples were diluted 1:10 and analyzed by an ICP-MS to determine the presence of any possible metals in the samples. Results and discussion of ongoing work will be presented

64. Crystallographic effects of doping early transition metals (V, Nb, Mo) into MnO_2 (2x2 tunnel, OMS-2)

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Purpose. Manganese oxide octahedral molecular sieves (OMS) are inexpensive, non-toxic materials with applications in catalysis, batteries, sensors, and ion sieves. Literature results already indicate that doping the 2x2 tunnel variant, OMS-2, with the early transition metals vanadium, molybdenum, and niobium, increases the material's catalytic activity. Our objectives were to determine the maximum doping of various early transition metals into OMS-2, and understand the morphological effects of these dopants.
Methods. Powder x-ray diffractometry (PXRD), x-ray fluorescence (XRF), scanning electron microscopy (SEM).
Results**.** The maximum doping of niobium into OMS-2 was determined to be 12.5% via XRF, and this degree of doping was also observed to decrease the amount of potassium present in the structure. Determination of maximums for double-doped samples is

ongoing. Doping the material with niobium was found to simultaneously increase the maximum possible percentage of another dopant, and materials that took advantage of this property in a direct 1:2 ratio of dopant to niobium were found to have a distinct crystal shape in SEM, forming very small, rice-like needles. Materials that attempted to invert this ratio became visibly amorphous in SEM, while those that included no niobium or a much higher percentage of niobium exhibited clusters of globular crystals. The undoped OMS-2 stands out as the only sample to have needle-like crystals of medium size, suggesting that any degree of doping has profound morphological effects which vary based on dopant identity, percentage, and ratio. When compared to the diffraction pattern of the undoped material, each of the doped samples examined retained its crystallinity, maintaining the diffraction pattern of monoclinic OMS-2. The exception to this pattern was the aforementioned 2:1 ratio of dopant to niobium, which unlike the same samples using a 1:2 ratio, became amorphous. This again suggests that niobium may open OMS-2 to greater percentages of dopant.

Conclusion. Dopant identity, percentage, and ratio were all found to have varying and significant effects on sample morphology and crystal structure. Future research regarding these materials will include a determination of the maximums for double-doped samples using vanadium, molybdenum, and niobium, as well as determination of Lewis acid sites, and investigations of their conductivity and catalytic properties.

65. Design and characterization of a novel enzymatic immobilization structure

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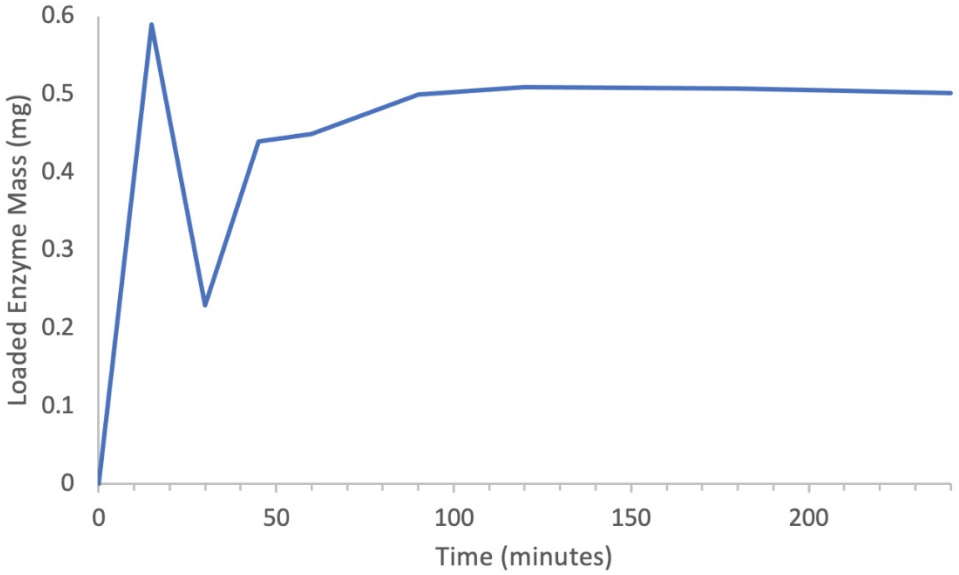
Organophosphate toxins are a class of organic toxins that pose a major threat to human, animal, and environmental health. By inhibiting acetylcholinesterase, organophosphates can cause a variety of neuromuscular problems. Though there are a variety of chemical and physical methods for the degradation of these toxins, many introduce other harsh chemicals into the environment or lack efficacy. Enzymatic degradation of organophosphates have shown to have higher conversion rates and are a promising, environmentally friendly alternative to conventional methods such as NaOH application. However, enzymes lack thermal and environmental stability, an issue encountered when attempting field application. Here, we introduce and characterize a novel method for the immobilization of enzymes within the pores of a mesoporous manganese oxide structure, Mn-UCT-450. Mn-UCT-450 offers suitable mesopores for the containment of Organophosphorus Acid Anhydrolase (OPAA), a phosphotriesterase enzyme capable of degrading organophosphate toxins. UV-vis spectroscopy was used to track the uptake of OPAA by Mn-UCT-450 and protein quantitation was accomplished via the Bradford Assay. Characterization of OPAA-loaded and unloaded of Mn-UCT-450 was accomplished via powder X-Ray Diffraction (XRD) and single area electron diffraction (SAED). Results demonstrate that Mn-UCT-450 is capable of relatively quick OPAA uptake and high enzyme loading efficiency. The discovery of UCT as a promising structure for the immobilization of enzymes points towards its use in the degradation of organophosphate toxins, introducing a cheap and easy way to degrade a variety of harmful chemicals.



Mass of OPAA loaded in Mn-UCT-450 over time in presence of 0.2 mg/ml OPAA solution.

66. Systematic analysis of nanoparticle synthesis in reverse micelles using CdS quantum dots as a model system

*Courtney L. Johnson[1], Augustino V. Scorzo[1], Nakoa K. Webber[2], **Alex R. Calabrese**[1], calabr24@students.rowan.edu, Aubrie Weyhmiller[1], Taylor V. Douglas[1], Nathaniel V. Nucci[1,2]. (1) Physics & Astronomy, Rowan University, Glassboro, New Jersey, United States (2) Molecular & Cellular Biosciences, Rowan University, Glassboro, New Jersey, United States*

Reverse micelle systems are utilized for a wide range of chemical applications, including nanoparticle synthesis. The rate at which reverse micelles collide and exchange contents plays an important role in the kinetics of the chemical processes that occur in the aqueous reverse micellar interior. Though many theoretical models have been presented and much is known about the fast kinetic processes in these systems, relatively little is known about the long-term evolution of chemical processes, especially the synthesis of nanoparticles. Here, we present a systematic analysis of cadmium sulfide quantum dot synthesis using the reverse micelle approach as a model for understanding how exchange processes influence nanoparticle evolution and quality over long time frames. The effects of compositional variables such as water loading, organic solvent viscosity, and initial precursor loading are analyzed via a comprehensive, statistical macroanalysis. The well-known relationship between the reverse micelle water content and the final nanoparticle size is reproduced, but the data also reveal that the bulk solvent viscosity significantly alters the prevalence of surface defects in the resulting nanoparticles. Higher viscosity solvents reduce the evolution of surface defects thus revealing the impact of ongoing exchange processes after initial nanoparticle growth. The combined outcome of these findings shows that this system may be used for more comprehensive modeling of exchange-related chemical processes that have previously been challenging to visualize. Additionally, the potential for controlling both size and surface character of nanoparticles synthesized by this method is revealed.

67. Heme model compound peripheral group interactions in low dielectric medium

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The role of heme *b* peripheral groups such as the vinyls, propionates, and the formyl in heme *a* is still a subject of debate. Quantification of specific heme-amino acid residue interactions are difficult because the protein hosts a wide variety of heme-amino acid interactions. A way of quantifying a specific interaction with a peripheral group on the heme is to study model heme compounds in an aprotic solvent, with ligands that can interact specifically with that group. The nonpolar and aprotic properties of the solvent facilitate the evaluation of hydrogen bonding and electrostatic interactions between

ligands and the peripheral groups of hemes. Using this approach, we have carried out a study of the hydrogen bonding interactions to the acetyl groups of a heme model compound, iron 2,4- diacetyl deuteroporphyrin IX dimethyl ester (DAH) in dichloromethane. The heme model compounds were studied as bis-methylimidazole complexes with 1 M *N*-methylimidazole. To quantify the acetyl group interactions, we used low-current voltammetry to determine the iron (III) to iron (II) reduction potential ($E_{1/2}$) in dichloromethane and in the presence of 5 M phenol. As a control, we used iron protoporphyrin IX dimethylester (PPDME). In dichloromethane, the measured $E_{1/2}$ for DAH and PPDME were -590 and -790 mV vs ferrocene, respectively. In the presence of 5 M phenol, the measured $E_{1/2}$ for DAH and PPDME were -545 and -850 mV vs ferrocene, respectively. Thus, hydrogen-bonding interaction between phenol and DAH contributes +100 mV to the reduction potential, relative to PPDME. This study shows the importance of the formyl group in heme *a* as a modulator of the electrochemical properties of the heme, which is key to proton pumping in cytochrome *c* oxidase.

68. Thin layer chromatography and column chromatography in the advanced inorganic laboratory

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An undergraduate inorganic laboratory where column chromatography coupled with thin layer chromatography (TLC) as the main separation techniques is presented. Students are introduced to the concept of liquid chromatography and to the “art” of making “silica gel columns” correctly in order to separate components of a reaction mixture where the Wilkinson catalysis - $RhCl(PPh_3)_3$, -, *cis*- and *trans*-$Pt(NH_3)_2Cl_2$, and cis-Diammineiodoplatinum (II) complexes are present. This experiment has been created to challenge students to evaluate the strengths and weaknesses of these techniques when they are applied to different coordination compounds.

69. Ruthenium(II) based water-oxidation catalyst supported on graphene oxide composites

***Claudio Amaya**, claudioas095@gmail.com, Yosra M. Badiei, Wanlu Li. Chemistry Department, Saint Peter's University, Jersey City, New Jersey, United States*

The continuous emission of greenhouse gases, due to the rapid increase in global energy demand, is linked to climate change. Artificial photosynthesis (AP) is a promising method to reduce greenhouse gas emissions and combat climate change. To develop a practical AP process, there is a need to build an efficient solar powered water-oxidation system. Previous studies have focused on designing homogeneous molecular catalysts for water splitting, but few studies have used heterogeneous composite materials that incorporate these catalysts. This research is focused on studying the immobilization of ruthenium complexes for water-oxidation on the surface of graphene oxide composites, with the goal of making a hybrid catalyst that can be incorporated in an AP electrochemical device. In

this study, reduced graphene oxide (rGO) will be used as a substrate for anchoring a Ru(II)-based polypyridine water-oxidation catalyst. We hypothesize that intermolecular interactions are due to π-π stacking between the Ru(II) complex and rGO. Additionally, binding can occur between the Ru complex and the oxygen functional groups on the graphene surface. The surface coverage, conductivity nature of the rGO-Ru composite, and its performance towards water-oxidation will be studied by electrochemical experiments such as cyclic voltammetry, UV-visible spectroscopy and bulk electrolysis. Future directions will explore the photocatalytic potential of Ru(II) complexes to develop a hybrid system capable of performing the water oxidation reaction.

70. *In vitro* evaluation of a potential Ruthenium-based chemotherapeutic agent for triple negative breast cancer

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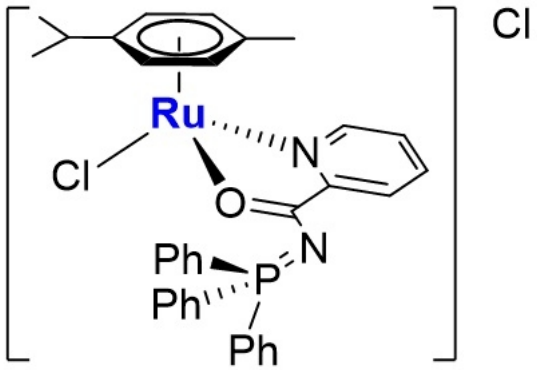
A water-soluble ruthenium compound containing an iminophosphorane ligand (**1**) was tested in multiple cell lines and analyzed for its cytotoxicity *in vitro* and *in vivo*. The compound was found to be significantly cytotoxic to cisplatin resistant cell lines. Furthermore, the compound was tested on triple negative breast cancer (TNBC) MDA-MB-231 xenografts in mice resulting in a 56% tumor mass reduction with low systematic toxicity and preferential accumulation in the tumor but not in kidney and liver. Taking into account these promising data and that cancer deaths are mainly due to metastatic cancers, we sought to clarify the mechanism of action of compound **1** in TNBC, a highly aggressive and invasive breast cancer, by using different TNBC cell lines from Caucasian (CA) and African (AA) ancestry (MDA-MB-231 and HCC1806, respectively). A further understanding of the biological basis of response to treatment for TNBC is needed that considers racial differences. Additionally, we will report on the results of testing **1** against the National Cancer Institute 60 cell line panel. We will specifically report on the anti-proliferative, antimetastatic and anti-angiogenic properties of complex **1** in different TNBC cell lines**.** Overall, the results point out that the compound is anti-metastatic as well as cytotoxic whereas other known Ruthenium complexes, such as NAMI-A, are only known to be anti-metastatic and exhibit low cytotoxicity. Importantly, the compound seems to have similar biological activities on the AA cell line which is of relevance, due to the higher incidence and mortality for TNBC in populations of African ancestry.



1

Ruthenium(II)-Iminophsphorane: A Ruthenium-based potential chemotherapeutic agent for the

71. Organometallic MRI contrast agents

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Transition metal compounds are used as magnetic resonance imaging (MRI) contrast agents to elucidate malignant tissue. Contrast agents used clinically are based on the lanthanide metal gadolinium and are known as potential neuro- and nephro-toxins. Gadolinium's noxious qualities necessitate the development of an alternative contrast agent with reduced toxicity that maintains effective magnetic properties for MRI. We have synthesized several contrast agents using iron(II), which is a comparatively benign transition metal, and measured their magnetic susceptibility. We report that manipulation of the surrounding ligand environment of these iron(II) compounds imparts significant control of their magnetic properties. We believe the ability to tune these iron-based MRI contrast agents may aid medical technicians monitor both the structure and temperature of patient tissue, facilitating both diagnosis and treatment of patients.

72. Development of a colorimetric assay for the carcinoembryonic antigen

***Brett Berger**, Baberger11@gmail.com, Joshua Smith. Math and Science, Alvernia University, Douglassville, Pennsylvania, United States*

Early and accurate detection can significantly increase the chance of surviving many serious ailments, including cancer. The carcinoembryonic antigen (CEA) is present in the bloodstream of healthy adults at low levels. High CEA concentrations indicate that cancer is present in the body, either from new cancer or residual from failed treatment. Current CEA testing involves the use of relatively large volumes of blood taken from the patient's arm. Our system has the potential to allow for the direct detection of CEA from the blood resulting from a small finger prick. The test can be done without the need for expensive laboratory testing equipment or highly trained staff. Gold nanoparticles (AuNPs) have been used for easy and cost-effective colorimetric detection of target molecules. Gold nanoparticles are combined with DNA-aptamers which have a high affinity and selectivity. This testing platform provides a colorimetric response in nature because of the color-changing properties that AuNPs possess. When the target is introduced, the AuNPs in positive tests remain a red color. While a negative test results in a blue color. This color difference is clear to the naked eye. The integration of microfluidic paper-based analytical devices (uPADS) with the AuNP platform allows for a self-contained test that both separates the blood components and delivers the sample to the detection reagents. The full integration of these two platforms allows for the detection of CEA on a cheap, portable, and easy to read device.

73. Synthesis of meso-Tetraphenylporphin (H_2TPP): A quest for better yield and purification

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The 5,10,15,20-tetraphenyl-21H,23H-porphyrin, or 'meso-tetraphenylporphyrin (H_2TPP) is the starting material of many inorganic synthesis where porphyrin ring is the final product. Unfortunately this synthesis starting from pyrrole and benzaldehyde does not give a high yield and it usually does not come with a pure product. We have developed a procedure for an inorganic undergraduate laboratory where the yield of this compound can be increased and the purity can be monitor using UV-vis spectroscopy, IR, 1H NMR and energy-dispersive X-ray spectroscopy (EDX). This laboratory experiment can take a total of seven hours were students will also practice on purification techniques as column chromatography, and sublimation.

Undergraduate Poster Session: Measurement and Data Science

74. Random forest model prediction of compound oral exposure in the mouse

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An early hurdle in the evolution of small molecule chemical probes and drug discovery entities is the attainment of sufficient plasma exposure in mice post oral administration of the compound. Machine learning approaches have attempted to predict molecular properties that influence the mouse pharmacokinetic (PK) profile, including aqueous solubility and liver microsome stability. In this presentation, we will present a machine learning approach that focuses on predicting the oral exposure of a compound measured in the mouse snapshot PK assay. A random forest model was found to produce the best cross-validation and external test set statistics following a data preprocessing step, optimization of model features, and selection of model hyperparameters. The modeling approach outlined should be useful to predict the PK profile of small molecules of translational significance.

75. Mechanistic investigation of fragmentation of protonated of nitroanisoles by mass spectrometry

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Nitroanisoles are widely used as synthetic intermediates and components of explosives. Criminal bombings adversely impact public security and safety. Thus, unambiguous identification of nitroanisole-based explosives used in a bombing incident is an important analytical challenge faced by forensic teams. Mass Spectrometry provides an efficient way to identify explosives. We found that ortho, meta, and para isomers of nitroanisole can be unequivocally distinguished by their collision-induced dissociation mass spectra recorded under positive-ion-generating electrospray-ionization conditions. Generally, radical losses from even-electron ions are considered unfavorable. In other words, ions with an even number of electrons tend to eliminate even-electron fragments, not radicals. In this respect, the fragmentation of protonated 4-nitroanisole is unique because it demonstrated three consecutive radical losses from the protonated percussor. The spectrum recorded from mass-selected *m/z* 154 ion showed peaks at *m/z* 137, 107, and 92 for consecutive losses of $\cdot OH$, $NO\cdot$, and $CH_3O\cdot$ H_3, respectively. Results from computational studies and data from stable-isotope-labeled ring isomers of nitroanisole will be presented to support proposed fragmentation mechanisms.

76. Evaluate the effectiveness of washing strategies on pesticide removal from skin and flesh of strawberries, apples, and grapes using QuEChERS and LC-MS/MS analysis

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Pesticide residues in foods are warned widely to cause negative impacts on human health. Although organic fruits follow stricter agricultural practices, they remain expensive, less accessible, and often with a limited variety for the majority of consumers. Therefore, a washing method that can be implemented easily in the home on non-organic fruits is a promising solution. This work is investigating simple washing strategies including tap water, a baking soda solution, and a dilute Clorox solution that can be applied to three commonly consumed fruits – strawberries, apples, and grapes. After fruits undergo a washing treatment, they are also peeled and separated into two parts: skin and flesh. Each part is processed exclusively using a standard QuEChERS extraction followed by LC-MS/MS analysis. Ten fungicides and insecticides commonly found in these fruits by the USDA Pesticide Data Program (PDP) are under study. Preliminary findings in unwashed grapes, apples, and strawberries show significantly higher concentrations of pesticides on the skins compared to the flesh. This data also provides a baseline to

understand the extent of pesticide residue removal that is possible from the outer-layer of the fruit as well as the percentage removed by each washing strategy. Data will be carefully evaluated to determine if a single washing method is effective for pesticide removal from the skin of all three fruits, or if different fruits or pesticides respond differently to each washing strategy.

77. Development of a method for the quantitation of carbohydrates in aquatic systems

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Carbohydrates, specifically glucose, galactose, arabinose, mannose, xylose, fructose, and rhamnose, are some of the most abundant dissolved organic carbon (DOC) sources in aquatic ecosystems and are a major food source for organisms. DOC have become a major pollutant in aquatic systems. Therefore, the concentration of these carbohydrates in aquatic waters may correlate to the health of the ecosystem. The goal of this project is to develop a method to quantify the seven carbohydrates listed in aqueous solution. The system used consisted of all Dionex instrumentation; it included an AS50 Autosampler, a LC30 Chromatography oven, an ED50 Electrochemical detector, and a GD50 Gradient Pump. The eluents were 18MΩ resistance purity water, 200mM NaOH, and 16mM NaOH. The separation method utilized high performance anion exchange chromatography, although mannose and xylose could not be separated. The detection method utilized pulsed amperometric detection. When analyzing, the method created the linear range, coefficient of determination (R2), reproducibility, and accuracy of an unknown for each carbohydrate were examined. A preconcentration method involving resuspension and a filter (.45μM nylon) were also examined and determined to not statistically alter the concentration of the carbohydrates. Then, real world samples were run to validate the method.

78. Analysis of benzodiazepines used in drug facilitated crimes

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Benzodiazepines are a class of antianxiety drugs including drugs commonly known as Rohypnol, Xanax, and Valium. They are also known as predator or date-rape drugs used in Drug Facilitated Crimes (DFCs) – crimes that include robbery, the maltreatment of the elderly and children, as well as rape and other sexual assaults. Identification of these drugs, or their metabolites in biological specimens such as urine, blood, saliva and hair of victims is commonly proof of exposure to the drug.
Like other psychoactive drugs used in DFCs, benzodiazepines are highly potent and have short half-lives. The combination of potency and short half-life makes the time window for when the drug is still detectable in biological samples very small. Victims of DFCs usually

experience short-term memory loss and often report the crime days after they have happened, which adds to the challenge of detecting the drugs in the biological samples by the currently used analytical methods in forensic toxicology laboratories. The goal of the current project is to develop a method for detection, identification and quantification of 17 benzodiazepines, including 7-aminoflunitrazepam, 7-aminoclonazepam, Alpha-hydroxyalprazolam, Lorazepam Glucuronide, Alprazolam, Bromazepam, Chlordiazepoxide, Clonazepam, Diazepam, Flunitrazepam, Lorazepam, Nitrazepam, Norchlordiazepxide, Nordiazepam, Oxazepam, Temazepam, and N-desmethylflunitrazepam, at very low concentrations in aqueous solutions, which can be applied to the analysis of these drugs and their metabolites in biological samples such as urine and blood.

79. Tongue cancer viability in organic tea tree and alma treatments

***Raul Gonzalez** , rgonzalez@caldwell.edu. Biology, Caldwell University, Caldwell, New Jersey, United States*

Oral squamous cell carcinoma is an aggressive illness. According to The Oral Cancer Foundation approximately 54,000 people in the United States will be newly diagnosed with oral cancer in the year 2021. Not to mention the 12,000 additional new cases per year. Besides the existing medicinal approaches of chemotherapy and surgery, alternative therapies can be utilized to mitigate or even prevent tongue cancer. In fact, a study conducted by Asian Pacific Journal of Cancer Prevention endorsed that a diet enriched with fruit and vegetables can reduce the risk of developing major cancers. A similar approach is taken here; to evaluate the effect of Melaleuca alternifolia (Tea Tree) oil and the herbal extract of Emblica officinalis (Alma) on the tongue cancer cell line, SCC154. The culture was grown over a period of 7 days at 37oC in 5% CO2 using EMEM medium supplemented with 10% fetal bovine serum, L-Glutamine (2 mM), Amphotericin B (2.5 µg/mL), and Gentamicin (50 µg/mL). The confluency was recorded using an inverted light microscope. The cultures were trypsinized and stained using trypan blue to count the dead (blue) and live (clear) cells using a hemocytometer and light microscopy. The total cell count average and concentration for both alive and dead cells were recorded, as well as the overall live cell percentage. Results show that increasing concentration of the treatments Tea Tree and Alma reduced the total number of live cancer cells. Our study demonstrated that these treatments may be effective remedies to prevent oral cancer or even mitigate its effects once progressing.

Undergraduate Poster Session: Organic Chemistry

80. Synthesis of phenyl pyridines, pyridazines and pyrimidines to test for their inhibition on the enzyme Uridine Nucleoside Ribohydrolase (UNH)

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Trichomoniasis, a common sexually transmitted disease is caused by a parasite Trichomonas vaginalis. In order for this parasitic protozoan to reproduce, it has to obtain specific nucleobases from its host. For this reason, a potential inhibition for this parasite would be the inhibition of enzymes that produce such nucleobases, such as uridine nucleoside ribohydrolase (UNH). A preliminary result had shown that a compound, 3-(3-methylpyridin-2-yl) benzonitrile, showed significant inhibition of UNH, with an IC50 value of 14 μM. Derivatives similar to this molecule were made using Suzuki cross-coupling reaction. A phenylboronic acid was reacted with an aryl bromide and palladium as catalyst to synthesize phenyl pyridines, pyridazines, pyrazines and pyrimidines. Synthetic results using Suzuki reactions and biological data of the derived compounds obtained against UNH will be discussed.

81. Investigation of pyridine-based bis-benzimidazoles as potential chemotherapeutic lead compounds

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Cancer is one of the major public health problems and continues to affect the health and well-being of millions of people in the U.S. and worldwide. It is defined by the uncontrolled growth of cells and known to metastasize to various tissues and organs. Cancer is the second leading cause of death, and responsible for the death of more than 600,000 people in the U.S. alone. Despite the availability of various therapeutic approaches to battle cancer, many chemotherapeutics currently used in clinical settings exhibit severe adverse effects. Moreover, drug resistance to anticancer agents is also becoming another roadblock to cancer therapy. To address some of these limitations regarding cancer therapy, scientists are continually developing new and improved anticancer agents. The Yoganathan lab has become interested in studying a class of heterocycles, called benzimidazoles as potential anticancer agents. Benzimidazole core is a privileged scaffold and is found in many therapeutic agents. It is also extensively utilized during small molecule-based drug discovery. We are interested in the synthesis and biological evaluation of pyridine containing bis-benzimidazoles as an unexplored class of potential anticancer compounds. These classes of molecules have the ability to exist as a 'planar' structure due to the overlap of pi-orbitals of the aryl rings, or twist to give a 'non-planar' structure if the benzimidazole nitrogen is substituted with a sterically bulkier motif. Due to the structural uniqueness, we designed a library of analogs to synthesize and assess the structure activity relationship (SAR) around the benzimidazole aryl ring, and alkylation of the benzimidazole nitrogen. Our lab has effectively developed a simple chemical method to synthesize a small library of bis-benzimidazoles from commercially available 2,6-pyridine-dicarboxylic acid and diverse 1,2-diaminobenzenes. The chemical methodology is scalable, and we readily acquired various analogs in gram scale for our initial SAR studies. Currently, our efforts are focused on establishing a small library of analogs via

gram-scale synthesis. We also plan to perform a preliminary anticancer study against a panel of tumor cell lines in the near future. Moreover, biologically active analogs from our anticancer studies will be evaluated for the mechanism of cell death. This bioactivity guided approach will enable us to fine-tune the structure and better understand the SAR of this pyridine-based scaffold.

82. Greener synthesis of pterostilbene derivatives as drug candidates for the treatment of Alzheimer's

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Alzheimer's disease is a progressive neurodegenerative disorder that causes deterioration of cognitive function in over 6 million people in the United States. It accounts for over 60% of all cases of dementia and ranked third cause of death among the elderly. Resveratrol, a naturally occurring compound in red wine, and its dimethyl derivative, pterostilbene, are known for their anti-aging properties and may be beneficial in the quest for discovering better treatment for Alzheimer's disease. Our colleagues have established two transgenic models of Alzheimer's disease through expression of the human APP-AP42 gene in the eye and in cell post mitotic neurons of Drosophila melanogaster. They have observed eye degeneration in the GMR model and have found resveratrol derivative treatments improve locomotion in the ELAV model flies. Encouraged by these results, we have synthesized new pterostilbene derivatives as potential drug candidates with a special focus on cost effectiveness and the application of green chemistry principles. The strategy uses the traditional Wittig protocol with significant differences in the reaction conditions. This approach avoids the use of strong often pyrophoric bases such as butyl lithium, expensive glassware, anhydrous solvent, and several hours of laboratory time. A microwave synthesis reactor was used to run the Wittig reaction with deionized water as the solvent and potassium carbonate as the base. The advantages are operational simplicity, high robustness, efficiency, and turnover frequency. The inexpensive, safe and milder conditions provide expedient access to a library of pterostilbene derivatives for therapeutic evaluation.

83. Ni-catalyzed oxidative esterification of allylic sp^3-carbon

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Esters are a class of compounds which have some of the widest array of real-world applications. They are used for their fragrance in products like perfumes and air fresheners, and for their flavor in food products. Among various esters, the synthesis of allylic esters has been studied widely in the literature due to their role as important scaffolds for bioactive molecules as well as pharmaceuticals. Inthe past decades, the advancements in the transition metal catalyzed C-H functionalization boosted the area of C**-**C and C-X (X = C, O, N, P, S) bond formation reactions Particularly the area of

oxidative coupling approach for the direct C-H activation have been an area of great interest. It has emerged as one of the most important strategies for the development of new and greener synthetic methodologies in organic synthesis in recent years. In this current study, we would like to report the successful use of nickel metal as catalysts for oxidative esterification of cyclohexene and its derivative with various carboxylic acids. In our attempts to carry out the reaction by reacting benzoic acid with cyclohexene in presence of $NiBr_2$(10 mol%) and Di-tert-butylperoxide (as oxidant), moderate to good yields of the product was obtained.

84. Novel conversion of 1,3-thiaza-4-ones to dimeric thioacetals

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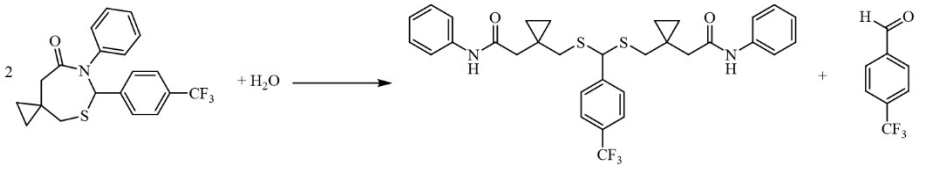
The novel conversion of 1,3-thiaza-4-ones to dimeric thioacetals was first observed during NMR analyses. In this poster, further exploration of this reaction is discussed.



85. Synthesis of 2-(2-methylpyridin-3-yl)phenol derivatives as uridine nucleoside ribohydrolase inhibitors

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Trichomoniasis is a sexually transmitted disease that is caused by a parasite called Trichomonas vaginalis. The parasite does not create nucleobases and will obtain them from the host to reproduce. Uridine nucleoside ribohydrolase (UNH) is one of the salvage pathway enzymes used by the parasite to obtain nitrogenous bases. There are treatments for trichomoniasis but some strains of the parasite are growing resistant and new treatments are needed. Using a different pathway, potential inhibitors can be used as treatment against the parasitic infection. 2-(2-Methylpyridin-3-yl)phenol was found to inhibit UNH with an IC50 value of 1.9 μM. Using this scaffold, derivatives were made using the Suzuki reaction. Suzuki reaction is a cross-coupling reaction that combines a boronic acid and an aryl halide with a palladium catalyst, to create biaryl compounds. After the compound was made, they were tested against the parasite to obtain an IC50. The goal is to create a compound that can inhibit UNH at a sub micromolar IC50 value.

86. Synthesis of phenyl pyzaroles for the inhibition of unh in trichomonas vaginalis

***Kevin Nelson**, jeannelson00@gmail.com. Chemistry, Adelphi University, Garden City, New York, United States*

Trichomoniasis, one of the most common sexually transmitted diseases in the world, is caused by the parasitic protozoan Trichomonas vaginalis. Current treatments use 5-nitroimidazoles to damage DNA residues, but due to increasing resistance over time, there has been a need to find new methods. Another potential is by inhibiting the function of the parasite's nucleoside ribohydrolases, specifically the UNH, which is important for metabolizing uridine from host cells. Compounds from a fragment collection were tested for inhibition of UNH. Out of the many fragments, a phenyl pyrazole, 4-(1-methylpyrazol-4-yl)benzamide, was seen to have caused moderate inhibition. To increase inhibition at lower concentrations, compounds were synthesized with a change to the position and/or type of functional group on the phenyl ring of the aforementioned fragment by way of a Suzuki reaction. This reaction was done by combining an aryl bromide with an aryl boronic acid or ester using a palladium catalyst. Inhibition was observed at a lower concentration when a hydroxyl or nitrile group was placed on the 2-position of the phenyl ring. New compounds will be synthesized by replacing the aryl bromide used for synthesis, being the 4-bromo-1-methylpyrazole, and attempting reactions with 3-bromo-1-methylpyrazole or 5-bromo-1-methylpyrazole. Based on the aforementioned observations, those with functional groups on the 2-position of the phenyl ring are expected to show higher inhibition of UNH than others.

87. C-glycosides synthesis by coupling C-linked glycosyl crotylboronates with simple aldehyde

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Glycans acting as polypeptide ligands are related to various disease conditions by inducing excessive repeated signaling cascades. This increased the demand for modified carbohydrates that can act on protein's active site as temporary or permanent competitive inhibitors by preventing ligand binding. C-glycosides (artificially synthesized carbohydrate residues connected by "CH_2" linkage instead of the traditional glycosidic "O" bond) among other altered linkage glycans gained high interest due to their intrinsic ability in resisting denaturation in acidic and basic mediums or hydrolyzation by various lysozymes in comparison to their "O" linked counterparts. These properties rise the value for exploring the candidacy of these glycans as drugs for disabling various enzymes and understanding the nature of the substrate-enzyme interaction. Nevertheless, building these molecules is challenging due to their complex chemical synthesis pathway that involves the formation of a carbohydrate on the already existing one in the glycan chain from aliphatic precursor. The established methodology of forming C-glycosides used in this experiment implemented coupling between C-linked glycosyl crotylboronates with simple aldehyde. This paper will focus on the formation of C-linked Alpha-gal (galactose-α-1,3-galactose), a

disaccharide of immunological relevance. The precursor C-linked glycosyl E-crotylboronate was obtained in six steps from D-galactose with the key $PdCl_2$ catalyzed reaction of glycosyl allylic chloride with bis-(pinacolato)diboron to give the glycosyl E-crotylboronate. Followed by the crotylation reaction of the E-crotylboronate with 1,2-O-isopropylidene D-glyceraldehyde. Details of this synthesis and subsequent ones to form the final product of Alpha-gal will be presented.

88. Use of heme proteins in bioremediation efforts: Turning heme green

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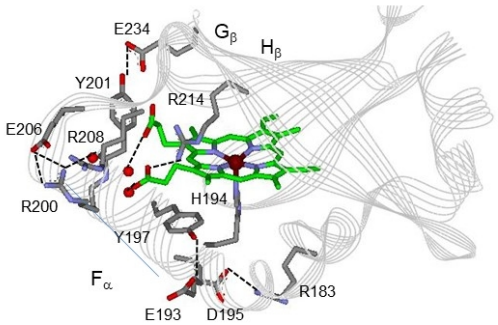
Modern industry has significantly polluted water sources with its production of textile dyes (citation). Historically, the methods of incineration and chemical degradation have been less than satisfactory, as they are costly and cause further harm to the environment. So, there is a blatant call for more efficacious bioremediation methods. Dye-decolorizing peroxidases (DyPs) are a variation of heme proteins that are capable of oxidizing textile dyes. It is proposed that the heme environment of DyPs contains a proximal histidine heme ligand and a distal histidine-arganine diad that, with the cooperative efforts of other residues in the catalytic pocket can catalyze dye degradation similarly to classical heme peroxidases. Unfortunately, DyPs are considered relatively slow catalysts which function at a narrow, acidic pH range. This research project is focused on the genetic engineering of the heme-Pas protein SmFixL. which contain heme domains that are like DyPs where hydrogen peroxide and substrate binding and catalysis occur. Ultimately, we strive to design a more effective heme enzyme dye degradation catalyst, to better restore the integrity of polluted water sources.



89. Desolvation pathways of four niclosamide solvates

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Many Active Pharmaceutical Ingredients (APIs) crystallize with solvent molecules yielding solvates, or water molecules yielding hydrates. The intentional removal of solvent/water from these phases can be used to create novel solvent-free solid forms. However, the solid state pathways by which these processes occur and the solvent-free products which result are difficult to predict *a priori*. Here we examine the desolvation of four different solvates of niclosamide, an anthelmintic drug on the World Health Organization's List of Essential Medicines. Using a combination of analytical methods including optical and hostage microscopy, thermal analysis, and powder X-ray diffraction, the solid state desolvation reaction kinetics and mechanisms were investigated. Results are discussed in the context of the structural and topological differences across these solvated forms.

90. Non-precious metal-based MOFs as catalysts for decarboxylative coupling reactions

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Decarboxylative coupling refers to a reaction in which a new carbon-carbon bond formation happens with the loss of a CO2 molecule. The reaction requires a base, oxidant, and a metal catalyst. Developments in this research area have recently established the frequent use of carboxylic acids, generally benzoic acid derivatives, as they are readily available and non-toxic, with a stable nature. Most of the research in the area has been done using precious metals, which limits the scope of these reactions due to their limited availability, cost, and impact on the environment. During the initial phase of this project, we have focused on the detailed study of the published reports to develop an outline of my project. The ultimate goal in the current research is to understand and explore the use of non-precious metals (such as Ni, Mn, Zn) as catalysts for the decarboxylative coupling reactions. To extend this project, we also want to explore the potential of non-precious metal-based MOFs as catalysts. The use of metal-organic frameworks (MOFs) to catalyze various reactions among organic and inorganic chemistry has been gaining attraction in recent years. A common drawback, however, is the use of precious metals during the synthesis of these metal-organic frameworks. These precious metals include iridium, platinum, ruthenium, etc., and are very expensive to come across and not very environmentally friendly. To overcome this drawback, the idea to use metal-organic frameworks, created by the heterogenization of metal complexes onto the organic framework using more affordable and reusable metals.

91. From natural to synthetic: Photophysical improved cyanine dyes and their bright future

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Cyanine fluorophores have been drawing more and more attention due to their applications in multiple scientific fields, such as engineering, pharmacology, biology and medicine. Since the first synthesis of cyanine dye 160 years ago, cyanine dyes have been playing interesting roles in everyday life. They have been used as cosmetic pigment and acid-base indicator, even dyes for DVD-R and CD-R discs. The synthesis of early generation cyanine dyes was carried out in harsh conditions with nonpolar building blocks. The cyanine products were also symmetrical and hydrophobic. About 30 years ago, the synthesis of sulfonic cyanine dyes marked a breakthrough. With two or more sulfonic groups installed on the dye molecules, these fluorophores finally became hydrophilic enough for many biological and medicinal applications. To keep up with the fast advancement in instrumentation and computer science, chemists are now facing new challenges and opportunities to make better and brighter synthetic fluorophores. Novel synthetic cyanine species have been reported constantly. In recent years, improved cyanine dyes have been used as light source in a new imaging technology called *single-molecule* Förster resonance energy transfer (smFRET). For example, the asymmetrical dyes with triplet state quenchers covalently attached render high brightness, long life-span, improved photophysical properties, higher hydrophilicity, and specific labeling. These new compounds combined with smFRET technology have made many previous impossible experiments possible and enabled unprecedented insights into mechanisms of bio-functions.

92. Synthesis of sulfoxides from 2,3-diphenyl-2,3-dihydro-1,3-thiaza-4-ones

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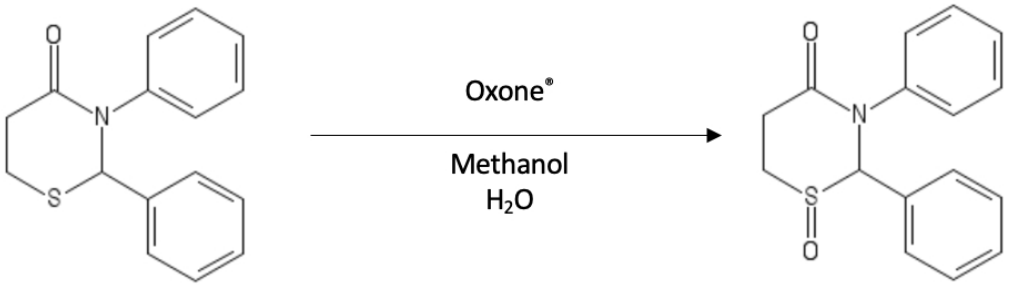
The purpose of this project is to discuss the use of previously made compounds to perform oxidation reactions to produce sulfoxides. The starting materials are 2,3-diphenyl-2,3-dihydro-1,3-thiaza-4-ones. The oxidant used in the reactions is Oxone®. The poster will discuss the selectivity of the synthesis of sulfoxides in certain reaction conditions and the results of the oxidations. Below is an example of a possible scheme producing a sulfoxide performed during the semester.



93. Synthesis of 1(benzotriazolyl)ethyl ferrocene: A potential cancer growth inhibitor

***Anuj Aryal**, anujaryal452@gmail.com, Marjorie Squires, Darryl Aucoin. Caldwell University, Caldwell, New Jersey, United States*

Ferrocene (Fe(C5H5)2) is an interesting organometallic compound because it chemically can be easily modified. This versatility allows Ferrocene complexes to serve as catalysts, fuel additives, and as beneficial pharmaceuticals. Ferrocene salt and Amine/Amide derivatives are suggested to inhibit cancer cell growth. In this project, 1(benzotriazolyl)ethyl ferrocene was synthesized using a three steps synthesis, purified via chromatography and recrystallization, and analyzed spectroscopically. The toxicity of this compound was tested using E. coli as a model organism in the Kirby-Bauer assay. The results showed a mild and dose dependent toxicity which was evident from the diameters of the kill zones. 60.3 g/L of 1(benzotriazolyl)ethyl ferrocene in ethanol resulted in kill zones of 6mm, 12mm, and 15mm when 1µL, 5µL, and 10µL of the samples were used respectively. The toxic activity of 1(benzotriazolyl)ethyl ferrocene against our model organism suggests its potential efficacy against cancer cells. Its mutagenic properties were also tested using the AMES test and the results will be discussed. Further research will focus on evaluating the effect of 1(benzotriazolyl)ethyl ferrocene on cancer cells.

94. Benzylic functionalization electrochemical oxidation

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Compared to traditional reagent-based transformations, synthetic organic electrochemistry provides approaches with high functional group tolerance, mild conditions, and high sustainability. A new methodology for the electrochemically promoted benzylic functionalization under relatively mild conditions has recently been developed. Benzylic-Tempo reagents were first prepared in good yields; a variety of nucleophiles can be utilized to react with the benzylic-Tempo reagents under electrochemical conditions to furnish the desired the benzylic functionalization products. Oxygen, nitrogen, and carbon nucleophiles will be screened for the formation of benzylic C-O, C-N and C-C bonds. This approach features mild reaction condition, high efficiency, and excellent functional group compatibility.

95. Using NMR titrations to assess halogen-bonding strength as a function of molecular structure towards sensor development

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Intermolecular forces such as halogen bonding (XB) require a fundamental, experimental understanding before they can be utilized in biological, chemical, and physical applications. XB is an orthogonal, electrostatic interaction between a region of positive electrostatic potential (δ+) on a halogen atom (XB donor) and a Lewis base (δ-) (XB acceptor). In this work, ^{19}F and ^{1}H NMR titrations are used to quantitatively assess the strength of XB interactions in solution by determining association constants (K_a) for a strategic series of XB donor and acceptor pairs. The panels of molecules are specifically selected to identify and optimize structural requirements of the XB donor, including specific halogen atoms and electron withdrawing groups, as well as properties of the XB acceptors such as electronegativity, that promote strong XB interactions. The role of solvent interactions is also explored. The experimental results are compared to computational modeling. With a thorough understanding of structure-optimized XB, one can envision harnessing XB donors with specific structures within sensing schemes designed to target molecules able to engage in XB interactions.

96. Design of ionic liquids bearing thioether side chains

***Mehreen Mughal**[1], MEHREEN.MUGHAL27@student.qcc.cuny.edu, James F. Wishart[2], Edward W. Castner, Jr.[3], Sharon I. Lall-Ramnarine[1]. (1) Chemistry, Queensborough Community College, Bayside, New York, United States (2) Chemistry Division, Brookhaven National Laboratory, Upton, New York, United States (3) Chemistry, Rutgers The State University of New Jersey, New Brunswick, New Jersey, United States*

Ionic liquids (ILs) are being extensively investigated as potential electrolytes in electrochemical devices, including rechargeable lithium cells, solar cells, and supercapacitors. However, most ILs have significantly higher viscosities than electrolytes based on conventional solvents, resulting in slower charge transport. Replacing IL alkyl side chains with ether groups has been known to improve transport properties, and recent reports on ILs with short *thioether* side chains have shown that replacing the ether O atoms with *S atoms lowers IL viscosity even more* in imidazolium ILs, but not in pyrrolidinium and phosphonium ILs.
We report here on a literature review and design process for the synthesis of novel thioether ionic liquids and plans for the methods we will use to prepare them. Research reveals opportunities to contribute information that to date is largely missing from the chemical literature on the synthesis and characterization of thioether-substituted ILs of varying structural types, particularly those with poly-thioether side chains covalently linked to the N atom of imidazolium and pyrrolidinium cation rings. There is also a lack of comprehensive temperature-dependent characterization of critical IL physical,

thermodynamic and transport properties.
This work is a part of a larger collaborative project where we seek to examine the atomistic origin of viscosity by comparing ILs with ether and thioether side chains. Results are expected to make important contributions to the design of ILs optimized for larger scale use in energy storage devices such as batteries.

97. Preparation and characterization of ionic liquid–polymer gels

Shameir Nembhard[1]*, SHAMEIR.NEMBHARD21@student.qcc.cuny.edu, Nicole Zmich*[1]*, Jasodra D. Ramdihal*[1]*, James F. Wishart*[2]*, Edward W. Castner, Jr.*[3]*, Sharon I. Lall-Ramnarine*[1]*. (1) Chemistry, Queensborough Community College, Bayside, New York, United States (2) Chemistry Division, Brookhaven National Laboratory, Upton, New York, United States (3) Chemistry, Rutgers The State University of New Jersey, New Brunswick, New Jersey, United States*

Ion gels comprising ionic liquids (ILs) and block copolymers have found unique and important applications in diverse fields of science and engineering, such as for energy storage materials and for separations chemistry. We report on the preparation and physical characterization of selected ion gels. Ionic liquids based on tetraalkyl-phosphonium and -ammonium cations and bis(trifluoromethylsulfonyl)amide anions are synthesized and purified in our labs. The alkyl groups on the IL cations were selected by design to form a significant non-polar region, and thus optimized for use as gas separation membranes. The polymeric material used in the ion gels is a common battery development diblock copolymer, PDVF-*co*-HFP, ^{1}H and ^{13}C NMR was used to confirm the structure of the IL gels. Physical characterization of ion gel films included differential scanning calorimetry. This work was supported in part by the NIH Bridges to the Baccalaureate program at Queensborough Community College, and the work at BNL was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences under contract DE-SC0012704.

98. Determination of asymmetrical viral capsid morphology through computational modelling of cryo-EM data

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In recent years, the experimental technique cryogenic electron microscopy (Cryo-EM) has helped to elucidate the morphology of viruses such as Ebola virus, Marburg virus, HPV, and more. The missing wedge artifact in Cryo-EM is a limiting factor to the single particle reconstruction of asymmetrical viral particles such as HIV-1 capsids. Without a computational strategy to interpolate missing protein positions, the structural biology of the mutagenic HIV-1 nucleocapsid continues to be an elusive concept. Despite a lack of knowledge of patterns in the fullerene HIV-1 nucleocapsid architecture, chemists and mathematicians have studied the mathematical properties of carbon fullerenes extensively. Through differential geometry and quantum chemistry minimization, we can describe the topology of the HIV-1 nucleocapsid by modeling its skeletal structure as a

carbon fullerene. Construction of the convex hull and the use of a topology-representing network, the growing neural network gas, are effective strategies in providing information about the structural biology of HIV.

99. Enhanced ionic liquid- single-walled carbon nanotubes mixtures for energy storage applications

***Zheyong Piao**, zheyong.piao42@qmail.cuny.edu, Tirandai Hemraj-Benny. Chemistry, Queensborough Community College, Bayside, New York, United States*

Currently, energy storage devices with high energy density and high-power density are in great demand. Compared to traditional batteries, supercapacitors are more advantageous due to their higher power density and longer life cycles. For supercapacitors to be more widely used in practical applications, more effective electrodes and electrolytes need to be identified and studied. Single-walled carbon nanotubes (SWCNTs) and ionic liquids (ILs) have shown great promise to serve as efficient electrodes and electrolytes, respectively. Although imidazolium-based ILs may be excellent solvents for the dispersion of SWCNTs in energy storage devices, the existing interactions that result in the nanotubes' de-bundling are not fully understood. Herein, a review of the enhanced conductivity properties observed for mixtures containing SWCNTs and various imidazolium ionic liquids is presented. Moreover, the specific interactions, such as cation-π interactions or π-π interactions that may exist between SWCNTs and imidazolium ILs are presented. Future spectroscopic analyses of mixtures containing SWCNTs and ILs of imidazolium cations coupled with bis(trifluoromethylsulfonyl)amide (NTf_2^-) or bis(fluorosulfonyl)amide (FSA^-) anions will be discussed to contribute to the development of optimal electrodes and electrolytes for energy storage devices.

100. Assessing the long-term effects of the cellular environment on HIV-1 pNL4-3 capsid

***Chaitanya A. Sheopurkar**, chai@udel.edu. Engineering, University of Delaware, Newark, Delaware, United States*

The HIV-1 capsid is the house for the genetic material of one of the world’s most known virus. The capsid also tells us a story through the amino acids that mutate in it. The objective of our analysis is to understand the effects of MT2 and MT4 Human T cells (8 MT-2 cells and 8 MT-4 cells) on the genomic code of the HIV-1 cells. Using data gathered from the analysis of cell cultures collected over a period of 3 years, we aim to derive a mechanistic knowledge of the capsid function. From the data of the entire genome only the data pertaining to the virus’ capsid protein was chosen. Then, identification of the mutations was performed, and the total number of mutations for each line were counted. Further analysis was done, to prove that there is a significant effect of the environment in which the virus is growing, and the mutation history also plays a role in the new mutations that occur in the capsid protein.

101. Antibacterial activity of sulfur-doped carbon/g-C_3 N_4 composite under visible light

***Muhammad Moueed Haider Mirza**, mhaidermirza19@saintpeters.edu, Adam Daoud, Wanlu Li. Saint Peter's University, Jersey City, New Jersey, United States*

Carbon-based nanomaterials have been widely developed into innovative antimicrobial agents since it provides a key solution to the problems caused by drug-resistant bacterial infections. Their advantages also include a high surface-to-volume ratio and unique properties such as photoactive properties. The nanocomposite of Sulfur-doped carbon/graphitic carbon nitride (SC/g-C_3 N_4), a free-metal photocatalyst, was synthesized through heat treatment and its antibacterial activity against Escherichia coli (E. coli) was investigated. The antibacterial ability of the SC/g-C_3 N_4 composite was compared with that of g-C_3 N_4after visible light irradiation. The composite showed a dramatic increment in the surface area (326 m 2 /g) and total pore volume (0.248 m 3 /g). Photocurrent generation and impedance spectroscopy (EIS) characterization revealed that the introduction of S-doped carbon lowered the band gap (2.66 eV) and facilitated more photogenerated electrons, thus directly improving the bactericidal ability of SC/g-C_3 N_4. This study helps an in-depth understanding of the mechanism of visible-light-driven disinfection and provides a good candidate sterilizing agent for treating microbial-contaminated water.

102. Single-particle tracking measurements in poly(ethylene glycol) hydrogels: Does size matter?

***Kathryn Foreman**, kforem4@students.towson.edu, Khanh-Hoa Tran-Ba. Towson University, Towson, Maryland, United States*

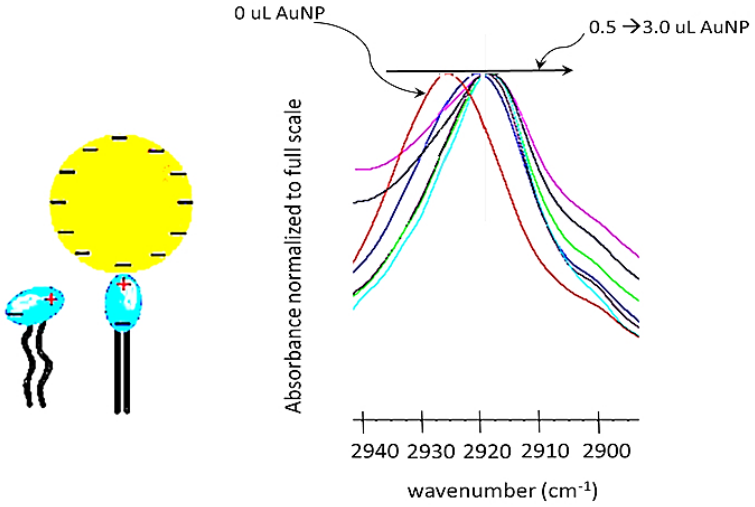
The interactions of drug particles within the human body are of great interest in drug delivery, as such phenomenon is known to define the efficiency that a drug can be delivered to its target. In this study, the diffusion behaviors of a series of polystyrene microspheres of varied diameters are systematically investigated in poly(ethylene glycol) hydrogels by using single particle tracking methods. We aim to gain a deeper understanding on how the steric interactions define a particle’s transport behavior in the PEG hydrogels, which was done by using microspheres of 2, 5, and 15 μm in diameter. The PEG hydrogels that are used to model the human body in the simplest fashion, are prepared by using previously reported approaches involving the UV-crosslinking of a 40 wt% poly(ethylene glycol) diacrylate solution for 5 min. Microsphere doping of as-prepared PEG hydrogels occur by adding a 10 μL drop of a diluted microsphere solution (0.1 μg/L, milli-Q water) on top of the hydrogel. SPT measurements in PEG hydrogels are conducted by tracking the Brownian motion of single diffraction-limited fluorescent spots in PEG. Quantitative data analysis of the recorded SPT data offers the assessment of the microspheres’ diffusivity via the measured diffusion coefficients (D). Our results show an inverse relationship between the microsphere diameter and the recorded D, as anticipated. Interestingly, our recorded video data also reveals the presence of two distinct populations of probes that explore the different pore environments in the PEG hydrogels.

The results of our work are suggested to aid to the development of better drug delivery platforms and further demonstrate the power of SPT in the advanced characterization of synthetic hydrogels.

103. Absorption IR spectroscopy tracks the effect of gold nanoparticles on the ordering of phospholipids

Karishma Kalloo[1]*, kkalloo000@citymail.cuny.edu, Sean Finn*[1]*, Najae Escoffery*[1]*, Qi Lu*[2]*,* ***Robin Helburn***[1]*, rhelburn@sfc.edu. (1) Chemistry & Physics, St Francis College, Brooklyn, New York, United States (2) Physics & Engineering, Delaware State University, Dover, Delaware, United States*

The interactions between a lipid bilayer and metal nanoparticles hold environmental and biomedical significance. Here, we probe the mechanism of interaction by following spectroscopically the dynamic ordering of a lipid layer from its constituent monomers in the presence of citrate stabilized gold nanoparticles (AuNPs). Solutions of DPPC (1,2-dipalmitoyl-sn-glycero-3-phosphatidylcholine) and DMPC (1,2-dimyristoyl-sn-glycero-3-phosphatidylcholine) in $CDCl_3$ were titrated individually with 0.5 µL aliquots of pure water, D_2O and respective solutions with and without AuNPs. The gradual lipid ordering was followed in individual FTIR experiments. Absorption bands for C-H, C=O and asymmetric PO_2^- vibrations were monitored throughout the titration. The observed pronounced shifting in band positions for C-H vibrations toward lower frequencies, consistent with transition to a more ordered crystalline orientation of C_{16} chain (on DPPC) on interaction with AuNPs, supports an electrostatic model of the lipid-AuNP orientation process. The results are consistent with a recently reported model of bilayer fluidity (in response to AuNP). Discussion of solvation mechanisms along with corroborating UV-vis spectra of the AuNPs and hyperspectral imaging also are presented.



Shift of C-H vibrations for DPPC in $CDCl_3$ to lower frequencies on interaction with AuNPs in D_2O.

104. Solvent-assisted nanochannel encapsulation of a natural phase change material in polystyrene hollow fibers for high-performance thermal energy storage

Dev K. Patel[1]*, pateld27@students.rowan.edu, Harmann S. Singh*[1]*, Ping Lu*[2]*. (1) Biomedical Engineering, Rowan University, Glassboro, New Jersey, United States (2) Chemistry and Biochemistry, Rowan University, Glassboro, New Jersey, United States*

This work demonstrates a green method for the encapsulation of a natural phase change material (PCM), lauric acid (LA), in polystyrene (PS) hollow fibers through a solvent-assisted diffusion process inside fiber nanochannels. The obtained LAPS composite fibers had a melting enthalpy of up to 147.8 J/g, which was 82.0% the heat storage capacity of pristine LA (180.2 J/g). This capacity was higher than the values (generally less than 60%) reported in the literature. The LA content in the composite fibers could be controlled by the solution concentration and the solvent. On the contrary, encapsulation time had little effect on the final LA loading beyond 1 h due to the rapid diffusion of the LA solution. The optimal LA loading (82.2%) was achieved in 0.4 g/mL LA ethanol solution for 1 h, which was more than 4 times the weight of PS fibers. Simultaneous TGA−DSC, ATR, Raman, and SEM measurements confirmed the homogeneous distribution of LA inside the fibers across the whole membranes. Further, the LAPS composite fibers showed a long-lasting stability during cycling without storage capacity deterioration, as well as an exceptional structural stability without LA leaking and fiber rupture during 100 heating−cooling cycles. The energy-dense and form-stable LAPS composite fibers have a great potential for various thermal energy storage applications like “temperature-smart” buildings and textiles.

105. In-air polymerization and crosslinking of monomers during electrospray deposition

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Electrospray deposition (ESD) is a coating method by which a solution is passed through a capillary, and a charge is applied to the opening of the capillary. This causes a charge build-up in the solution, resulting in its dispersion into a spray due to a series of “Coulomb fissions,” in which each parent droplet splits into children droplets until an equilibrium is reached between droplet surface tension and charge. This method can be used in micro and nanoscale coating, and creates films with complex properties, including various morphologies from spheres to nanowires (in the case of specific solutes such as methylcellulose), porous or dense films, and the ability to coat all parts of 3D objects in a process known as self-limiting electrospray deposition (SLED). Though useful, ESD has several downsides as a manufacturing method. Only certain solvents can stably spray, such as 2-butanone (MEK), ethanol, and chloroform, and the loading of solutes can cause the spray to become unstable even at low weight percentages. Likewise, sprays can only

remain stable at certain low flow rates, meaning these low solute percentage sprays require a long period of time and a lot of solvent to fully deposit a film. Loading solvents with monomers and polymerizing agents can solve these problems. By introducing monomers such as methyl methacrylate (MMA) into MEK and other solvents, high amounts of the monomer can be loading into the solvent and polymerized in mid-air by loading in a photo initiator (PI) and cross-linker and spraying under ultraviolet (UV) light. For example, we were able to spray up to 50 wt% of MMA and photoinitiator from an MEK solution, as compared to spray of PMMA polymer which typically occurs at <5 wt%. In addition, by substituting 10% of the monomer with a difunctional acrylate, poly(ethylene glycol) diacrylate (PEGDA), we were able to create crosslinked films. Because of the in-air polymerization and cross-linking, we can form spray films in a much shorter period with the option of incorporating hierarchical texture by selection of curing kinetics. Using mid-spray polymerizing methods like this can allow for quicker sprays at higher loading capacities, use a much lesser amount of wasted solvent, and make complex spray film morphologies.

106. Study of nanocomposites of PolyRhodanine/Palladium/Cobalt: Synthesis and application

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Rhodanine (Rh) monomer is a heterocyclic derivative from thiazolidine containing 5-membered ring. Rh has several coordinating sites, sulfur, oxygen, and nitrogen and hence it is an excellent adsorbent of heavy metals and dyes. PolyRhodanine (pRh) shows corrosion inhibition properties, is antibacterial, anti-diabetic, anti-viral, antimicrobial, antihistaminic, and HVC inhibitor. Core-shell nanoparticles have two phases, an inner core structure and an outer shell which is made up of a different material. Core-shell nanoparticles are highly functionalized material and the purpose of the coating is to increase the stability and dispersibility of such material and to increase their functionality. Core-shell nanoparticles have applications in the optics, catalysis, pharmaceutical and the biomedical fields. Synthesis of such material required multiple step synthesis; Type 1, core formation is completed first and then reactants are added to form the shell *in situ*. In Type 2, the core particles are synthesized separately, and their surface is modified to coat with shell material. In our lab, polyRhodanine (pRh) core-shell nanocomposites were successfully synthesized *in situ* by an oxidation-reduction reaction with Cu (II), Pd(II) and Co(II) salts. The reactions took place efficiently in a microwave, accelerated by $KMnO_4$. The morphology of the materials was analyzed via Infra-red (IR) spectroscopy, SEM (Scanning Electron Microscopy), EDX (Energy Dispersive X-ray spectroscopy) and TEM (Transmission Electron Microscopy) analysis. This presentation will also include future plans for testing these materials for anti-viral, anticancer and antimicrobial activity.

107. G3-G5 PAMAM dendrimer demulsification studies of known oil compositions in water emulsions

***Mohamed A. Salah**, msalah1@gaels.iona.edu. Iona College, New Rochelle, New York, United States*

Separation of oil and water is desired for a variety of applications, including oil/gas extraction or oil spill cleanup. Our studies will investigate the chemical properties of an ideal demulsifier. We will use three generations of a known biocompatible PAMAM dendrimer, varying in molecular weight, and phenanthrene in hexadecane oil compositions to better understand how the dendrimer interacts with the oil layer and if there is a dependence on the oil composition in addition to dendrimer size demulsification efficiency. We hope to discover either a dendrimer generation demulsification dependence and/or an oil composition demulsification dependence through these initial studies.

108. Interactions of CO_2 with polymer surfaces for sequestration: A computational study

***Ramesh B. Komma**[2], rvk5518@psu.edu, Lorena Tribe[1]. (1) Penn State Berks, Reading, Pennsylvania, United States (2) Penn State Erie The Behrend College, Erie, Pennsylvania, United States*

Many materials have been considered in the search of systems that will capture CO_2 from the atmosphere and from sources such as carbon-burning power plants, including physisorbing materials like zeolites, activated carbon, alumina, metal-organic frameworks, and novel materials like BN, and chemisorbing ones such as amine solutions and amines on sorbents. Here we explore in detail the interaction of CO_2 with PEI to determine the structure and dynamics of the adsorbate-surface interaction. Electronic structure calculations were used to develop models for the transition of CO_3^{2-} to HCO_3^- at the surface driven by the presence of water molecules. A detailed understanding of the dynamics of this transition will allow for future calculations of the kinetics of the reaction.

109. Polyaniline nanofiber-metal nanoparticle composites for the catalytic degradation of congo red and other targets: A mini-review

***Devani Mahabir**, devani.mahabir99@student.qcc.cuny.edu, David M. Sarno. Chemistry Department, Queensborough Community College, Bayside, New York, United States*

We are developing a method for the formation of polyaniline nanofiber-ruthenium nanoparticle composites (PANI-NFs/Ru-NPs). PANI nanofibers provide a matrix to immobilize and disperse metal NPs, preventing their aggregation. These high surface area, electrically conductive composites may find use as a catalyst for the degradation of congo red, an azo dye that is toxic to many aquatic organisms and highly resistant to biodegradation. Ru-NPs were synthesized from Ru-salts by microwave irradiation in water at > 100 °C in the presence of $NaBH_4$ and pre-formed PANI-NFs. SEM images suggest that NP formation is favored by shorter microwave time and higher temperature, as well as

pre-adsorption of Ru-salts onto dispersed PANI-NFs; however, laboratory closures have prevented us from optimizing our method. Instead, we have conducted a literature review of relevant metal-polymer nanoscale composites. This poster provides an overview of our methods, as well as some of the studies we have drawn from. It also outlines our research plan to determine if our materials can be used as proposed.

110. Porous microspheres of polyaniline and its derivatives as a material for cargo loading and delivery: A mini-review

***Miaolan Chen Weng**, miaolan.chenweng03@student.qcc.cuny.edu, David M. Sarno. Chemistry Department, Queensborough Community College, Bayside, New York, United States*

We have prepared porous microspheres of polyaniline and several of its derivatives through a single surfactant water-in-oil-in-water (W/O/W) double emulsion method. When the crude granular polymer is dispersed in acidic solution with unreacted monomer, it is instantaneously converted into porous spheres by addition of excess ammonium hydroxide. This one-pot method produces a wide size distribution, but it can be significantly narrowed by a multi-step method that limits the amount of available polymer. Having applied the process to several polymers, we had hoped to test these porous particles as possible materials for cargo loading and delivery; however, laboratory closures have prevented us from pursuing this research. Instead, we have conducted a literature review of relevant polymer systems that successfully demonstrate cargo loading by permeation or encapsulation, as well as different delivery methods. This poster describes our W/O/W preparation method, including characterization by SEM and FTIR. We also present some of the studies we have drawn from, and outline our research plan to determine if our materials can be used as proposed.

BILL Talk: Barbara Morgan

111. Transition from chemist to business director: Leadership lessons

***Barbara Morgan**, barbara.morgan@lubrizol.com. LLS Health, Lubrizol Advanced Materials Inc, Cleveland, Ohio, United States*

Dr. Barbara Morgan received her PhD in Organic Chemistry from the University of Pennsylvania but opted to focus her career in the area of Business Management. She has worked with LLS Health, a Lubrizol Life Science Company, since 2014 and was named General Manager of CDMO Services in 2018. In addition, she has a larger global role serving as the Global Business Director for all of Lubrizol Life Science's pharma businesses, facilitating a strong relationship between the different business units. Dr. Morgan is going to provide a BILL^{TM} talk (Business, Illumination, Longevity and Laughs) discussing leadership lessons followed by a networking event in order to spread thought provoking, worthy concepts, foster professional growth, and make collegial connections.

112. Recent success stories from the women of Merck small molecule process research and development

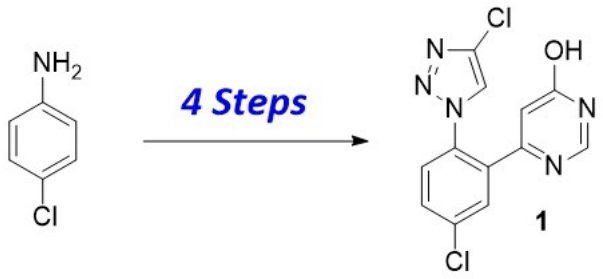
***Jamie McCabe Dunn**, jamie.mccabe.dunn@merck.com. Merck & Co Inc, Kenilworth, New Jersey, United States*

The influence of female mentorship and sponsorship as well as being surrounded by other women is vital in a women's career. This is particularly important in fields, like chemistry, that are lacking female representation. This presentation will describe several short stories of recent scientific accomplishments from women within small molecule process and development at Merck.

113. Chemical process development innovations to expand patient access to transformative medicines: Recent examples from the Janssen pipeline

***Jaume Balsells**, jbalsell@its.jnj.com, Simon Wagschall, Diego Broggini, Robert Panish, Shane L. Plunkett. Chemical Process Research & Development, Janssen Research and Development LLC, Raritan, New Jersey, United States*

Beyond the incredible challenge of inventing any new medicine, Process Chemists are tasked with designing the best chemical process for every product in the pipeline. In many cases, a completely redesigned novel synthetic route is needed to meet this objective. Chemists at Janssen working on the Development of a novel FXIa inhibitor demonstrated a 4-step process to intermediate **1**, drastically simplifying the synthesis of this compound. New chemistry developed to enable the preparation of differently substituted triazoles found application in Discovery chemistry to expand the understanding of this chemical space.



114. Flavonids revisit

***Ving J. Lee**, VLee@adesisinc.com. Adesis Inc, New Castle, Delaware, United States*

The 1,4-Benzopyrone scaffold (4H-chromen-4-ones) is the basis for various bioactive natural products. As some of these natural products are ubiquitious, some have been studied as possible pharmaceutical agents. However pleiotropic activities have detracted from their viability. This presentation will discuss attempts to modulate biological selectivity of several natural products, including some chemistry observations.

115. Withdrawn

116. Development of a scalable process for insecticide Tyclopyrazoflor

Xiaoyong Li[1]*, Xiaoyong.Li@corteva.com, Qiang Yang*[2]*, Beth A. Lorsbach*[3]*, Kaitlyn Gray*[1]*. (1) Process Science &Technology, Corteva Agriscience, Indianapolis, Indiana, United States (3) Discovery Chemistry, Corteva Agriscience, Indianapolis, Indiana, United States*

The development of a scalable process for the lead route to sap-feeding insecticide Tyclopyrazoflor is described. This process features a [3 + 2] cyclization of 3-hydrazinopyridine-2HCl and methyl acrylate as well as a radical initiated highly regio-selective thiol-ene reaction. The key impurities were identified and successfully controlled after fit for purpose optimization. The overall yield for this 7-step synthesis of Tyclopyrazoflor was improved from 10% to 41%. The optimized process presented an excellent advantage in process safety and economics.

117. Overview of agricultural discovery at FMC

Travis McMahon*, TRAVIS.MCMAHON@FMC.COM. Discovery Chemistry, FMC Corporation, Philadelphia, Pennsylvania, United States*

As the fifth largest agrichemical company in the world, FMC is committed to finding new, innovative and sustainable solutions to meet farmers evolving needs. Our Discovery organization utilizes a variety of approaches aimed at finding new proprietary areas of biologically active chemistry that can be developed and delivered to growers. In this presentation we will give an overview of Discovery research at FMC.

Empowering Chemists with Disabilities

118. Communicating chemistry content effectively to the blind

Cary A. Supalo*, csupalo@ets.org. Educational Testing Service, Princeton, New Jersey, United States*

We take for granted that chemistry concepts are communicated in both two- and three-dimensional representations that are non-ambiguous in nature. However, visual

representations can be innately biased towards sighted and non-print disabled scientists. Further, ways to represent and teach chemistry content can further be designed to limit the print disabled individual from fully comprehending and participating in the chemistry community.

This presentation will discuss two different group's efforts to make the communication of chemistry content available in more non-ambiguous ways to the blind or print disabled community. These groups are the Braille Authority of North America (BANA) chemistry ad hoc committee and the World Wide Web (W3C) Consortium Chemistry Community group. All these efforts are designed to make learning chemistry more efficacious to the print disabled learner in the hopes of opening more doors of opportunity for the blind and print disabled in the chemistry profession.

119. Computational biophysical chemistry for researchers who are visually-impaired

*Olivia R. Shaw, **Jodi A. Hadden-Perilla**, jhadden@udel.edu. Department of Chemistry & Biochemistry, University of Delaware, Newark, Delaware, United States*

Through collaboration of an undergraduate student who is blind with a faculty member in the Department of Chemistry and Biochemistry at the University of Delaware, we have developed strategies for individuals who are visually-impaired to participate in research and education in computational biophysical chemistry. Our approach utilizes molecular model kits, 3D printing, variable-height tactile graphics, and the TactViz software, which we developed to render Protein Data Bank structures on refreshable tactile displays and to print textual descriptions of biomolecules accessible with screen-readers and Braille devices. Combining these tools and resources, our undergraduate student was enabled to carry out computational biophysical chemistry research, including performing molecular dynamics simulations on a national supercomputer, analyzing and interpreting simulation results, and preparing two manuscripts for publication. Our TactViz software, a plugin for the widely-used, freely-available Visual Molecular Dynamics (VMD) code, is publicly available on GitHub for researchers and educators everywhere to support inclusion of individuals who are visually-impaired in STEM fields like chemistry, where they are significantly underrepresented.

An Assistant Professor at the University of Delaware collaborates with an undergraduate student who is blind to improve accessibility of computational biophysical chemistry for individuals who are visually-impaired.

120. Voice control of a raman microscope with Commercial Off the Shelf (COTS) software

Karl S. Booksh[1]*, kbooksh@udel.edu, Rachael McCormick*[1]*, Deanna Greco*[2]*. (1) University of Delaware, Newark, Delaware, United States (2) The Catholic University of America, Washington, District of Columbia, United States*

There is a persistent need to make capital instrumentation accessible to students with physical or visual disabilities in academic settings. Compared to consumer goods, such as cell phones, the small market for scientific instrumentation limits manufacturers motive to natively embed accessibility options into the instrumentation operating software. These issues are compounded with major instrumentation such as Raman or FTIR microscopes where the controlling software are often not written with concerns for compatibility with third-party products for accessibility. The logical, best case scenario, for economically increasing major instrument accessibility is thus through commercial off the shelf (COTS) software. In this talk we will present the control of a Horiba LabRAM HR Evolution Raman Microscope by Dragon Dictate. This was accomplished during a summer Research Experience for Undergraduates (REU) program.

121. Well succeed experience in teaching chemistry to deaf students in Brazil

Hélder V. Silva*, helder.carneiro@ufpe.br. Department of Fundamental Chemistry, Universidade Federal de Pernambuco, Recife, PE, Brazil*

The teaching of sciences to Brazilian students requires targeted actions that go far beyond those provided today by public policies present in the country. This work aims to narrate the successful experience in teaching chemistry to deaf students in a preparatory course, allocated at the Federal University of Pernambuco, in the city of Recife. The GRADAÇÃO Project, created in 2019, has as one of its main objectives to provide the inclusion of students with disabilities in preparatory courses for Brazilian public universities, in classes composed of hearing and non-hearing students. The project is mostly organized by undergraduate students, with the supervision of a faculty member. In its first year of operation, the project had x students, x of whom were deaf. More than 100 undergraduate students were responsible for classes, logistics, class organization, and translation to sign language services. Specifically, in chemistry classes, there was a joint work between teachers and translators, with the development of educational devices and signs to a better understanding of subjects. The use of many experimental classes and intensification of visual resources played a fundamental role in the students' development. Also, the use of these tools increased the hearing students' curiosity about chemistry, a discipline that does not usually cause this reaction. The beginning of 2020 brought great news for the project. Among the fifteen approved students, two of them were deaf students. One of the deaf students was approved in the first place overall in the degree course in chemistry, being a reason of great joy for all of the team. The goal now is to ensure that more students are reached and built a more equal society.

122. Panel discussion: Making career decisions during the pandemic

***Karl S. Booksh**, kbooksh@udel.edu. University of Delaware, Newark, Delaware, United States*

This panel discussion will probe the impacts of the COVID pandemic on the decision making process for students with disabilities as they selected graduate programs, chose to attend graduate school or chose to leave a graduate program. The college-to-graduate school transition is stressful for many students under optimal conditions and choosing the right program / advisor can have long-term implications for future success. This is especially true for students with disabilities who must find programs and advisors who are accommodating to their needs and will help place the students in an environment where they can succeed. With quarantines, cancelled visitation weekends, and remote interviews, it is additionally difficult to gather information for confident decision making. In light of the COVID-related uncertainties, We will talk with students with disabilities about why they made particular decisions, what resources helped inform the decisions, and what advice they offer to programs and other students to support transition planning for prospective graduate students.
Students with

Inorganic and Organometallic Young Investigator Symposium

123. Design and synthesis of highly porous coordination cages

***Eric D. Bloch**, edb@udel.edu. Chemistry & Biochemistry, University of Delaware, Newark, Delaware, United States*

Porosity in network solids, including zeolites, activated carbons, and metal-organic frameworks, has been widely interrogated for decades. In molecular metal-organic systems, however, it is a relatively novel phenomenon. This is somewhat surprising given the fact that porous organic cages can display surface areas that rival those of metal-organic frameworks. This talk will focus on the design, synthesis, and characterization of highly porous coordination cages for small molecule storage applications. Further, it will detail the intriguing interplay between surface area and solubility in a class of paddlewheel-based cages. We have recently shown that these materials, which conceptually serve as soluble metal-organic framework analogs, display impressive porosity under specific synthesis and activation conditions. Although these cages are typically amorphous upon desolvation, the utilization of pillaring ligands endows the materials with high crystallinity and compatibility with diffraction methods for the identification and optimization of gas binding sites. The design, synthesis, and characterization of an exciting new class of materials, porous salts, will also be discussed.

124. Molecular strategies to modulate the electrode-electrolyte interface in heterogeneous electrocatalysis

***V. Sara Thoi**, sarathoi@jhu.edu. Chemistry, Johns Hopkins University, Baltimore, Maryland, United States*

Extraordinarily efforts have been placed on developing novel electrocatalysts for transforming energy-relevant small molecules. Catalysts particles are stabilized by surfactants and supported on carbon materials. The roles of these molecular additives and heterogeneous supports are often considered negligible or worse yet, not considered at all. Herein, we demonstrate that cationic surfactants play a significant role in modulating the electrode-electrolyte interface during carbon dioxide reduction. We further illustrate that the type of carbon support affects the structural transformation of the metal surface. Moreover, we will present new strategies to probe the electrode-electrolyte interfaces in electrocatalysis using advanced electrochemical techniques such as in-situ vibrational spectroscopy and electrochemical impedance spectroscopy. Our studies highlight molecular strategies to tune complex heterogeneous interfaces and opens up new avenues for directing catalytic performance.

125. Photoswitchable extended network materials

***Kate M. Waldie**, kate.waldie@rutgers.edu. Chemistry and Chemical Biology, Rutgers The State University of New Jersey, Piscataway, New Jersey, United States*

Extended network materials such as metal-organic frameworks (MOFs) and covalent organic frameworks (COFs) enable precise control over their structure and properties through particular selection of the framework components. Next-generation functional materials will exhibit tunable properties in response to an external stimulus. Light is an especially attractive stimulus due to its high spatial and temporal resolution; thus, the introduction of organic photochromic molecules as framework components in MOF and COF materials is of special interest in order to obtain optical control over the material structure by simply applying light irradiation at different wavelengths. In this talk, I will present our efforts to prepare a series of highly aromatic, organic molecules that undergo photoisomerization upon exposure to visible light and their installation into extended network materials. This photoisomerization reaction is accompanied by a large decrease in their π-conjugation, and thus the two photoisomers have significantly different electronic absorption characteristics and electrical conductivities. By directly incorporating these molecules as the organic linkers in MOF and COF structures, their photoisomerization has direct impact on the structure and properties of the networks. Characterization of these new functional materials provides key insights into understanding photoisomerization reactivity in constrained environments.

126. Developing hydrolytic mini-metalloenzymes using *de novo* proteins

***Katherine Buettner**, kbuettne@gettysburg.edu. Chemistry, Gettysburg College, Gettysburg, Pennsylvania, United States*

Metallohydrolases are metal-dependent enzymes that catalyze the hydrolytic cleavage of a range of biologically relevant substrates, including esters, organophosphates, polynucleotides, peptides, and CO_2. They are found throughout all kingdoms of life and their biological functions make them valuable potential targets for drug design (e.g., osteoporosis, cancer, cystic fibrosis), antibacterials, and bioremediation catalysts (e.g., degradation of pesticides or nerve gases). While metal ions are not required for hydrolytic cleavage reactions, they can be particularly powerful catalysts due to their high Lewis acidity, resulting in a metal-bound hydroxide at neutral pH. When placed within a protein scaffold, the resultant highly reactive hydroxide ion can be positioned for optimal nucleophilic attack on a substrate, allowing for hydrolysis under room temperature and neutral pH conditions. Metallohydrolases can be mononuclear or multinuclear, and function with a wide range of metal ions, including Mg^{2+}, Ca^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Cu^{2+}, Ni^{2+}, and Zn^{2+}. Binuclear metallohydrolases contain two metal ions spaced 3-4 Å apart coordinated primarily by a combination of Asp, Glu, and His amino acids. Utilizing the *de novo* designed Due Ferri single chain (DFsc) scaffold, we have made a series of proteins, which feature these residues in a binuclear active site, and have further modified this site to include a tyrosine, which is found in the active site of purple acid phosphatase, and known to bind and stabilize hydrolysis-prone metals. We have tested the effect of this substitution on both metal binding and hydrolytic activity, making mini-metalloenzymes (MMEs). We have tested metals commonly used by nature, like Zn^{2+}, as well as metals underutilized by nature like Ti^{4+} and V^{5+} for their ability to bind to these protein scaffolds, and have seen differential binding in constructs containing this tyrosine substitution vs. those that do not. We have also studied the effect of both metal and protein sequence on their ability to hydrolytically cleave DNA and have seen both successful cleavage and increased activity with the tyrosine substituted proteins.

127. Olefin metathesis with vanadium(V) alkylidenes: Current possibilities and limitations

***Wesley Farrell**, wfarrell@usna.edu. Chemistry, US Naval Academy, Annapolis, Maryland, United States*

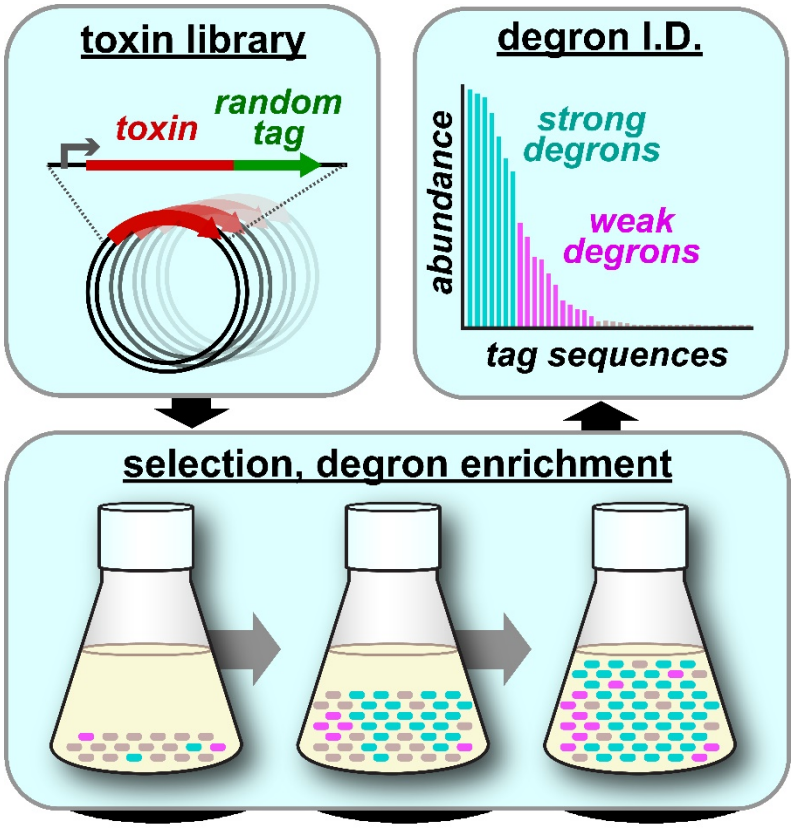
Cross metathesis (CM) is a widely used tool in organic synthesis, allowing for the construction of carbon-carbon double bonds with high precision. While such transformations have long been catalyzed by ruthenium and group 6 compounds, analogous transformations mediated by abundant, inexpensive, and environmentally-friendly vanadium complexes are less well-known. This talk will detail the current state of olefin metathesis generally, and CM specifically, with vanadium alkylidenes. Limitations resulting from decomposition of key intermediates will be discussed, along with suggestions for preventing such issues.

Protein Quality Control

128. Systematic discovery of terminal sequences that mark proteins for proteolysis in *E. coli*

*Patrick C. Beardslee[2], **Karl R. Schmitz**[1,2], karl.schmitz@gmail.com. (1) Biological Sciences, University of Delaware, Newark, Delaware, United States (2) Chemistry & Biochemistry, University of Delaware, Newark, Delaware, United States*

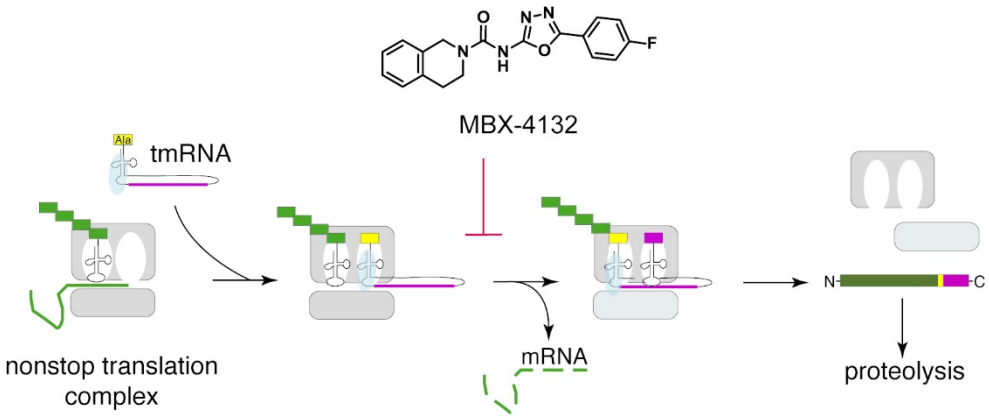
ATP-dependent proteases carry out targeted destruction of cytosolic proteins in all bacteria, and have emerged as promising antibacterial and antivirulence drug targets. While some aspects of their function are well understood, the critical initial step in regulated proteolysis – *substrate selection* – remains poorly characterized. Many substrates are recognized through direct interactions with short targeting sequences, termed degrons. The full complement of functional degrons remains unknown. Using a cell-based approach that links survival to degron recognition and proteolysis, we systematically identified functional degrons in *E. coli* from a randomized library of terminal sequences. Our study reveals a vast catalog of novel functional degrons in *E. coli*, and highlights the unique ability of the protease ClpXP to robustly recognize an array of sequences similar to the ssrA tag.



129. Co-translational protein quality control is a target for new antibiotics

Kenneth Keiler[1], *kkeiler@psu.edu, John N. Alumasa*[1], *Mynthia Cabrera*[1], *Zachary Aron*[2], *Christine Dunham*[3]. *(1) Biochemistry & Molecular Biology, The Pennsylvania State University - University Park Campus, University Park, Pennsylvania, United States (2) Microbiotix Inc, Worcester, Massachusetts, United States (3) Emory University, Atlanta, Georgia, United States*

Problems during transcription or translation can result in a ribosome stalled on the mRNA with an incomplete nascent polypeptide still engaged. Bacteria use *trans*-translation to target the nascent polypeptide for degradation and rescue the stalled ribosome. During *trans*-translation, tmRNA, a specialized RNA molecule, and SmpB, a small protein, act first as a tRNA and then as an mRNA to divert the ribosome onto a reading frame within tmRNA. Translation of this reading frame adds a sequence to the nascent polypeptide that is recognized by proteases, which degrade the incomplete protein. The ribosome is released at a stop codon within tmRNA. Because *trans*-translation is essential in most bacteria but is is not found in higher eukaryotes, this pathway could be a target for antibiotic development if appropriate small molecule inhibitors were available. We used a high-throughput screen to identify a family of acylaminooxadiazoles that specifically inhibit *trans*-translation and not translation. Optimization of the pharmacokinetic properties of these compounds resulted in MBX-4132, which had potent broad-spectrum antibiotic activity. In a mouse infection model for gonorrhea, bacteria were cleared after a single oral dose of the compound. Single particle cryo-EM structures showed that the acylaminooxadiazoles bind to a unique site near the peptidyl-transfer center and significantly alter the conformation of ribosomal protein bL27, suggesting a novel mechanism for specific inhibition of *trans*-translation by these molecules. These results show that *trans*-translation is a viable therapeutic target and reveal a new conformation within the bacterial ribosome that may be critical for ribosome rescue pathways.



MBX-4132 inhibits *trans*-translation and has broad-spectrum antibiotic activity *in vivo*.

130. Proteasomal conformation controls unfolding ability

Julianna Cresti, Abramo Manfredonia, Christopher Bragança, Joseph Boscia IV, Christina Hurley, Mary Cundiff, ***Daniel Kraut****, daniel.kraut@villanova.edu. Chemistry, Villanova University, Villanova, Pennsylvania, United States*

The 26S proteasome is the macromolecular machine responsible for the bulk of protein degradation in eukaryotic cells. As it degrades a ubiquitinated protein, the proteasome transitions from a substrate-accepting conformation (s1) to a set of substrate-processing conformations (s3-like), each stabilized by different intramolecular contacts. Tools to study these conformational changes remain limited, and although several interactions have been proposed to be important for stabilizing the proteasome's various conformations, it has been difficult to test these directly under equilibrium conditions. Here we describe a conformationally sensitive FRET assay in which fluorescent proteins are fused to Sem1 and Rpn6, which are nearer each other in substrate-processing conformations than in the substrate-accepting conformation. Using this assay, we find that two sets of interactions, one involving Rpn5 and another involving Rpn2, are both important for stabilizing substrate-processing conformations. Mutations that disrupt these interactions both destabilize substrate-processing conformations relative to the substrate-accepting conformation and diminish the proteasome's ability to successfully unfold and degrade hard-to-unfold substrates, providing a link between the proteasome's conformational state and its unfolding ability.

131. Countering deleterious phase transitions in ALS/FTD

James Shorter*, jshorter@pennmedicine.upenn.edu. University of Pennsylvania, Philadelphia, Pennsylvania, United States*

Here, I will present our latest endeavors counter deleterious phase transitions in ALS/FTD.

Spectroscopy: From Molecules to Macrostructures

132. Properties of solar energy and spintronic materials from DFT

Leah Bendavid*[1], lebendavid@vassar.edu, Owen T. Fauth[1], Austin O. Atsango[1,2], Reid W. Smith[1]. (1) Chemistry, Vassar College, White Plains, New York, United States (2) Chemistry, Stanford University, Stanford, California, United States*

We present two projects that use computational quantum chemistry to design better nanomaterials for solar energy and spintronic applications. In the first project, we use density functional theory (DFT) to examine CdS/graphene photocatalytic interfaces. Using DFT calculations, we study the interfacial properties of CdS(0001)/graphene and a CdS/graphene bilayer, and examine whether doping with B/N can strengthen interfacial adhesion. The CdS/graphene bilayer is found to exhibit high interplanar distances and low

adhesion energies, characteristic of dispersion-dominated interfacial adhesion. Doping graphene does not significantly modify the strength of adhesion, but it does enable modulation of the band edge and Fermi level alignments. The CdS(0001)/graphene interface is found to be similarly adhered via dispersion interactions, but here, doping with B strengthens interfacial adhesion. In the second project, we study how strain-engineering can be used to tune the properties of dilute magnetic semiconductors formed by doping transition metal dichalcogenides with Mn. Specifically, we focus on Mn-doped MoS_2 and $MoSe_2$. We find that strain changes the optoelectronic properties primarily by decreasing the optical gap and changing the nature of the gap from direct to indirect. Increasing tensile strain will also increase local magnetic moments and may strengthen the exchange coupling that stabilizes ferromagnetic alignments over antiferromagnetic alignments.

133. Surface supportive metal-organic framework as a drug delivery system

*Steven G. Guillen, Angela Bui, **Fangyuan Tian**, fangyuan.tian@csulb.edu. Department of Chemistry & Biochemistry, California State University Long Beach, Long Beach, California, United States*

Metal-organic frameworks (MOFs), a class of hybrid materials, exhibit ultrahigh porosity, structural diversity and multiple functionalities, making them excellent candidates for a variety of applications, such as gas storage and separation, catalysis, and drug delivery. Recent progress in making surface supportive MOFs has dramatically expanded their uses ranging from molecular devices to biomedical applications. Here, we reported a type of iron-based MOF materials as drug carriers. Attaching MOFs onto substrates offers a wide variety of chemical functionality and controllable structural and mechanical versatility. However, the challenges associated with chemically binding MOF films relating to homogeneity, orientation, thickness, and stability that are hard to accommodate all in one system. We utilize surface science and coordination chemistry as guidance during the formation of MOF films. In this work, we compared the drug loading and releasing capabilities of MIL-88B and MIL-53 with ibuprofen as a model drug. We found that MIL-88B exhibits a high encapsulation rate (19.5 wt%) with a controllable releasing rate over 10 days. Furthermore, we attached MIL-88B on a COOH-terminated self-assembled monolayer modified Au substrate. The prepared MIL-88B film was studied for ibuprofen loading and releasing performance. Additionally, the binding mechanism of MIL-88B on the functionalized Au substrate was explored with cluster calculations based on the density functional theory (DFT). The interactions between MIL-88B and ibuprofen were studied with frontier orbital analysis to simulate the drug loading environment.

134. Time-resolved X-ray spectroscopy studies of long lived photoinduced charge separation in redox active metal organic frameworks

***Jenny V. Lockard**, jlockard@andromeda.rutgers.edu, Lauren Hanna. Department of Chemistry, Rutgers University - Newark, Newark, New Jersey, United States*

Metal organic frameworks are hybrid solid state materials that are composed of metal ions or clusters connected by organic molecules to form crystalline microporous networks.

Their diversity in chemical makeup and tunable, permanent porosity make MOFs attractive candidates for traditional adsorption-based applications such as chemical separation and storage. Efforts to engender redox or photoredox properties offer new opportunities for applications that rely on MOF conductivity, stable electron transfer and/or long-lived charge separation such as resistive sensors, electrochromic devices, and single site electro- or photocatalysis. Synthetic strides in developing frameworks with these properties have, however, far outpaced the progress in advancing the fundamental understanding of their electronic structure and excited state dynamics. Consequently, there are often significant ambiguities in the structure/function relationships that give rise to their utility. In our research, we use a targeted set of spectroscopy methods to make those connections by producing molecular level understanding of observed MOF behavior. Specifically, the talk will introduce two types of MOF systems containing potential photoredox sites and present time resolved X-ray and optical spectroscopy studies that elucidate the nature and dynamics of their charge separated excited states.

135. Imaging partially ordered molecular materials through vibrational nano-spectroscopy

Eric A. Muller[1]*, ericantonmuller@gmail.com, Brian T. O'Callahan*[2]*, Johna Joseph*[1]*, Tarik Cigeroglu*[1]*. (1) Chemistry, Colgate University, Hamilton, New York, United States (2) EMSL, Pacific Northwest National Laboratory, Richland, Washington, United States*

Order and disorder spanning multiple length scales determine the function and performance in molecular materials. However, the nanometer length scales and low energies of interaction particularly at surfaces and interfaces have remained an experimental challenge. Infrared scattering-scanning near-field optical microscopy (IR s-SNOM) overcomes these limitations through super resolution imaging as well as through sensitivity to molecular vibrations from ensembles as small as 100 vibrations. We describe the use of molecular vibrations as intrinsic labels, providing nanoscale measurement of order, local environment, and orientation. We use strong coupling induced splitting of vibrational exciton modes to measure few-nm domain sizes and phase coexistence. Using the combination of vibrational labels and nanoscale imaging, we measure from molecular scale to long-range ordering in molecular materials and interfaces.

136. High-resolution, rotationally-resolved spectroscopy of the 3300 cm^{-1} band of astrochemically-relevant HCN

Jess Palko, Thomas Howard, ***Leah G. Dodson****, ldodson@umd.edu. Chemistry & Biochemistry, University of Maryland at College Park College of Computer Mathematical and Natural Sciences, College Park, Maryland, United States*

Hydrogen cyanide (HCN) is ubiquitous in the interstellar medium and planetary atmospheres where its abundance and reactivity are of great astrochemical interest. We have developed a safe, robust synthesis and characterization procedure for pure HCN gas, which is necessary for carrying out further studies on the reactivity of HCN. I will present the high-resolution, rotationally-resolved vibrational spectrum of gaseous HCN

obtained with a Nicolet iS50 Fourier-transform infrared (FTIR) spectrometer and describe our line-by-line frequency and spectral intensity analysis based on data from the HITRAN database. Finally, I will describe our progress toward using a cryogenic buffer-gas beam composed of pure HCN doped in rare gases to explore low-temperature HCN reactivity both in the gas phase – through reactions with atomic metal ions – and in a matrix.

137. Gas-surface interactions of Hg(II) compounds probed by mass spectrometry

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Gaseous oxidized mercury (GOM) is a family of poorly characterized Hg(II) compounds formed in the atmosphere through photochemical oxidation of Hg(0). Our focus on gas-surface interactions of GOM is driven by two principle reasons. First, the uptake of GOM by surfaces of aerosols may play a major role in the removal of mercury from the atmosphere to land and ocean. However, the rate of GOM uptake has not yet been quantified. Second, adsorption on surfaces is a common approach to increase the concentration of atmospheric GOM before analysis due to its extremely low atmospheric abundance. We hypothesize that surface-sorbed GOM species can engage in exchange reactions with the surface, each other, or co-adsorbed atmospheric chemicals, changing the chemical composition of GOM and leading to analysis artifacts. To address these questions, we measured the rate of GOM surface uptake and investigated its exchange in aqueous solutions and on surfaces, We used $HgCl_2$, $HgBr_2$, HgI_2 as GOM surrogates and analyzed exchange reaction products by ion drift - chemical ionization mass spectrometry and electrospray ionization - mass spectrometry. We found that the interaction of $HgCl_2$ with inorganic salts surfaces is governed by a two-step (adsorption/reaction) Langmuir-Hinshelwood mechanism and the rate of uptake varies strongly with the surface composition. Using experimental uptake rates, we estimated GOM lifetime with respect to removal by urban and marine aerosols to range from hours to days, outcompeting the removal by direct dry deposition to the land and oceans. Furthermore, we observed a rapid exchange of mercury (II) halides both in aqueous solutions and on surfaces, producing volatile HgBrCl, HgBrI, and HgClI. Thus, we propose that a similar exchange can occur during atmospheric sampling, completely scrambling up the original GOM speciation.

Plenary: Dan Nocera

138. Complete artificial photosynthesis: Sustainable and renewable carbon, nitrogen and phosphorus cycles for fuel and crop production

***Daniel G. Nocera**, dnocera@fas.harvard.edu. Harvard University, Cambridge, Massachusetts, United States*

Hybrid biological | inorganic (HBI) constructs have been created to use sunlight, air and water as the only starting materials to accomplish carbon and nitrogen fixation, thus enabling distributed and renewable fuels and crop production.

The carbon and nitrogen fixation cycles begin with the Artificial Leaf, which was invented to accomplish the solar fuels process of natural photosynthesis – the splitting of water to hydrogen and oxygen using sunlight – under ambient conditions. To create the Artificial Leaf, self-healing catalysts were created to permit water splitting to be accomplished under benign conditions and thus the system may be easily interfaced to bioorganisms to convert carbon dioxide and nitrogen from air, along with the hydrogen produced from the catalysts of the Artificial Leaf, into liquid fuels and ammonia, respectively. The HBI, called the Bionic Leaf, operates at carbon- fixing and nitrogen-fixing efficiencies (×10 of nature), greatly exceeding the 1% yield of natural photosynthesis. The organism can also fix phosphorus from waste sources. By interfacing energy with agriculture, we show that for a 400-acre farm, that the budget saving of carbon dioxide is 253,000 lbs while enhancing crop yields.

The science that is presented will show that using only sunlight, air and water, a distributed and renewable system may be designed to produce fuel (carbon neutral) and food (carbon negative) within a sustainable cycle for the biogenic elements of C, N and P. The innovation described in this talk is particularly useful to the poor of the world, where large infrastructures for fuel and food production are not tenable.

Biophysical Chemistry

139. Atomistic dynamics of a viral infection process: Release of membrane lytic peptides from a non-enveloped virus

***Eric R. May**, eric.may@uconn.edu. Molecular and Cell Biology, University of Connecticut, Storrs, Connecticut, United States*

Molecular simulations have played an instrumental role in uncovering the structural dynamics and physical properties of virus capsids. In this work we move beyond equilibrium physicochemical characterization of a virus system to study a stage of the infection process which is required for viral proliferation. Despite many biochemical and functional studies, the molecular mechanism of host cell entry by non-enveloped viruses remains largely unresolved. Flock House Virus (FHV) is model system for non-enveloped

viruses and is the subject of the current study. FHV infects through the acid-dependent endocytic pathway, where low pH triggers externalization of membrane disrupting (g) peptides from the capsid interior. Employing all-atom equilibrium and enhanced sampling simulations, the mechanism and energetics of g peptide liberation and the effect of pH on this process is investigated. Our computations agree with experimental findings and reveal nanoscopic details regarding the pH control mechanism which are not readily accessible in experiments

140. Differential thermodynamics and kinetics of prefusion spike proteins of SARS-CoV-1 and 2

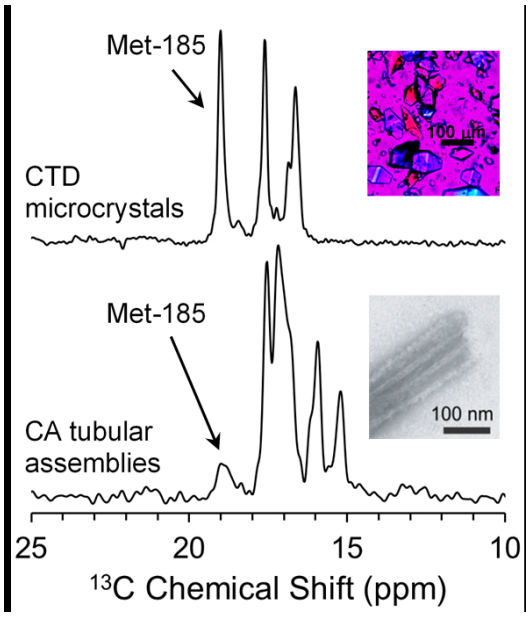
Vivek Govind Kumar, Dylan Ogden, Ugochi Isu, Adithya Polasa, James Losey, ***Mahmoud Moradi****, moradi@uark.edu. Chemistry and Biochemistry, University of Arkansas Fayetteville, Fayetteville, Arkansas, United States*

Within the last two decades, severe acute respiratory syndrome coronaviruses 1 and 2 (SARS-CoV-1 and SARS-CoV-2) have caused two major outbreaks. For reasons yet to be fully understood the COVID-19 outbreak caused by SARS-CoV-2 has been significantly more widespread than the 2003 SARS epidemic caused by SARS-CoV-1, despite striking similarities between the two viruses. One of the most variable genes differentiating SARS-CoV-1 and SARS-CoV-2 is the S gene that encodes the spike protein, which mediates a crucial step in the infection, i.e., host cell recognition and viral entry. Recent structural and functional studies have shed light on the differential binding behavior of the SARS-CoV-1 and SARS-CoV-2 spike proteins. In particular, cryogenic electron microscopy studies show that angiotensin converting enzyme 2 (ACE2) binding is preceded by a large-scale conformational change in the spike protein to expose the receptor binding domain (RBD) to its binding partner. Unfortunately, these studies do not provide detailed information on the dynamics of this activation process. Here, we have used an extensive set of unbiased and biased microsecond-level all-atom molecular dynamics (MD) simulations of SARS-CoV-1 and SARS-CoV-2 spike protein ectodomains in their prefusion state to determine the differential behavior of spike protein activation in the two viruses. Our results indicate that the two proteins are associated with substantially different thermodynamic and kinetic properties. The active form of the SARS-CoV-2 spike protein is considerably more stable than the active SARS-CoV-1 spike protein and the energy barrier between the active and inactive states is significantly higher for the SARS-CoV-2 spike protein, indicating a slower kinetics. Employing state-of-the-art path-finding algorithms, we also observe that the conformational transition pathway associated with the activation process is drastically different for the two proteins. Based on these results we postulate that the effective binding process should not be reduced to the binding of ACE2 receptor to the RBD region, but the activation process, which involves not only the RBD but also the rest of the protein, should also be considered as an important part of the binding process. This hypothesis has important implications in spike-based vaccine and therapeutic development as the activation/deactivation process can be targeted as a way of inhibiting the binding process.

141. Protein interface flexibility in pleomorphic viral assemblies via solid-state NMR spectroscopy

Guivert Michel, Jeremy Gonzalez-Roman, Carlos A. Figueroa Morales, Naomi Rodriguez-Marino, ***Marvin J. Bayro****, marvin.bayro@gmail.com. Department of Chemistry and Molecular Sciences Research Center, Universidad de Puerto Rico Recinto de Rio Piedras, San Juan, San Juan, Puerto Rico*

The structural proteins of the human immunodeficiency virus type 1 (HIV-1) are characterized by their capacity to self-assemble and restructure themselves during the infectivity cycle. To understand the structural mechanisms that drive these protein assemblies, novel methods have been developed for the elucidation of molecular structure and dynamics. In this presentation, I will describe solid-state nuclear magnetic resonance (NMR) spectroscopy experiments for the analysis of the mature and the immature protein lattices of HIV-1 at the atomic level, with emphasis on the interactions that stabilize self-assembly and the mechanisms that facilitate structural reorganization in the critical maturation step of the virus infectivity cycle. I will also describe the application of solution NMR spectroscopy to guide batch-crystallization of proteins for solid-state NMR analysis of conformation and flexibility, focusing on the interfaces that give rise to variable curvature in asymmetric protein lattices. Our results demonstrate a highly tailored spectroscopic approach to characterize the plasticity of protein interfaces.



Identification of curvature-dependent structural heterogeneity in dimerization interface of HIV-1 CA-derived assemblies based on solid-state NMR spectra

142. All-Atom MD simulations of the HBV capsid: Revealing mechanisms of function and disruption

***Jodi A. Hadden-Perilla**, jhadden@udel.edu. University of Delaware, Newark, Delaware, United States*

The hepatitis B virus (HBV) capsid is an attractive drug target, relevant to combating viral hepatitis as a major public health concern. Among small molecules known to interfere with capsid assembly, the phenylpropenamides, including AT130, represent an important antiviral paradigm based on disrupting the timing of genome packaging. Here, all-atom molecular dynamics simulations of an intact AT130-bound HBV capsid reveal that the compound increases spike flexibility and improves recovery of helical secondary structure in the spike tips. Regions of the capsid-incorporated dimer that undergo correlated motion correspond to established sub-domains that pivot around the central chassis. AT130 alters patterns of correlated motion and other essential dynamics. A new conformational state of the dimer is identified, which can lead to dramatic opening of the intradimer interface and disruption of communication within the spike tip. A novel salt bridge is also discovered, which can mediate contact between the spike tip and fulcrum even in closed conformations, revealing a mechanism of direct communication across these sub-domains. Altogether, results describe a dynamical connection between the intra- and interdimer interfaces and enable mapping of allostery traversing the entire core protein dimer.

143. Updating the CHARMM lipid force field and modeling membrane leaflet composition asymmetry

*Yalun Yu[2], Min-Kang Hsieh[1], **Jeffery B. Klauda**[1], jbklauda@umd.edu. (1) Chemical and Biomolecular Engineering, University of Maryland, Silver Spring, Maryland, United States (2) Biophysics, University of Maryland at College Park, College Park, Maryland, United States*

Although the CHARMM36 (C36) lipid force field (FF) has been extended to incorporate various lipids with a high-level of accuracy, the development of the FF was based on cutoffs in the long-range dispersion energies. This works reasonably well with bilayers but fails to represent the properties of lipid assemblies that require long-range dispersion, i.e., lipid monolayers with an air-acyl chain interface. A method to optimize lipid FF parameters in a semi-automated approach is presented to refit the C36 lipid FF to simultaneously reproduce lipid bilayer and monolayer properties. The optimization uses thermodynamic reweighting with regularization to the original C36 FF. The ability to quickly obtain an accurate set of parameters for phosphocholine (PC) lipids in the manner of months allowed us to quickly develop a revised C36 with a Lennard Jones particle mesh Ewald (LJ/PME) approach for long-range dispersion. This approach has been used to develop parameters for PC, phosphatidylethanolamine (PE), phosphatidylglycerol (PG), and ether lipids that agree with structural and dynamical properties of bilayers and monolayers. This presentation will also present work on asymmetric leaflet models of plant plasma

membranes and bacterial inner membranes. Natural membranes are known to have a varied composition between leaflets that is important to structure and function of membranes. Models for the plasma membrane of *Arabidopsis thalina* (a widely used model to study plant biology) are developed based on past lipidomic work. These models have eight lipids (including sitosterol) with two glycolipids residing on the outer leaflet. We also will present work on the composition asymmetry for the inner membrane of *E. coli*. The lipid diversity in this simple organism is reduced compared to plants but important to the function of this membrane and driving force for transmembrane protein orientation. Biophysical properties will be presented for these two models and how they differ from simple symmetric membrane models. These models are currently being developed to apply towards auxin (plant hormone) partitioning and transmembrane protein orientation.

144. Identifying structurally-resolved lipid fragments through molecular simulation

*Thomas T. Joseph[4], Mark Arcario[3], John Petroff[3], Wayland Cheng[3], Jerome Henin[2], **Grace Brannigan**[1], grace.brannigan@rutgers.edu. (1) Rutgers University, Camden, New Jersey, United States (2) LBT, IBPC - CNRS, Paris, France (3) Washington University in St Louis, St Louis, Missouri, United States (4) University of Pennsylvania Perelman School of Medicine, Philadelphia, Pennsylvania, United States*

Many, if not most, transmembrane proteins select for certain lipids in their lipid annulus. These specific lipids can also bind and modulate transmembrane proteins like ligands. Yet understanding these modulatory mechanisms introduces several challenges. The membrane environment emphatically violates most of the traditional assumptions underlying classic receptor-ligand binding models. Furthermore, while high-resolution structures reveal fragments of specifically-bound lipids, the bound lipid species cannot be identified. For example, multiple pentameric ligand-gated ion channel structures include bound lipids, but only the glycerol backbone and part of the headgroup are resolved. Finally, native mass spectrometry may reveal the species of bound lipids but not where the lipid binds. Here I will briefly summarize a generalized theoretical framework and a robust molecular simulation approach for predicting the species of lipids revealed in crystal structures, using fully atomistic resolution. This approach is an extension of the Streamlined Alchemical Free Energy Perturbation (SAFEP) implementation that we had previously developed for calculating free energies of cholesterol for sites on multiple G protein-coupled receptors. I will further present the application of SAFEP toward the identification of the lipid species for multiple structurally-resolved phospholipid sites on a lipid-sensitive pentameric ligand-gated ion channel. Finally, I will quantitatively predict how varying the bulk membrane composition will affect the bound lipid species, a task that is straightforward and remarkably efficient using SAFEP.

145. Plasma membranes are asymmetric in lipid unsaturation, packing and protein shape

***Ilya Levental**, il2sy@virginia.edu. MPBP, University of Virginia, Charlottesville, Virginia, United States*

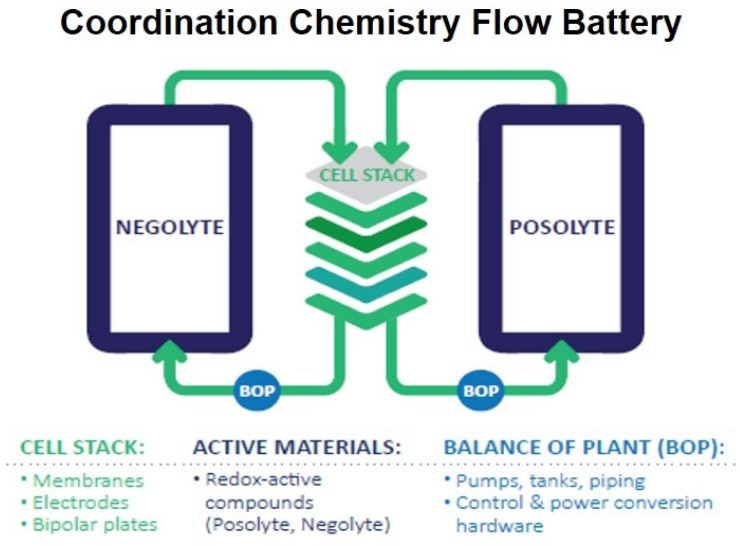
A fundamental feature of cellular plasma membranes (PMs) is an asymmetric lipid distribution between the bilayer leaflets. However, neither the detailed, comprehensive compositions of individual PM leaflets nor how these contribute to structural membrane asymmetries have been defined. We report the distinct lipidomes and biophysical properties of both monolayers in living mammalian PMs. Phospholipid unsaturation is dramatically asymmetric, with the cytoplasmic leaflet being approximately twofold more unsaturated than the exoplasmic leaflet. Atomistic simulations and spectroscopy of leaflet-selective fluorescent probes reveal that the outer PM leaflet is more packed and less diffusive than the inner leaflet, with this biophysical asymmetry maintained in the endocytic system. The structural asymmetry of the PM is reflected in the asymmetric structures of protein transmembrane domains. These structural asymmetries are conserved throughout Eukaryota, suggesting fundamental cellular design principles.

Energy Catalysis

146. Coordination chemistry flow battery

***Steven Reece**, streece80@gmail.com. Lockheed Martin Corp, Bethesda, Maryland, United States*

Lockheed Martin is commercializing the GridStar Flow Battery for long-duration grid energy storage. The product is based on Coordination Chemistry Flow Battery (CCFB) technology, which leverages aqueous metal ligand coordination complexes for affordable, durable, and safe energy storage systems for utility-scale projects (MW-scale and larger). The company has successfully fielded GSF Serial Number 01 (S/N01) a 0.5MW, 5hr pilot system. This talk will present background on the technology, including a primer on flow batteries, and the role chemistry can play in developing affordable solutions to grid-scale energy storage.



147. Anti-catalysis: Applications of the kinetic inhibition of water splitting

***Michael P. Marshak**, michael.marshak@colorado.edu. Department of Chemistry, University of Colorado Boulder, Boulder, Colorado, United States*

For many electrochemical energy storage and conversion processes, catalytic water splitting is often a parasitic side reaction that limits efficiency. Here, I demonstrate the consequences of chelation to kinetically stabilize highly reduced metals in aqueous electrolyte. This approach has led to high voltage flow batteries with the performance, efficiency, cost, and scale to enable long-duration energy storage for the grid. Beyond energy storage, these metal chelate electrolytes have the potential (both literal and figurative) to disrupt common approaches to electrochemical energy conversion processes.

148. Sustainable and efficient energy storage using a flow battery assembly based on iron, air, and water

***Linh Tran**[1], linhtran@udel.edu, Joel Rosenthal[2]. (1) Chemistry and Biochemistry, University of Delaware, Newark, Delaware, United States (2) Dept of Chemistry Biochemistry, University of Delaware, Newark, Delaware, United States*

Fuel cells (FCs) represent important electrochemical energy conversion devices that couple the oxidation of hydrogen at the anode with the oxygen reduction reaction (ORR) at the cathode to generate electricity and yield water as the sole emission byproduct. While FCs are important for certain applications, their commercial implementation remains limited due to the lack of facilities to store, transport, and supply hydrogen gas. We proposed a new and practical hybrid device called the redox flow fuel cell (RFFC), which combines the design and chemistry of a FC with that of a redox flow battery (RFB). In the RFFC, ORR at the cathode is coupled with oxidation of inorganic and/or organometallic complexes at the anode. In the devices we will describe, O_2 from air serves as the positive electrolyte and the negative electrolyte is comprised of highly concentrated aqueous solutions of redox active complexes of iron. The iron, air, and water that are required for function of the RFFC are all earth abundant and low-cost. Under mild condition (room temperature and 0.1 M HCl), the RFFC distinguishes itself as a safe, inexpensive, and energy-dense energy conversion device that can operate at 150 Wh/L with exceptionally high coulombic efficiencies (99%) and competitive voltage (33-51%) and energy (32-53%) efficiencies.

149. Insights into electrocatalytic oxidation reactions using first-row transition metal complexes

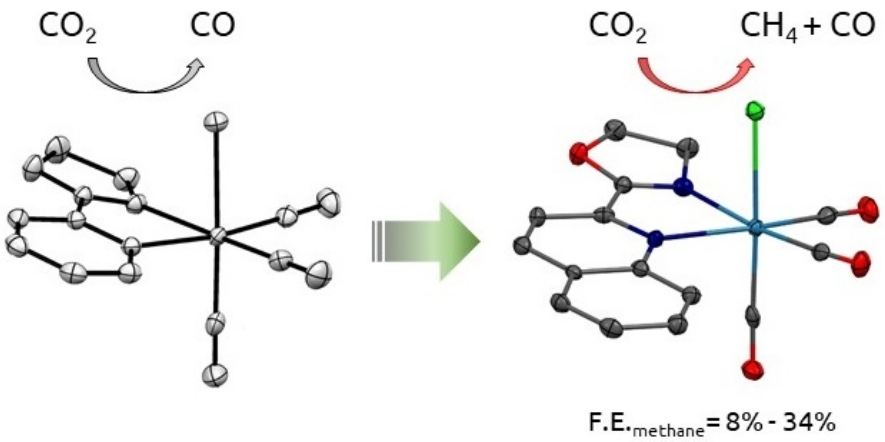
***Kate M. Waldie**, kate.waldie@rutgers.edu. Chemistry and Chemical Biology, Rutgers The State University of New Jersey, Piscataway, New Jersey, United States*

As we transition away from fossil fuel combustion as our primary means of energy production, the development of more efficient methods for harvesting useable energy from synthetic chemical fuels will be needed. The electrochemical oxidation of hydrogen using a fuel cell is a promising option. Fuel cells based on liquid carbon fuels such as formic acid and methanol are also attractive due to their high volumetric energy densities, ease of handling, and established storage and transportation infrastructure. Additionally, while formic acid and methanol are currently produced from fossil fuel resources, both liquids could in principle be synthesized from carbon dioxide to establish a carbon-neutral cycle. However, current fuel cell technologies are based on expensive noble metal catalysts that are cost-prohibitive for large scale applications, and the development of robust electro-oxidation catalysts based on first-row transition metals has been extremely challenging. In this talk, I will discuss our efforts to utilize hydride transfer reactivity at molecular, first-row metal complexes based on cobalt and iron to facilitate the oxidation of hydrogen, formic acid, and alcohols under mild conditions. By tuning the outer coordination sphere of the metal complex, we are able to control the favorability of the hydride transfer step, which can be quantified using thermodynamic and kinetic hydride affinities. Following hydride transfer, the resulting metal-hydride complex serves as a key catalytic intermediate, from which oxidative deprotonation completes the electrocatalytic cycle.

150. Recent developments in the application of oxazoline-containing ligands in CO_2 reduction catalysis

***Alfredo M. Angeles Boza**[1], alfredo.angeles-boza@uconn.edu, John K. Nganga[1], Kyle A. Grice[2], Mehmed Z. Ertem[3]. (1) University of Connecticut, Storrs, Connecticut, United States (2) Chemistry Deparment, DePaul Unviersity, Chicago, Illinois, United States (3) Brookhaven National Laboratory, Upton, New York, United States*

The tunability of ligands to control the reactivity of metal centers is a compelling reason to develop homogeneous catalysts for challenging reactions such as the electrochemical reduction of carbon dioxide. In this presentation, I will report on our collaborative work on oxazoline-containing ligands and their rhenium complexes. These compounds catalyze the reduction of CO_2 to carbon monoxide and methane depending on the structure of the ligand. A joint experimental and theoretical study has been carried out to investigate the mechanistic aspects that lead to the different catalytic activities. The insight gained is expected to facilitate the development of more robust catalytic systems that produce fuels from CO_2.



151. Anion induced surface structuring of copper cathodes as a means to control the selectivity and activity of electrochemical CO_2 reduction

Lu Xiong[1]*, luxiong@udel.edu, Thabiso Kunene*[2]*, Joel Rosenthal*[3]*. (1) Chemistry and Biochemistry, University of Delaware, Newark, Delaware, United States (3) Dept of Chemistry Biochemistry, University of Delaware, Newark, Delaware, United States*

Electrochemical reduction of CO_2 into reduced carbon species is a sustainable strategy to synthesize fuels and commodity chemicals using renewable energy sources. Ionic liquids (ILs) have been established as effective promoters for the electrocatalytic reduction of CO_2. Our laboratory has shown that switching electrolyte additive from organic cations comprised of 1,3-dialkylimidazolium cations to a protic amidinium derived from 1,8-diazabycyclo[5.4.o]undec-7-ene (DBU), enables a switch in CO_2RR at inexpensive Bi cathodes from CO to $HCOO^-$. To further understand how electrolyte composition can attenuate the efficacy and selectivity of CO_2RR, we probed how varying the identity of the anion used with $[DBU–H]^+$ containing electrolytes influences CO_2 activation on Cu cathodes. We observe a surface restructuring takes place when Cu cathodes are polarized in $[DBU–H]^+$/MeCN electrolytes under CO_2. Further, the selectivity and kinetics of reduction of CO_2 to CO shows a large dependence on the types of anions in the electrolysis bath, with ClO_4^- supporting a Faradaic efficiency of FE_{CO} ~ 80% (j_{co}=18 mA/cm^2), and PF_6^- showing a much lower FE_{CO} ~ 10% (j_{co}=2 mA/cm^2). Ex-situ XPS characterization demonstrates anion dependent surface structuring, which is correlated to differences in CO_2RR selectivity and activity. We have also used electrochemical impedance spectroscopy to probe the dynamics involving the Cu cathode and the electrolyte solution at the electrode-electrolyte interface and to provide insight into the pathway(s) by which these systems activate CO_2. The manner in which the electrolyte anions interact with the Cu electrode and control the selectivity and activity of electrochemical CO_2 reduction will be discussed.

152. Approaches to the catalytic synthesis of weak bonds

Paul J. Chirik*, pchirik@princeton.edu. Dept of Chem, Princeton University, Princeton, New Jersey, United States*

Weak chemical bonds are found in intermediates relevant to nitrogen fixation, arene and CO_2 hydrogenation and other catalytic processes. Making these bonds from hydrogen at or near thermodynamic potential is a challenge for catalysis and molecular science. Proton coupled electron transfer from appropriately designed metal hydrides is an attractive strategy. My presentation will focus on our efforts in the design of metal hydride reagents designed to activate H_2 then promote PCET to various substrates including arenes and various intermediates in nitrogen fixation. Both thermal and photochemical methods will be described.

153. Umpolung approaches to aryl ether synthesis via electrophilic oxygen species

***Sarah Wengryniuk**, sarahw@temple.edu. Chemistry, Temple University, Philadelphia, Pennsylvania, United States*

Aryl ethers are a ubiquitous functional group in bioactive molecules. The synthesis of these motifs via C(sp2)–O bond formation is well established, however these approaches commonly rely on the use of expensive transition metal catalysts and pre-functionalized arene coupling partners. As a part of our laboratory's efforts in developing reverse polarity or "umpolung" approaches to C–O bond formation, we have developed several approaches to aryl ether synthesis leveraging an electrophilic oxygen intermediate enabled by the use of a unique class of nitrogen-ligated I(III) reagents, or N-HVIs. This talk will discuss our recent efforts in the synthesis of functionalized chromanes using this approach, resulting in a net double C–H functionalization starting from simple, acyclic alcohol starting materials. Computational studies support the intermediacy of an electrophilic oxygen species and a novel umpoled cyclization event.

154. Fe-catalyzed multicomponent Radical cascades/cross-coupling accelated by a computational and experimental approach

***Osvaldo Gutierrez**, ogs@umd.edu. University of Maryland at College Park, College Park, Maryland, United States*

In this talk, I will focus on our use of high-level quantum mechanical calculations, rigorously calibrated against experimental data, to interrogate the mechanisms and to guide the development of (asymmetric) three-component iron-catalyzed radical cascade/cross-coupling reactions.

155. New methods for the development of novel ingredients

***Kimberly Steward**, Kimberly_Steward@cargill.com. Cargill Inc, Minneapolis, Minnesota, United States*

Significant changes in the demand for agriculture and food products are being driven by the growing population, lifestyle changes, rising incomes and regulatory environment. This continual evolution of consumer trends presents unique challenges for food and non-food ingredient producers to meet their expectations. This has resulted in the industry rethinking how to formulate products and source ingredients and stepping up the pace of R&D by shortening innovation cycles. Chemistry plays an integral role in the emerging trends of cleaner labels (food and cosmetics), the increased demand of plant-based meat alternatives (taste, texture, and mouthfeel), and the reduction of salt, fat and sugar from the diet. As a leader in the food industry, Cargill provides innovative solutions to solve these challenges. This talk will highlight recent method developments in the production of

ingredients for the food, bioindustrial and cosmetic segments, with a particular focus on sustainability.

156. New reactions for installing heteroatoms in complex molecules

***Donald A. Watson**, dawatson@udel.edu. Chemistry/Biochemsitry, University of Delaware, Newark, Delaware, United States*

Complex molecules are of vast importance in modern society and serve as the basis for many pharmaceuticals and agrochemicals that both treat human diseases and feed our growing population. Heteroatoms are critical components of these molecules, as heteroatoms allow of binding, specificity, and bioavailability of bioactive molecules. In addition, heteroatoms provide sites of reactivity in the molecular precursors that are used to assemble the increasingly complex structures of modern drugs and crop protectants. In this lecture, I will discuss my group's on-going efforts to design new reactions that install heteroatoms into complex molecular settings, and that enable the conversion of simple starting materials into complex structures in step-efficient and atom-economical ways.

157. Oxygen driven fragment coupling for the synthesis of natural products and antibacterials

***Marisa Kozlowski**, marisa@sas.upenn.edu. Univ of Penn, Philadelphia, Pennsylvania, United States*

Nature uses oxidative couplings to construct carbon-carbon, carbon-oxygen, and carbon-nitrogen bonds with a high degree of efficiency. Surprisingly, few laboratory equivalents are as selective or as efficient as the biological versions. The use of parallel microscale screening to discover selective and efficient catalysts for such processes using oxygen as the terminal oxidant will be discussed. The unexpected outcomes obtained highlight the value of interrogating large numbers of rationally selected variables under the umbrella of general hypothesis. The development of selective catalytic processes for phenol coupling, alkenyl phenol coupling, asymmetric phenol coupling, enol coupling, , and alkyl C–H activation that utilize oxygen as the terminal oxidant will be discussed. Applications in total synthesis of honokiol, chaetoglobin, and pyrolaside B will be presented. Finally, studies on the mechanisms of these transformations will be described with the goal of understanding the governing principles and how they might be used to discover further new transformations.

158. Innovation in the synthesis of complex pharmaceutical agents

***Martin D. Eastgate**, martin.eastgate@bms.com. Chemical Development, Bristol-Myers Squibb, New Brunswick, New Jersey, United States*

Modern pharmaceuticals are both increasingly complex and increasingly diverse. Today's clinical candidates often contain challenging stereochemistry, unique molecular architectures, and uncommon heterocyclic frameworks; they range from small molecules

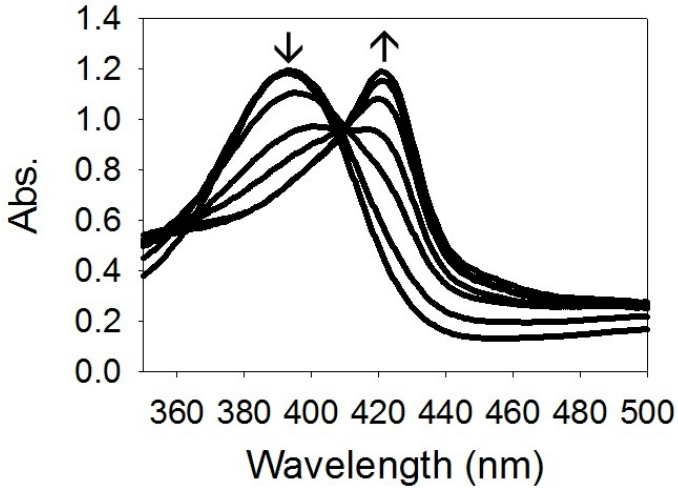
to natural products, peptides, oligonucleotides, antibody-drug conjugates and other modalities. Developing safe, scalable and sustainable routes to molecules, in the context of increasingly short development timelines, requires an approach focused on maximizing impact through innovative chemical solutions – so called ‘disruptive innovations’. However, increases in molecular complexity bring new challenges to the decision making process, complicating our ability to identify the synthetic strategies which will produce the most sustainable outcomes. These decisions can be aided by predictive decision making tools, cognizant of potential environmental impact, and recent advances have begun to establish such methodologies.

This presentation will cover the synthetic strategies and chemical innovations developed to address several clinical candidates from the Bristol Myers Squibb portfolio. Our approach has led to the invention of several new synthetic approaches, new chemical methods, and new concepts in predictive data analytics.

159. Salt bridge between a conserved arginine and a heme propionate plays a key role in the oxygen sensing mechanism of the FixL protein from *Sinorhizobium meliloti*

***Mark Reynolds**, mreynold@sju.edu. Chemistry, Saint Joseph's University, Philadelphia, Pennsylvania, United States*

The oxygen sensing FixL protein from *S. meliloti,* SmFixL, is part of the heme-PAS family of gas sensing heme proteins which regulate key biological processes such as nitrogen fixation, circadian rhythm and virulence. FixL is a histidine kinase that phosphorylates the response regulator FixJ , that is part of a two-component system that regulates nitrogen fixation and micro aerobic respiration in the root nodules of alfalfa plants. We probed the role of a conserved arginine, arginine 200, in the heme domain of SmFixL, that forms a salt bridge with a nearby heme propionate, by substituting it with the amino acids glutamine, histidine, glutamate and alanine, that have differing abilities to hydrogen bond. We then studied the cyanide (CN^-) and CO bound forms of wild-type SmFixL and these arginine variant proteins with UV-vis and Circular Dichroism spectroscopy and Photoacuistic Calorimetry. The results of our studies suggest that the salt bridge between the conserved arginine 200 and the heme propionate in the heme domain of SmFixL plays a key electronic role in transmitting the gas binding signal to the kinase domain of FixL. These results are important for heme-PAS family of proteins that regulate many important biological processes and serve as a model for signal transduction in heme- based gas sensing proteins.



160. PubChem for drug discovery in the age of big data and artificial intelligence

***Sunghwan Kim**, kimsungh@ncbi.nlm.nih.gov, Evan Bolton. National Library of Medicine, National Institutes of Health, Bethesda, Maryland, United States*

With the emergence of the age of big data and artificial intelligence, biomedical research communities have a great interest in exploiting the massive amount of chemical and biological data available in the public domain. PubChem (https://pubchem.ncbi.nlm.nih.gov) is one of the largest sources of publicly available chemical information, with +270 million substance descriptions, +110 million unique compounds, +285 million bioactivity outcomes from more than one million biological assay experiments. PubChem provides a wide range of chemical information, including structure, pharmacology, toxicology, drug target, metabolism, chemical vendors, patents, regulations, clinical trials, and many others. These contents can be accessed interactively through web browsers as well as programmatically using computer scripts. They can also be downloaded in bulk through the PubChem File Transfer Protocol (FTP) site. PubChem data has been used in many studies for developing bioactivity and toxicity prediction models, discovering polypharmacologic (multi-target) ligands, and identifying new macromolecule targets of compounds (for drug-repurposing or off-target side effect prediction). This presentation provides an overview of PubChem data, tools, and services useful for drug discovery.

161. Theranosis of liver fibrosis in non-alcoholic fatty liver disease (NAFLD) with collagen-targeted thermoresponsive assembled protein

***Andrew Wang**[1,2], alw643@nyu.edu, Edward Fisher[3], Jin K. Montclare[1]. (1) New York University Tandon School of Engineering, Brooklyn, New York, United States (2) Biomedical Engineering, SUNY Downstate Health Sciences University, New York City, New York, United States (3) Medicine, New York University School of Medicine, New York, New York, United States*

Non-alcoholic fatty liver disease (NAFLD) is the leading cause of chronic liver disease worldwide due to its strong association with obesity and diabetes. Because NAFLD develops insidiously, it can be difficult to detect, and diagnosis is often incidental. As the disease progresses however, inflammation and fibrosis lead to liver failure. Although there is no approved treatment beyond lifestyle modifications, there is evidence that pharmacological therapy may improve outcomes when initiated at an early to moderate stage of the disease. Therefore, **there is a need for *improved diagnostic monitoring* of disease progression *in vivo,* coupled with the capacity for *controlled intervention* at desired timepoints.** Thermoresponsive assembled protein (TRAP) is a versatile protein construct developed by the Montclare Lab that self-assembles into micelles above body temperature at 37°C, and is engineered to release cargo with increasing temperature up to 42°C. Here we have recombinantly expressed a collagen-targeting nonapeptide tag on the micellar surface that will target TRAP toward liver fibrotic deposition. Collagen-binding

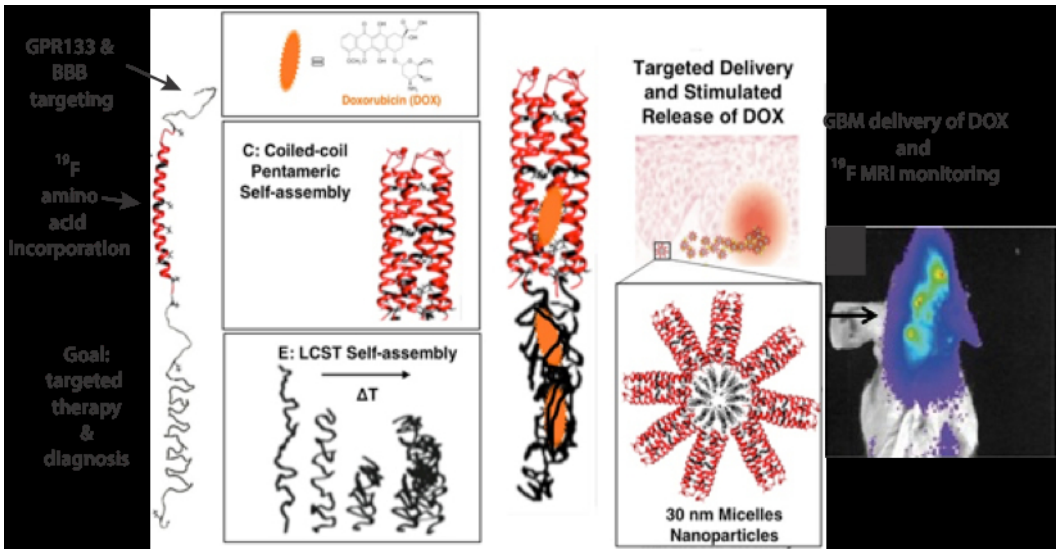
assays in vitro and biodistribution studies in diabetic mouse models of NAFLD will be used to establish targeting and differential accumulation of particles at various time points in disease progression. All non-solvent exposed methionine residues were mutagenized to isoleucine; the impact on protein secondary structure was modeled computationally using Rosetta software. Functionalized iron oxide nanoparticles were then conjugated to azidohomoalanine residues expressed in place of solvent-exposed methionines, enabling magnetic resonance imaging (MRI) visualization of particle (Col1-FeO-TRAP) accumulation. The degree of MRI contrast enhancement will be quantified with T1/T2 relaxivity measurements. Liraglutide will be studied as a model drug for reducing fibrosis and steatosis in NAFLD when incorporated into Col1-FeO-TRAP. Drug release will be initiated using locally applied high-intensity focused ultrasound (HIFU). Our preliminary experiments demonstrate that Col1-TRAP-FeO has strong potential to be a combined diagnostic and therapeutic agent for NAFLD.

162. Engineering fluorinated thermo-responsive assembled protein (F-TRAP) for theranostic applications in glioblastoma multiforme

Aparajita Bhattacharya[1,2]*, ab8288@nyu.edu, Youssef Z. Wadghiri*[3]*, Dimitris Placantanokis*[3]*, Jin K. Montclare*[1,3,4]*. (1) Chemical and Biomolecular Engineering, New York University Tandon School of Engineering, Brooklyn, New York, United States (2) SUNY Downstate Health Sciences University, New York City, New York, United States (3) Department of Radiology, NYU Langone Health, New York, New York, United States (4) Department of Chemistry, New York University, New York, New York, United States*

Gliomas account for roughly 27% of all brain tumors and there is an urgent need to develop new therapeutic modalities. A glioblastoma multiforme (GBM) prognosis signifies a survival time of 14-16 months with only 5% of patients surviving more than 5 years. A significant challenge for GBM is the inability to: a) treat tumor cells with cytotoxic drugs due to poor solubility and their lack of blood brain barrier (BBB) permeation; b) specifically target tumor cells while avoiding normal tissue with such cytotoxic agents; and c) monitor GBM status and therapy non-invasively. Theranostic agents which can both deliver drugs and monitor disease progression can address these requirements but treatments specific to GBM do not currently exist. While considerable efforts have been made in developing protein-based systems as drug-delivery carriers or as diagnostic agents, we are investigating a fundamental new insight that is helping us develop a single protein-based system combining drug delivery capabilities with the ability to cross the BBB and remain at cancer site due to the enhanced permeation and retention (EPR) effect. This biomaterial also incorporates functional groups detectable via magnetic resonance (MR) spectroscopy and imaging as well as near-infrared fluorescence (NIR) to enable visualization during treatment. Recently, we have engineered a protein-based theranostic agent called fluorinated thermo-responsive assembled protein (F-TRAP) bearing a non-canonical fluorinated amino acid (trifluoroleucine) that can self-assemble into a micellar structure and encapsulate hydrophobic drugs. Circular dichroism and dynamic light scattering were performed to observe F-TRAP secondary structure and micelle formation, as well as ^{19}F magnetic resonance imaging (MRI) to visualize F-TRAP and determine pharmacokinetic

properties in a GBM mouse model. Results indicate that F-TRAP has an alpha-helical secondary structure and forms micelles 30 nm in size. F-TRAP showed favorable pharmacokinetic data with a half-life of 112 minutes and high plasma retention. Data also revealed the ability of F-TRAP to cross the BBB to be imaged inside the brain.



163. Potential muscarinic antagonist antidepressants that lack cognitive deficits in rodents

Chad R. Johnson[1], *cjohn167@umaryland.edu, Brian Kangas*[2], *Emily Jutkiewicz*[3], *Gail Winger*[4], *Jack Bergman*[2], *Andrew Coop*[1], *James Woods*[4]. *(1) Pharmaceutical Sciences, University of Maryland Baltimore, Baltimore, Maryland, United States (2) Psychiatry, McLean Hospital, Belmont, Massachusetts, United States (3) Pharmacology, University of Michigan, Ann Arbor, Michigan, United States (4) Pharmacology, The University of Texas Health Science Center at San Antonio, San Antonio, Texas, United States*

Approximately 16% of Americans are diagnosed with major depressive disorder, a mental disorder thought to be caused by a combination of genetic, biological, environmental, and psychological factors. While counseling and antidepressant medication can be effective treatments, current selective serotonin re-uptake inhibitors (SSRI's) take weeks before therapeutic effects are observed. This "delay" period of action is not well understood and presents a significant challenge for medical professionals in the management of major depression.
The cholinergic nervous system has been implicated in mood disorders, which is evident in the fast-onset antidepressant effects of scopolamine, a potent muscarinic antagonist, in clinical studies (nimh.nih.gov). A disadvantage to the use of scopolamine in the treatment of depression is its detrimental effects on cognition due to its anticholinergic properties, especially since such effects might aggravate already existing cognitive deficits that occur with depression itself.

Our goal is to identify a muscarinic (mAChR) antagonist that may be able to relieve depression without disrupting cognitive effects. In order to probe the orthosteric site of the mAChRs we designed a large library of compounds and evaluated them via a battery of pharmacological assays to confirm both their antidepressant and cognitive effects. This resulted in the identification of a known mAChR antagonist, L,687-306, and a mAChR antagonist of our own design, CJ2100, that were as effective as scopolamine in antagonizing the bradycardia effects of the muscarinic agonist arecoline in cardiovascular studies, its discriminative-stimulus effects, and rate-decreasing effects in behavioral studies. Additionally, both antagonists were equally effective to scopolamine in decreasing immobility in the forced swim test (FST), a preclinical indicator of potential antidepressant activity. However, both compounds were much less disruptive at equally effective or even larger doses than scopolamine in assays of cognition-related behavior. Additionally, the compounds displayed high specificity for the mAChRs with few off-target binding sites, and CJ2100 showed modest affinity across the mAChRs compared to L-687,306 and scopolamine. These data emphasize the different pharmacological profiles evident across antimuscarinic compounds and novel mAChR antagonists' utility for the improved treatment of depression. (Supported by NIMH Grant 107499)

164. Chemical approaches for understanding the landscape of RNA modifications

***Emilia Arguello**, emiliaarguellop@gmail.com, Ralph Kleiner. Chemistry, Princeton University, Princeton, New Jersey, United States*

The chemical modification of central biomolecules plays a critical role in cellular physiology. Eukaryotic mRNA in particular is extensively tuned post-transcriptionally with a diverse collection of epitranscriptomic modifications. Of these, the nucleobase N^6-methyladenosine (m^6A) is known to regulate mRNA stability, translation, splicing, and localization and is also implicated in disease. Still, our understanding of the molecular mechanisms by which m^6A impacts RNA function and of its broader role in biological processes is limited. This gap stems from the challenge in understanding the effect of these marks on the protein-RNA interactome. Our research thus far contributes with complementary approaches to study m^6A-regulated RNA-protein interactions.

First, we developed a chemical proteomics method relying upon photocrosslinking with synthetic diazirine-containing RNA probes and quantitative proteomics to profile mammalian ‘reader’ proteins of m^6A. Aside from identifying m^6A interactors, namely the YTH-domain-containing proteins and the m^6A ‘eraser’ ALKBH5, we also showed that the disease-associated proteins FMR1 and LRPPRC can ‘read’ this mark. In addition, we found that stress granule proteins G3BP1/2, USP10, CAPRIN1, and RBM42 interact preferentially with unmethylated RNA. Second, we established a high-throughput platform based on *in vitro* selection with a site-specifically modified random RNA library and next-generation sequencing, to survey the binding specificity of m^6A reader proteins. We applied this scheme to characterize the m^6A-dependent recognition motifs of ‘reader’ proteins YTHDF2 and YTHDC1 and found overlap with the canonical DR(m^6A)CH motif,

but overall distinct binding preferences for each protein.

Taken together, these findings reveal some of the biochemical mechanisms underlying m^6A function and provide a detailed understanding of the sequence determinants critical for m^6A recognition by its 'readers', suggesting that the m^6A interactome is more complex than previously appreciated. In a similar vein, the current m^5C-based work will be key to understand how m^5C metabolism is regulated in RNA. Ultimately, we envision that these approaches can be deployed together to characterize other modified RNA-protein interaction networks in an unbiased fashion and to incrementally decode the function of the RNA epitranscriptome.

165. Fluorescent probe design for targeting and imaging carbonylation in live cells

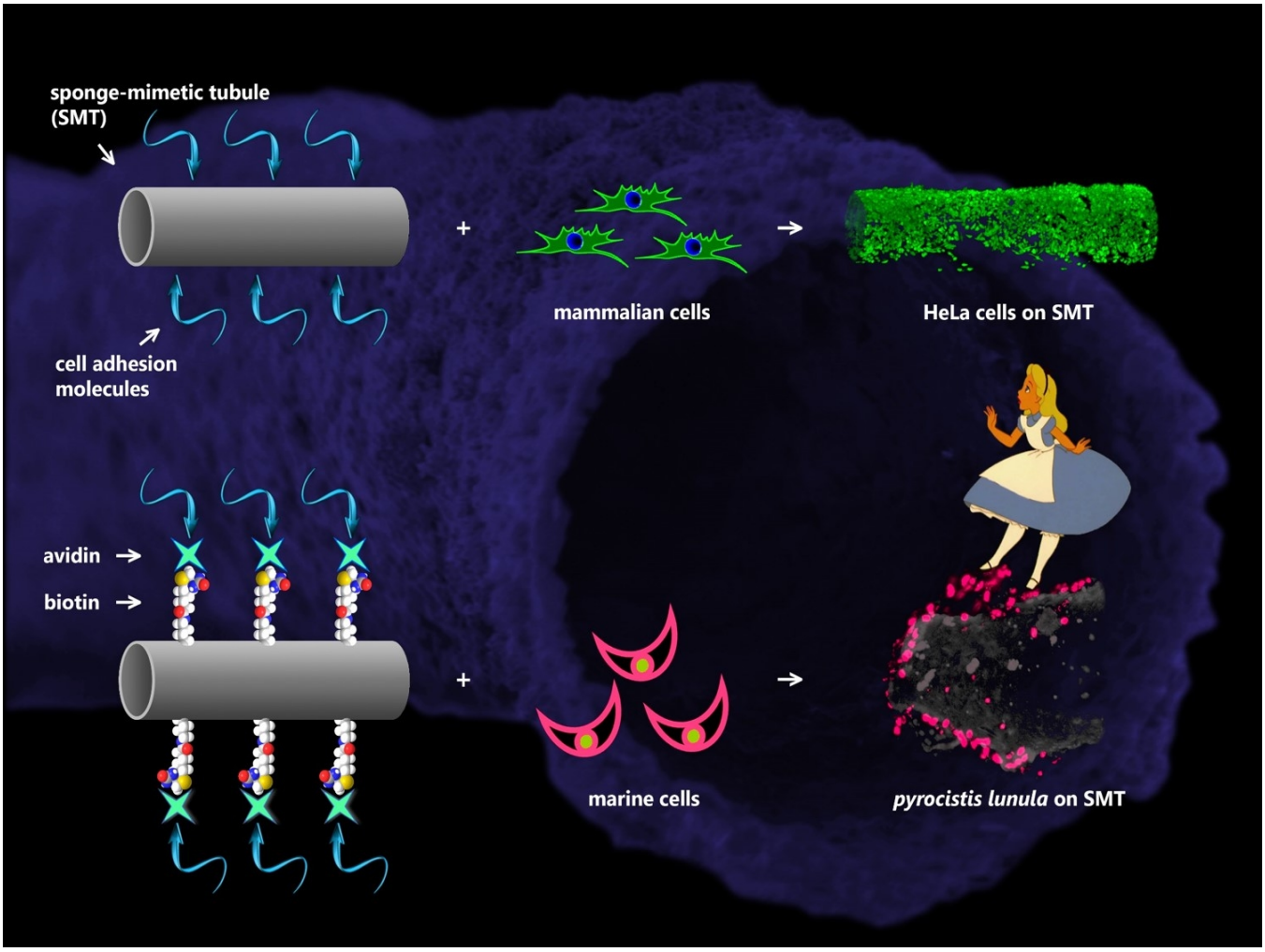
*Hazel Erkan[1], Dilek Telci[2], **Ozlem Dilek**[3], ozlem.dilek@udc.edu. (1) Department of Biophysics, Medizinische Universitat Graz, Graz, Steiermark, Austria (2) Department of Biotechnology, Yeditepe Universitesi, Istanbul, İstanbul, Turkey (3) Chemistry, University of the District of Columbia, Washington, District of Columbia, United States*

Fluorescent probes have been used for a wide range of biomedicine, pharmaceutical research and clinical diagnostics including bioconjugation, drug discovery, selective tagging of biomolecules in cells. As a key element of fluorescent imaging, probes should have distinct unique characteristics to be effectively used in living systems: high stability, less toxicity, rapid reaction, large Stokes shifts, reasonable quantum yields, drastic changes on absorption and emission spectra and minimal perturbation. We synthesized a turn off/on fluorescent probe which can react fast with the carbonyl moieties of biomolecules through a click reaction to produce a fluorescent product inside cells so that we can able to visualize carbonylation process in various cancer cell lines. Microscopic and spectrofluorometric analyses were used to differentiate the exogenous and endogenous ROS induced carbonylation profile in human dermal fibroblasts along with A498 primary site and ACHN metastatic site renal cell carcinoma (RRC) cell lines. We have found that our fluorophore can selectively detect carbonylation level that differs in response to exogenous and endogenous stress in healthy and cancer cells. Use of click chemistry to monitor carbonylation with a fluorescent probe has proven itself to be superior in satisfying many criteria (e.g., biocompatibility, selectivity, yield, stability, and so forth); we therefore successfully applied to fluorescent imaging in live cells. This approach will not only expand the library of ideal probes as imaging agents, but also advance the broad approaches of fluorescent imaging to understand biological events in cellular systems.

166. Sponge Mimetic Tubules (SMT) to explore biomorph templated evolution of animal life

***Krishnaswami S. Raja**, krishnaswami.raja@csi.cuny.edu. Dept of Chem 6S 332A, College of Staten Island CUNY, Staten Island, New York, United States*

Sponges are considered as the earliest form of animal life. Biologists propose that unicellular choanoflagellates which can form multicellular clumps evolved to produce early ocean sponges. Scientists have been constraining themselves to one discipline in an attempt to explain animal evolution without taking into account that the animal form is many orders of magnitude more complicated than a simple clump of one cell type. It is proposed that nature employs a multidimensional approach to produce animal life. Unicellular organisms, cell adhesion molecules, bacteria which serve as food and biomorph scaffolds in a vast oceanic buffer are her toolkit. In the biomorph templated evolution theory proposed unicellular organisms with stem cell like qualities are assembled together on a biomorph scaffold. The organisms co-evolving on the scaffold would possess the exponential increase in sophistication necessary to produce animal life. Such a supra-cellular entity would have the collective shape memory of a tubue (in the case of a tubular sponge) necessary to make copies of itself. Stromatolites which resemble sponge scaffolds are natural bio-hybrid tubules produced by the co-precipitation of salts at hydrothermal vents with the debris of dead cyanobacteria. Sponge/Stromatolite-Mimetic Tubules (SMT) were generated by chemobrionic chemistry to form biomaterial-intercalated silicate phosphate tubes. Incorporation of biopolymers in the SMTs was confirmed by EDS and IR and further charecterized by X-ray diffraction and SEM. SMT's were employed to test the hypothesis of biomorph templated evolution of ocean sponges. The choanoflagellate cell line *Salpingoeca rosetta* was cultured on the SMTs. The viability of marine cells on SMTs was confirmed by live cell imaging and confocal laser scanning microscopy. The findings suggest that stromatolites can support eukaryotic life and lend validity to the theory of a chemobrionic-linked origin of ocean sponges. T



Adventures down the Sponge Mimetic Tubule

167. Visible light promoted tryptophan photoconjugation using donor-acceptor pyridinium salts

***Caleb Hoopes**, croopes@outlook.com, Akash Sarkar, Nicholas Kuehl, Nicole Collins, Michael Taylor. Chemistry, University of Wyoming College of Arts and Sciences, Laramie, Wyoming, United States*

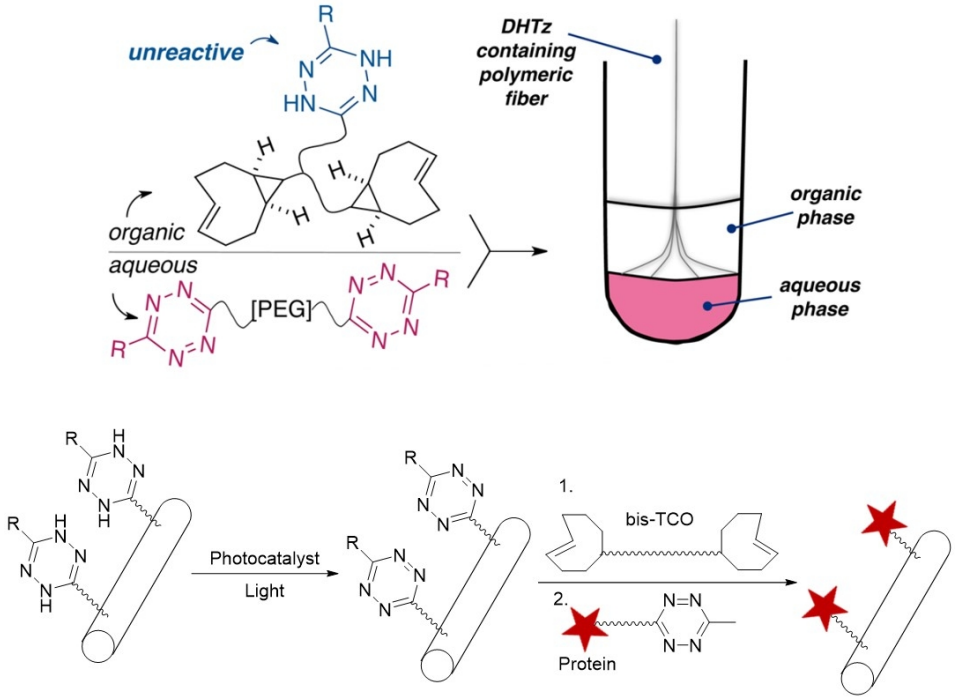
Small molecule probes that are photochemically activated have become essential tools in the investigation of the complex environment inside living systems. Recently, our group reported a light promoted reaction between N-carbamoyl pyridinium salts and tryptophan residues involving a photoinduced electron transfer (PET) event that installs a detectable functional group to the surface-exposed Tryptophan (Trp) residues of native proteins. The probe's absorbance and photo-redox properties were found to be closely linked to the extent of pyridinium conjugation. Here, we report a new generation of pyridinium salts that feature a donor-acceptor structural motif, causing a bathochromic shift of the absorption spectrum. These pyridinium salts enable the use of visible light in tryptophan photobioconjugation. Under micromolar concentrations, the photolabeling process occurs with enhanced kinetics at conditions that are an order of magnitude more dilute than previous work. A scope of ten peptides and proteins ranging from 1-29 kDa were modified.

Tandem MS experiments of labelled proteins indicated that the chemical transformation is highly selective to tryptophan, even in an abundance of other residues that participate in photo-redox processes, such as tyrosine. Additionally, we assessed the suitability of the probes, which are inherently fluorescent, for intracellular labelling chemistry. We found that the probes maintained their fluorescent properties, indicating biological stability, while also localizing in the mitochondrion of the cell. The cytotoxic effects of the pyridinium salts were found to be acceptably low, having essentially no toxicity in cultures of H9C2 cells that were incubated for 12 hours in media with 100 μM of probe. The probes were then functionalized to deliver detectable reporters, which did not compromise the high yielding in vitro reactivity. Intracellular and lysate chemoproteomics were then performed using a biotin functionalized derivative of the new generation of pyridinium salts.

168. Post-polymerization modification of hydrogel microfibers synthesized via interfacial tetrazine ligation

***Paramesh Ramaraj**, paramesh@udel.edu. Chemistry and Biochemistry, University of Delaware College of Arts and Sciences, Newark, Delaware, United States*

Rapid biorthogonal reactivity allows for interfacial polymerization to create hydrogel-based microfibrous scaffolds for tissue engineering applications. The inverse electron demand Diels-Alder (IEDDA) reaction between bis-*trans*-cyclooctene carrying dihydrotetrazine and poly(ethylene glycol) (PEG) derived bis-tetrazine allows for the formation of microfibers at the solvent-water interface. In this work, polymer fibers functionalized with dihydrotetrazine were photocatalytically oxidized to tetrazine for reaction with bis-*trans*-cyclooctene for further modification with tetrazine functionalized proteins. HaloTag and Nanoluciferase were evaluated and found to maintain activity on the fibers for fluorescence and luminescence, respectively. The results indicate that this approach can be extended to incorporate extracellular matrix proteins in the microfibers for attachment, division, and contact guidance of cells.



169. Electrogenetic control and regulation of a synthetic *Escherichia coli* consortia

Eric VanArsdale[1,2]*, esv5009@terpmail.umd.edu, Juliana Pitzer*[1]*, Sally Wang*[1,2]*, Kristina Stephens*[1,2]*, Gregory F. Payne*[2]*, William E. Bentley*[1]*. (1) Fischell Department of Bioengineering, University of Maryland at College Park, College Park, Maryland, United States (2) Univ of Maryland Biotech Inst, College Park, Maryland, United States*

Manipulation of genetic programs within microbes has allowed for the development of robust cell factories that can produce products and therapeutics on command. Many of these systems are either constitutively active, or are activated by the addition of chemical inducers. As the genetic programs employed to make products have become more sophisticated and complex, they have also involved the addition of many new functions that can easily overtax the metabolic machinery of the host cell. To overcome this challenge, there is growing interest in dividing functions among two or more host cell populations, so that the overall function is parsed into subgroups which can be individually fine-tuned. These opportunities, however, are balanced by the novel challenge of regulating the composition of each subgroup within the consortium. In this work, we demonstrate the use of electrogenetics to guide consortia composition and product formation. We show that by altering electrochemical inputs, such as time and voltage, we can differentially activate OxyR-based genetic circuits through the 2-electron oxygen reduction reaction known to generate the signaling molecule hydrogen peroxide. This molecule is generated locally and is then degraded, precluding its transmission deep into a culture. The information can then be transmitted throughout an *E. coli* consortium via

production of acylhomoserine lactones (AHLs) that persist longer than the initial signal and activate different populations. Using this general “transmitter/receiver” model, we demonstrate that we can alter the composition of an *E. coli* culture by using AHLs to regulate the growth rate of particular subsets of the consortia. Similarly, we were also able to use this control structure to regulate the production of the small molecule, tyrosine, which can also be measured electrochemically. In this work, we demonstrate how these methodologies can be employed separately, or combined, to increase overall control of tyrosine production.

Spectroscopy: From Molecules to Macrostructures

170. Oxidation of $Cu_2O(111)$ by NO_2 : An ambient pressure x-ray photoelectron spectroscopy study

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Metal oxide catalysts, particularly CuO_x, are preferred in industrial chemical processes due to their low cost and availability compared to the noble metal-based catalysts. CuO_x is also used in gas sensors and in air filtration materials to absorb toxic gas molecules and chemical warfare agents. CuO_x can be used to capture NO_x pollutants in urban areas to mitigate health risks for individuals. Synchrotron-based ambient pressure x-ray photoelectron spectroscopy (APXPS) and near-edge x-ray absorption spectroscopy fine structure (NEXAFS) were used to investigate the interactions of NO_2 species with a $Cu_2O(111)$ surface at atmospherically relevant pressures. The surface begins to oxidize to CuO after introducing minimal pressure of NO_2. Four different chemical states of NO_2 are observed on the surface, indicating the decomposition of NO_2 to NO and O and further decomposition to N and O. The results are applicable to several applications, including gas filtration, catalysis, and environmental chemistry.

171. Investigating plasmonic resonances in metal-semiconductor heterostructures

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Metal/semiconductor heterostructures have shown promise in the field of plasmonics, with possible applications towards solar energy conversion, opto-electronics, and photocatalysis. In particular, plasmon-induced transfer of carriers from the metal to semiconductor components of the system is not yet well understood, let alone the material

properties that would most enhance this plasmon-induced transfer. Therefore, ultrafast spectroscopic measurements on various heterostructures with tuned properties are required. The chosen systems of study are two-dimensional Au/Cu2O hemispherical nano-heterostructure arrays. By varying the semi-shell thickness, we can tune the plasmonic resonance, and ultimately the plasmonic coupling and the corresponding charge transfer processes. Charge transfer mechanisms of these systems are studied with transient absorption spectroscopy (TAS) and time-domain terahertz spectroscopy (TDTS). Hot hole dynamics are extracted from the TAS measurements, while TDTS further investigates the plasmonic properties. Results show that wavelength-dependent hot hole transfer that occurs after the localized surface plasmon undergoes Landau damping, and that terahertz emission from these nano-heterostructure arrays are dependent on the metal atom used for the core as well as the core-shell size. This study could be expanded to a broader range of metal-semiconductor hybrids, where the fine-tuning of their properties can lead to the design of optimized plasmonic materials.

172. Reactions of boric acid and 4-fluorophenylboronic acid with H- and Cl-terminated Si(100) surfaces

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The reactions of boric acid and 4-fluorophenylboronic acid in solution were studied in order to understand the interaction of these molecules with hydrogen- and chlorine terminated Si(100) surfaces. The reactions were mainly followed by X-ray photoelectron spectroscopy (XPS) which shows that both molecules react preferentially with Cl-Si(100) compared with H-Si(100) at identical conditions. On Cl-Si(100), both reactions introduce boron onto the surface forming a Si-O-B structure. Density functional theory calculations were used to supplement the experimental findings, showing that the reaction of boric acid and 4-fluorophenylboronic acid is more favorable with the Cl- versus H- terminated surface, and on Cl-Si(100) the reaction with 4-fluorophenylboronic acid is ~55 KJ/mol more thermodynamically favorable than the reaction with boric acid. This work provides a fundamental understanding of boron incorporation into silicon surface via Si-O-B bonds, which can be used for further functionalization or as a means of selective-area monolayer doping.

173. Pump-degenerate four wave mixing spectroscopy of the interfacial electron transfer on perylene-sensitized TiO_2 surfaces

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Pump-Degenerate four wave mixing (pump-DFWM) spectroscopy is applied on a recent measurement for studying the interfacial electron transfer (IET) on perylene-sensitized TiO_2 Surfaces. Acrylic acid linkers were used for binding the dye molecule and mesoporous anatase. A broadband pulse with over 500 nm full width half maximum was generated results in a sub-13 femtosecond probe pulse. The compressed probe allows the system to measure the vibrational states at up to 1800 cm^{-1} wavenumber with high signal-to-noise. The pump on/off spectrum of the sensitized film, corresponding to the cationic/neutral form of the sensitizer, was measured at different time delay after the actinic pump, covering the process of IET. This result is used to compare with calculated Raman spectra (B3LYP level, 6-31G* basis set) of the sensitizer. Some shifts between the ground state and cation predicted from calculation agree qualitatively with the measurement.

174. Comparison of spectral unmixing algorithms applied to simulated and measured frequency domain dynamic fluorescence reaction monitoring of semiconductor quantum dot surface passivation

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Multivariate curve resolution (MCR) is a data analysis methodology used in many scientific disciplines to isolate overlapping signals in multivariate data. Several MCR algorithms have been developed by investigators from diverse communities. However, in most cases, the application of these algorithms has been limited to the field in which they originated because of inconsistent communication across fields and the absence of systematic approaches to selecting the appropriate algorithm for a specific data type. In spectrochemical analysis, multivariate curve resolution–alternating least squares (MCR-ALS) is the widely used algorithm. Non-negative matrix factorization (NMF) is more widely used in image analysis and signal processing applications. Comparisons of the performance of these algorithms contribute to the development of systematic guidelines for selecting MCR algorithms for specific data analysis problems.
In this report, the performance of these two algorithms is compared systematically using simulated and experimental matrix-formatted fluorescence decay data. Wavelength-resolved frequency-domain decays can be arranged as complex Fourier-transform emission-decay matrices (FT-EDM) from which component spectra, photokinetic rates, and relative intensities can be resolved using MCR methods. Increasing the number of components, measurement noise, and overlap of component spectra or decay profiles all increase the difficulty of resolving the sample components. FT-EDMs collected during the progress of selected steps in the synthesis of ZnS passivated CdTe semiconductor quantum dots (QDs) capped with mercaptopropionic acid (MPA) ligands are used as experimental data sets. Monitoring and resolving the emission of semiconductor quantum dots during synthetic processes, such as surface passivation, clarifies the links between

emission properties and structural features. Simulated FT-EDMs, are modeled after the QD data, but with varying numbers of fluorescent components, degrees of component profile overlap and levels of noise. The performance of the MCR-ALS and NMF algorithms in resolving the component profiles from the simulated data is measured by the correlation between the resolved profiles and the input profiles used to simulate the data.

175. Mapping preferential adsorbate interactions at electrodeposited Cu interfaces via shell-isolated nanoparticle enhanced raman spectroscopy

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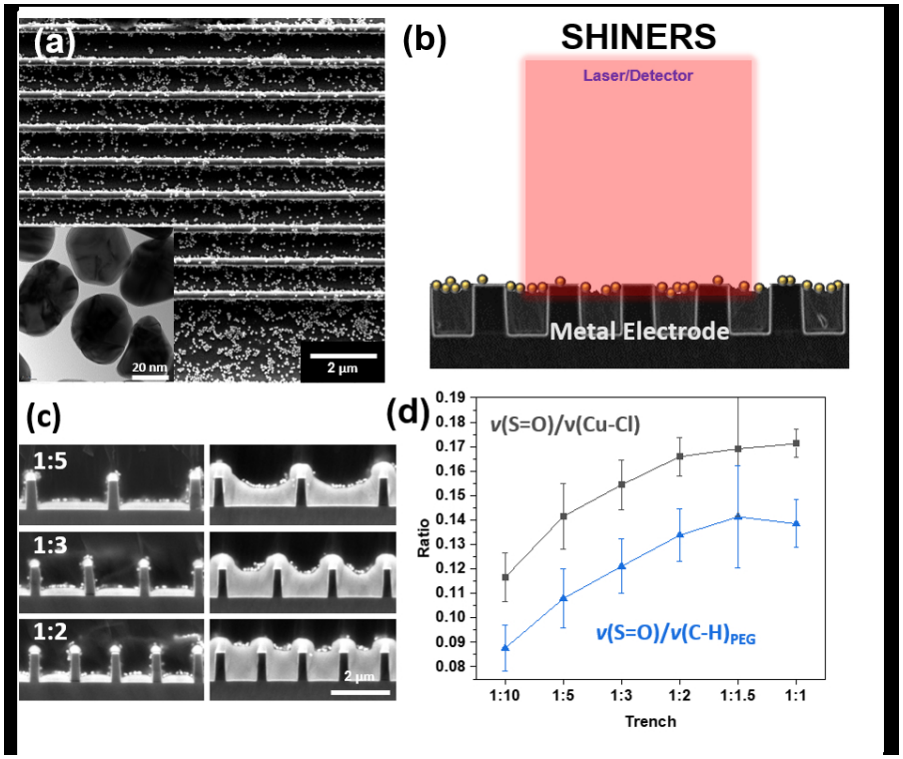
Additive adsorbates are widely used as surfactants to steer interactions at interfaces, especially microstructural evolution during electrochemical deposition of thin films. In many fields the mechanistic understanding of the interface is relatively limited, even though some strategies have been used for decades. Modern spectroelectrochemical methods, like surface-enhanced Raman and infrared spectroscopies (SERS and SEIRAS, respectively), are enabling significant insight into the composition, structure, and dynamics of the surfactant adsorbates through vibrational signatures on nominally static surfaces. However, each strategy is limited to specimen geometry; SERS is closely linked to the use of rough plasmonically active surfaces while SEIRAS measurements is constrained to thin IR transparent metal films. In the last decade, a significant advance was the introduction of nanoparticle reporters, based largely on silica coated Au nanoparticles, that enable Raman spectroscopy studies on well-defined single crystal surfaces whereby the nanoparticle serves to channel the plasmonic energy to the nanoparticle-substrate interface. The silica or alternative coating materials are designed to be inert with respect to the chemistry of the adsorbate species under study while remaining thin enough to allow effective focusing of the optical energy. The present work demonstrates the use of $Au@SiO_2$ (core-shell) nanoparticles, also known as SHINERS (Shell-Isolated Nanoparticle-Enhanced Raman Spectroscopy) to enable spatially resolved vibrational spectroscopic measurements of nominally smooth electroplated surfaces. The study reveals an interesting regime at the boundary between analytical surface chemistry and composite electroplating, promising to be a powerful technique to resolve complex site-specific interfacial interactions.



(a) Electron micrographs, (b) SHINERS, (c) cross-sections. and (d) spectroscopic relationships of a $Au@SiO_2$ covered Cu electrodeposit.

Poster Session: Innovations in Chemical Biology

176. Toward a mechanistic understanding of ferrous iron transport: Deciphering the function of FeoA

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Iron is an essential transition metal to nearly all living organisms and is utilized for a variety of biological processes. Under anoxic and/or reducing conditions, Fe^{2+} is the predominant form of iron available to bacteria. The ferrous iron transport (Feo) system has been identified as the predominant prokaryotic Fe^{2+} transport system and cellular studies have linked the Feo system to bacterial survival, intracellular colonization, and virulence. Canonically, the Feo system comprises three proteins: FeoA and FeoC, two small, cytoplasmic proteins of unknown function and FeoB, a polytopic transmembrane protein that transports Fe^{2+}. FeoB also contains a cytosolic G-protein domain and a GDI domain (termed NFeoB). Though rare, some *feo* operons encode for a fusion of FeoA to the G-protein domain of NFeoB, suggesting that FeoA and FeoB interact and that FeoA may be involved in regulating the function of FeoB. We leveraged the soluble domain of the naturally-occurring FeoAB fusion protein from *Bacteroides fragilis* (*Bf*NFeoAB), a

commensal organism implicated in drug-resistant peritoneal infections, to investigate FeoA-NFeoB interactions and to determine the role of FeoA in the iron transport process. Using SAXS, HDX-MS, and NMR we show that FeoA and NFeoB interact in a nucleotide-dependent manner and that FeoA serves to slow down the rate of GTP hydrolysis by NFeoB. Furthermore, we mapped the potential FeoA-NFeoB interactions to structural models of *Bf*NFeoAB. We posit that FeoA binds to NFeoB upon GTP binding, slows the rate of GTP hydrolysis thus leaving FeoB in the 'on' state, which subsequently allows for FeoB-mediated Fe^{2+} transport. Upon nucleotide hydrolysis, FeoB returns to the 'off' state and FeoA dissociates from NFeoB. Our work serves as the first biochemical and structural characterization of any fusion protein and provides functional and structural insight into Feo-mediated Fe^{2+} transport.

177. Withdrawn

178. Study of dopamine-induced functional adaptations in astrocytes

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Dopamine is one of the major neurotransmitters in the central nervous system and plays a central role in the dopamine reward pathway. Many drugs of abuse interact with dopamine neurons present in the midbrain leading to the release of dopamine via the mesocorticolimbic pathway. Additionally, alterations in dopamine levels are connected to various neurological conditions such as Parkinson's disease, Schizophrenia, and Alzheimer's. While elevated dopamine levels have been shown to induce morphological changes in astrocytes in culture, the role of dopamine-activated astrocytes in neuroinflammation is not clearly understood. Astrocytes act as mediator cells in the brain. During pathological conditions, both microglia and astrocytes are activated, but astrocytes communicate with neurons and play a crucial role both in the protection and destruction of neurons. We performed a series of studies showing time-dependent modifications of astrocytic processes resulting from dopamine exposure. We tracked changes in the fine astrocytic process using atomic force microscopy and found dopamine-induced remodeling in fine astrocytic processes. We also observed concentration-dependent overexpression of GFAP and of IL6 cytokine release in dopamine-treated astrocytes. However, we did not find detectable levels of the proinflammatory cytokine TNFα production even at high concentrations of dopamine. We also discovered that dopamine-treated astrocytes are more cytotoxic to neurons from our experiments of treating astrocyte conditioned media in neuroblastoma N2a cells.

179. Aptamer based label-free and sensitive detection of miRNA

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We selected an aptamer against a fluorogenic dye called Thioflavin T (ThT). Aptamers are single-stranded DNA that can bind a specific target. We selected the ThT aptamer using

graphene oxide-assisted SELEX and a low-cost Open qPCR instrument. We optimized, minimized, and characterized the best aptamer candidate against ThT. The aptamer, ThT dye, and the enzymatic strand displacement amplification (SDA) were used in a label-free approach to detect the micro RNA miR-215 in saliva and serum. The aptamer confers higher specificity than intercalating dyes but without expensive covalently modified DNA probes. This isothermal, low-cost, simple method can detect both DNA and RNA. The target, miR-215, was detected with a limit of detection of 2.6 nM.

180. Epigenetic modifications of histones in a yeast amyloid-beta overexpression model

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Alzheimer's disease, the most common type of dementia, is a neurodegenerative disease whose mechanism has yet to be fully elucidated. With 95% of patients having the sporadic form of AD, new methods of investigation must be considered besides standard genetic approaches. Presently, studies in the epigenetics of AD focus mainly on DNA methylation. Another form of epigenetic modulation are histone post-translational modifications such as methylation, acetylation, and phosphorylation. Here we utilize a yeast amyloid-beta model to map out the changes in the histone PTM landscapes that arise between several amyloid-beta isoforms. Our preliminary data suggests that these amyloid-beta isoforms allow for different epigenetic landscapes, which may serve as novel markers to track disease progression.

181. Indirect downregulation of MCL-1 via targeted PROTACs

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Acute myeloid leukemia (AML) is a progressive bone marrow cancer that has resulted in over 11,000 deaths and almost 20,000 new cases in the U.S. in 2020. Although the FDA has recently approved several treatments for AML, these provide only short clinical responses; venetoclax (VEN), which inhibits the anti-apoptotic BCL-2 protein and is now a component of the standard treatment for AML, provides a median survival of only 17 months due to the onset of resistance; a prominent mechanism is compensatory upregulation of the sister anti-apoptotic protein MCL-1, an important target in AML and other cancers since its overexpression contributes to chemoresistance in general. Accordingly, discovery of direct/competitive MCL-1 inhibitors has been a long sought after goal towards new cancer therapies. However, knockdown of MCL-1 is embryonic lethal and is essential for cardiomyocyte and hepatocyte survival among others; need for sub-

nanomolar affinities of direct MCL-1 inhibitors has rendered this a challenging goal and, unfortunately, potent inhibition of one inhibitor chemotype has resulted in cardiotoxicity and one fatality. We propose to circumvent problems associated with direct MCL-1 inhibition by indirectly downregulating the protein – rather than complete inhibition – and integrating this strategy with the emerging platform of proteolysis targeting chimeras (PROTACs). Such chimeras comprise a ligand for the protein of interest (POI) linked to a ligand that recognizes an E3 ubiquitin ligase, which is responsible for polyubiquitinating, or "tagging", the POI for destruction via the proteasome. There are several advantages to the implementation of this strategy versus conventional inhibitors. Notably, lower doses of these therapeutics may be used because the PROTAC mechanism is catalytic, and they may be more refractory to upregulation and point mutations, two common resistance mechanisms. We aim to synthesize a library of PROTACs using ligands selected to indirectly target MCL-1 on the transcriptional, translational, or post-translational level. This will be accomplished by using established CDK5/CDK9, PI3K/Akt/mTOR, and MAPK inhibitors, respectively, which will be coupled to three different E3 ligases (CRBN, MDM2, and von Hippel-Lindau ligands), and compounds will be evaluated in the appropriate kinase assays and several AML cell lines. Furthermore, lead PROTACs will be tested in combination with VEN because of the crucial role MCL-1 plays in VEN resistance.

182. PROTAC strategy to rescue venetoclax sensitivity in AML-resistant cells

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Venetoclax, which is now a standard-of-care drug for the treatment of acute myeloid leukemia (AML), is a potent inhibitor of the anti-apoptotic BCL-2 protein. Venetoclax functions by specifically recognizing sub-pockets p2–p4 on the surface of BCL-2 that are crucial for engagement with pro-apoptotic family members. However, clinical responses are short (~17 months median survival). This is primarily due to a compensatory upregulation of the anti-apoptotic family member MCL-1, but is also a result of drug-induced mutations within the BCL-2 protein. The most prominent mutation that is manifested in patients is present in the p2 pocket of BCL-2 where a G101V mutation causes a ~180-fold decrease in binding. Coupled with this, predictive resistance studies in mice have shown that various other mutations within BCL-2 could occur. For example, F104L and F104C cause a ~10-fold and 500-fold decrease of binding to venetoclax while BH3 binding is unhindered. While one strategy of restoring the efficacy of venetoclax in mutant BCL-2 proteins is for the small-molecule to undergo a targeted overhaul that focuses on responding to the specific changes to the protein surface, we propose an orthogonal strategy that does not depend on a significant redesign of this FDA-approved drug. Proteolysis-Targeting Chimera, or PROTACs, are bivalent inhibitors composed of a ligand for the protein of interest (POI) coupled to a ligand that recognizes an E3 ubiquitin ligase. The PROTAC results in the polyubiquitination of the POI and the subsequent recruitment to the proteasome for destruction. Potential benefits of PROTACs relative to the parent drug include: (1) they may be more refractory to point mutations, as observed

with a PROTAC-driven rescue of BTK mutational resistance to ibrutinib, and (2) the PROTAC mechanism is catalytic meaning lower doses for a therapeutic effect which could widen the scope for safe combination therapies as well as directly counter upregulation-mediated resistance. We aim to modify the solvent-exposed tetrahydropyran with various linkers tethering E3 ligase ligands, including the cereblon-specific thalidomide ligand. All PROTACs will be tested against wild-type and G101V mutant BCL-2 proteins, as well as in venetoclax-sensitive and resistant AML cells.

183. Structure-activity relationship studies of ketamine

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The *N*-methyl-D-aspartate receptor (NMDAR) modulates an extensive range of neurodegenerative and neuropsychiatric conditions, including Major Depressive Disorder and Alzheimer's disease. Existing treatment options for these disorders show minimal to moderate efficacy and varying levels of tolerability. As a result of these limitations, alternative therapies are actively being pursued. NMDAR antagonism is a viable pharmacotherapeutic strategy for central nervous system disorders, as exemplified by the use of memantine for the treatment of Alzheimer's disease, and both Ketamine and its *S* enantiomer Esketamine for use in clinical depression. Since its FDA-approval for use in both Major Depressive Disorder and Treatment-Resistant Depression, the Ketamine pharmacophore has continued to garner increasing interest. Specifically, Ketamine and Esketamine are chemically classified in the β-ketoarylcyclohexylamine pharmacophore. In spite of their clinical significance, the structure activity relationship studies on β-keto-arylcyclohexylamines as NMDAR antagonists are limited. To probe this pharmacophore and pave the way for the discovery of compounds with improved efficacy and tolerability, we have designed and synthesized a series of β-ketoarylcyclohexylamines. Currently, 16 analogs have been synthesized in 5 steps at gram scales and good yields, and have been fully analytically characterized. NMDAR affinities for these compounds were evaluated using competitive radioligand binding assays, with affinities ranging from 105 to 508 nM. Binding on other CNS receptors will also be evaluated in order to better understand the polypharmacological binding profiles of these compounds, which can give insight into possible side effects. We will also investigate *in vitro* metabolic and *in vivo* profiles of compounds exhibiting desired CNS receptor binding profiles.

184. Identification of diverse targets of arginine phosphorylation in *Mycolicibacterium smegmatis* by shotgun proteomics

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Tuberculosis remains a leading cause of worldwide infectious mortality, ranking above HIV/AIDS and Ebola, and is one of the top ten leading causes of death overall**.** Although medical advances have contributed to a reduction in morbidity and mortality, an increase in the prevalence of multidrug-resistant *Mycobacterium tuberculosis* (*Mtb*) infections has made it imperative to identify new drug targets. One such target is the ClpC1P1P2 protease, which degrades folded cytosolic proteins through the cooperation of the ATP-dependent unfoldase ClpC1 and the ClpP1P2 peptidase. Clp protease components are strictly essential for *Mtb* viability and are validated targets for anti-*Mtb* therapeutics. An expanded understanding of the physiological roles associated with ClpC1P1P2 - especially in terms of specific substrate recognition - would bolster efforts to develop antimicrobial compounds. Recent studies in *Bacillus subtilis* revealed that the orthologous ClpCP protease recognizes proteolytic substrates through post-translational arginine phosphorylation*.* Several lines of evidence suggest that ClpC1P1P2 similarly recognizes phosphoarginine-bearing proteins. However, the existence of phosphoarginine modifications in mycobacteria has remained in question. Here, we confirm the existence of post-translational phosphoarginine modifications in *Mycolicibacterium smegmatis* (*Msm*), a nonpathogenic surrogate of *Mtb.* Using a phosphopeptide enrichment workflow coupled with shotgun phosphoproteomics, we identify arginine phosphosites on a diverse collection of targets within the *Msm* proteome. Physicochemical and functional characterization of targets suggest that arginine phosphorylation is part of a proteome-wide quality control pathway. Our findings provide new evidence supporting the existence of phosphoarginine-mediated proteolysis by ClpC1P1P2 in mycobacteria and other actinobacterial species.

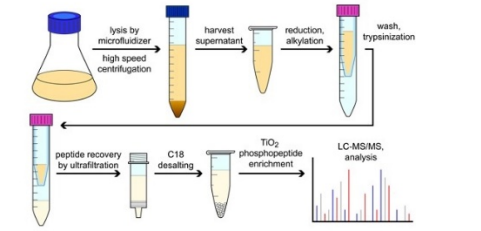

Figure 1: High resolution mass spectrometry was used identify protein arginine phosphorylation. Workflow for Discovery Arginine Phosphoproteomics in *Mycolicibacterium smegmatis* based on the filter-aided sample preparation (FASP) technique. All experiments were done in biological triplicates. Adaptation for acid-lability were applied at TiO_2 phosphopeptide enrichment and during liquid chromatography-tandem mass spectrometry (LC-MS/MS).

185. Mapping out histone post-translational modifications in a yeast prion model

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Prions are proteins with the ability to self-template into alternative folds, allowing them to operate outside the canonical steps of the central dogma of molecular biology. Interestingly, while these infectious protein species are responsible for causing several diseases in humans and animals alike, they have also been postulated to provide positive cellular outcomes in yeast. Because of proteins propensity to misfold and aggregate, prions could allow for environmental adaptiveness without directly affecting an organism's genome. However, the exact mechanisms by which these proteins could potentially lead to gene utilization changes are not known, and the extent of their roles in normal cellular biology has not been adequately investigated. Rnq1 and Swi1 are two such yeast prion proteins, each responsible for the propagation of the [PIN+] and [SWI+] prion states, respectively. Due to the ease with which prion states exchange, we hypothesize that they could be connected to particular changes in histone post-translational modifications (PTMs) to alter the way that genes are expressed, and thus could be the key to understanding how prions impact cellular phenotypes. Through previously published methods, we have begun to map out the changes in histone PTM levels between yeast prion states. Overall, [PIN+] yeast showed increased levels of H3K9ac, H3K18ac, and H3K56ac compared to [pin-]. Interestingly, all these modifications are correlated with increased gene transcription. In agreement, we find higher levels of total RNA in [PIN^{+}] yeast. Furthermore, [SWI+] yeast have shown a decrease in H3K56ac and H3K36me2 levels compared to [swi-] cells. Decreases in these marks generally represent decreased gene expression, which agree with the decrease in global RNA levels in [SWI+] compared to [swi-] samples. Furthermore, treatment with 1mM guanidinium hydrochloride (GuHCl) - to shut off or "cure" the prion state in yeast- reversed the observed histone PTM level changes. Here, we have effectively shown that the yeast epigenome is directly linked to prion states, further confirming the role of prions as another form of epigenetic modulation.

186. Functional characterization of undenatured type II collagen supplements : Are they interchangeable?

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Undenatured (native) type II collagen is a dietary supplement ingredient that has been clinically shown to support joint health. The purpose of this study was to compare the physicochemical and analytical characteristics of commercially sold native type II collagen supplements and to explore whether they might be sufficiently similar in their properties to yield similar benefits in promoting joint health.
Two commercial collagen type II ingredients (UC-II® and b-2cool®) and capsules

containing these two ingredients were examined for physical, chemical and microbiological assays. Total collagen content in the test product was analyzed using the hydroxyproline amino acid analysis method, while the undenatured type II collagen content was estimated by a validated ELISA method.
Analysis indicated that ingredients labeled as undenatured type II collagen were found to be markedly different in terms of size of collagen fibers as determined by transmission electron microscopy and antigenic configuration as measured by the ELISA assay. It was observed that the lots of b-2cool® contained negligible amounts of undenatured collagen (< 1%) in raw materials as well as in capsule products. On the contrary, the UC-II® raw material and the capsule reported levels of undenatured collagen, which aligns with its product specification (≥ 3%).
In conclusion, the data suggests that one should not assume that products labeled as undenatured (native) type II collagen are interchangeable. The difference in the undenatured type II collagen content in the material can potentially influence the efficacy and health benefits of the product.

187. Development and application of methods to classify Clp protease protein paralogs in actinobacteria

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Mycobacterium tuberculosis (Mtb), a highly infectious human pathogen, is the leading cause of mortality among infectious diseases worldwide. The emergence of drug resistance in Mtb drives a need for new antibiotics. Clp proteases have emerged as promising anti-virulence and antibacterial targets in several bacterial pathogens, including *Mycobacterium tuberculosis*. Multiple compounds have been identified that disrupt Clp protease activity, and some show promise as therapeutic leads. Clp proteases are composed of two distinct oligomeric components. Protein substrates are recognized and mechanically unfolded by an ATP-fueled unfoldase, such as ClpX, ClpA or ClpC. The unfoldase translocates the resulting denatured polypeptides into ClpP, an associated barrel-shaped peptidase, for degradation. The interaction between Clp unfoldase and peptidase is stabilized by LGF/IGF loops present on the unfoldase, which dock into hydrophobic pockets on the surface of ClpP. Through sequence analysis, I have identified a novel, conserved group of actinobacterial ClpC paralogs, with and without LGF/IGF loops. The novel ClpC paralogs lacking LGF/IGF loops presumably cannot associate with ClpP, and do not function in proteolysis. Our method is aimed to develop a bioinformatic method to classify ClpC paralogs and characterize their specialized function based on their sequence characteristics. This workflow can be applied to other sets of paralogs in other clades, and can help identify specialized functions paralogs and define their importance to organism viability.

188. Targeted, catalytic, near-IR light-triggered release from dihydrotetrazine precursors

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The targeted release of molecules such as fluorophores or drugs from stable precursors has proven to be useful in several fields. A majority of these release mechanisms rely on biological stimuli or UV light to initiate release. Since biological factors can vary from subject to subject and UV light is unable to safely penetrate tissues, an external, long wavelength light trigger is favored. Described here is a catalytic, near-IR (NIR) light-triggered intramolecular tetrazine ligation that results in release of a drug or fluorophore. Initiated by photocatalytic oxidation of the dihydrotetrazine (DHT) precursor, an intramolecular inverse electron-demand Diels-Alder (IEDDA) reaction occurs between the now oxidized tetrazine and vinyl ether, leading to liberation of the relevant molecule. Studies were performed with model compounds to determine rate and extent of release with various NIR photocatalysts. To examine drug release, cellular studies were completed to compare the response of cells treated with free drug to those treated with DHT precursor under diverse conditions. By targeting the photocatalyst to the nucleus, we were able to demonstrate successful intracellular release of the drug from the DHT system following light irradiation. The cellular response of the targeted release was similar to that of free drug resulting in unhealthy cells. Cells treated with the DHT prodrug in the absence of photocatalyst and light were healthy, similar to the vehicle control. To test the release of the fluorophore, a similar cell study was performed looking at fluorescence intensity following light irradiation. Samples containing the fluorogenic DHT precursor and photocatalyst showed significantly higher fluorescence intensity following light irradiation than that of conditions lacking either photocatalyst or light. Localization of photocatalyst combined with the NIR light trigger provides a spatiotemporally controlled, catalytic release system.

189. Exploring the relationship between temperature activated hydrogen-deuterium exchange and protein stability with SANS

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Hydrogen deuterium exchange, (HDX) is of increasing interest for characterization of protein dynamics in solution. In particular, the rapid development of HDX mass spectrometry (HDX-MS) has provided insight into protein flexibility and conformational changes by investigating the exchange of amide hydrogens with deuterium. Due to very large difference of the neutron scattering cross section between H and D, techniques such as small angle neutron scattering (SANS), offer an alternate approach to monitering HDX. Unlike HDX-MS, SANS allows for the continual measurement of HDX over time and is a non-invasive technique to investigate the HDX in solution. Even though SANS does not have the sensitivity to study the amino acid sequence specific exchange kinetics, it could

provide the spatial distribution information of exchangeable protons in a protein, as a function of the exchange time. With the use of SANS,we thermally probed the HDX of globular protein, bovine serum albumin, (BSA) over the course of a couple of days. The detailed analysis of the SANS data will be discussed. The exchange kinetics and the spatial distribution of exchangeable protons are determined using SANS. Additionally, the effect of the sample conditions, such as the temperature and buffer conditions, on the HDX will be presented.

190. Blood-brain barrier permeability and AChE inhibition of ionophoric polyphenols

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Alzheimer's disease (AD) is the most common form of dementia that affects more than 40 million people around the world. The incidence is expected to rapidly increase due to the lack of any effective treatment. In previous work we synthesized a family of five ionophoric polyphenols (compounds **1-5**) that targeted important aspects related to AD. Here, in order to gain insights into their potential therapeutic value, we have tested the ability of compounds **1-5** to cross the blood brain barrier (BBB), and to inhibit acetylcholinesterase (AChE), an enzyme that is reported to be involved in the progression of the disease. We performed BBB permeability and efflux mechanisms studies by means of the *in vitro* parallel artificial membrane permeability assay (PAMPA-BBB), as well as several *in silico* methods. AChE inhibition was spectrophotometrically studied. All compounds were found permeable to the BBB and moderate AChE inhibitors. Additionally, they displayed the ability to interact with several residues of the active site of the enzyme as revealed by docking and molecular dynamics simulations. Overall, our results suggest that these compounds could effectively cross the BBB to exert their anti-AD activity, including AChE inhibition.

191. High-throughput discovery of sequences that promote proteolysis in bacteria

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All bacteria possess multiple ATP-dependent proteases that degrade cytosolic proteins. These enzymes help maintain protein homeostasis and regulate discrete pathways, including the expression of virulence phenotypes in pathogenic bacteria, and have emerged as attractive antibacterial targets. ATP-dependent proteases are able to selectively recognize substrate proteins and ignore non-substrate proteins, minimizing harmful or wasteful off-target proteolysis. Many substrates are recognized directly by short, unstructured terminal sequences, termed degrons. While a small number of degrons have been identified, there is little known about the overarching rules that allow proteases to effectively discriminate between valid degrons and the millions of other

possible terminal sequences.

To address this gap in our knowledge, we have developed a cell-based screening platform that will allow us to interrogate global degron specificity and define the sequence-based rules that govern recognition of protein substrates by ATP-dependent proteases. Our method incorporates a novel selection-based screen, in which a library of protein toxin bearing a randomized terminal tag is expressed in host bacteria. Accumulation of toxin in host cells causes cell death. However, toxins bearing *bona fide* degrons are proteolyzed by endogenous proteases, allowing cell survival. Bacteria expressing valid degron sequences are enriched over time, and identified by Next-Generation Sequencing. Here we describe the efficacy of our method in *E. coli*, supported by preliminary NGS data from pilot screening experiments. The information gathered from this method we ultimately help us understand the roles that ATP-dependent proteases play in individual pathogenic bacteria.

192. Activation of tetrazines by a genetically encodable catalyst for intracellular spatially controlled bioorthogonal chemistry

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The tetrazine-*trans*-cyclooctene ligation is the fastest bioorthogonal reaction to date with a second order rate constant up to $k_2 = 10^6\ M^{-1}s^{-1}$ with strained *trans*-cyclooctene (s-TCO) derivatives and up to $k_2 = 10^7\ M^{-1}\ s^{-1}$ with *trans*-1-sila-4cycloheptene, far surpassing other biorthogonal reaction kinetics. While electron-deficient tetrazines increase the rate of the tetrazine-TCO ligation, they are only suitable as chemical probes instead of reporters. DHT is a stable precursor to tetrazine with a longer half-life in aqueous conditions. The Fox group developed a system to induce the catalytic oxidation of DHT to tetrazine in situ, enzymatically by horseradish peroxidase (HRP) or by photooxidation in the presence of a photocatalyst and light for subsequent biorthogonal chemistry with TCO. While HRP can enzymatically activate tetrazines, HRP is inactive when expressed in the reducing, calcium scarce mammalian cytosol which limits applications of this enzymatic system to mammalian endoplasmic reticulum and in vitro environments. We have developed a new enzymatic system that oxidizes DHT to tetrazine by utilizing an engineered ascorbate peroxidase (APEX2), as ascorbate peroxidase is naturally active in reducing environments. We have shown that APEX2 can oxidize a wide range of DHT substrates, have elucidated the hydrogen peroxide independent enzymatic mechanism, and have conducted site-directed mutagenesis to afford an APEX2 variant that is more active towards DHT oxidation. We have also shown that APEX2 can oxidize a series of DHT prodrug scaffolds where upon oxidation, an intramolecular inverse-electron demand Diels-Alder (IEDDA) reaction occurs to release a cytotoxic drug. This prodrug scaffold has been adapted to develop a fluorogenic DHT where upon oxidation by APEX2, a free fluorophore is released resulting in the turn on of fluorescence. We plan to utilize APEX2 to catalytically induce spatially controlled biorthogonal chemistry for imaging of proteins and

cellular compartments and decaging of prodrugs for drug delivery in different areas of the mammalian cell.

193. Application of Fundator's multidimensional time model to finding trace of fractional multidimensional Fokker-Plank equation dynamics in DNA replication in formation of CpG islands, analog bases, and repeats of G-quadruplexes

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Recent groundbreaking discovery by the author relates Poisson spike trains in dynamics of neural networks expressed by fractional multidimensional Fokker-Plank stochastic differential equation (fm FP SDE) to dynamics of DNA replication that can be expressed also by fm FP SDE and may result in formation in CpG and non-CpG islands, non-canonical bases, and repeats of repeats of G-quadruplexes. Benoit Mandelbrot was the first to apply fractional approach to statistical character of neural networks a year after FitzHugh's application of FP equation with complex functional term to neural networks as an alternative to Hodkin-Huxley model. The present abstract discusses application of the author's multidimensional time model to tracing similar dynamics of fm FP SDE in DNA replication and repair, e.g. methylation, or de- methylation, where the transport is controlled by fm advection dispersion equation.

194. Novel application of qPCR melt analysis following BRED

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Alexphander is a mycobacteriophage that primarily infects *M. smegmatis*. Its genome has been sequenced but not completely characterized. One of the uncharacterized genes is gene product 94 (gp94), which is classified as a MerR-like HTH DNA binding protein hinting at a gene regulation function. In order to characterize gp94, we will use Bacteriophage Recombineering of Electroporated DNA (BRED) to delete gp94 and thermal melt analysis to detect mutant phage populations with high sensitivity, as opposed to traditional PCR and agarose gel analysis. With proper primer design, gp94 regions of wildtype Alexphander, and the junction of gp94 in the mutant, will be amplified. If the gene is not essential for phage propagation, both wildtype and mutant populations will appear on the thermal melt analysis. The differences in melting temperature will distinguish between wild type and mutant phage populations in plated plaques. To delete Alexphander gp94, a 200bp substrate will be co-electroporated into *M. Smegmatis* with the Alexphander DNA. The electroporated cells will be plated and plaques will form as part of the infection process. These plaques will be harvested, and phage DNA will be amplified using qPCR then heated. Results on the deletion of gp94 using the BRED method and the novel application of thermal melt analysis to distinguish wild type and mutant populations will be presented.

195. Identification of a secondary binding site for acyldepsipeptide fragments within the bacterial Clp protease

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The increasing prevalence of drug-resistant bacterial infections is widely recognized as an impending public health crisis. As a consequence, there is an urgent clinical need for the development of new antibacterial therapeutics, and a related need to characterize novel drug targets. The Clp proteases, a widely distributed class of ATP-fueled proteolytic machines, have emerged as promising targets in a cross section of important bacterial pathogens. These enzymes degrade cytosolic proteins through the cooperation of an ATP-dependent unfoldase (e.g., ClpX) and the barrel-shaped ClpP peptidase. Multiple classes of compounds that kill bacteria by specifically inhibiting or dysregulating ClpP have been identified. The most widely studied class of these are the acyldepsipeptides (ADEPs), which are derivatives of naturally occurring non-ribosomally encoded peptides produced by some *Streptomyces.* Structural and biochemical studies have shown that ADEPs bind to the surface of ClpP and dysregulate Clp protease assembly and function. ADEPs typically consist of a complex peptide macrocycle linked to an N-acylphenylalanine substituent. Here, we examine the activity of ADEP fragments lacking the full macrocycle. We find that fragments with partial macrocycles retain considerable ability to bind and dysregulate ClpP. Curiously, some fragments appear to inhibit proteolysis at high concentrations, suggesting an alternate binding site at the peptidase active sites. Further, we report crystal structures of ADEP fragments bound to ClpP, which provide additional evidence for secondary inhibitory effects. Our findings open new possibilities for future ADEP development and provide a new area for ADEP structure optimization targeting an alternate location within the Clp protease.

196. Nipamovir: Synthesis and preclinical evaluation of an anti-HIV thiobenzamide prodrug

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Human immunodeficiency virus type 1 (HIV-1) is still a major public health concern. Highly active antiretroviral therapy (HAART) is a combination of antiretroviral drugs targeting the virus at multiple stages of its replication cycle which has helped reduce new HIV infections as well as AIDS-related deaths. However, its routine application has led to multi-drug resistance and the onset of adverse side-effects that results from long-term use. It is therefore crucial to continue the development of novel antivirals, particularly those that are inexpensive, nontoxic, and which are unlikely to result in viral resistance.
Thiobenzamide molecules like Amovir (Fig. 1) are chemically simple HIV inactivators targeting viral nucleocapsid protein 7 (NCp7), a 55 amino acid protein that performs essential functions during the assembly and maturation of new HIV virions. This class of molecule also shows low toxicity, and a high barrier to viral resistance. We developed Nipamovir (Fig. 1), a prodrug which protects the sulfur atom of Amovir in a manner similar to the clinically used immunosuppressant Azathioprine. Our molecule is very simple to reproducibly synthesize and has similar antiviral activity compared to Amovir and other thiobenzamides.
Here we report the synthesis, *in-vitro* and *in-vivo* preclinical evaluation of Nipamovir.

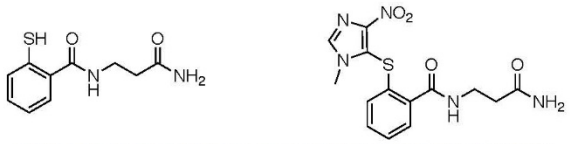

Figure 1. Left) Structure of active molecule: Amovir. Right) Prodrug Nipamovir.

197. New electron transport and biomedical applications for peptide amphipile materials

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Peptide amphiphiles, short peptides connected to a lipid tail, are a class of noncovalent biopolymer with applications in biomineralization, drug delivery, extra cellular matrix replacements, and more. In their polymeric form, the peptide amphiphiles we use form long ordered fibers in high pH conditions and are capable of binding the natural cofactor heme B, an Fe-centered cofactor that can undergo reversible oxidation and reduction. We seek to use this material to order heme B and develop electron transport functions. The malleability of the peptide segment will potentially allow for changes in conductivity with no change in the aspect ratios or size-parameters of fibers themselves. We hope to develop a new types of electronics based on these peptide polymers and use the functional diversity of peptides to introduce advanced transistor-type functions which will allow the peptide fiber itself to

Poster Session: Innovations in Chemistry Education

198. Case for case studies when teaching biochemistry

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It is generally accepted that active learning is superior to passive lectures when teaching General Chemistry, but this has not been well documented for higher level science classes. We are presenting our results using Case Studies and Active Learning activities to teach Biochemistry. Case studies provide a more integrated approach to the topics such as metabolism rather than the usual segregation of topics by pathways. This emphasis enables students to apply 21st Century skills and relate the topics to real life situations, disease states, and drug discovery. Active learning encourages interaction where students debate questions, explain their thinking to one another, and come to a consensus answer. These methods increase understanding and retention of the material and as a result students are better prepared for future opportunities in graduate school, medical school, academia, or industry. In all cases, they will need to interact with colleagues in other disciplines and must be able to interpret problems and collaborate on solutions.

199. Sustainability and safety in chemistry: An upper level undergraduate elective

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Many science students are drawn to an industrial, environmental, or safety-related career and seek out opportunities to expand their knowledge and experience related to sustainability and environmental issues in chemistry. We have developed an advanced elective course focusing on green chemistry, sustainability, and safety to serve these undergraduates. Students apply foundation-level coursework in organic and analytical chemistry as they are introduced to the field of green chemistry. The course incorporates a sustainability innovation team project in which students think critically about an environmental issue and develop a solution. This course provides an avenue to engage students and faculty in this vital area of science and technology.

200. Impact of recitation timing on student performance in undergraduate general chemistry

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This research investigates the impact of recitation timing on student exam performance in undergraduate general chemistry. Chemistry courses are typically designed in a way that requires some students to attend recitation before their lecture while other students have the opportunity to attend recitation after lecture. Given this, we investigated if there was a relationship between recitation timing and exam performance and found that across majors students who attend recitation before lecture typically experience a higher exam performance across exams. Welch's t-test was utilized in order to analyze the mean difference in performance between the recitation before lecture (RBL) and the recitation after lecture group (RAL) and found that on average students in the recitation before lecture group achieved exam scores nearly 2% higher than the RAL group on average across the three mid-term exams. This indicates that there is an intrinsic benefit experienced by students who were in the recitation before lecture group even when controlled for major and placement exam performance. Given the difference in performance between the two groups, we have reason to believe that student performance is affected by recitation timing and may be due to the fact that students who attend recitation before lecture have a chance to develop a foundational understanding of the content prior to attending lecture which enables the students to get more out of the lecture thus leading to higher performance on exams.

201. Hybridization of C-H bonds is directly related to electronegativity of substituents

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Chemistry courses often teach hybridization of an atom in a molecule can be found by drawing its Lewis structure and counting electron pairs with complete neglect of electronegativity [EN]. Acetonitrile [CH_3CN] is said to have sp^3 and *sp* C atoms

respectively. A dipole moment of 3·92 D shows it to be strongly polarized. The pK_a of its CH bond, ~25, is similar to that of ethyne [24] which is said to be *sp* hybridized. pK_a of methane, [sp^3 hybridized] is ~56. HCN, is said to be *sp* hybridized based on drawing its Lewis structure and counting electron pairs. $^1J_{CH}$ for HCN is 269 Hz; its C-H bond is $sp^{0.86}$ hybridized. Its pK_a [9.4] is 15 orders of magnitude greater than ethyne, the standard for *sp* hybridization. Cyanide [CN^-] is a good nucleophile. Replacing an H of CH_4 with CN^- yields CH_3CN; it is not sp^3 hybridized [Bent's rule]. Neglecting EN, the methylene C of $CH_2(CN)_2$ [malononitrile] is said to be sp^3; its pK_a = 11·1 and the methine C of $CH(CN)_3$ [cyanoform] also is implied to be sp^3; its pK_a = -5·1. Stating C is sp^3 hybridized instead of C has four sp^3 hybridized orbitals in CH_4 is FALSE. We cannot measure hybridization due to EN of atoms involved in a bond directly. Lauterbur [inventor of MRI] pointed out that *s* orbitals have a finite probability of being in the nucleus while *p*- orbitals don't [Fermi contact]; NMR [$^1J_{CH}$] coupling is related to hybridization. Calibration of this relationship with methane, ethene and ethyne yielded the equation: $^1J_{CH}$ = 5x [% *s* character] of a CH bond. Pauling showed CH_4 is sp^3 hybridized; the C-H bonds have 25% *s* character; its $^1J_{CH}$ = 125 Hz. $^1J_{CH}$ for CH_3CN is 136.1 Hz; its C-H bonds are $sp^{2.67}$ hybridized. It has three C-H bonds with hybridization $sp^{2.67}$ thus its C-C bond is $sp^{3.98}$ [12-3(2.67)], i.e. it has 20% *s* and 80% *p* character. A C atom cannot have two different hybridizations; the different hybridization of the C-H and C-C bonds of the CH_3 group in CH_3CN is proof that atoms are not hybridized; only bonds are. Bonds have no angles [e.g. N_2 and O_2]. The claim that interbond angles can be predicted from hybridization also is FALSE. The hybridization of the C-C bond of CH_3CN [~sp^4] is similar to the C-C bonds in cyclopropane [C_3H_6]. Interbond angles in these molecules are vastly different. Prediction of hybridization from interbond angles is not possible. EN is not the only predictor of hybridization; angle strain also is directly related to hybridization.

202. Teaching hands on chemistry labs to the visually impaired

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Teaching Chemistry Labs to the Visually Impaired normally consists of the student just taking down notes and observation through a lab partner with no real hands on experience in the lab. This can lead to frustration for the student and a feeling of being "left out". This, in turn, makes the visually impaired student lose interest in Chemistry and have a feeling that chemistry is not a field for them.
Teaching hands on labs in developing countries can be even more trying. Though there are talking lab sensors that can give student temperature readings etc. the costs are extremely high and prohibitive in developing countries where access to chemistry laboratory is very limited for most rural areas.
To combat these problems, two students from rural Kenya who were visually impaired were given a series of basic hands on lab experiments that ranged from basic measurement techniques to making standard solutions. Their data was analyzed and compared to known values.

203. Strategies for the photoreduction of Tc-99 pertechnetate to low valent Tc by Keggin polyoxometalates

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Technetium-99 (^{99}Tc) is a high yield (~6%) product of Uranium-235 fission and is a weak beta emitter (βmax= 0.29 MeV) with a half-life of $2.1x10^5$ years. When exposed to air, ^{99}Tc is most prevalent in its oxidized Tc^{VII} form, which exists predominantly as pertechnetate (TcO_4^-) and is highly mobile in the environment. The immobilization of Tc in the environment has usually been achieved via reduction of the prevalent TcO_4^- anion to relatively insoluble TcO_2, Tc^{IV} species. In this work, we report the use of small metal oxide clusters called Keggin polyoxometalates (POMs), $XM_{12}O_{40}^{n-}$(X= P, Si, Al, n=3, 4, 5) to both reduce and stabilize the reduced Tc species. Specifically, we report on the mechanism by which the reduction of technetium occurs and find that PW_{12}, SiW_{12}, and AlW_{12} promote the reduction of TcO_4^- to lower valent states. X-ray absorption spectroscopy was used to confirm a combination of Tc^{IV} {in the form of $TcO_2 \bullet 2H_2O$ and $Tc_2(\mu\text{-}O)_2^{4+}$} and Tc^V, which is subsequently complexed into a POM defect as a Tc^V=O species. The examination of Keggin POMs to photocatalytically reduce TcO_4^- will lead to investigation of solid-state materials for photocatalytic reduction of TcO_4^-.

204. Mathematical aspects of application of fractional multidimensional Fokker-Plank equation to the theory of rate of chemical reactions based on spectroscopy experiments with examples

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Different types of spectroscopy experiments carried by multiple teams suggest some discrepancies between one-dimensional (1D) Kramers' theory for the rate of chemical reactions with hydrodynamic Stokes-Einstein friction model. The disagreement continued despite multidimensional (multi-D), or non-Markovian, or not-exactly hydrodynamic modifications by Grote-Hynes, Hubbard, and other authors. The proposed fractional dimensional modification to multi-D model is based on theoretical and experimental findings of dimensional disagreement and deceptive simplicity between curves for barrier crossing at equilibrium and the boundary of the curves. Comparison of less anomalous fractional derivative exponents of 1.9 and 1.7 with more anomalous of 1.5 and 1.3 suggest Sierpinski carpet, Cesaro's, and different attractors' curves.

205. Optimizing the properties of sol-gel based silica nanoparticles

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Sol-gel is a synthetic method that can generate a solid matrix having extremely high porosity, which is transparent, chemically inert and mechanically stable. This technique has been used extensively in material science. More recently it was shown that under certain conditions, proteins and other biochemical molecules can be encapsulated within these sol-gel matrices and not only remain functional but show enhanced stability under harsh conditions, thereby opening the door for a range of applications from biosensors to drug delivery. Expanding the silica based sol-gel synthetic method to the fabrication of sol-gel based silica hybrid nanoparticles (nanogels) represents a leap forward as it marries the sol-gel advantageous properties with those of nanoparticles, mainly their small size and increased surface area. We, as well as many other research groups, have developed different synthetic methods for the fabrication of silica based nanoparticles with varying properties. Here we explore and contrast different fabrication protocols for the generation of monodisperse nanogels with improved hydrophilicity, size control, stability and flexibility in trapping biomolecules of interest all while retaining their non-toxic and biocompatibility properties. Methods explored include tetramethyl orthosilicate or tetraethyl orthosilicate as precursor, acid or base catalyzed, precursor exclusion (PE) approach, biomimetic approach and integration of additives such as chitosan or PEG. The results and existing challenges will be discussed.

206. Electron microscopy of platinum-based anti-cancer drugs: Cisplatin, oxaliplatin, and carboplatin

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Cisplatin, oxaliplatin, and carboplatin are common drugs in chemotherapy, and they are widely used to treat many kinds of cancers. In general, particle count, particle size and compound distributions of a pharmaceutical drug are among key parameters that determine the quality of the final product since they heavily affect the dissolution rate for the solid dosage form. Scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS) and transmission electron microscopy (TEM) imaging for materials characterization have been used in this experiment to create concentration maps to help having a better understanding of the morphology, possible polymorph identification, and crystal defects in these three platinum-based anti-cancer drugs.

207. Development of heterometallic platinum(IV)-gold(I) compounds as potential chemotherapeutics against specific genitourinary cancers

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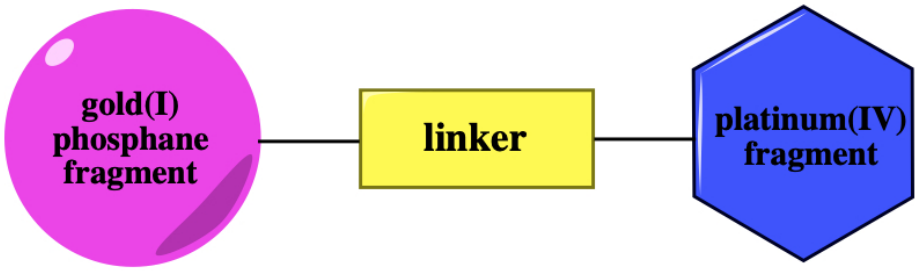
Platinum-based drugs have governed the anticancer organometallic field for more than half-century now. Numerous structural designs using platinum(II) oxidation state have been synthetized since the FDA approval of cisplatin [cis-diaminediiodo platinum(II)] in 1978. Cisplatin is currently used to treat of 40-80% of cancers (alone or in combination therapy) with a minimal spectrum of activity and acquired or intrinsic resistance and known to cause numerous side effects in patients due to its non-selective mechanism of action.[1] A long-term exploration for less toxic platinum(II)-derived drugs lead to strategies such as modification of ligands coordinated with platinum(II) center as well as the change of platinum oxidation state to platinum(IV) derivatives.[1,2] Platinum with the oxidation state of +4 provides structural axial-bonds for the coordination of functionalized axial ligands. The axial position offers 1) a way to reduce secondary mechanisms (with reactive sulfur-, nitrogen- or oxygen-containing species) from the equation, therefore, eliminating side-effects in the extracellular environment of the tumor and 2) a dual mechanism or synergetic effect by the release of the axial ligands into the intracellular environment of the cancerous cells.[2] Recent literature described mono- and bimetallic platinum(IV)-based anticancer compounds, including Ru(II)[3] and Gd(III)[4] heterometallic compounds. Our laboratory has successfully developed heterometallic complexes containing gold(I) and metals such as Ti(IV) and Ru(II), which have resulted in extremely efficient in renal cancer in vitro and in vivo and have shown a synergistic effect of the different metallic fragments.[5] Thus, we present the initial attempts to develop novel bimetallic Pt(IV) and Au(I) containing compounds with promising chemotherapeutic effects. We present the synthetic work of new Pt(IV)-Au(I) complexes and computational studies for the development of these heterometallic Pt(IV)-Au(I) complexes.



208. Two-dimensional materials based photocatalysts for light-induced H_2 production

***Jingrun Ran**, jingrunran@gmail.com. The University of Adelaide, Adelaide, South Australia, Australia*

The global energy crisis and environmental problems drive the aggressive search for a clean and renewable energy source to replace fossil fuels. The production of clean and carbon-free hydrogen energy from inexhaustible solar energy through photocatalytic water splitting is a 'dream technology' to address the worldwide energy shortage, environmental contamination and the greenhouse effect. The core challenge of this advanced technology lies in the development of low-cost and environmentally benign photocatalysts with sufficiently high activity and stability to produce hydrogen at a cost comparable to the conventional fossil fuels. Recently, emerging two-dimensional (2D) materials such as MXene, phosphorene, 2D metal-organic framework (MOF) and ReS_2 have attracted tremendous attention due to their outstanding characteristics of ultrathin thickness, large surface area, high-aspect ratio and abundant active sites. Therefore, the rational design and synthesis of 2D materials based photocatalysts to achieve efficient and stable light-induced H_2 production is highly promising. Furthermore, both advanced characterizations (*e.g.,* aberration-corrected atomic-resolution transmission electron microscopy, synchrotron-based X-ray absorption spectroscopy and femtosecond fluorescence spectroscopy) and density functional theory based theoretical computations are adopted to investigate the atomic-level structure/composition-performance relation in photocatalysts. Finally, a general principle to develop high-performance photocatalysts for efficient solar-to-hydrogen energy conversion is concluded.

209. Designing silicon substrates for area-selective deposition of TiO2

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Atomically precise and area-selective deposition processes play crucial role in miniaturization of devices in modern electronics. The surface-selectivity of titanium deposition precursor molecules in atomic layer deposition (ALD) of TiO 2 was investigated using ex situ X-ray photoelectron spectroscopy (XPS) and in vacuo Fourier-transform infrared (FT-IR) spectroscopy. We established that TiCl 4 readily chemisorbs onto Si(111) and Si(100) surface terminated with hydroxyl groups but is relatively inert towards Cl- and H-terminated surfaces, allowing for area-selective deposition. In tandem with XPS analysis, density functional theory (DFT) chemisorption simulations characterized TiCl 4 adsorption geometries and identified the factors influencing differences in reactivities. Thermal atomic layer deposition (ALD) of TiO 2 based on TiCl 4 and water was also compared with the commercial processes that utilize other titanium precursors and oxidation half-cycles.

210. Interplay between mesoscale architecture and catalytic output in CO_2 gas-diffusion electrolyzers

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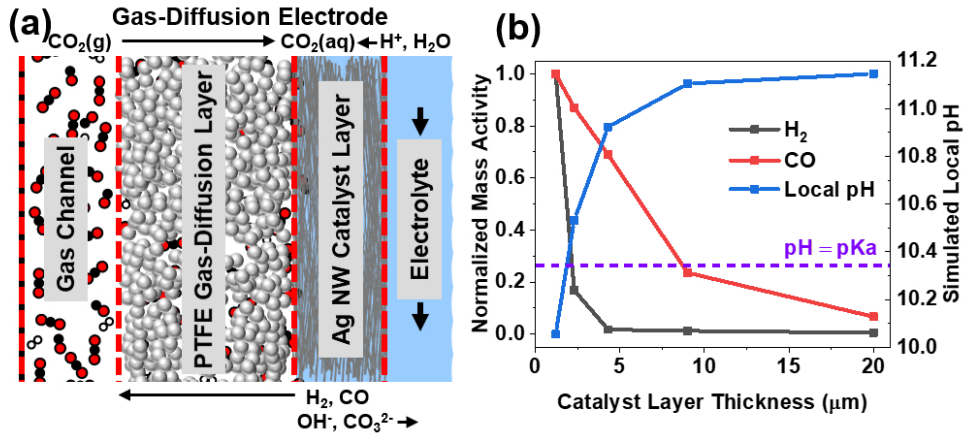
In June 2019, California produced the most solar energy on its grid, but also took the most solar power offline because of insufficient need. As intermittent renewable energy becomes increasingly competitive with conventional platforms, we will need to address how peak energy can be utilized or stored. By using CO_2 as an electron sink, electrochemical CO_2 could effectively utilize this excess peak energy while reducing atmospheric CO_2 levels to produce transportable fuels that can be used during off peak hours, mitigating reliance on fossil fuels. For this process to be economically viable, production of selective, high throughput, durable electrolyzers must be realized. High surface area nanocatalysts combined with conductive carbon-based gas-diffusion layers (GDL) enable high CO_2 flux and conversion, but can suffer from ineffective catalyst utilization, premature degradation and flooding of the conductive carbon-based GDL that limit electrolyzer operation. We address this challenge by using self-conducting networks of nanowires (Ag or Cu) on a non-conductive gas-diffusion layer (Figure 1a) as a gas-diffusion electrode (GDE) for CO2 conversion. Optimization of catalyst layer thickness demonstrates a fine line between suppression of parasitic hydrogen evolution (≈20x) and CO_2 depletion events that cause a ≈15x decrease in CO evolution (Figure 1b). A 1-D model of the electrode morphology and microstructure quantitatively captures the steady-state compositional gradients within the catalyst layers supporting the role of thickness on microenvironment. This model, along with additional experiments, indicate that proton dissociation from bicarbonate contributes significantly to the hydrogen evolution at modest overpotentials. The combination of a self-conductive nanowire catalytic network and robust hydrophobic porous support structure combined with predictive computational simulations provide an effective platform for the development of heterostructured, meso-scale catalysts and microenvironment for improved performance and durable CO_2 electroreduction.



(a) Ag NW/PTFE GDL for CO_2 conversion and (b) catalytic output vs simulated local pH

211. Immobilization of water-oxidation catalysts on plasma grafted poly(acrylic) acid modified anodes

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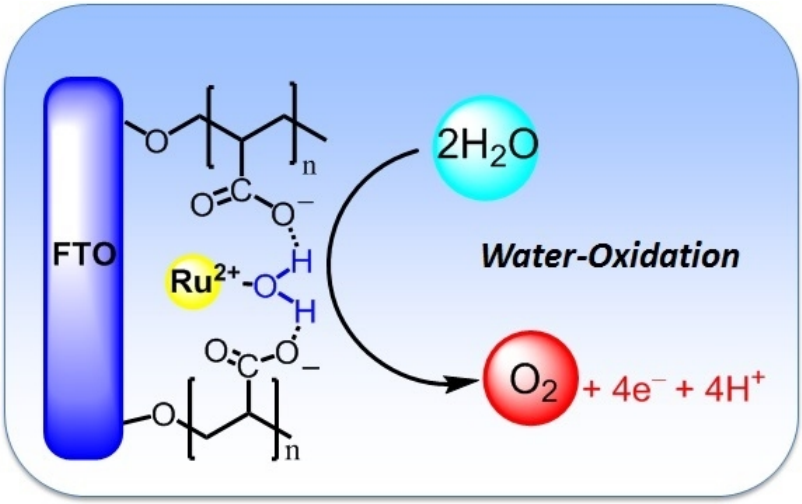
Water-oxidation ($2H_2O \rightarrow O_2 + 4H^+ + 4e^-$) is a mechanistic bottleneck for solar powered hydrogen production by water splitting. Significant progress has been made in the fundamental understanding of the O-O bond formation step in water-oxidation using Ru(II) homogeneous water-oxidation catalysts. For practical integration in electrocatalytic or photoelectrosynthetic fuel production devices, interfacing these known molecular catalysts onto conductive solid supports is necessary. The traditional approach for surface attachment to conductive oxides (e.g. fluorine doped tin oxide, FTO) is via synthetic modification of the ligand architecture to incorporate functional groups such as carboxylic acids or phosphonates prior to immobilization. In this work, argon plasma-induced graft polymerization of polyacryclic acid (PAA) films onto the FTO conductive glass were constructed as a robust platform for the immobilization of "underivatized" molecular water-oxidation catalysts (WOCs). Electrochemical studies and surface characterization of the modified electrodes reveal the prescence of H-bonding between the water ligand in the immobilized complex and the carboxyl groups of the poly(acrylic acid) brushes which attributes to surface catalysis and stability.



212. Mechanism and kinetics of the MAX etching reaction for MXene synthesis

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Since their discovery in 2011, the family of two-dimensional (2D) transition metal carbides, nitrides, and carbonitrides, MXenes, have grown to encompass more than 100 stoichiometric compositions, providing materials for a variety of applications such as energy storage, wireless communication, and photothermal therapy because of their redox-active surfaces, high electrical conductivities of >15,000 S cm^{-1}, and plasmon resonance behavior. The next step to expand upon such promising results is to integrate MXenes into devices for commercial and consumer use, which will rely on scaling up the synthesis of MXenes to industrial levels. This transition will require understanding the MAX etching mechanism and kinetics to determine the limiting parameters, understanding the relationship between the extent of reaction and chemistry and properties of the resulting MXenes, and speeding up the synthesis process to reduce costs. Moreover, while the synthesis protocols for the first and most widely studied MXene, $Ti_3C_2T_x$, were developed through years of systematic experiments, reaching the same level of optimization for every member of the MXene family would be time-consuming. Thus, there is a need to develop new strategies for correlating MAX composition with etch-ability. To address the above problems, herein, we develop a simple H_2 gas collection system for the in-situ monitoring of the MAX etching reaction. We use this system to correlate the effect of various parameters such as temperature, hydrofluoric acid concentration, and MAX particle size on the properties of the resulting MXenes and by fitting with Avrami reaction kinetic models, to better understand the reaction mechanism. Overall, our results reveal that for Ti_3AlC_2, etching time can be decreased without significant oxidation or degradation of the resulting $Ti_3C_2T_x$ MXene. Fundamentally, our results reveal a new basis for optimizing the MXene synthesis process which can be used to investigate MAX phases that have not been etched successfully, like Cr_2AlC, which is predicted to have interesting magnetic properties.

213. Flexible approach to fabricate a well-ordered array of Metal/Semiconductor hemispherical nano-heterostructures

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Novel methods for fabricating plasmonic systems like metal/semiconductor heterostructures have contributed immensely to wider applications in the field of solar energy conversion, photodetection, optoelectronics, and photocatalysis. However, the absence of precise control over the size, shape, interparticle spacing, and shell-thickness during the fabrication of these core-shell heterostructures using conventional experimental methods poses a huge challenge. Herein, we present a flexible approach that combines a nanosphere lithographic (NSL) technique with a kinetically controllable, solution-based electrodeposition method on a non-conductive glass and fused silica substrate.
The well-ordered array of Au or Ag nanoparticles, which form the core of the hybrid

structure, is fabricated using the NSL technique, accommodating the manipulation of the core sizes. Semiconductor shell is grown by employing a solution-based, electrochemical deposition process using the metal nanoparticle array on the substrate as a seeding template.
Steady-state absorption measurement has shown that the modification of the core size, interspacing, and importantly, the semi-shell thickness of the heterostructures results in the tunability of their plasmonic property from the visible region through the near and mid-infrared. The result observed makes this approach very flexible in fabricating metal/semiconductor heterostructure with desired property and functionality.

214. *In situ* adsorption studies of anisole on NiMo oxide catalysts under hydrodeoxygenation reaction conditions

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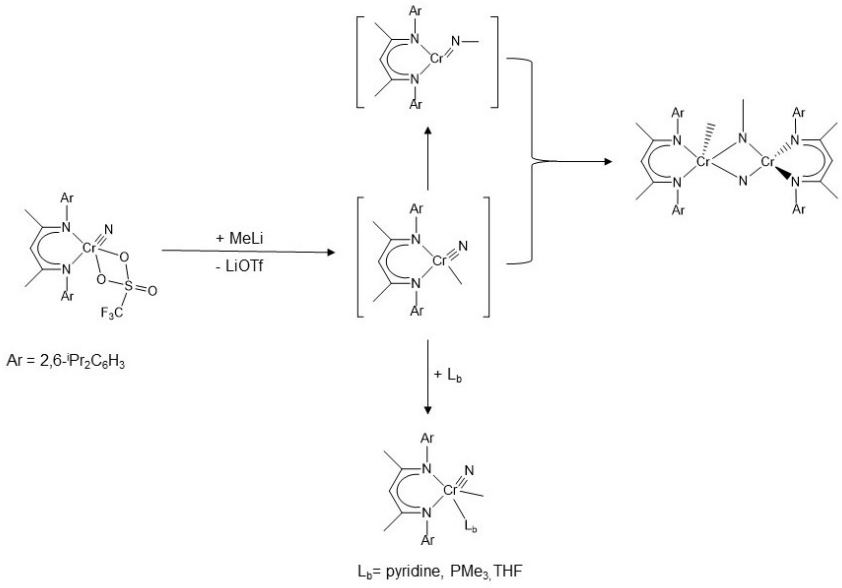
Mo oxide catalysts provide a viable approach for enhancing reactivity and selectivity of biofuel production from biomass. It has been found that the addition of Ni further improves the performance of catalysts in the hydrodeoxygenation (HDO) reaction of anisole, a model compound for lignin biomass; however, an in-depth understanding of the role of Ni or Mo is unclear in the industrially used nickel molybdenum oxide catalysts. Three oxide catalysts, including Ni only, Mo only, and combined nickel molybdenum catalysts, were characterized using *in situ* infrared (IR) spectroscopy and ambient pressure X-ray photoelectron spectroscopy (APXPS) to give a direct comparison of surface species and chemical behavior during the HDO of anisole. The adsorption behavior of anisole from room temperature to 350 °C was studied in addition to HDO reaction conditions. Ni only catalyst featured a different pathway of anisole adsorption at room temperature, while Mo only and NiMo catalysts showed similar behaviors. Most organic species desorbed from the surface of all catalysts above 200 °C, with the exception of a methoxy group. The sharp feature at 1020 cm^{-1} in the IR data grew with increasing temperature and time on Mo only and nickel molybdenum catalysts. The IR data show a decrease in the Mo=O groups while the formation of Mo^{4+} and Mo^{5+} are seen in the APXPS data, indicating the reduction of Mo^{6+} plays a key role in the catalysis. The combined results of *in situ* IR and APXPS characterizations of oxide catalysts during the HDO of anisole show that Mo reduction plays a primary role in the enhancement of the catalysis.

215. C-N bond formation by nitride migratory insertion into Cr-C bond

Le Zhang*, zhleang@udel.edu, Klaus H. Theopold. CBC, University of Delaware, Newark, Delaware, United States*

Owing to the prevalence of nitrogen-containing target molecules in the areas of natural product synthesis, medicinal chemistry, and organic materials, the development of facile

methods for the formation of C-N bond is an important subject in organic synthesis. We have discovered a rare example of C-N bond formation by nitride migratory insertion into a Cr-C bond. The reaction of $L^{iPr}Cr(N)OTf$ with MeLi unexpectedly yielded the dinuclear complex $L^{iPr}Cr(Me)(\mu\text{-}N)(\mu\text{-}NMe)CrL^{iPr}$ (L^{iPr} = $[ArNC(Me)]_2CH$, Ar = 2,6-$^{i}Pr_2C_6H_3$). We propose a three-step mechanism for this reaction: 1) methyl group substitution for the triflate ligand produces intermediate alkyl $L^{iPr}Cr(N)Me$, 2) nitride migratory insertion into the Cr-C bond generates $L^{iPr}Cr(NMe)$, and 3) trapping of the latter with $L^{iPr}Cr(N)Me$ yields the final product $L^{iPr}Cr(Me)(\mu\text{-}N)(\mu\text{-}NMe)CrL^{iPr}$. We have shown that intermediate $L^{iPr}Cr(N)Me$ may be stabilized by Lewis bases, yielding $L^{iPr}Cr(N)(Me)L_b$ (L_b= pyridine, PMe_3, THF), which have been structurally characterized. In this presentation, we will describe our findings regarding the reaction mechanism and analogous reactions.



Poster Session: Innovations in Measurement and Data Science

216. Fluorescence reaction progress monitoring of solid-phase asymmetric ionic nanoscale probe synthesis

Claudia Von Suskil[1]*, cvonsusk@udel.edu, Sharon L. Neal*[2]*. (1) University of Delaware, Newark, Delaware, United States (2) Chem Biochem, Univ of Delaware, Newark, Delaware, United States*

Reactive oxygen species (ROS) are byproducts of metabolic reactions involving oxygen that are involved in many natural and anthropogenic processes. Overproduction of ROS is known to cause oxidative stress, cell damage, and disease. In addition, ROS are highly reactive and short-lived by nature, making them important, but challenging, analytical targets.

Asymmetric ionic materials (AIM), which include ionic liquids and solid-phase materials, are organic salts whose ions are mismatched in size and shape. While ionic liquids have been widely studied, solid-phase AIMs (including nanoscale materials comprised of asymmetric salts) are lacking robust investigation, in spite of their potential for use in sensor development and adaptive spectral and physical properties. Probes based on nanoscale asymmetric salts offer a promising avenue for tunable fluorescent probes for ROS, as reported in the literature, but more research is needed to identify and evaluate these types of sensors.
The work reported here uses time-dependent multichannel UV-Vis absorbance and frequency-domain dynamic fluorescence measurements to evaluate and compare two types of nanoscale solid-phase AIMs by monitoring the evolution of their spectral properties during their synthesis. Anionic exchange reactions are used to associate both the target (imidazolium with 2,7'-dichlorodihydrofluorescein) and reference AIM (1,1'-diethyl-2,2'-cyanine with bis(trifluoromethanesulfonyl)imide) in a biphasic solution of DCM and water. Analyzing the resulting multivariate spectral data sets via curve resolution identifies changes in the number and properties of the reaction mixture components, facilitating optimization of reaction conditions, detection of reaction completion, and correlation of spectral changes to the probes' structures. These methods will also be used to evaluate and compare the responsiveness of the target AIM to ROS.

217. Photodegradation of semiconductor quantum dots in microheterogeneous media using wavelength- and frequency-resolved fluorescence decay measurements

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Semiconductor quantum dots (QDs) have generated substantial research interest in the past two decades because of their connection to various applications such as: cancer treatments, photovoltaics, bio-labeling, and fluorescence microscopy. Specifically, cadmium-containing luminescent quantum dots (QD) are being widely used because of their relatively simple synthesis and enhanced photophysical properties. However, there is significant concern about the impact that cadmium containing luminescent QDs can have on natural systems and human health as they degrade i.e., "weather" in the environment. Previous work by others has demonstrated that combining time resolved fluorescence measurements with quantum yield determinations and peak width determinations provides valuable information regarding semiconductor QD as they grow and degrade. However, the use of single channel, time-resolved fluorescence measurements provided limited utility as a stand-alone analytical technique for quantum dots because the spectral response to simultaneous changes in QD properties can produce ambiguous spectral results.

In this research, multichannel, broadband, frequency-domain dynamic fluorescence

measurements are used to compare the photodegradation of ZnS passivated CdTe semiconductor quantum dots (QDs) with mercaptopropionic acid (MPA) ligands in microheterogeneous media. Microheterogeneous media have been observed to mimic the environments encountered in cell membranes and other complex samples, suggesting these solvents are viable in studying ROS production and aggregation of QDs. Wavelength- and Frequency-Resolved Fluorescence Decay Measurements of QDs in phosphate buffer and phosphate buffer saturated octanol are used to investigate the impact of solvent microheterogeneity on QD weathering processes. Monitoring the photodegradation of QDs using wavelength- and frequency-resolved fluorescence decay processes produces Fourier-transform emission-decay matrices (FT-EDMs), which can be analyzed numerically for the spectra, decay rates and relative intensities of the fluorescent sample components with minimal *a priori* assumptions. The comparison of the spectra, decays and relative intensities of fluorescent components resolved from FT-EDMs collected as passivated CdTe semiconductor quantum dots (QDs) with mercaptopropionic acid (MPA) ligands are photodegraded in phosphate buffer and phosphate buffer saturated octanol will be described.

Poster Session: Innovations in Organic Chemistry

218. Deaminative reductive methylation of alkylpyridinium salts

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Alkyl amines are highly versatile, widely abundant feedstock chemicals. The ease in which they can be carried throughout multistep syntheses make them a highly sought-after candidate for further functionalization. Recently, we have discovered a powerful transformation of alkyl amines via the carbon–nitrogen (C–N) bond mainly to form $C(sp^3)$–$C(sp^2)$ bonds. Due to the high degree of saturated carbon–carbon bonds in bioactive molecules, methods to form alkyl–alkyl bonds have become highly desirable. We recently developed a nickel-catalyzed cross-coupling of Katritzky's alkylpyridinium salts and alkylzinc halides to create new $C(sp^3)$–$C(sp^3)$ bonds. Notably, this method provides a method to transform a simple amine into a methyl group. However, the harsh conditions limited the functional group tolerance including radiolabeled ^{11}C. Inspired by overcoming these limitations, we have now developed a reductive cross-coupling utilizing alkylpyridinium salts and a simple methylating agent. By providing an accessible route to install methyl groups, this method enables our collaborator, Zibo Li at the University of North Carolina Chapel Hill, for the radiolabeling of bioactive compounds which are used to detect and measure molecular interactions through positron emission tomography (PET). The optimization, scope and mechanistic understanding of this transformation will be presented.

219. Synthesis and evaluation of biaryl compounds as inhibitors of nucleoside hydrolases to treat trichomoniasis

***Melissa A. Vanalstine-Parris**, mvanalstine@adelphi.edu, Vanesa Abrego, Erum Ajmal, Ari Gil, Kevin Nelson, Rebekah Shin, Davi Vanegas, Edina Saljanin, Carlos Ventura, Brian J. Stockman. Chemistry, Adelphi University, Garden City, New York, United States*

Trichomoniasis is the most prevalent non-viral sexually transmitted diseases. It is caused by the parasitic protozoan *Trichomonas vaginalis*. Current treatments use 5-nitroimidazoles to damage DNA residues, but due to increasing resistance over time, there is a need for a novel treatment. *T. vaginalis* is incapable of de novo synthesis of nucleobases and therefore needs to acquire them from the host. *T. vaginalis* uses salvage pathway enzymes to metabolize the host's nucleosides, converting them into ribose and the corresponding nucleobase. Two enzymes involved in this salvage pathway are Uridine Nucleoside Ribohydrolase (UNH) and Adenosine-Guanosine Nucleoside Ribohydrolase (AGNH). Screening of a fragment diversity library against both UNH and AGNH resulted in multiple classes of compounds with IC50 values of ~100 μM. Multiple hits from the fragment screen were biaryl compounds, with phenyl pyridine and phenyl pyrazole as two common ones. Using Suzuki coupling we were able to synthesize a variety of analogs and test them against UNH and AGNH. We will report the synthesis and biological activity of these biaryl compounds on UNH and AGNH.

220. Reactions of isocyanates and isothiocyanates with 2-bromoallylamines: Investigations into the synthesis of 1,3-dihydro-2*H*-imidazol-2-ones and 4-imidazoline-2-thiones

***Todd J. Eckroat**, tje146@psu.edu. School of Science, Penn State Erie The Behrend College, Erie, Pennsylvania, United States*

Five-membered heterocyclic rings are abundant in natural products and pharmaceuticals. Thus, continued investigation of new heterocyclic ring forming reactions are of interest to the synthetic community. 1,3-Dihydro-2*H*-imidazol-2-ones and 4-imidazoline-2-thiones have found a diverse array of biological applications, including analgesic, antiserotonin, antioxidant, and herbicidal activity. Undoubtedly, other activities remain to be explored. Current synthetic access to these scaffolds is varied. Based on a recent report of a cascade reaction involving Cu-catalyzed S-vinylation with N-(2-bromoallyl)butylamine and CS_2, it was hypothesized that isocyanates and isothiocyanates could undergo a similar cascade reaction involving heteroatom-vinylation to access 1,3-dihydro-2*H*-imidazol-2-ones and 4-imidazoline-2-thiones. Preliminary results show that N-(2-bromoallyl)butylamine reacts readily with phenyl isocyanate and phenyl isothiocyanate in the presence of CuI in one-pot to form the resulting 1,3-dihydro-2*H*-imidazol-2-ones and 4-imidazoline-2-thiones, respectively, in moderate yield. The role of copper in the reaction is not essential, as the desired products are still produced in the absence of any copper species. Reaction temperature appears important, as the reaction produces 1,3-dihydro-2*H*-imidazol-2-ones and 4-imidazoline-2-thiones at 120 °C but a mixture of isomers and

intermediates at lower temperatures. Progress on the investigation of heteroatom-vinylation between N-(2-bromoallyl)butylamine and isocyanates and isothiocyanates will be reported. Optimization of reaction conditions and substrate scope will be detailed. This previously unreported one-pot reaction will enhance synthetic access to important heterocycles.

221. One-pot chemoenzymatic reactions in water enabled by micellar encapsulation

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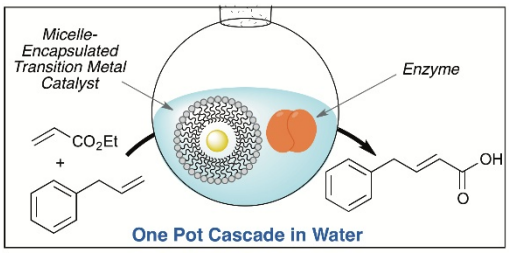
The use of micellar conditions to enable one-pot reactions involving both transition metal and enzymatic catalysts is reported. Representative enzymatic transformations under micellar conditions are unaffected by the presence of non-ionic surfactants, including designer surfactants such as TPGS-750-M. Furthermore, the presence of enzymes has negligible effect on transition metal catalysis under micellar conditions in water. Finally, three one-pot chemoenzymatic reactions in water are reported in which the micelle-forming surfactant TPGS-750-M is a crucial factor for reaction efficiency.



222. Photochemical and photophysical study of *bis*-alkylated lumazine and pterin photosensitizers

María José Sosa[3], Mariana Vignoni[3], María Noel Urrutia[3], Matías I. Quindt[4], Sergio Bonesi[4], Dobrushe Denburg[5], Alexander Greer[1,2], Andrés H. Thomas[3], ***Edyta Greer***[6]*, edyta.greer@baruch.cuny.edu. (1) Chemistry, Brooklyn College, Brooklyn, New York, United States (2) Ph.D. Program in Chemistry, CUNY The Graduate Center, New York, New York, United States (3) Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas (INIFTA), Departamento de Química, Facultad de Ciencias Exactas, Universidad Nacional de La Plata (UNLP), CCT La Plata-CONICET, La Plata, Argentina (4) CIHIDECAR-CONICET, Departamento de Química Organica, FCEyN, Universidad de Buenos Aires, Buenos Aires, Argentina (5) Natural Sciences, Baruch College, New York, New York, United States (6) Baruch College, New York, New York, United States*

A *bis*-decylated lumazine and pterin have been synthesized and characterized. Namely, *bis*-decyl chain 1,3-didecylpteridine-2,4(1*H*,3*H*)-dione and decyl 4-(((2-amino-4-(decyloxy)pteridin-6-yl)methyl)amino)benzoate conjugates were synthesized. The synthesis was carried out by nucleophilic substitution (S_N2) reactions of 1-iododecane with lumazine and pteroic acid, in *N,N*-dimethylformamide (DMF) and *N,N*-dimethylaniline (DMA) solvent respectively. Decyl chain coupling arises in a sequential manner, without DMF or DMA condensation. Experimental data from NMR (1D and 2D), HPLC, UV-vis,

fluorescence, as well as theoretical data (density functional theory) will be presented to compare the two *bis*-decylated sensitizers with the notion to add to strategies for increasing sensitizer lipophilicity for use in antimicrobial photodynamic inactivation and photodynamic therapy.

223. Adjuvant compound analysis for mechanistic insight to promote photodynamic action

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A review of adjuvants for enhanced photodynamic activity will be presented. Addition of adjuvants (NaBr, KI, NaN_3, $NaNO_2$, KSCN, 8-methylnon-7-ene-1 sulfonate, as well as amino acids, vitamins, and repurposed drugs) can enhance phototoxicity towards tumor cells, microbe cells, fungi, and also acceptor compounds in microemulsions. We will discuss candidate reactive oxygen intermediates that are responsible for the enhanced photodynamic action. In the case of bacteria and fungi, antimicrobial agents and their combination with sensitizers leads to improved outcomes for photoinactivation. In the case of tumor cells, exogenous addition of aminolaevulinic acid as a pro-sensitizer along with adjuvants such as vitamins leads to increased formation of the endogenous photosensitizer protoporphyrin IX. Adjuvants act through different mechanisms to amplify the photodynamic effects, as will be discussed.

224. Superhydrophobic antimicrobial photodynamic inactivation of bacterial biofilm with airborne singlet oxygen

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Due to limitations of conventional antimicrobial photodynamic therapy (aPDT) in the treatment of periodontal disease, we have developed a superhydrophobic (SH) technique that generates cytotoxic airborne singlet oxygen for the eradication of bacterial biofilms. One advantage of the SH-aPDT technique is that there is no staining by the sensitizer molecules in the dental tissues and periodontal pocket. Furthermore, SH-aPDT creates

channels for air to diffuse through the sensitizer sites within the plastron for the formation of singlet oxygen as a gaseous species to potentially deep hypoxic biofilm environments. An *in vitro* study was carried out with SH-aPDT against a multi-species periodontopathogenic biofilm model (*Streptococcus mutans, Actinomyces naeslundii* and *Porphyromonas gingivalis)*. The biofilms were cultured on hydroxyapatite discs and exposed to airborne singlet oxygen generated by SH surfaces loaded with chlorin e_6 photosensitizer. Illumination was carried out with a 664 nm LED under various light doses. The CFU/mL results of SH-aPDT showed enhanced killing and a dose-dependence for both the Gram-positive and Gram-negative bacteria in the multi-species biofilm, with >5-log reduction of all bacterial species. The results demonstrate that the novel SH-aPDT is a promising tool to disinfect and treat periodontal disease.

225. Deaminative nickel-catalyzed one-carbon homologation of alkyl amines

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Until recently, alkyl amines have been an underutilized substrate class despite their ubiquity and ease of synthesis. One-carbon deletion to give alkyl amines is well known via the Curtius rearrangement; however, the insertion of one carbon into alkyl amines is more limited. Currently, the installation and subsequent reduction of a nitrile traditionally through S_N2 chemistry can give an alkyl amine, but has many limitations and safety precautions. In 2017, our group described a Suzuki-Miyaura cross-coupling utilizing alkyl amines as novel electrophiles. We have now developed a nickel-catalyzed cyanation of Katritzky alkylpyridinium salts via C–N bond activation. This reaction demonstrates broad functional group tolerance in the scope allowing for the synthesis of functionalized alkyl nitriles which offers an opportunity to prepare new amines. The optimization and scope of this transformation will be presented.

226. Development of a hiyama cross-coupling of highly substituted vinylsilanes

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A method to synthesize geometrically defined tri- and tetrasubstituted alkenes through a Hiyama cross-coupling is reported. Easily prepared and handled tri- and tetrasubstituted vinylsilanes bearing four carbon substituents on the silicon center can be coupled with a variety of aryl halides, without the requirement of undesirable additives such as 18-crown-6 ether or fluoride salts, to achieve high-yields of highly substituted alkene products.

227. Computational design of foldamer based water channels

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Water shortage is one of the serious challenges of this century and is primarily due to growing demand of clean water and depletion of freshwater resources. Water desalination using reverse osmosis has been used for water recycling, but current membranes performance follows permeability/selectivity trade-off and suffers from high cost. Therefore, the development of highly permeable yet selective water transport channels is essential. In this research, we aim to computationally design aromatic foldamer channels for high permeability and selectivity in transporting water, comparable to natural water channels, aquaporins (AQPs). Aromatic foldamers are inexpensive and easy to synthesize. They are tunable and can be adjusted to desirable length and pore size by using aromatic units with proper backbone curvature angle. The inner surface of the channels can be readily modified to introduce functions, showing potentials for further investigations which might lead to the new generation of water purification materials. We carried out molecular dynamics simulations to characterize the structural and dynamical properties of these helical arylamide foldamers for transporting water and ions. Analysis reveals interesting structure-function relations such as the number and position of certain substituents on inner pore of the channels influence the flow of the water and ions activity. We have also obtained a series of sequences that are potential water transport channel with high permeability and selectivity against monovalent ions such as Na^+ and Cl^-.

228. Development of ^{19}F fast magic-angle-spinning NMR spectroscopy for structural characterization of protein assemblies

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Protein structure determination by NMR spectroscopy relies on distance restraints extracted from ^{13}C, ^{15}N and ^{1}H based correlations. This approach is limited to proteins comprising single domains, while in multi-domain proteins and protein assemblies long-range restraints are needed. Fluorine is an attractive nucleus for protein structure analysis, due to its 100% natural abundance and high gyromagnetic ratio. We have exploited these favorable magnetic properties to develop ^{19}F magic-angle-spinning (MAS) NMR spectroscopy as a probe of structure in proteins and protein assemblies. We have incorporated 4F-Trp residues as reporters into Oscillatoria aghardii agglutinin (OAA), a

protein with potent anti-HIV activity also used by our team as an excellent model system. With fast MAS frequencies of 50-62 kHz, we acquired high-resolution ^{13}C-^{19}F and ^{19}F-^{19}F correlations, from which we have assigned the ^{19}F chemical shifts of the 4F-Trp residues. We have recorded DANTE-RFDR exchange curves to measure ^{19}F-^{19}F distances in the microcrystalline OAA. The measured distances are consistent with X-ray crystal structure of 4F-OAA determined by us demonstrating the power of this approach for proteins with unknown structures. Our approach is broadly applicable for structural characterization of proteins and protein assemblies containing fluorotryptophan residues.

229. ^{19}F magic angle spinning NMR spectroscopy to probe protein-ligand interactions

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Fluorine is an exquisitely sensitive, background-free NMR probe, ideally suited for structural characterization of complex systems, such as proteins and protein assemblies and their complexes with small-molecule ligands. Here we demonstrate the power of ^{19}F fast magic angle spinning (MAS) NMR for investigations of protein/ligand interfaces in the crystalline carbohydrate binding domain of galectin-3 (galectin-3C) in complex with fluorine containing diastereomeric ligands. The ^{19}F MAS NMR spectra acquired at the spinning frequency of 60 kHz exhibit excellent sensitivity and resolution. Two-dimensional ^{13}C-^{19}F and ^{1}H-^{19}F correlation experiments revealed correlations at the protein/ligand interface and permit site-specific assignments of the protein residues in the vicinity of the ligand. ^{19}F chemical shift tensor parameters reveal distinct environments for the two fluorine atoms in each ligand. The ^{19}F MAS NMR approach presented here is envisioned to broadly applicable for structural investigations of protein-ligand complexes.

230. Determination of histidine protonation states in proteins by fast magic angle spinning NMR

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Histidine residues play important roles in structure and functions of proteins, such as comprising active sites of enzymes, mediating proton channels activity and metal–protein interactions. Many of these functions are mediated by the protonation/tautomeric forms of His residues. While determination of protonation states is a challenging problem for most biophysical techniques, NMR ^{13}C, ^{15}N and ^{1}H chemical shifts can be exploited as unique reporters of His protonation and tautomeric states, both in solution and in magic angle spinning solid-state (MAS) NMR experiments. Here we present a new approach for characterization of protonation and tautomeric states of His in proteins. We combined fast MAS NMR at frequencies of 40-62 kHz and ^{1}H detection with selective magnetization inversion techniques and transferred echo double resonance (TEDOR) – based signal filtration, in 2D heteronuclear correlation experiments. We demonstrate, for two proteins, HIV-1 CA tubular assemblies and HIV-1 CA CTD-SP1 in the microcrystalline state, that these experiments unequivocally inform on the protonation states of individual His residues and indicate the coexistence of multiple forms for some residues. We anticipate that the approach described herein to be particularly useful for determination of His protonation states in large proteins and protein assemblies.

231. Towards the atomic resolution structure of a novel disulfide-rich biomaterial

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Eggshell membrane (ESM) is a composite proteinaceous biomaterial lining the avian eggshell. ESM comprises three layers, which are discernable by their orientation, thickness, and morphology. Both the inner and the outer layers are formed by fibers of about 2-8 μm in diameter, as is clear from electron micrographs. While proteins are a major constituent of ESM (80-85% by weight), the nature and the structure of the individual protein building blocks remain unknown.

Combining reductive alkylation and aggressive proteolytic digestion led our laboratories to the identification of a series of peptides with unusually repetitive patterns. The corresponding Cysteine-Rich Eggshell Membrane Protein (CREMP) contains about 14% Cysteine residues (Cys) in a total of 4127 amino acids. Chicken CREMP (UniProt ID A0A3Q2UC95), which is the subject of our studies, has 133 modules each containing two disulfides. Herein, we present the protocol for successful expression and purification of 4 consecutive modules of CREMP in *E*. coli SHuffle cells with high yield (~25 mg/L in LB media). We prepared U-^{13}C,^{15}N labeled 4-module CREMP for 3D structure determination by solution NMR spectroscopy. The 2D and 3D triple-resonance NMR spectra indicate that the protein is monomeric and well-folded. Remarkably, despite the highly repetitive sequence, the spectra are well resolved, and the overwhelming majority of peaks (103 out of 121 residues) were detected in the HSQC spectra. We will present assignments of chemical shifts and distance restraints, from which we will calculate the first atomic-resolution structure of this protein fragment. We anticipate that the 3D structure of 4-mod CREMP will provide clues about the arrangement of modules in the full-length CREMP.

232. Thermal dry etching of CoFeB alloy thin films using chlorine and acetylacetone (acacH)

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The initial steps of thermal dry etching of CoFeB alloy thin films using Cl_2 and acetylacetone (acacH) were investigated. CoFeB alloy is commonly used in magnetic random-access memory (MRAM) technology. The etching was done on chlorinated alloy surfaces using 2,4-pentadione (acacH) and the pathway was followed by detecting expected desorbing fragments during a heating ramp via temperature-programmed desorption (TPD) experiment. The chemical properties of the etched surfaces were then analyzed with ex situ X-ray photoelectron spectroscopy (XPS). The morphology of the surface was studied with microscopic techniques such as scanning electron microscopy (SEM) and atomic force microscopy (AFM). Comparison of the reaction of acacH with oxidized and clean (non-oxidized) surfaces suggested that partially oxidized surface is necessary for thermal etching of the CoFeB alloy thin films. On a clean surface, the only possible pathway for the organic precursor molecule is to be decomposed. The overall mechanism of thermal etching on partially oxidized alloy thin films is quite complicated as the desorbing products may have a combination of chlorine and organic ligand, and their general formula can be expressed as $M(acac)_xCl_y$. It was also shown that annealing at elevated temperatures results in substantial morphology changes with producing microscopic level defects (pits).

233. Realistic SARS-CoV-2 liposomes via *VesGen*: an efficient tool for modeling large and complex lipid membranes

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Experimental challenges in both structural and quantitative lipidomic studies have led to a disparity in data available to computational researchers compared with biomolecules such as proteins. Coupled with the immensity of biological membranes, computational lipid modeling routinely employs coarse-grain (CG) models. Further, lipidomic detail is simplified due to poor diversity of lipid species in most force fields. Here we present *VesGen*, an efficient and user-friendly tool and part of VMD which can generate coarse and atomistic lipid membranes of arbitrary size and lipidomic complexity. *VesGen* supports a variety of parametrizations and features such as membrane protein embedding. The tool supports GROMOS, Martini, PACE, SIRAH, and CHARMM formatted force-fields, allowing simulation within NAMD. Here, we employ *VesGen* to construct a the SARS-CoV-2 bilayer vesicle, yielding novel insights into the physical properties of the viral envelope and serving as the basis for a detailed, multiscale model of the SARS-CoV-2 virion.

234. Molecular determinants of Ebola nucleocapsid stability from molecular dynamics simulations

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Ebola virus (EBOV) is a human pathogen with the ability to cause hemorrhagic fever and bleeding diathesis in hosts. The life cycle of EBOV depends on its nucleocapsid. The Ebola nucleocapsid consists of a helical assembly of nucleoproteins (NPs) encapsidating single-stranded viral RNA (ssRNA). Knowledge of the molecular determinants of Ebola nucleocapsid stability is essential for the development of therapeutics against EBOV. However, large degrees of freedom associated with the Ebola nucleocapsid helical assembly pose a computational challenge, thereby limiting the previous simulation studies to the level of monomers. In the present work, we have performed all-atom molecular dynamics (MD) simulations of the helical assembly of EBOV nucleoproteins in the absence and presence of ssRNA. We found that ssRNA is essential for maintaining structural integrity of the nucleocapsid. Other molecular determinants observed to stabilize the nucleocapsid include NP–RNA and NP–NP interactions and ion distributions. Additionally, the structural and dynamical behavior of the nucleocapsid monomer depends on its position in the helical assembly. NP monomers present on the longitudinal edges of the helical tube are more exposed, flexible, and have weaker NP–NP interactions than those residing in the center. This work provides key structural features stabilizing the nucleocapsid that may serve as therapeutic targets.

235. Impact of cavity losses on nonadiabatic couplings and dynamics for many molecules coupled to a single photon in polaritonic chemistry

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Light is a basic tool for the investigation of molecular properties. The physical and chemical properties of molecules can be investigated via chemical modifications and/or coupling the molecules strongly to light. The strong interactions between molecules and quantized photons create polaritons which are hybrid light-matter states and do not have a purely material or light nature. Instead, they have properties of both light and matter constituents that can have different properties and reactivities. In our previous work, we developed a non-Hermitian formalism (CQED Hamiltonian) that explicitly considers the photonic dissipation and applied this formalism to the system of azobenzene strongly coupled to a single quantized photon. We showed that cavity dissipation strongly alters cis to trans isomerization rate of azobenzene molecule. Herein, we modified our non-Hermitian approach for the model system with the coherent interaction of many molecules that couple strongly with the confined and same quantized photon. When many molecules are coupled to a photonic mode, the new hybrid light-matter potential energy surfaces develop with new critical points, i.e., new intersections or avoided crossings, and different couplings between surfaces; these new features may suppress or enhance the reactivity

compared to the single-molecule system. We hypothesize that our model will confirm that many molecules strongly coupled to a photon will demonstrate all of these features depending on the photon's details and its confinement. We predict that our approach will support that the photonic dissipation can significantly alter the polaritonic nonadiabatic couplings that are responsible for cis−trans isomerization of azobenzene molecules for low and moderate dissipation rates.

236. All-atom MD simulations of CpAM-bound HBV capsids reveal allosteric mechanisms relevant to assembly regulation and inhibitor binding

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Hepatitis B virus (HBV) is a major cause of liver damage, affecting over 250 million people worldwide. A detailed study of the HBV life cycle and how it can be disrupted is fundamental to developing a definitive cure for the disease. The assembly of the HBV core particle is a promising drug target. The core particle consists of a capsid -- an icosahedral shell built by 120 protein homodimers -- that contains the virus's genome. Core particle assembly can be disrupted in vitro by small molecules called core protein allosteric modulators (CpAMs). Here, we perform microsecond all-atom molecular dynamics (MD) simulations of empty, intact HBV capsids to investigate their biological function and disruption by three CpAMs, namely AT130, HAP1, and HAP18. Our simulations reveal changes in capsid dynamics and morphology in the presence of CpAMs and provide improved, statistical characterization of CpAM binding modes. This information is important for understanding the CpAMs' mechanism of action and designing or optimizing new small molecules against the capsid. The simulations also reveal a homodimer conformation never observed in experimental structures, which may explain an allosteric mechanism known to be important for efficient core particle assembly.

237. Development of novel xanthate-modified and unmodified exchangers for remediation of effluent in contaminated water within Enugu State metropolis

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Freshly processed powder of *raphia farinifera* inflorescence was separately modified with xanthate acid (XMRFi), subsequently characterized with Fourier Transform Infra-Red (FTIR) Spectroscopy and other physical properties. The competitive adsorption capacity of Pb (II), Cu (II), and Dyes onto a novel xanthate-modified XMRFi and unmodified Raphia farinifera inflorescence (RFi) was thoroughly examined in contaminated water. The equilibrium results showed that XMRFi removed higher amounts of the pollutants than unmodified Raphia farinifera inflorescence with maximum adsorption capacity (96.9, 82.5,

80.8 and 79.98) and (80.9, 61.5, 40.8 and 50.98) mg/g, respectively. The result also show that equilibrium followed Freundlich model and sorption was in the order of Pb (II) > Cu (II) > Dyes. The Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectra (XPS), Scanning electron microscope (SEM) and Thermogravimetric analysis (TGA) studies showed that the xanthate and hydroxyl group participated in the adsorption of Pb(II), Cu(II) and Dyes present in contaminated water in Enugu State metropolis.

238. Three conformationally distinct models of the full-length SARS-CoV-2 spike protein with representative post-translational modifications

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Severe acute respiratory syndrome coronavirus 2 (SARS-CoV-2) is a ß-coronavirus responsible for COVID-19, an infectious disease which has claimed the lives of an estimated 2.8 million individuals worldwide. The spike protein on SARS-CoV-2 is a homotrimer that plays a significant role in the process of cellular entry by binding the ACE2 receptor and facilitating membrane fusion. Here, we present three full-length models of the spike protein, with distinct conformations of the Receptor Binding Domains

(RBDs) based on observed cryo-EM structures. Missing regions, including numerous loops, the stalk, transmembrane domain, and cytoplasmic tail, were built using the ROSETTA software, integrating experimental information into the process where available. Each structure is decorated with 66 N-linked glycans according to available glycoanalytic data, and the cysteine-rich cytoplasmic tail was palmitoylated at two sites according to available data on homologous coronavirus spike proteins. The models were embedded in a 100 nm diameter lipid envelope as part of the construction of a physiologically representative SARS-CoV-2 virion and are being examined in their native environment via large scale all-atom molecular dynamics simulations.

Poster Session: Innovations in Polymers & Soft Materials

239. Conductive hydrogels based on a water-soluble EDOT derivative

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Conductive hydrogels, particularly those containing poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS), have sucessfully gained popularity in hydrogel bioelectronics because of their remarkable electrical and mechanical properties over inorganic, graphene oxide and other conducting hydrogel networks. Conductive hydrogels are soft three-dimensional polymeric networks due to their high-water content but can be either too fragile at low crosslinking density or too “hard” when large amounts of conducting polymer are incorporated, which limits their integration in devices and biological interfaces. A simple method for obtaining conductive hydrogels with high conductivity and tunable mechanical properties is still lacking. Here, we report a simple approach to incorporate a conductive PEDOT-derived polymer in PSS-containing hydrogels. We first synthesized a mono-pegylated derivative of EDOT (EDOT-PEG). This water-soluble monomer, unlike EDOT, is easily polymerized inside any hydrogel using a mild oxidant such as sodium hypochlorite. The resulting hydrogels show good electrical conductivities (0.23 S m^{-1} in PBS), and mechanical, electrical and electrochemical stability.
This method proves to be a simple and rapid approach which does not require blending PEDOT:PSS with hydrogels nor crosslinking it, and addresses the lack of solubility of PEDOT in water. These materials could be promising candidates in diverse applications including bioelectronics, energy storage and actuators.

240. Degradable multiblock copolymers as scaffolds for conductive polymers

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Biodegradable electronic devices can be used to alleviate the harmful nature of electronic waste (e-waste) in the environment, but often suffer from limited conductivity. Poly(3,4-ethylene dioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) is a conductive polyelectrolyte complex that is commonly used in organic electrochemical transistors (OECTs), organic field-effect transistors (OFETs), and other organic electronic devices. While the stability of PEDOT:PSS is an important feature, it also means that PEDOT:PSS is not a degradable material. To address this lack of degradability, we synthesized multiblock copolymers of poly(lactic acid) (PLA), a bio-based and biodegradable polymer, with PSS to serve as scaffolds for PEDOT, affording PEDOT:$[(\text{PSS-}b\text{-PLA})_n]_m$. The telechelic blocks of PLA and PSS blocks are synthesized by ring-opening polymerization and atom-transfer radical polymerization (ATRP) respectively, then combined using Click chemistry to access the final multiblock copolymer. While studies of this material are still underway, we are hoping that it will combine conductivity and degradability. We believe that this material could be integrated into transient electronic devices and could minimize environmental pollution related to e-waste.

241. Synthesis of stimuli-responsive and conducting polyelectrolyte complexes

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Stimuli-responsive block copolymers have been developed for applications ranging from drug delivery to actuators and shape-memory materials. Common stimuli for these materials include light and temperature, which can often prove impractical for integration in actuating devices (e.g., for soft robotics). Instead, we are developing a conductive thermo-responsive material which can be actuated electrically by Joule heating. This approach would lead to easier integration in actuating devices because a separate source of heating would not be needed. In addition, being flexible and light-weight, this material would enable a more portable device, thus eliminating a drawback of electronic actuators that require metals and alloys for actuation. Our approach uses a thermo-responsive block copolymer as a matrix for a conductive polymer. We first synthesized the thermo-responsive block copolymer poly (*N*-isopropylacrylamide)-*block*-poly(styrene sulfonate) (PNIPAM-*b*-PSS) by reversible addition-fragmentation chain transfer (RAFT) polymerization. PNIPAM was chosen for its thermal response close to body temperature—it exhibits a lower critical solution temperature transition in water above 32°C. The addition of the PSS block in the copolymer serves as a stabilizer and matrix to enable the dispersion of the doped conductive polymer, poly(3, 4-ethylene dioxythiophene) (PEDOT), in water. Together, PEDOT:PSS-*b*-PNIPAM is a thermo-responsive and conductive polyelectrolyte complex. In this presentation, we will discuss the optimization of the RAFT polymerization (initiators, RAFT agents and solvent systems). We are currently

characterizing PEDOT:PSS-*b*-PNIPAM samples for their thermal response, particle size, electrical conductivity and self-assembly. These conductive polyelectrolyte complexes could prove useful as materials for actuators in assistive robotics and stimuli-responsive mixed-ionic conductors for bioelectronics.

242. Tunable microfibers via interfacial tetrazine ligation

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Fibrous materials are important components within hierarchical biomaterials of the native extracellular matrix (ECM). We sought to create hybrid peptide-polymer microfibers that compositionally, structurally, and mechanically resemble fibrous proteins found in the ECM, with added tunability and processability introduced by synthetic polymer constituents. To promote cell growth and differentiation, synthetic materials should exhibit cell adhesive properties similar to that of natural proteins found in the native ECM. Here, we introduce two platforms for fabricating such tunable microfibers based on the tetrazine ligation, an exceptionally fast biorthogonal reaction between strained trans-cyclooctene (TCO) and s-tetrazine (Tz). In the first, multiblock copolymer microfibers are synthesized via interfacial polymerization employing tetrazine ligation. The modular approach allows for straightforward incorporation of bioactive peptide sequences and degradable synthetic polymer repeats to guide cell-material interactions. In part two, Tetrazine ligation-based layer-by-layer deposition is utilized to generate core-shell structure microfibers with hydrophilic and soft hyaluronic acid (HA) shell and stiff polycaprolactone (PCL) backbone, which is served as a platform for treatment of vocal fold scarring.

243. 3-D cytocompatible network construction mediated by long wavelength photocatalytic activatable bioorthogonal reactions

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Due to their exceptional reaction rates and high selectivity, the inverse-electron-demand bioorthogonal Diels-Alder cycloaddition between tetrazines (Tz) with strained alkene and alkyne dienophiles was more and more applied in 3-D network construction *in vivo* environment. In the same time, the reduced form of Tz, dihydrotetrazine (DHTz) is proved to be capable of fast photooxidation under far-red/near-infrared irradiation. Even though with some issues of cytotoxicity and side-reactions associated with singlet oxygen sensitization, this photoinitiated method provides a promising way to construct 3-D network system with precise spatial and temporal control. The long wavelength light which triggers the oxidation enables the application of cytocompatible network construction in vivo for the deep tissue penetration. In the presented work, we explored gentler photo-initiated oxidation system with sila-rhodamine (SiR) derivatives. DHTz and trans-

cyclooctenes (TCO) conjugated hyaluronic acid (HA) (HA-DHTz and HA-TCO) and SiR aqueous solutions were mixed as the pre-gel solution. Human prostate cancer (LNCap) spheroids were resuspended in the solution and irradiated with 660nm light for 10 min to form 3-D cell-laden hydrogel. After 14-day incubation, spheroids presented high viability and continuously increased size. Also, fluorescent dye (Cy7) tagged pre-gel solution was injected into mice and hydrogel was successfully formed after irradiation, stable during 7-day culture. In conclusion, SiR dyes were first developed as photocatalysts and successfully served in this photoinitiated cytocompatible 3-D network construction system, providing a promising platform for further application.

244. Impact of the molecular structure of poly(styrene sulfonate) on the mixed ionic-electronic conduction of PEDOT:PSS

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Organic mixed ionic electronic conductors (OMIECs) are crucial semiconducting material able to efficiently transport ionic and electronic charge, and transduce ionic and electronic signals across the living/nonliving interface. OMIECs have therefore been successfully used as the channel materials in organic electrochemical transistors (OECTs) for biological sensing applications. The polyelectrolyte complex and OMIEC, poly(3,4-ethylene dioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) has been extensively used in OECTs due to its stable dispersed form in water and good electrical conductivity. However, the complex structure of PEDOT:PSS makes it difficult to study its structure-property relationships with regard to mixed ionic-electronic coupling. Moreover, the commercial formulation of PEDOT:PSS does not specify important molecular parameters such as molecular weight, dispersity, and degree of sulfonation of PSS. To address these challenges and establish an understanding of the interconnection between hydrophobic PEDOT domains and hydrophilic PSS domain, we synthesized precise PSS samples and determined their effect on the mixed ionic-electronic conductivity and morphology of PEDOT:PSS films. Our studies show that the conductivity of PEDOT:PSS is closely related to the molecular weight and dispersity of PSS, with and without secondary dopants. We believe that our studies will pave the way to a better understanding of ionic-electronic coupling in PEDOT:PSS and will ultimately provide design guidelines for OMIECs in bioelectronics.

245. Celebrating the 100th Anniversary of the Delaware ACS Section

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The Delaware Section celebrated its 100th Anniversary in 2017. It has a rich tradition and list of accomplishments during those 100 years. It has many members from industry, academia and the governmentment that have contributed to its success and the success American Chemical Society. This presentation will give a brief history of some of the section's members, significant contributions they have made, events that occurred and places where they occured The section was once the "Chemical Capitol of the World"

during World War I and the center for the discovery of the miracle fiber,"Nylon". After the war many of the members contributed and participated to the development of new technologies, advances in education and environmental regulations. There were many members both from industry and academia who served on local section committees and as advisors to the section's outreach activities that heve made an impact on students lives and professional careers in chemistry. The presentation will also share some of the activities that occurred during the celebration that may be of interest to other local ACS sections considering celebrations and potential involment of senior chemists in their section. As a memember of the Senior Chemist Committee and their liason for the MARM meeting I will provide information on their strategic plan and how senior chemists can contribute and participate tn sustaining the future of our society and future chemists.

246. Electrochemical behaviour of polymer nanocomposite on differents electrode substrates

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Carbon nanomaterials with high surface areas and excellent electrical conductivity have been widely used in fabrication of electrochemical sensors and biosensors. The carbon nanofibers(CNF) present excellent mechanical, thermal and electrical properties; it has been used as modified material of electrodes for electrochemical sensing. Conducting polymers, especially aromatic diamines, have been a field of intensive studies due to their unique properties, as well as possible applications in electrocatalysis, electrochromic devices, capacitors, batteries, and sensors**.**
Polymer (1,5-diaminonaphthalene)/CNF nanocomposites can be prepared by different routes, including in situ electropolymerization, solution processing.
Herein, the aim of this paper is to study in detail the behavior of nanocomposites poly(1,5-DAN)/CNFs at different substrates electrodes (carbon paste, glassy carbon, platinum…), its electropolymerization in acidic medium HCl 0,1M, characterization and electroactivity in Fe^{2+}/Fe^{3+}, $Fe(CN)_6^{4-/3-}$. The results were achieved by means of SEM, cyclic voltammetry and electrochemical impedance spectroscopy.

Carothers & Regional Award Symposium

247. Lessons learned from nature: From biomineralization to biomaterials

Allison Campbell*, lablover2b@gmail.com. None, Kennewick, Washington, United States*

Nature has the ability to build mineral systems such as bones, teeth, and shells at ambiant conditions by utilizing proteins to facilitate and direct the biomineralization process. Unraveling this process then adapting it to artifical systems is the focus of this talk. We will

explore how proteins control enamel formation, then utilize those concepts to develop a biomimetic route to control the deposition of calcium phosphate on surfaces. This process is then applied that process to the development of orthopedic biomaterials. The efficacy of the biomaterials to facilitate bone growth will be shown. Antimicrobial agents, incorporatied to reduce infection, will be shown as highly effective. The talk will close by highlighting commeriaclization opportunities and status of the intellectual property.

Alternative Grading in the Chemistry Curriculum

248. Getting started with mastery grading

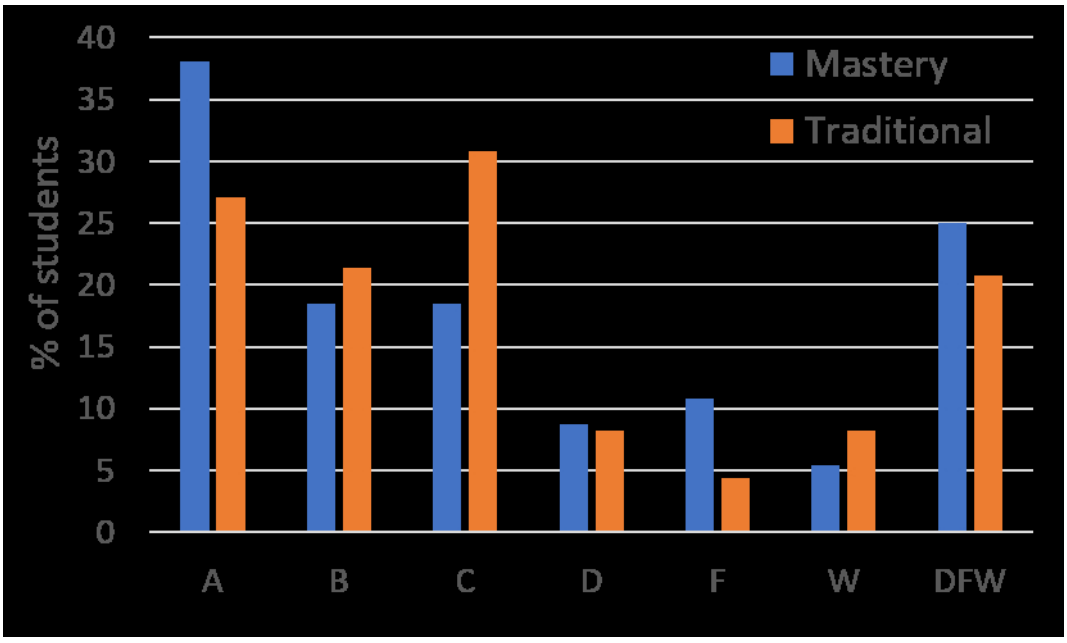
***Alice Deckert**, adeckert@allegheny.edu. Chemistry, Allegheny College, Meadville, Pennsylvania, United States*

In a mastery grading system, grades are based on students' ability to demonstrate mastery of a well-defined list of learning objectives. Typically students have multiple opportunities to meet these objectives and are not penalized for failures on previous attempts. In this talk, I will describe the key components of a mastery grading system, highlighting how such a system supports the student learning cycle, promotes a growth mindset, and reinforces the value of productive failure. I will describe the approach I have taken in both General Chemistry and Physical Chemistry courses and highlight the evolution of my approach based on lessons learned in my first few attempts.

249. Implementation and outcomes of mastery-based grading in general chemistry

***Erin E. Wilson**, wilsonee@westminster.edu. Biochemistry and Chemistry, Westminster College, New Wilmington, Pennsylvania, United States*

General Chemistry is the gateway course into the chemistry curriculum in many chemistry programs. It is vital that students succeed in General Chemistry, and it is equally important that they master the concepts presented in this course to have a solid foundation for subsequent chemistry curriculum. Many students making the transition into undergraduate-level chemistry (and often college) struggle to adjust to the rigorous academic expectations at this level. In a traditionally-graded course, this can translate to poor initial exam scores, and the cumulative nature of the curriculum makes it that much more difficult to recover. In addition, the human learning process is one that involves failures, as in the attempt-feedback-reattempt cycle of learning. Yet traditional exams are a make-or-break, one-time attempt scenario. At Westminster College, Mastery-Based Grading was fully implemented in some sections of the one-semester General Chemistry course starting in the fall of 2017. In this grading model, all work is pass/fail. Students may retake assessments, which are linked to 21 Learning Objectives, as many times as necessary to master the Learning Objective. Likewise, laboratory reports and write-ups may be resubmitted after revisions are made. A student's grade is linked to how many passes are achieved. In this way, failure becomes a normal part of the learning cycle, and students who struggle to master a Learning Objective have grade-based motivation to go back and solidify their understanding before moving to subsequent topics. The evolution of the course over seven semesters will be presented, and outcomes of the Mastery-Based grading sections compared to traditional sections of the same course will be discussed. In particular, there was a strong gender-based effect, with women showing measurable improvement in outcomes and men performing similarly to the traditional sections.



250. Student-centered grading practices and the journey to (mostly) gradeless chemistry labs/lectures

***Courtney J. Sobers**, cj.sobers@rutgers.edu. SASN-Chemistry, Rutgers The State University of New Jersey, Newark, New Jersey, United States*

There are 2 elements to grading: assessment design and evaluation. The “grading” in my courses has been motivated by pedagogical approaches including: peer-to-peer, gamification, POGIL (Process Oriented Guided Inquiry Learning), CURE (Course-based Undergraduate Research Experience), active learning, and most recently, ungrading. For the design element, I have experimented with two-stage exams, escape room final exams, using peer created materials, poster presentations, and practical exams. For evaluation, I have explored peer evaluation, contract grading, summative grading, and for the Spring 21 semester, ungrading. The public discussion around each of these approaches comes with a caveat of primarily being used in small enrollment (40 or fewer students) or humanities/writing intensive classes. I have used them in chemistry lab and lecture classes ranging from 8 to 400+ students. This talk will discuss the reasons for using these grading elements as well as some practical considerations for using them in courses where enrollment is greater than 300 but less than 1,000 students.

251. Bundle up! Using bundled grading in a remote organic chemistry course

***Stephen A. Habay**, sahabay@salisbury.edu. Chemistry, Salisbury University, Middletown, Delaware, United States*

The COVID-19 pandemic has pressed many instructors to adapt their courses for remote or hybrid instruction. It is critical that any course redesign include a feasible plan for grading and assessment. When moving a course to remote instruction, relying on traditional timed exams as valid assessments becomes more problematic because of challenges with equity, technology, and academic integrity. Additionally, assigning grades based on accumulation of points and partial credit does not directly measure if a student has achieved the learning outcomes of the course. The specifications (SPECS) grading method has emerged as an alternative that better reflects achievement of learning outcomes, increases student engagement, reduces student stress, and promotes a growth mindset through cycles of revision and reassessment. Using SPECS grading, final letter grades can be assigned based on “bundles” of assessments successfully completed, rather than points accumulated, that are directly linked to learning outcomes achieved. This talk will describe an organic chemistry course redesign for remote instruction that implemented bundled grading and alternative assessments. Course structure, design and implementation of alternative assessments, course management, and student outcomes and perceptions will be discussed.

252. Techniques for getting students to meet the “specification” in specifications grading

W Christopher Hollinsed*, chollinsed@gmail.com. Department of Chemistry, Howard University College of Arts and Sciences, Washington, District of Columbia, United States*

Students often wait until they take an exam to find out that there are gaps in their learning. When they take the exam, they are often disappointed to discover that there are topics and concepts that they have not studied well enough. Their grade does not reflect their ability to understand the topics and concepts but only the efficacy of their studying for the specific content on the exam. In the past several years, techniques aimed specifically at developing for the students an understanding of what they know and don’t know, as well as how to fill those gaps, so that they will be able to be more prepared for their individual exams have been applied to this problem. Specifications grading is used to set common criteria that they will need to meet in order to be successful.

253. Five year study using specifications grading in an undergraduate chemistry curriculum

Heidi J. Fletcher*, hfletche@waynesburg.edu. Waynesburg University Department of Chemistry, Waynesburg, Pennsylvania, United States*

Specifications (specs) grading is gaining popularity to assess student learning in chemistry by educators and students alike. It helps the learner master essential concepts that are foundational for success while eliminating the possibility of partially learning concepts that will inevitably show up in future courses and challenge the student. Five years ago, our department implemented specs grading into general chemistry II as a pilot study. Since then, almost all courses within the department have implemented, in one form or another, specs grading through assessment quizzes. Students are required to pass assessment quizzes with 88% or higher competency, as it varies from course to course. This study looks at graduating senior students’ feedback for the past two years who have been subjected to taking assessment quizzes for a large portion of their chemistry coursework. The results of this study will help direct the future use of the assessment quizzes used in these courses. Student feedback will be presented and compared between the use and effectiveness of essential skills assessments in: (1) general chemistry to see if students felt they had a foundational understanding in essential core concepts to be successful in future chemistry courses, and (2) advanced chemistry courses to help students master content within the course itself and perform well.

254. Mapping glycoconjugate interactions in native cellular environments

*Eugene Joeh[1], Weichao Li[1], Christopher Parker[2], **Mia Huang**[1], miahuang@scripps.edu. (1) Molecular Medicine, Scripps Florida, Jupiter, Florida, United States (2) Chemistry, Scripps Florida, Jupiter, Florida, United States*

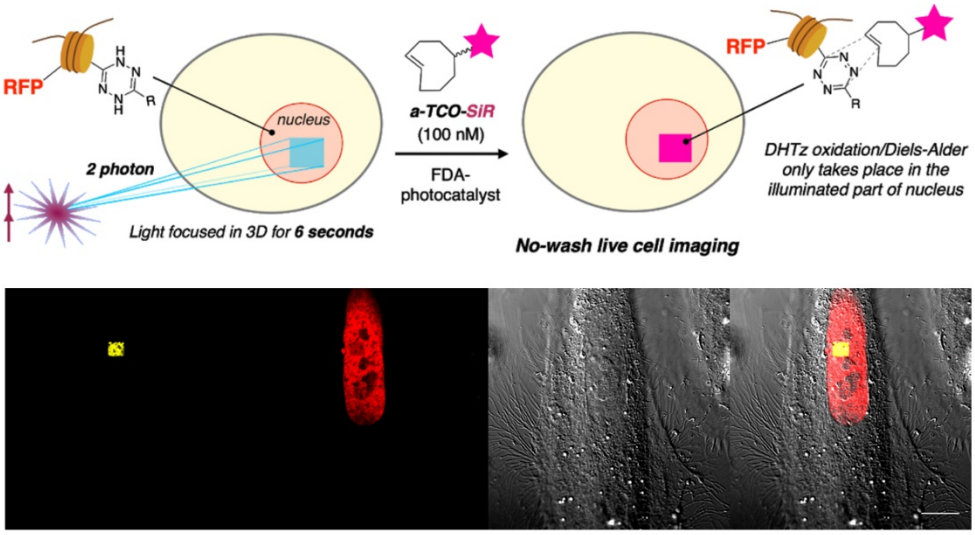
The interactions between glycans and proteins, as well as those between small molecules and glycoproteins are central to many important biological events, yet the structural heterogeneity imparted by glycosylation often precludes their study in live cells. Thus, glycan-protein interactions are typically surveyed in artificially reconstituted formats, devoid of the physiological presentation of ligands. As such, it is challenging to assign the proteins carrying the requisite glycan ligands, and elucidation of the full mechanism of how these interactions orchestrate biological events beyond initial binding analyses is hampered. Here, we will demonstrate that a proximity tagging approach using recombinant fusions of peroxidase enzymes and glycan-binding proteins permits the determination of glycoprotein counter-receptors in live cells. Importantly, this approach has allowed us to decipher the key glycoproteins co-opted by galectin-3 to activate hepatic stellate cells, a crucial step in the progression of liver fibrosis. In a similar vein, we will also describe our efforts to use chemoproteomic approaches to identify proteins that experience changes in small molecule ligandability as a function of glycosylation.

255. Catalytic activation of bioorthogonal chemistry with light (CABL) enables rapid, spatiotemporially-controlled labeling and no-wash, subcellular 3D-patterning in live cells using long wavelength light

***Andrew W. Jemas**, ajemas@gmail.com. Chemistry and biochemistry, University of Delaware, Newark, Delaware, United States*

We report a spatiotemporally controlled labeling and patterning of biomolecules in live cells through the catalytic activation of bioorthogonal chemistry with light, referred to as “CABL”. Here, an inactivated dihydrotetrazine (DHTz) is photocatalytically oxidized in the cellular environment by ambient O_2 to produce a tetrazine ‘on demand’ that immediately participates in *in situ* biorthogonal chemistry with a *trans*-cyclooctene (TCO) dienophile. Previously, CABL was only possible in the extracellular environment. Key to success in live cells was the development of 6-(2-pyridyl)-dihydrotetrazine-3-carboxamides as DHTz reagents that are cell permeable, highly stable in the intracellular environment, and upon oxidation produce the most reactive tetrazines ever used in live cells with Diels-Alder kinetics exceeding k_2 10^6 $M^{-1}s^{-1}$. Photocatalysts for CABL are based on fluorescein or silarhodamine dyes with activation at 488 or 660 nm, respectively. The HaloTag self-labeling platform was used to introduce DHTz tags to proteins localized in the nucleus, mitochondria, actin or cytoplasm in live cells, and CABL in the presence of a TCO-fluorophore was used to demonstrate selective and high yielding activation/labeling on these subcellular targets. Focused light can be used to promote CABL at the subcellular level, and by using fluorescein diacetate and 2-photon excitation it is possible to

selectively pattern subcellular structures in 3D. Cells were imaged live under no-wash conditions enabled by nearly instantaneous labeling at very low concentration (100 nM) of TCO-fluorophore. 2-Photon CABL is light-dose dependent, and subcellular labeling by a TCO-fluorophore can be monitored in live cells with $t_{1/2}$ ~ 3 sec. Beyond spatiotemporally controlled labeling, CABL is also able to improve the efficiency of 'ordinary' tetrazine ligations by rescuing the reactivity of commonly used 3-aryl-6-methyltetrazine reporters that become partially reduced to DHTzs in the intracellular environment. The spatiotemporal control and fast rates of photoactivation and labeling associated with CABL should enable a range of biomolecular labeling applications in living systems.



256. Modified *N*-acetyl muramic acid probes for improved bacterial peptidoglycan metabolic incorporation

***Ashley R. Brown**, arb@udel.edu, Kimberly Wodzanowski, Cintia C. Santiago, Stephen N. Hyland, Julianna L. Follmar, Catherine L. Grimes. Chemistry and Biochemistry, University of Delaware, Newark, Delaware, United States*

Metabolic labeling of the peptidoglycan (PG) of genetically engineered bacteria with *N*-acetyl muramic acid (NAM) probes permits the visualization of the structural details of this dynamic macromolecule as well as the detection of naturally generated fragments implicated in innate immune signaling. In order to improve the uptake and decrease the amount of probe required, we asked if mammalian strategies could be used in the bacterial setting. Here we developed an improved, scalable synthesis of the peptidoglycan building blocks, allowing preparation of immunostimulatory peptidoglycan fragments and masked NAM precursors. The data show that converting the carboxylic acid to a methyl ester, masks the ionic character of probe, allowing for more efficient uptake and utilization

of probe. Interestingly, the data suggest that acetylated NAM probes are not tolerated by bacterial esterases. As a result of the investigation, we were able to reduce the amount of probe by 10-fold. We speculate that bacteria appear to have endogenous esterases capable of converting the methyl ester probe to the accessible acid form utilized by the PG biosynthetic and recycling enzymes. These results will allow for more efficient preparation and labeling of NAM probes for studying bacterial PG and its immunological impact.

257. Development of chemical biology probes for applications in drug discovery

***Christopher Am Ende**, Christopher.amEnde@pfizer.com. Pfizer Inc., Mystic, Connecticut, United States*

Chemical biology tools and techniques have shown immense value in drug discovery. For example, photoaffinity and electrophilic probes can help explore small molecule/protein interactions and have been used for identifying new druggable targets, binding site elucidation and to understand selectivity of lead matter. This presentation will highlight a series of vignettes including the use of clickable photoaffinity probes to find the protein target of a small molecule from a phenotypic screen and analysis of the off-target profiles, as well as the exploration into covalent degraders of protein targets. Additional emphasis on the development of new chemistry to access chemical biology probes and examination into their reactivity will also be discussed.

258. Programmable technologies to retune gene expression at the RNA level

***Krysten Jones**, krysten.jones@gmail.com, Yang Cao, Simone Rauch, Bryan C. Dickinson. Chemistry, The University of Chicago, Chicago, Illinois, United States*

Genome-targeting therapies are revolutionizing the study and treatment of human diseases. After decades of work optimizing gene therapies and “first-wave” programmable nucleases such as zinc fingers, the discovery and characterization of the “Clustered Regularly Interspaced Short Palindromic Repeats” (CRISPR) bacterial defense systems has rapidly accelerated progress in the field. While permanently altering a patient’s DNA is a viable approach in diseases that are monogenic, challenges with safety or efficacy limit the clinical applicability of DNA-targeting therapies. Additionally, the transient nature of many disease states, many of which require coordination of cell repair and recovery processes, renders permanent DNA alterations inappropriate and ineffective. For example, diseases that require subtle alterations to many genes or that involve genes too risky to permanently alter, remain challenging to drug. Targeting information flow at the RNA level overcomes these hurdles through the ability to halt and/or titrate treatment in response to any emergent side effects, target genes that are otherwise too risky to alter at the DNA level, and manipulate gene expression without permanently changing the patient’s genome.

Inspired by CRISPR-Cas, we recently developed CIRTS, as a smaller, human derived moiety that exploits RNA regulatory mechanisms to control the transcriptome. CIRTS relies on guide RNA complementarity to bind a target of interest and deliver a tethered

cargo effector protein that acts on the targeted RNA in a proximity-dependent manner. To expand and diversify CIRTS functionality, we have developed a small molecule-controllable CIRTS for temporal control of RNA regulation and are screening new candidate RNA regulatory systems for improved performance. These efforts are being coupled with the development of delivery strategies for CIRTS for improved RNA targeting of clinically relevant endogenous transcripts.

259. Activity-based proteomics: Target and ligand discovery on a global scale

***Ben F. Cravatt**, cravatt@scripps.edu. The Scripps Research Institute, La Jolla, California, United States*

Advances in DNA sequencing have radically accelerated our understanding of the genetic basis of human disease. However, many of human genes encode proteins that remain uncharacterized and lack selective small-molecule probes. The functional annotation of these proteins should enrich our knowledge of the biochemical pathways that support human physiology and disease, as well as lead to the discovery of new therapeutic targets. To address these problems, we have introduced chemical proteomic technologies that globally profile the functional state of proteins in native biological systems. Prominent among these methods is activity-based protein profiling (ABPP), which utilizes chemical probes to map the activity state of large numbers of proteins in parallel. In this lecture, I will describe the application of ABPP to discover and functionally annotate proteins that contribute to human diseases, such as cancer and autoimmunity. I will also discuss the generation and implementation of advanced ABPP platforms for proteome-wide ligand discovery and how the integration of these global 'ligandability' maps with emergent human genetic information and phenotypic screening can expand the druggable fraction of the human proteome for basic and translational research objectives.

Innovations in Organic Chemistry

260. New methods for the synthesis of tetraarylmethanes

***Arthur J. Catino**, arthur.catino@scranton.edu, Jake D. Selingo, Maria J. Fadelici. Chemistry, University of Scranton, Scranton, Pennsylvania, United States*

Tetraarylmethanes contain four aryl groups (typically phenyl) bonded to a central carbon atom. They are used in a wide range of high-tech materials including OLEDs, organic solar cells, and hydrogen storage devices. Despite their importance, there are only a few methods available for their preparation. Our group has reported a general method to prepare tetraarylmethanes with all-phenyl groups and diverse substitution/electronics using an intramolecular Friedel-Crafts reaction followed by a nickel-mediated desulfurization. Herein, we describe our progress toward developing a second-generation approach that does not require desulfurization, as well as an enantioselective variant to prepare chiral tetraarylmethanes.

261. Deaminative alkyl–alkyl cross-couplings of alkylpyridinium salts and alkenes

***Kristen Baker**, bakekr@udel.edu, Diana Lucas Baca, Shane L. Plunkett, Mitchell E. Daneker, Mary P. Watson. Chemistry & Biochemistry, University of Delaware, Newark, Delaware, United States*

Alkyl amines are inexpensive and widely abundant chemicals in organic synthesis, making them attractive substrates for further functionalization. Functionalization via cleavage of the carbon–nitrogen (C–N) bond has recently been discovered as a powerful transformation of these abundant, easily protected alkyl amines. Due to the prevalence of $C(sp_3)$–$C(sp_3)$ bonds in bioactive molecules, methods to create alkyl–alkyl bonds have become increasingly desirable. By using High-Throughput experimentation interfaced with traditional reaction optimization, we have developed a nickel-catalyzed cross-coupling of alkyl pyridinium salts with an alkyl boron species formed in situ from an alkene. The optimization, scope, and mechanistic understanding of these reactions will be presented.

262. Rapid synthesis of diverse imidazoles through microwave-assisted multicomponent reaction

***Jacqueline A. Smith**[1], jsmith@bowiestate.edu, Madeline Rotella[2], Mayowa Osunsanya[1], Ikechi Nwadike[1], Brenda Tankeu[1], Osvaldo Gutierrez[2]. (1) Bowie State University, Bowie, Maryland, United States (2) University of Maryland at College Park, College Park, Maryland, United States*

The GBB multicomponent reaction is a well-known route to synthesize imidazoles. In this study, the Strecker-like GBB was employed to synthesize a variety of imine substituted imidazoles including 5-aminoimidazoles and 2,5-diaminoimidazoles. When conducted with microwave-assistance, this reaction can become one of the most efficient and facile methods to create 2-, 4- and 5-functionalized imidazoles. Using benzamidine, we have expanded the scope of this reaction by employing various ortho- and para-benzaldehydes. However when guanidine is used an unexpected product was found for some substrates. Other amidines (H, CH_3, CF_3) are unreactive under these conditions. Computational models are used to understand the alternative pathway of the guanidine reaction.

263. Diastereoselective alkynylations of β-(Bromo)iminium ions via Copper(I) catalysis

***Samantha O. Santana**[1], sosantana2012@gmail.com, Weiye Guan[2], Mary P. Watson[3]. (1) Chemistry and Biochemistry, University of Delaware, Newark, Delaware, United States (2) University of Delaware, Newark, Delaware, United States (3) Chemistry & Biochemistry, University of Delaware, Newark, Delaware, United States*

We have developed a diastereoselective copper-catalyzed alkynylation of cyclic β-(bromo)iminium ions, formed in situ from aminals, to deliver trans-difunctionalized products. β-(bromo)aminal substrates are readily prepared via facile bromination of cyclic enamine precursors, allowing an efficient route from dihydropiperidines and

dihydropyrrolidines to highly functionalized heterocycles. Piperidine and pyrrolidine derivatives can be prepared with high diastereoselectivity and good functional group tolerance.

264. Study of the solubility of hypervalent iodine reagents and synthesis of hypervalent iodine reagents with increased solubility in non-polar solvents

Daniel L. Silverio*, dsilverio@adelphi.edu, Ivan D. Hyatt, Vanie Seecharan, Lyse Armand, Jennifer Noorollah, Nirvanie Singh, Andrew Zhang, Kevin Freddo, Nicholas Spatola, Sailesh Prasad, Azka Chaudhry, Su Wint War. Chemistry, Adelphi University, Garden City, New York, United States*

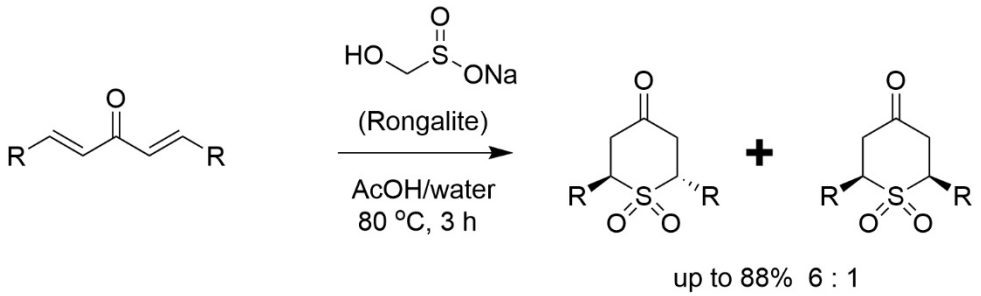
Hypervalent iodine (HVI) reagents are employed in many different reaction types in organic chemistry. Despite the utility of such reagents, the application of HVI reagents, especially phenyliodonium diacetate (PIDA), has been limited due to its perceived poor solubility in a variety of solvents. To address and investigate these limitations, we synthesized HVI reagents where the substituent of the carboxyl group were longer alkyl chains, specifically an *n*-propyl and *n*-nonyl group. The solubility of these reagents, as well as the commonly used PIDA and phenyliodonium bis(trifluoroacetate) (PIFA), were measured in dichloromethane, acetonitrile, diethyl ether, tetrahydrofuran, toluene, and hexanes. The HVI reagents derived from the less polar decanoic acid were more soluble in hexanes and less soluble in acetonitrile than the other reagents. Such differing solubility will allow reactions involving HVI reagents to occur in a wider variety of solvents, empowering chemists to be able to better optimize the solvent in such reactions. Additionally, the measured solubilities of PIDA and PIFA will be useful to the synthetic chemistry community.

265. Withdrawn

266. Cyclic sulfones from double conjugate addition of Rongalite

***Magnus Bebbington**, bebbingtonm@montclair.edu. Department of Chemistry and Biochemistry, Montclair State University, Montclair, New Jersey, United States*

Rongalite™ (sodium hydroxymethanesulfinate) is a commodity bleaching agent prepared from electrochemical reduction of sulfur dioxide. In the synthetic laboratory, it has been used as a low cost, low-odor masked equivalent for the unstable hyposulfite (SO_2^{2-}) ion. Although its first use for organic synthesis was at least 50 years ago, interest in Rongalite has increased sigificantly in the last decade, in the light of the ongoing pursuit of more sustainable chemical processes. We have found that it reacts via double conjugate addition with dienones to give 6 membered cyclic sulfones in good yields, without the need for the preparation of an intermediate sulfide and a subsequent vigorous oxidation. The reaction occurs readily in an open flask. The current scope and stereochemistry of the reaction will be discussed.



267. Practical implementation of predictive retrosynthesis in ReaxysCchemistry database

***Irakli Samkurashvili**[1], i.samkurashvili@elsevier.com, Steven E. Dueball[2]. (1) Life Sciences, Elsevier Inc, New York, New York, United States (2) Elsevier BV, Des Plaines, Illinois, United States*

Synthetic Chemists would embrace a tool which accelerates both new reaction discovery and the synthesis of new molecule. Numerous attempts have been made to develop such tools, generally called Computer Aided Synthesis Planning or CASP, for 40 years. Although the CASP idea has been very attractive conceptually the practical implementation of CASP has been burdened with technical challenges. One of the biggest problems was to define rule set on which predictive algorithm is based. Traditional approach where manually coded rules have been used proved to be less than ideal solution for predictive retrosynthesis. The latest advances in the AI research and the significant increase in computational power contributed in the development of new neural network based algorithms. The combination of these algorithms with the high quality

training datasets seem to produce promising predictive retrosynthesis tools (RT) with very high prediction accuracy. Novel AI based Predictive retrosynthesis engine has been successfully integrated in the Reaxys chemistry database. We will discuss typical examples of how to use Reaxys Synthesis Planner and Retrosynthesis Tool to quickly identify synthesis plans with high degree of accuracy. The discussed scenarios would be very useful for both novice and expert Reaxys users and can give valuable insight how predictive retrosynthesis works. We also briefly discuss benefits and limitations of predictive retrosynthesis tools.

268. Photoredox catalysis for the synthesis of ambiphilic polymers via decarboxylative fluorination

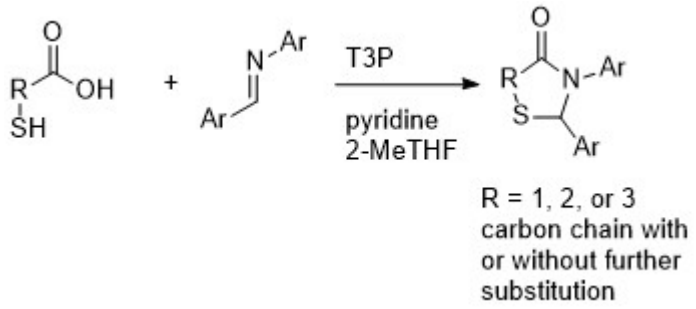
Michael Talley[1]*, mtalley90@gmail.com, Craig Machado*[2]*, Weiye Guan*[1]*, Thomas H. Epps*[2]*, Mary P. Watson*[3]*. (1) Chemistry and Biochemistry, University of Delaware, Newark, Delaware, United States (2) Chemical Engineering, University of Delaware, Newark, Delaware, United States (3) Chemistry & Biochemistry, University of Delaware, Newark, Delaware, United States*

Fluorinated polymers are unique compounds that boast a wide range of utility for their anti-fouling, hydrophobic and chemically resistant properties. However, they are generally synthesized via harsh methods requiring toxic peroxyfluoro reagents, hydrofluoric acid or high-energy conditions like electrical discharge. We've discovered that photoredox catalysis utilized on small molecules can be employed for the decarboxylative fluorination of commercially available poly(acrylic acid) to make ambiphilic poly(acrylic acid)-co-poly(vinyl fluoride). Solvation of all components proved to be critical to fully fluorinate PAA. Additionally, light exposure could be tuned to vary the degree of fluorination to synthesize a library of fluorinated PAA with unique ambiphilic properties. Thus we demonstrate the impact of photoredox catalysis on post-polymerization functionalize for the synthesis of PAA-co-PVF.

269. T3P promoted synthesis of 2,3-diaryl-2,3-dihydro-1,3-thiaza-4-ones

Lee J. Silverberg*, ljsilverberg@verizon.net. Chemistry, Pennsylvania State University, Allentown, Pennsylvania, United States*

Preparation of five, six, and seven-membered *N*-aryl 2,3-dihydro-1,3-thiaza-4-ones is more difficult than the *N*-alkyl compounds. In this presentation it is demonstrated that 2,3-diaryl-2,3-dihydro-1,3-thiaza-4-ones can be easily prepared from thioacids and diarylimines with stoichiometric amounts of T3P as promoter. The reactions work at room temperature using a variety of thioacids and imines.



Nanoparticles: Characterization & Applications

270. Plasmonic electricity: Fluorophore-induced plasmonic current

***Chris D. Geddes**, chrisgeddes72@gmail.com. Suites 3017-3021, Institute of Fluorescence, Baltimore, Maryland, United States*

Fluorophore-induced plasmonic current is generated when an excited fluorophore in close proximity to a metal nanoparticle film non-radiatively transfers energy to the metal, resulting in an induced electrical current across the film. Although a growing literature reports the use of surface plasmons for fluorescence enhancement (Metal-Enhanced Fluorescence) as well as plasmons for current generation, little has been reported *hitherto* regarding the electrical current generation via the fluorophore excitation of plasmons. Our *"plasmon to current"* technique utilizes electron transport between closely spaced metal nanoparticles, generating a measureable electrical signal upon excitation of a proximal fluorophore. This induced electrical signal is found to be strongly dependent on the magnitude of the fluorophore extinction coefficient. In other words the electrical signal contains photophysical information pertaining to the fluorophore, potentially leading to the direct detection of fluorescence without the need for traditional detectors such as photomultiplier tubes and charge coupled devices. Such a realization would have profound implications in optical detection strategies. In addition, we demonstrate the dependence of this current on fluorophore concentration, excitation laser polarization, background solution dielectric, temperature and choice of metal etc. Finally, we will demonstrate the inverse relationship between plasmonic current and metal-enhanced fluorescence generation.
Fluorophore-induced plasmonic current holds significant potential as a novel molecular detection platform with simplified instrumentation, compatible with a variety of fluorescent probes.

271. Visualizing dynamic changes in metal nanoparticle surface chemistry

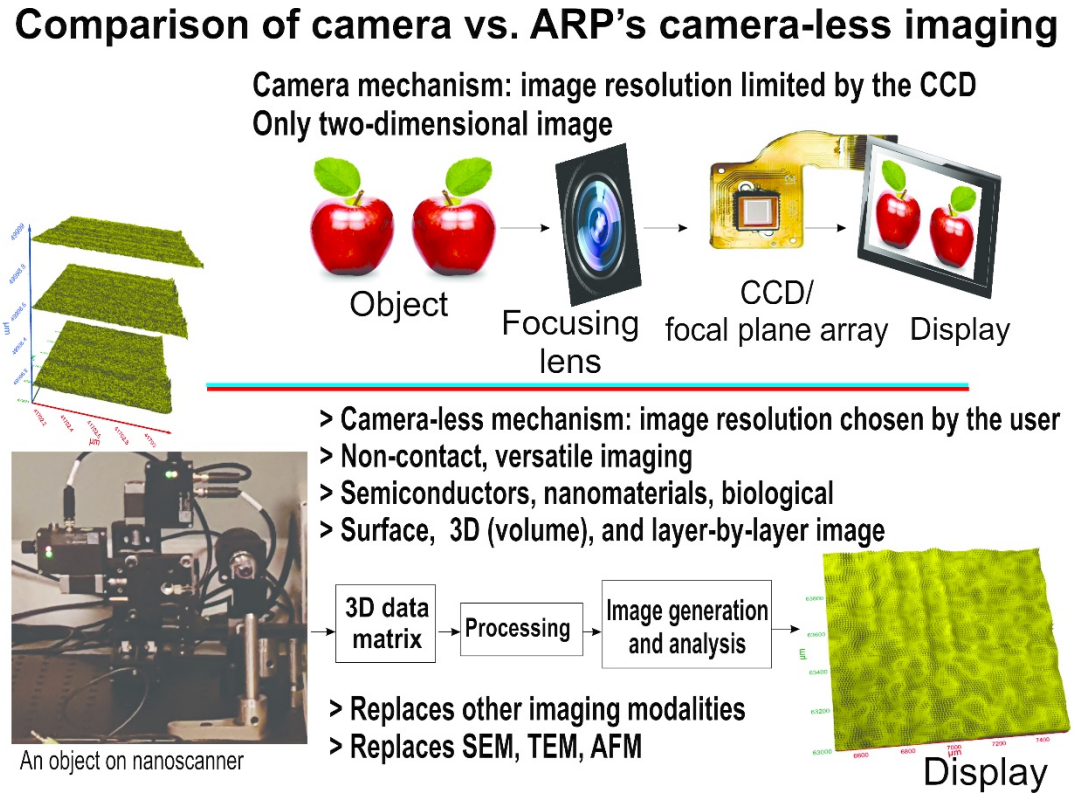
***Katherine A. Willets**, kwillets@temple.edu. Chemistry, Temple University, Philadelphia, Pennsylvania, United States*

Metal nanoparticles are of paramount importance across a multitude of applications, from catalysis to sensing to electrochemistry. Reactions that change the chemistry at the nanoparticle surface can have adverse effects on their function, requiring techniques that can monitor and benchmark nanoparticle performance in situ. This talk will describe how optical microscopy provides a simple platform for characterizing nanoparticle surfaces under both chemical and electrochemical control, allowing us to visualize changes in surface chemistry and monitor reaction kinetics in real time.

272. Terahertz camera-less imaging of semiconductors overcoming the Abbe diffraction limit

***Anis Rahman**, a.rahman@arphotonics.net. Applied Research and Photonics, Harrisburg, Pennsylvania, United States*

This talk will outline a new terahertz technology for camera-less, lattice-resolution imaging of semiconductors, overcoming the Abbe diffraction limt. Main principle of the camera-less imaging modality will be discussed. Examples of practical system will used for illustration in terms of surface images, sub-surface images, volume images, and layer-by-layer images.



Main mechanism and comparison between a camera and camera-less image formation

273. Synthesis and characterization of carbon dots and their application in dye sensitized solar cell (DSSC)

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Due to their small size and high surface-to-volume ratio, nanoparticles turn to have unique physical and chemical properties which make them useful in several applications. Carbon dots (CDOTs), for example, are nanoparticles that are increasingly becoming popular in areas ranging from sensing and bioimaging to electronics. The interesting optical properties of CDOTs make it vital to explore their potential in the development of sustainable energy. In this work, one-step hydrothermally synthesized CDOTs were used as a sensitizing agent in the fabrication of dye-sensitized solar cells. The fabrication of the CDOT-based dye-sensitized solar cell and its performance characteristics are explored in depth. The fabricated dye-sensitized solar cell performance in terms of efficiency, voltage, and the current was evaluated using a standard illumination of air-mass 1.5 global (AM 1.5 G) having an irradiance of 100 mW/cm. The photon-to-current conversion efficiency (η) of only the carbon dot sensitized solar cell was 0.10% whereas the efficiency of the solar cell fabricated with a sensitizing dye made up of CDOT and N719 was 0.19%. As compared with the performance DSSCs fabricated with only 719 dye, it was observed that when CDOT was used in combination with N719 as sensitizing dye, the open-circuit voltage increases yet the overall efficiency of the resulting solar cells decreases. It is clear from the result that CDOT could be used as a sensitizing dye in DSSCs. However, it is not very useful when used in combination with other sensitizing dyes due to energy transfer.

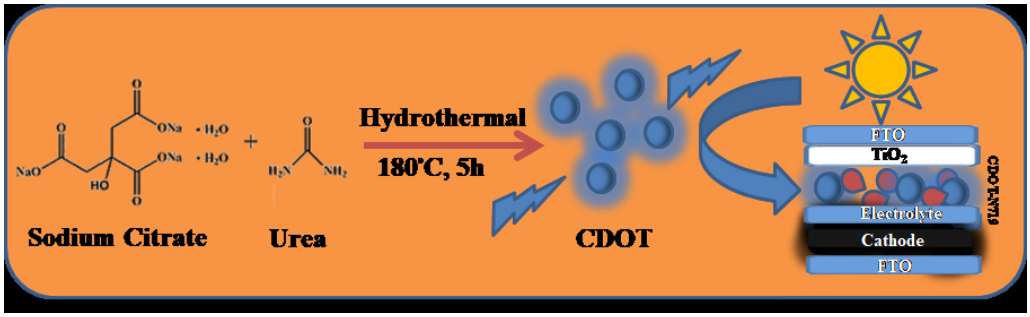

Figure 1. Schematic diagram of the synthesis of CDOT and its use in dye sensitized solar cell

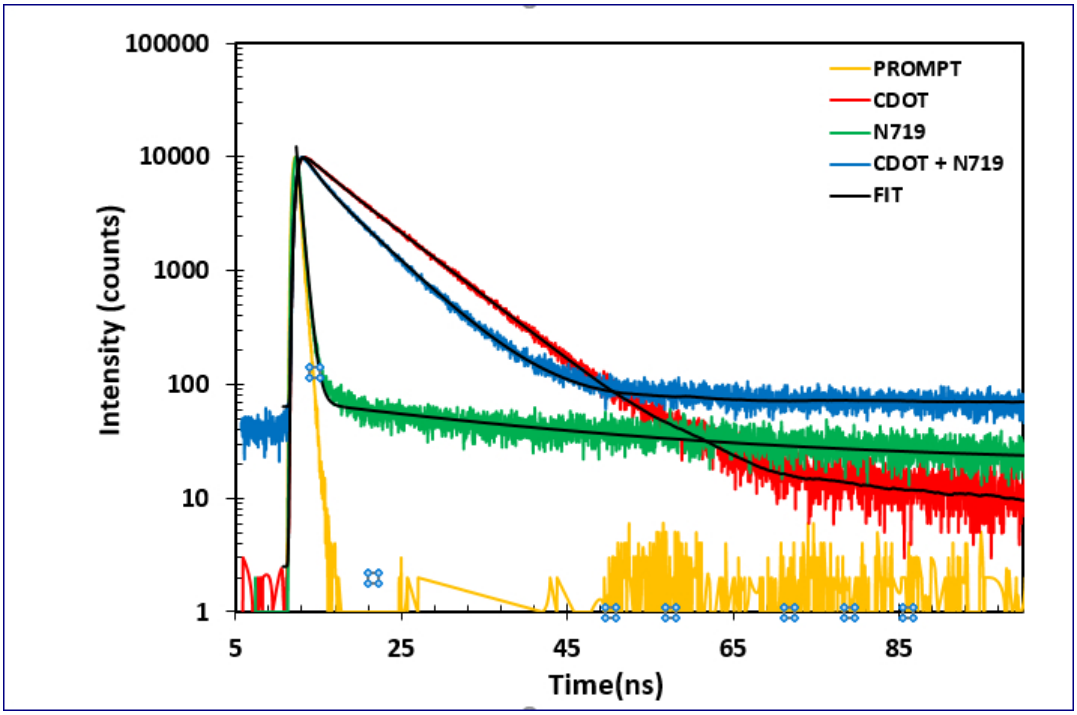

Figure 2. Fluorescence lifetime measurement of CDOT, N719 and CDOT/719

274. Enhanced catalytic activity of nickel nanoparticles explained by bimetallic effect on carbon nanotube formation

Carly Byron[1], *cbyron@udel.edu, Magali S. Ferrandon*[2], *Gokhan Celik*[8], *Rachael McCormick*[1], *Jennifer Sloppy*[3], *Karl S. Booksh*[4], *Massimiliano Delferro*[5], *Chaoying Ni*[6], *Andrew V. Teplyakov*[7]. *(1) Chemistry and Biochemistry, University of Delaware, Newark, Delaware, United States (2) Chemical Sciences and Engineering, Argonne National Laboratory, Lemont, Illinois, United States (3) W. M. Keck Center for Advanced Microscopy and Microanalysis, University of Delaware, Newark, Delaware, United States (6) Materials Science and Engineering, University of Delaware, Newark, Delaware, United States (8) Chemical Engineering, Orta Dogu Teknik Universitesi, Ankara, Turkey*

Supported metal nanoparticles are excellent catalysts for a variety of applications, and nickel deposited on MgO and Al_2O_3 supports has shown to be a promising catalyst for the dry reforming of methane (DRM). Nickel is often paired with another transition metal to enhance surface and catalytic properties and is typically thought to hinder carbon nanotube “whisker” formation. However, the chemical explanation for this effect is often unclear. An in-depth analysis of the coke formation on promoted nickel catalysts may help us better understand the chemistry behind this phenomenon, therefore this work provides microscopic and spectroscopic characterization of the coke formed on various promoted nickel catalysts during the DRM reaction. It was determined that bimetallic promotion of nickel significantly altered the morphology of thewhiskers formed, and that those whiskers

did not affect catalytic activity due to the orientation of the nickel nanoparticle at the whisker tips.

275. Algorithm for soot aggregate restructuring

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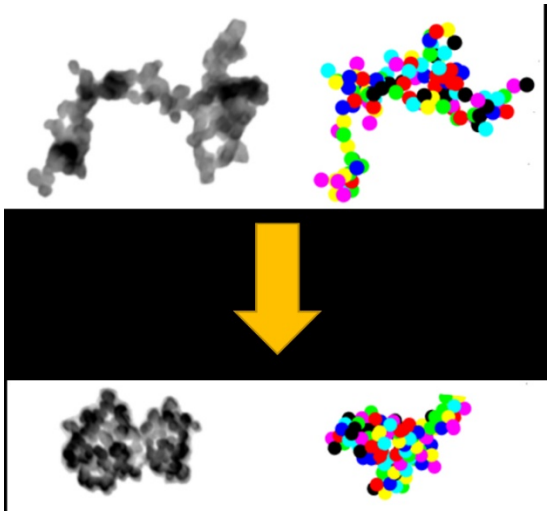
Soot aggregates, derived from the incomplete combustion of fossil fuels and biomass burning, are ubiquitous in the atmosphere and adversely impact air quality and global climate. The fractal-like structure of soot aggregates undergoes significant restructuring due to interaction with condensable trace-gas chemicals during atmospheric aging. This morphological change affects the properties of soot aggregates including their light scattering and absorption, surface chemistry, cloud nucleation efficiency and atmospheric lifetime. In this study, we develop an algorithm to simulate the condensation-induced restructuring of soot aggregates. The restructuring algorithm accounts for adhesion forces between soot monomers, capillary forces due to coating trapped in junctions between monomers, and viscous dissipation forces. We test our restructuring algorithm on an ensemble of initially fractal aggregates and track the morphological evolution of the aggregate backbone. We also compare our predictions of final aggregate morphology against compact aggregates generated directly via traditional Diffusion Limited Cluster Aggregation (DLCA) methods. The results of our findings will provide a framework that facilitates predictions of morphologically dependent soot properties.



Porous Materials

276. Design of functional sites in porous framework materials for energy storage

***V. Sara Thoi**, sarathoi@jhu.edu. Chemistry, Johns Hopkins University, Baltimore, Maryland, United States*

Despite their high theoretical specific energy of 2,600 Wh kg^{-1}, the commercialization of Li-S devices is hindered by irreversible capacity loss from the dissolution of polysulfide intermediates in the electrolyte solution. We report novel strategies to design reactive sites for polysulfide adsorption in metal-organic frameworks (MOFs) to improve capacity retention and ionic conductivity. Incorporation of redox-active moieties in the framework further enable fast charge and discharge capabilities. We will present our efforts in identifying structure-property-function relationships in tunable molecular platforms with the goal of developing chemical strategies that can be translated across electrochemical storage technologies.

277. Adsorption of small molecules in metal-organic frameworks

***Craig M. Brown**[1,2], craig.brown@nist.gov. (1) NIST Center for Neutron Research, Gaithersburg, Maryland, United States (2) Department of Chemical and Biomolecular Engineering, University of Delaware, Newark, Delaware, United States*

Adsorption of molecules in functionalized and high surface area metal-organic frameworks (MOFs) is of emergent technological importance in a multitude of areas ranging from chemical separations to energy storage. We have been studying the properties of MOFs and other porous materials for storage and separations of industrially important small molecules such as hydrogen, oxygen, carbon dioxide, noble gases, and short chain organics. Besides the geometrical and porosity control available in MOF chemistry, the properties of the frameworks can be tweaked to elevate electrostatic interactions by exposing open metal cation sites or through enhanced van der Waals contacts via functionalizing ligands and introducing flexibility. Here, we discuss the information accessible from neutron and X-ray scattering experiments on a selection of nominally rigid MOFs. The results illustrate the governing characteristics of these material properties and the interactions with the guest molecules.

278. Perspective on novel porous materials scale-up: Practical challenges in manufacturing and commercialization

***Matthew Kapelewski**, mtk180@gmail.com. Process Technology Department, ExxonMobil Research and Engineering Company Annandale, Annandale, New Jersey, United States*

Moving novel porous materials from conceptualization and discovery to manufacturing is a challenging aspect to any research program. Many important considerations drive the scale-up of materials including raw materials sourcing, equipment availability, cost, and environmental and safety regulations, among others. Thus, the scale-up of new materials

has many challenges beyond technical feasibility that ultimately determine the manufacturing and commercial viability of a given material. Translation of bench- and even pilot-scale experiments to commercial scale is quite challenging and requires significant effort to ensure product quality and cost-efficiency. Additionally, controlling emissions and properly disposing of waste is also crucial to the overall process, and many of the equipment and materials choices will dictate how this proceeds. This presentation will outline some of these challenges and give perspective on the requirements of moving novel porous materials to scale-up and commercialization.

279. Tunable Metal-Organic Framework (MOF) nanoparticles as inhaled drug delivery vehicles

*Zachary Stillman[2], Bader Jarai[2], Gerald Decker[1], Lucas Attia[2], Eric D. Bloch[1], **Catherine Fromen**[2], cfromen@udel.edu. (1) Chemistry & Biochemistry, University of Delaware, Newark, Delaware, United States (2) Chemical Engineering, University of Delaware, Newark, Delaware, United States*

Metal-organic frameworks (MOFs), in particular MOF nanoparticles (NPs), have recently been used in drug delivery applications because of their flexibility in design, though they have seldom been adapted as inhalable therapeutics. In collaboration with the Bloch group at University of Delaware, we have begun to evaluate of a range of MOF NPs for aerosol drug delivery applications. We have synthesized a suite of UiO-66, a Zr-based MOF with terephthalic acid ligands, of constant NP size (100 nm) and varying missing linker defectiveness (extent of missing terephthalic acid linkers from 0% to 20%). Through this synthetic handle tuning defectiveness, we have evaluated the role of NP porosity on diffusivity through various fluid media. UiO-66 NPs showed promising results for pulmonary administration, having aerodynamic diameters between 1 and 1.5 micron as a dry powder formulation with high cargo loading capacities of up to 0.2 mg cargo/mg UiO-66. We find UiO-66 NPs are biocompatible both *in vitro* and *in vivo* experiments, with no acute airway inflammation observed 24-hrs after orotracheal administration and rapid Zr clearance completed by 1 week in a murine model. Uniquely, UiO-66 NPs selectively release cargo in environments mimicking intracellular pH, while retaining cargo in extracellular pH environments, promoting tunable cargo release. Accordingly, we believe that UiO-66, and potentially other MOF NPs, show great promise for use in pulmonary administration, and are continuing our evaluation of other MOF NPs for a wide range of pulmonary inhalation applications.

280. Microporous nanocomposite emulsion thermosets for multi-material, multifunctional porous composites

***Yogin K. Patel**, ykp11@scarletmail.rutgers.edu, Jonathan Singer. Mechanical and Aerospace Engineering, Rutgers The State University of New Jersey, New Brunswick, New Jersey, United States*

Multifunctionality can be achieved by responsive materials sensitive to stimuli such as temperature, stress, and light, shape memory materials, or architectures with structurally

programmed function, among other methods. However, integrating different functions in one material system in a desired macroscopic form is a fundamental challenge, especially if those functions seem to exclude each other. We have developed microporous nanocomposite emulsion thermosets (MiNET), a new class of composite resins made from epoxies and nanoparticles, a liquid porogen, and a small quantity of surfactant. These ingredients form an intermediate between a conventional surfactant a Pickering emulsion to create a bicontinuous network of oil and epoxy composite throughout the processing. After a room temperature cure and usage of different functional nanoparticles, based on the performance requirements of a given application, it is possible to design a composite with a range of functionality like flexibility, inertness and conductivity. Further extraction of the oil phase through rinsing, MiNETs can be converted into porous (30~60% open volume) structures without considerable volume shrinkage (~1~5%). The pore size (between 100~10,000 nm) and chemical functionality of the pores is tunable by the constituent nanoparticles, allowing for, for example, hydrophilic or hydrophobic pore surfaces, high thermal or electrical conductivity, piezoelectricity, or the incorporation of antimicrobial particles. Simultaneously, the matrix resin can change mechanical properties and use of silicone nanoparticles as a filler can establish flexible behavior. The molding of these novel thermosets enables new form factors, such as injectable filters or parallel-processed electrospray emitters. Through the use of silicone and photolithographic templates, we have employed this property to create structures from the centimeter to micrometer scale that possess interconnected pore networks through the entire component and even, through fusing, multiple characteristic pore sizes. This approach is potentially an arbitrarily scalable means of rapid micro/nanomanufacturing of a materials-agnostic functional materials.

281. Kinetic and deactivation mechanisms of isostructural MIL-101 for organic small-molecule oxidations

*Rachel Yang, **Michele L. Sarazen**, msarazen@princeton.edu. Chemical and Biologial Engineering, Princeton University, Princeton, New Jersey, United States*

Metal-organic frameworks (MOFs) are a class of crystalline solids that exhibit promising activity for diverse applications, owing to the high modularity of their building blocks; metal nodes and organic ligands can form unique porous structures with tailored physiochemical properties. We focus on a thermochemically tenable class of MOFs, metal-terephthalate MIL-101, for styrene oxidation by hydrogen peroxide, a probe reaction for liquid-phase aryl oxidative chemistries utilizing green oxidants. Specifically, we elucidate the effects of metal identity on intrinsic reactivity and stability between isostructural Cr and Fe MIL-101 that serve as heterogeneous analogs for conventional molecular transition-metal organometallics that encounter sustainability challenges in catalyst recovery and reuse. Pseudo-first order rate constants for styrene consumption, normalized by total metal loading, are an order of magnitude higher for MIL-101(Fe) compared to MIL-101(Cr) at 323 K. These rate constants are kinetic in nature, with calculated Weisz-Prater numbers less than 0.1. Oxygenate product distributions also depend on metal identity, as Cr is more pathway selective, preferring epoxide (styrene oxide) formation over aldehyde

(benzaldehyde) formation at the α-carbon to the aromatic ring. Subsequent recyclability experiments show decreased styrene conversions with each cycle over both catalysts. However, consistent oxygenate production rates across cycles for MIL-101(Fe) indicate that conversion decreases are due to solid losses from reactivation procedures. Additionally, MIL-101(Fe) sites are more regenerable, as probed by UV-Vis and FT-IR. Decreases in styrene conversion on MIL-101(Cr) accompanied by increased production rates and different product distributions suggest a change in active site or mechanism. The presence of solvated Cr(III) complexes was observed via UV-Vis, indicating that chromium leaching dominates cycling inefficiencies. Overall, these observations elucidate relevant reversible and irreversible physicochemical changes that impact observed MIL-101(Fe) and MIL-101(Cr) reactivity and stability, which can be applied to conversion of other hydrocarbons and oxygenates to value-added products.

282. Stimuli-responsive 2D metal-organic frameworks prepared by chemical vapor deposition

Thomas J. Kempa[1,2]*, tkempa@jhu.edu. (1) Chemistry, Johns Hopkins University, Baltimore, Maryland, United States (2) Materials Science and Engineering, Johns Hopkins University, Baltimore, Maryland, United States*

The incorporation of metal organic frameworks into advanced devices remains a desirable goal, but progress is hindered by difficulties in preparing high quality, multifunctional metal-organic framework (MOF) films with suitable electronic performance. We demonstrate the direct growth of large-area, high quality, and phase pure single MOF crystals through chemical vapor deposition of a dimolybdenum paddlewheel precursor, $Mo_2(INA)_4$. These exceptionally uniform crystals cover areas up to 8600 μm^2 and can be grown down to thicknesses of 30 nm. Scanning tunneling microscopy indicates that the $Mo_2(INA)_4$ clusters assemble into a two-dimensional, single-layer framework. Devices fabricated from single vapor-phase grown crystals exhibit reversible nearly 10-fold changes in conductivity upon illumination at modest powers. Moreover, we identify vapor-induced single crystal transitions that are reversible and responsible for 30-fold changes in conductivity of the MOF as monitored by *in situ* device measurements. Gas-phase methods, including chemical vapor deposition, show broader promise for the preparation of multifunctional molecular frameworks, and may enable the integration of these materials into devices, including detectors and actuators.

283. Beyond nanostructured supports: Maximizing catalytic centers in metal-organic frameworks

Amanda J. Morris*, ajmorris@vt.edu. Chemistry, Virginia Tech, Blacksburg, Virginia, United States*

Metal-organic frameworks, composed of inorganic nodes and multi-dentate organic linkers, assemble into the highest surface area molecular scaffolds (and materials) currently known. In catalysis, we can exploit that surface area to potentially produce the highest geometric turnover frequencies. In the Morris group, we have explored

epoxidation chemistry, water oxidation, and chemical warfare agent degradation chemistries. In this paper, we will explore the lessons learned from these fundamental studies, including the dual-nature of MOFs, mass transport and diffusion limitations, the mechanism of electron transport, and the ability for post-synthetic modification to manipulate mechanistic pathways.

284. Metal-organic frameworks at the interface of medicinal and materials chemistry

*Mary Zick[2], Ruth Mandel[2], Faith Chen[2], Joshua Woods[2], Jung-Hoon Lee[3], Miguel Gonzalez[4], Ever Velasquez[1], Adam Uliana[1], Jesse Hsu[2], José Fuentes-Rivera[2], Jeffrey R. Long[6], Justin J. Wilson[5], **Phillip J. Milner**[2], pjm347@cornell.edu. (1) Chemistry, UC Berkeley, Albany, California, United States (2) Chemistry and Chemical Biology, Cornell University, Ithaca, New York, United States (3) Korea Institute of Science and Technology, Seongbuk-gu, Seoul, Korea (the Republic of) (4) Harvard University, Cambridge, Massachusetts, United States (6) University of California, Berkeley, Oakland, California, United States*

Metal-organic frameworks (MOFs) are an exciting class of porous, crystalline materials that are constructed from organic linkers and inorganic nodes. Owing to their tunability and well-defined structures, MOFs are promising next-generation materials for a range of industrial applications, including chemical separations, gas storage, and catalysis. However, their applications in synthetic organic and medicinal chemistry remain comparatively underdeveloped. Here, we will discuss new strategies to leverage the tunability of MOFs to enable the synthesis, purification, and delivery of biologically-active molecules. We will discuss how MOFs enable the separations of fluorinated compounds, which are critical to the pharmaceutical industry because approximately 30% of small molecule therapeutics contain a C-F bond. In addition, we will discuss the utility of MOFs for delivering biologically-active hydrogen sulfide, which has untapped therapeutic potential for treating diseases involving oxidative damage, under physiological conditions. In both cases, we will discuss how the molecular-level interactions of biologically-active molecules enables their separation or delivery under relevant conditions.

Plenary: LaShanda Korley

285. Manipulating hierarchy, mechanics, and function in polyurea-peptide hybrids

***LaShanda Korley**, lkorley@udel.edu. University of Delaware, Newark, Delaware, United States*

Inspired by natural materials, we have designed a series of polymer-peptide polyurethane/ureas to explore the hierarchical arrangement critical to energy absorption and mechanical enhancement. We have developed chain-extended and non-chain extended peptide-polyurea hybrids with tunable secondary structure, modulating extensibility, toughness, and stiffness. The sheet-dominant hybrid materials were typically tougher and more elastic due to intermolecular H-bonding, while the helical-prevalent systems generally exhibited higher modulus. We have also explored the impact of a molecular design strategy that overlays a covalent and physically crosslinked architecture in these hybrids, demonstrating that physical constraints in the network hybrids influences hydrogen bonding and morphology. Additionally, tailored physical associations within the soft and hard phases were engineered as a function of peptide content, leading to a rheological response dictated by block ordering and highlighting their potential as structural and injectable hydrogels. Recently, we utilized these hybrids to design thermoresponsive shape memory elastomers with shape fixity and shape recovery tuned by secondary structure. New efforts in water-responsive systems with adaptable mechanics and shape memory behavior are underway via the incorporation of nanofillers.

Dimensionality in Nanoscale Materials

286. Insights into reaction intermediates to predict synthetic pathways for shape-controlled copper nanocrystals

***Raffaella Buonsanti**, raffaella.buonsanti@epfl.ch. Chemical Sciences and Engineering, Ecole Polytechnique Federale de Lausanne, Lausanne, VD, Switzerland*

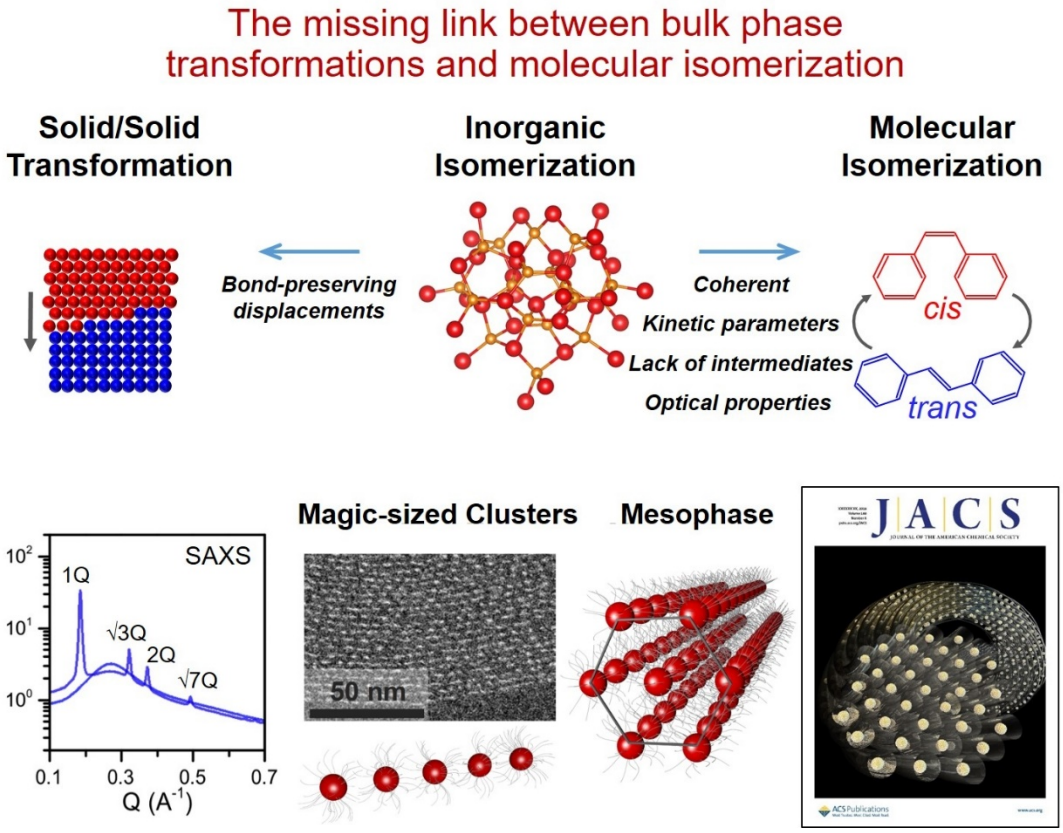
In this talk, I will present our recent group efforts towards the synthesis via colloidal chemistry of atomically defined copper nanocrystals (NCs) and their use as CO_2RR catalysts.
First of all, I will focus on our studies aimed at advancing the knowledge on the formation mechanisms of such Cu NCs, which is quite limited compared to the one acquired by the community for Au, Ag and other noble metals. I will present our integrated approach, which include *in-situ* X-ray absorption and scattering spectroscopy , along with *ex-situ* techniques (mass spectroscopy, NMR, electron microscopy), to identify reaction intermediates and then correlated their conversion kinetics to the subsequent nucleation and growth mechanisms of the Cu NCs.
I will then briefly illustrate how these NCs with precisely tunable shapes and sizes can

help to identify selectivity rules at the branching nodes which lead to C_1 and C_{2+} reduction products in CO2RR.

287. Chemically reversible isomerization in magic-sized clusters

***Richard D. Robinson**, rdr82@cornell.edu. MSE Department, Cornell University, Ithaca, New York, United States*

Structural transformations are ubiquitous at all length scales in chemistry, spanning from isomerization reactions of small molecules to solid-solid transformations in bulk crystals. Despite attempts to merge understanding of these disparate regimes by reducing domain size in solids to nanocrystalline dimensions, bulk-like solid-solid transformation behavior still predominates at length scales approaching those of molecules. In-between small molecules and nanocrystals, magic-sized clusters (MSCs) provide an advantageous experimental platform to study isomerization in well-defined atomically precise systems. Here we show here that a reversible transformation between CdS cluster isomers with distinct stable configurations possesses essential characteristics of both solid-solid transformations and molecular isomerization reactions. These isomers, termed α- and β-$(Cd_2S)_x$, interconvert (α-to-β/β-to-α) reversibly, as identified by a 140 meV shift in the species' excitonic energy gap, that is, the absorption edge and peak emission wavelength is precisely tunable and reversible. A characteristic displacive reconfiguration of the inorganic core (solid-solid transformation), as evidenced by our reconstruction of the atomic pair distribution function from x-ray scattering, accompanies the change in electronic structures. The first order kinetics of the transformation—indicative of molecular isomerization—are driven by a distortion of the ligand binding motifs due to the presence of hydroxyl species in the ligand shell. Chemical control over the surface energy boundary conditions *via* adsorbates appears to be the exclusive determinant of "phase" stability in this system. The reversible transformation of MSCs reported here presents the missing bridge between molecular isomerization and solid-solid transformations. The ability to dynamically tune light emission through controlled structural transformations holds promise in both fundamental research and device application areas.



288. Laser-made nanocatalysts with controlled properties

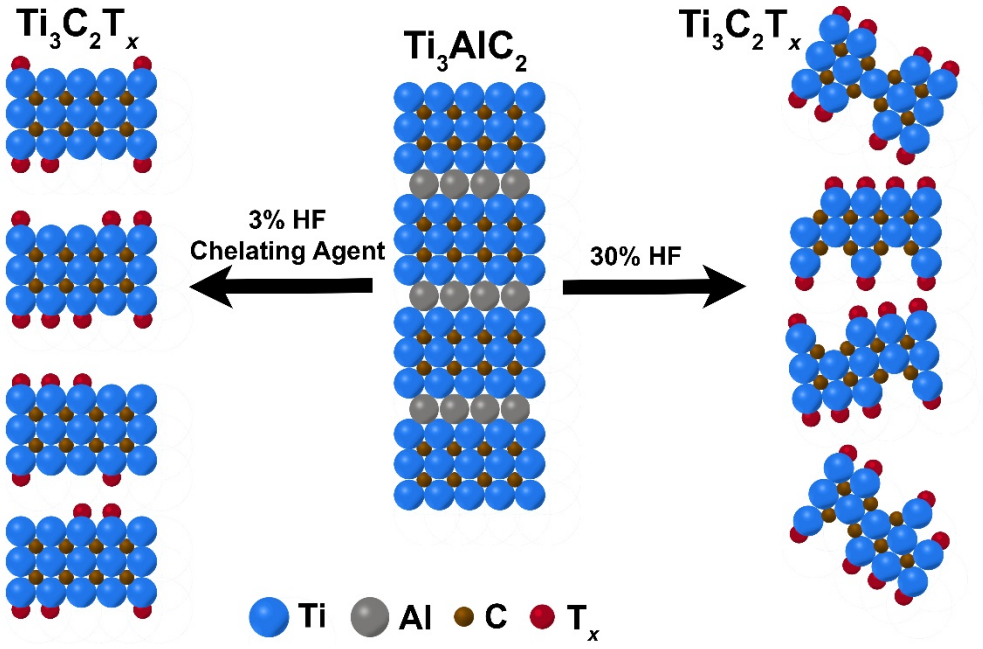
***Astrid M. Müller**, astrid.mueller@rochester.edu. Department of Chemical Engineering, University of Rochester, Rochester, New York, United States*

New synthetic approaches to make tailored nanomaterials with precisely controlled properties are much sought after. Development of new functional multicomponent nanomaterials requires a time-effective, controlled synthesis technique. Pulsed laser in liquids synthesis offers versatility, tunability, rapidity, control of size, composition, and crystallinity, unnecessity of surfactants, and ease of preparation of multimetal nanostructures. It permits the preparation of nanomaterials with precisely and independently controlled properties. Additionally, uniform metastable nanomaterials are accessible via optical and chemical control. Metastable materials are kinetically trapped phases or compositions with higher free energy than the thermodynamic equilibrium state; they have been shown to possess superior catalytic properties compared to equilibrium materials. The pulsed laser in liquids method provides sufficient energy and rapid cooling to synthesize uniform metastable nanomaterials, which cannot be obtained by conventional chemical routes.

289. Chelating agents in tandem with minimal concentrations of HF as an alternative method to produce highly crystalline MXene $Ti_3C_2T_x$ nanostructures

Luis R. De Jesus, *luisdejesus7@gmail.com, Thomas E. Mallouk. Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania, United States*

MXenes are a unique class of 2D layered materials with general formula $M_{n+1}X_nT_x$ (n=1–3) with proposed application as supercapacitors, Li-ion batteries electrode, and as a field effect transistor. These structures are derived from a parent MAX phase where the A layer (an element from groups 13–16) is removed by washing with an appropriate etching solution (most commonly used etching solution is 30% HF). MXene phases are comprised of an early transition metal M; *X* is carbon and/or nitrogen; and T_x stands for the surface termination (-F, -O, and/or -OH; attached by the etching process of the parent MAX phase). The electronic structure and crystallinity of the canonical MXene $Ti_3C_2T_x$ is strongly correlated to the nature of the surface composition and the number of layers which in turn depend on the etching and exfoliation processes. Herein, we demonstrate that the use of chelating agents in tandem with low concentrations of HF serves as an effective method to selectively etch aluminum whilst retaining high crystallinity of the sample. Additionally, the low concentrations of HF allow for the increased concentration of Ti-O and Ti-OH terminal groups. Since the Ti-O and Ti-OH termination on the basal plane surfaces resembles that of early transition metal oxides that bind strongly to late transition metal ions, crystalline $Ti_3C_2T_x$ serves as excellent support for the growth of late transition-metal oxides nanoparticles.



Schematic depiction of the production of MXene nanostructures with the use of minimal concentration of HF with chelating agent in comparison to high concentration HF

290. Design and synthesis of colloidal quantum dot nanostructures for photon upconversion

***Tory Welsch**, twelsch@udel.edu, Jill Cleveland, Matthew Doty. Materials Science and Engineering, University of Delaware, Newark, Delaware, United States*

Photon upconversion is a process by which two or more low-energy photons are absorbed and one higher-energy photon is emitted by a material. Materials that can achieve photon upconversion are desirable for many applications such as optoelectronic devices, drug delivery, and photovoltaics. A key advantage of using semiconductor nanoparticles for photon upconversion is their wide tunability in structure, which consequently affects their absorption and emission properties. We have synthesized colloidal quantum dot (QD) heterostructures for this purpose, in which two QDs with different bandgaps are separated by a wide-bandgap nanorod. While our CdSe(Te)/CdS/CdSe core/rod/emitter structures demonstrate near-infrared (NIR)-to-visible photon upconversion, their upconversion efficiencies show significant room for improvement. The performance of these structures can be enhanced through a better understanding of their underlying properties and the effects of these properties on upconversion efficiency while considering the constraints of available synthesis techniques. Synthesis parameters such as ion precursors, organic ligands, reaction time, and temperature, among others, can be tuned within well-studied procedures to create structures with the desired composition, structure, and resulting optical behavior. For example, introducing a bandgap gradient along the nanorod through doping has been found to funnel carriers to the emitter, increasing both quantum yield and upconversion efficiency. We have also found that charge carrier separation can be improved by controlling the position of the core along the rod and by optimizing the length of the rod. This has led us to explore spherical CdTe/CdS/CdSe core/shell/shell structures with varying shell thicknesses and gradients to further tune absorption and emission wavelengths. We present these synthesis methods and the resulting structures characterized by TEM, absorbance, and photoluminescence measurements. We describe how upconversion performance can be further enhanced through improved structural control, which will allow for future incorporation into various photonic device applications.

291. Energy-based applications of multi-functional nanoscale systems

***Stanislaus S. Wong**, stanislaus.wong@stonybrook.edu. SUNY Stony Brook, Stony Brook, New York, United States*

Our group is fundamentally interested in the design of a series of novel multi-functional nanoscale systems, using diverse chemical strategies. Such a multi-functional material often possesses unique catalytic and optoelectronic properties that are distinctive from and at times, superior to those of its individual constituent components. In essence, our hope and expectation is that chemical synthesis can be used to tune and tailor structure – property correlations. In this presentation, we focus on the applications of fundamental chemical principles with respect to the synthesis of metal-containing and metal-oxide-containing nanostructures. In particular, we describe advances in the use of

complementary, sustainable, and cost-effective solution-based methodologies that allow us to generate functional nanomaterials with high quality, purity, and crystallinity, in addition to control over size and shape. We have created a number of different architectures for gaining valuable insights into solar, fuel cell, and battery applications.

Diversity in Polymer Chemistry and Engineering

292. Merging organic synthetic and polymer chemistry: Toward accelerated catalysis and architecturally-diverse Sp^3-enriched polymers

***Elizabeth Elacqua**, eze31@psu.edu. The Pennsylvania State University, University Park, Pennsylvania, United States*

Efforts to develop synthetic methods that achieve robust materials (e.g., sequenced organic electronics, polymerizable renewable feedstocks, and/or sustainable cooperative catalysis) have generated a need to engineer strategies that merge organic synthesis and polymer chemistry to address grand challenges. This talk will detail our group's recent efforts at this interdisciplinary interface. We will first discuss our homogeneous polymer catalysts that are visible-light activated and feature significant rate acceleration in cooperative organic photoredox catalysis, ascribed to more efficient single-electron transfer. Our approach deviates from conventional methods, and tackles diffusion-limited cooperative catalysis, while enabling enhanced reactivity under polymer confinement. Second, we will disclose the synthesis of sp^3-hybridized 1D carbon-based polymers from simple petroleum-based or biomass-derived sp^2 feedstocks under pressure. In these studies, we have uncovered new robust materials from abundant aromatics (e.g., furan, phenol, pentafluorophenol) that are theorized to possess high tensile strength and chemical versatility.

293. Two-dimensional perovskites with bifunctional ligands yield efficient and stable solar cells

***Melissa Ball**[1], mlball@princeton.edu, Xiaoming Zhao[2], Arvin Kakekhani[3], Tianran Liu[2], Andrew M. Rappe[3], Yueh-Lin Loo[1,2]. (1) Andlinger Center for Energy & the Environment, Princeton University, Princeton, New Jersey, United States (2) Chemical & Biological Engineering, Princeton University, Princeton, New Jersey, United States (3) Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania, United States*

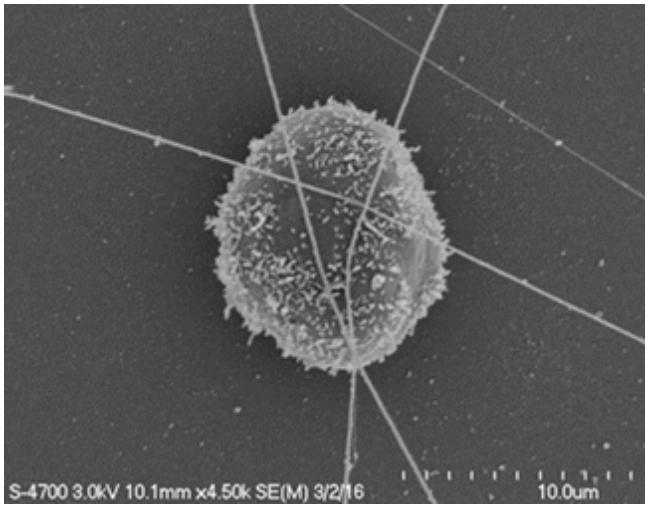
Organometal halide perovskites efficiently absorb light and generate electricity, with solar cells that comprise them possessing power conversion efficiencies now exceeding 25%. However, halide perovskites decompose when exposed to light, heat, or moisture, making them unsuitable for solar cells. Two-dimensional perovskites with organic ammonium spacer ligands are environmentally stable, but the power conversion efficiencies of solar cells that contain 2D perovskites as the active layer are low, reflecting inefficient charge transport. As the interactions between organic ligands and the perovskite octahedra affect

the octahedral tilts, directly affecting charge transport, there is an opportunity for a comprehensive molecular design strategy to manipulate organic-inorganic interactions, control octahedral tilting, enhance charge transfer, and impact device performance. In this talk, I will discuss our approach to molecular design. In particular, I will elucidate the role of the organic cation in controlling macroscopic properties. This design paradigm can guide future innovations in solution processable perovskite optoelectronics, with the goal of creating both high performing and stable next generation solar cells.

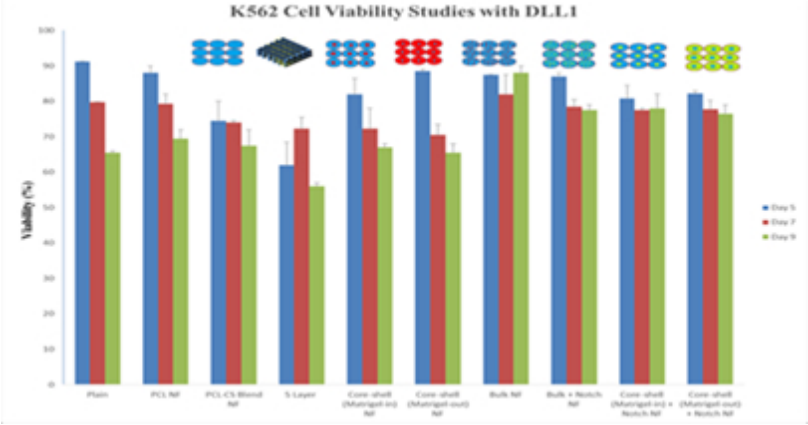
294. Polymeric nanofiber scaffolds as an ex-vivo method for CD34+ Hematopoietic Progenitor Stem Ccell (HPSC) growth and expansion

Cherese Winstead Casson*, cwinstead@desu.edu, Lewis Lott. Chemistry, Delaware State University, Dover, Delaware, United States*

Current treatment of Sickle Cell Disease (SCD) involves either a bone marrow or a stem cell transplant. The issues involved with bone marrow transplants, such as graft failure or difficulty in donor matching, suggest that stem cell transplants may be a more effective treatment approach. This work presents an ex-vivo approach for expansion of progenitor cells in the treatment of SCD. Polymeric nanofiber scaffolds incorporating Matrigel® and Notch-ligand have been developed to support CD34+ hematopoietic progenitor stem cell (HPC) growth and expansion. These nanofiber scaffolds were constructed using a 15% poly (ε-caprolactone) (PCL)-8% chitosan (CS) blend. Various nanofiber constructs were fabricated consisting of bulk and core shell orientations. FTIR was used to confirm the chemical composition of the scaffolds with characteristic bands attributed to chitosan and PCL, respectively. XRD analysis showed the formation of a semi-crystalline construct, with diffraction peaks corresponding to both PCL and chitosan occurring at 21.4, 23.7, and 38.5° 2θ. The surface morphologies of the scaffolds were studied using SEM, TEM, and CLSM and it was observed that the fibers are aligned, uniform, and measure between 100-400 nm in diameter. Cell viability studies show that the addition of Notch-ligand and matrigel into the nanofiber scaffold has a positive effect on cell survival rates (>90%). Preliminary findings show that the developed PCL-CS scaffolds show promise as successful substrates for enrichment and expansion of CD34+ hematopoietic stem cells.



CD34+ HPSC growth on polycaprolactone/chitosan (PCL/CS) blend nanofibers



295. Responsive polymer nanocomposites

***Shu Yang**, shuyang@seas.upenn.edu. University of Pennsylvania, Philadelphia, Pennsylvania, United States*

Stimulus-responsive polymers are of interests for a wide range of applications, including adhesives, biomedical devices, soft robotics, and smart wearables. The responses can be tuned by the materials chemistry, composition, intrinsic anisotropy, geometry, form (e.g. fibers vs. films), and the type of external stimulus; the direction and magnitude of the responses can be varied by geometric design and incorporation of functional nanofillers. Here, I will discuss different types of polymer nanocomposites and their applications as soft yet forceful actuators, color displays, and smart wearables. I will highlight the geometric designs, scalable manufacturing, and strategies to embed intelligence such that the nanocomposites can response to light (UV and IR), temperatures, and electrical fields.

296. Precision polyolefins and the circular economy

***Kathryn Beers**, beers@nist.gov. Materials Science and Engineering Division, NIST, Bethesda, Maryland, United States*

Radical change is coming to the plastics industry. Economic and environmental factors are challenging our approach to the entire supply chain. Polyolefins (predominantly polyethylene and polypropylene) represent the largest fraction of the market impacted by these changes. This talk will present several key efforts at NIST to facilitate change and help address some of the challenges, including economic and manufacturing support activities, support for accurate measurements of environmental impacts and fundamental polymer science. On the fundamental side, we study relationships between structure and properties though precision design of molecular structure, measurement of intrinsic properties (such as viscosity) and co-development of molecular dynamics simulations, training against experimental data sets, to improve transferability of calculations to physical (manufacturable) molecules. The primary dataset is obtained from 'perfectly' short-chain branched polyethylene with varying branch lengths prepared by ring-opening metathesis followed by hydrogenation. High temperature quadruple detection size exclusion, including refractive index, infrared spectroscopy, viscosity and light scattering provided key physical property measurements, and a program created at NIST called ZENO provided simulation data to match experimental results.

297. New family of guanidine based n-type dopants and the structural effects on doping efficiency

***Julia A. Schneider**[1], jschneider43@fordham.edu, Hidenori Nakayama[2], Hengbin Wang[2], Javier Read de Alaniz[3], Michael L. Chabinyc[3]. (1) Chemistry, Fordham University, New York, New York, United States (2) Mitsubishi Chemical Center for Advanced Materials at the University of California Santa Barbara, Santa Barbara, California, United States (3) Materials, University of California Santa Barbara, Santa Barbara, California, United States*

Doping conjugated polymers and small molecules is how we enhance and control their conductivities. Efficient doping is a critical part of using these materials in a variety of applications, especially in thermoelectric devices or as transport layers in solar cells and light-emitting diodes. When using chemical dopants, you ideally want uniform incorporation of the dopant without disrupting the supramolecular assembly of your semiconductor. With n-type dopants, you must also worry about the dopant being air-stable.

This talk will introduce a new series of n-type dopants based on the bicyclic guanidine-type structure, 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD). These stable dopants were shown to be effective dopants for a variety of materials, including the polymer P(NDI2OD-T2). It will also be demonstrated that structural changes in this series of dopants yield different physical properties, processabilities, and doping efficiencies.

298. Observing and reversing the cysteine-perfluoroarene S_NAr reaction: towards a traceless tag for isolating expressed peptides

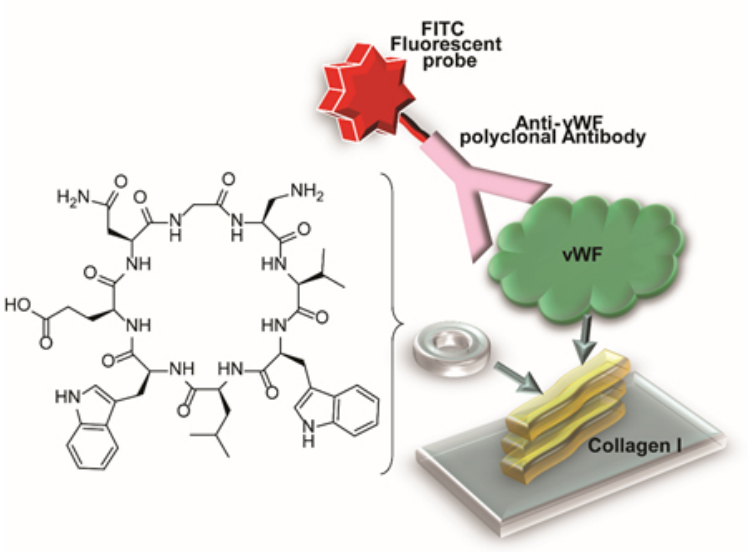
***Jason Gavenonis**, gavenonis@gmail.com. Chemistry, Dickinson College, Carlisle, Pennsylvania, United States*

The cysteine-perfluorarene S_NAr has recently found applications in peptide stapling and site-selective and sequence-specific protein tagging, but creates a covalent bond that is not easily cleaved. This presentation describes efforts toward the development of this reaction as a platform for the discovery of new S_NAr-reactive motifs as a traceless tag for peptide purification from microbial culture. The perfluoroaryl moiety may be removed from cysteine by either elimination or hydrogenolysis, as demonstrated in a simplified model system. Additionally, bifunctional probes have been synthesized to observe S_NAr reactions in microbial culture by reaction with a fluorescent protein bearing a known S_NAr-reactive sequence. Finally, efforts toward the detection of fluoride ions produced by this reaction will be described.

299. Good things come in small packages: Cyclic peptide inhibitors to a protein-protein interaction initiating thrombosis and novel short peptide helices and turns

***Danielle Guarracino**, danielle.guarracino@gmail.com. Chemistry, The College of New Jersey, Princeton Junction, New Jersey, United States*

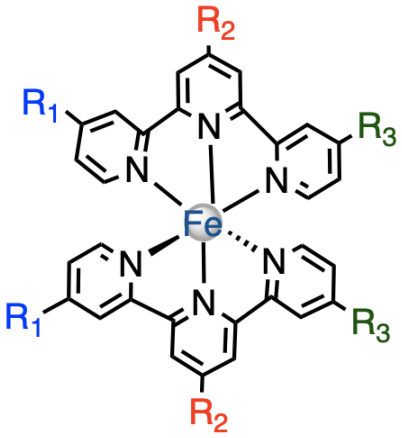
Peptide structure and function are intrinsically linked and exquisitely exploited in studies of protein-protein interactions. Understanding the link between these is pertinent in the development of novel first generation pharmaceuticals. The field of peptide pharmaceuticals is a hot-bed of activity; with an attractive pharmacological profile and excellent safety, tolerability and efficacy in humans, peptide therapeutics are on the rise. Macrocyclic arrangements provide added stability and many of the favorable characteristics sought after. We will describe the development of our head-to-tail cyclized peptides that inhibit the interaction between von Willebrand factor and collagen, which initiates thrombosis. Heart attacks and strokes, most of which are attributable to arterial blood clots, remain major health concerns in America. Current therapies and preventatives target platelet interactions at the site of the clot and are riddled with complications. Our peptides are moderately active in vitro and show remarkable stability when treated with peptide-degrading factors often found in the cell. The designs therefore provide a springboard for future advances in exceptionally stable, active cyclic peptide drugs. In independent work as part of an advanced undergraduate class, we have developed short alpha- and beta-peptide helical scaffolds and synthesized several peptides that use primary sequence to influence helical control. Additionally, we have defined a new minimal epitope for beta-turn motifs. Overall, our results from both major studies inform future peptidomimetic designs, especially in the development of short, structured peptides with biological function.

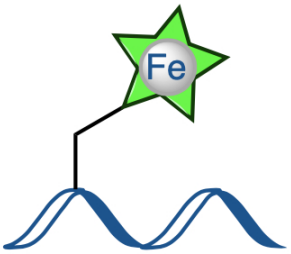


300. Designing 'intelligent' MRI contrast agents

Anthony J. Rojas*, ajrojas@salisbury.edu. Chemistry, Salisbury University, Salisbury, Maryland, United States*

Magnetic resonance imaging (MRI) is a non-invasive imaging technique that can provide information on the anatomy, function, and metabolism of tissues *in vivo*. With exclusively undergraduate researchers, we are designing a series of dynamic, activatable, or ‘intelligent’ MRI contrast agents based on iron(II) coordination complexes that undergo thermally induced spin-state crossover to provide local temperature data and tissue contrast. We are also developing iron(II) complexes integrated into a known peptide binder for cellular tumor protein P53 to direct accumulation of contrast agents in tumor tissue.





Aim 1

chemically tuning Fe(II) SCO contrast agents

Aim 2

incorporating contrast agents into peptide binders

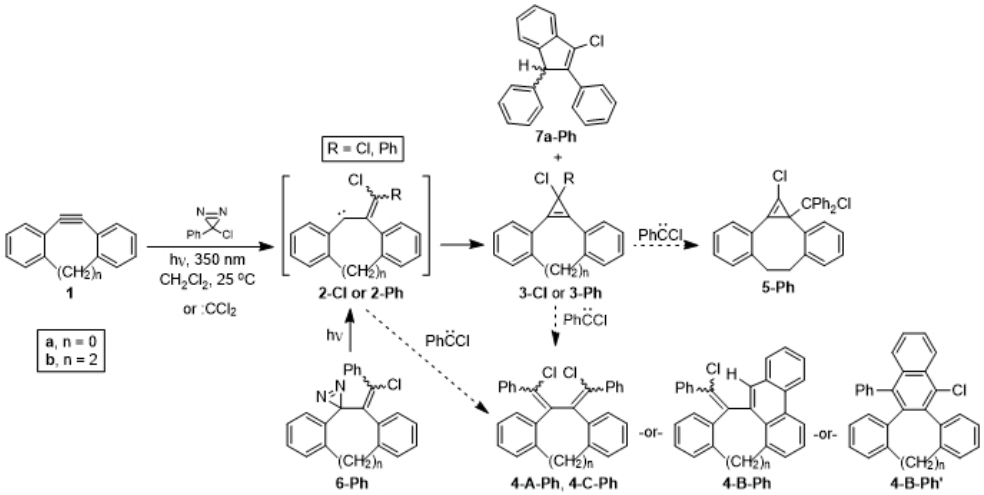
Focus

providing undergraduates experience in biomedical science research, complex synthesis, transition metal magnets, and chemical biology

301. Untangling the mechanisms of chlorocarbene additions to strained bonds

***Dina C. Merrer**, dmerrer@barnard.edu. Dept of Chemistry, Barnard College, New York, New York, United States*

The Merrer group uses experiment and theory to explore the mechanisms of chlorocarbene additions to strained carbon-carbon (C-C) π bonds. The reactions of carbenes with π substrates having strain in excess of 40 kcal mol^{-1} are influenced, if not controlled, by dynamic effects. Our current work investigates dichlorocarbene (CCl_2) and phenylchlorocarbene additions to dibenzocyclooctyne (DIBO; 1b). Our direct dynamics trajectories predict the formation of vinylcarbene 2b-Cl (4%) as well as the major reaction path to cyclopropene 3b-Cl (96%). Experimentally, the major addition product appears to come from the addition of two equivalents of PhCCl followed by HCl elimination, perhaps 4b-B-Ph or 4b-B-Ph'. Two isomeric products, proposed to be 4b-A-Ph and 4b-C-Ph, form in lesser amounts. We report our ongoing characterization efforts. We are also approaching this mechanistic scheme via a "midpoint" entry. Synthesis of diazirines 6b-Ph and open chain analogue 6a-Ph will allow unimolecular access to vinylcarbenes 2b-Ph and 2a-Ph, respectively. Calculations show 2a-Ph to form cyclopropene 3a-Ph or cyclopentene 7a-Ph preferentially. Experimentally, we report our progress on the syntheses of diazirines 6-Ph, and our recent calculations on these systems.



302. Bacterial capsule polymerases as tools for carbohydrate synthesis

***Pumtiwitt C. McCarthy**, pumtiwitt.mccarthy@morgan.edu. Chemistry, Morgan State University, Baltimore, Maryland, United States*

Neisseria meningitidis is one of the leading causes of bacterial meningitis worldwide. There are six-disease causing serogroups, each characterized by the capsular

polysaccharides surrounding the pathogen. Capsule polymerases are responsible for synthesizing these sugars. Our current focus is the *N. meningitidis* serogroup W (NmW) capsule polymerase which synthesizes a polysaccharide containing repeating units of sialic acid and galactose. An increased understanding of the serogroup W capsule polymerase can lead to its use as a tool to improve the enzymatic synthesis of carbohydrate structures. Our group uses interdisciplinary approaches to investigate activity of the *NmW* capsule polymerase. The overall goal is to modulate the biosynthetic activity of this enzyme to create size-controlled carbohydrates for applications in glycoconjugate vaccines and bioremediation of heavy metal cations. This presentation will describe our progress using chemoenzymatic strategies and bioinformatics tools to investigate catalysis by the NmW capsule polymerase enzyme.

303. From heterocycles to carbacycles: How to exploit nitrogen in small rings

Gustavo Moura-Letts*, moura-letts@rowan.edu. Chemistry and Biochemistry, Rowan University, Cherry Hill, New Jersey, United States*

Nitrogen-containing heterocycles are among the most important families of molecules due to their high occurrence in medicines. Despite efforts for the last 200 years, their synthesis remains a main challenge in the field of organic chemistry. Our group is interested in inventing new chemical reactions for the synthesis of nitrogen-containing small heterocycles and their respective reactivity patterns as substrates for the synthesis of more complex molecules. These efforts have shed light on some highly unprecedented reactivity pathways, thus providing access to previously inaccessible regions of chemical space. Clues have being found, reactions discovered, but the hunt continues.

Nanoparticles: Characterization & Applications

304. Manipulation of dimensionality, edge state, and strain in transition metal dichalcogenide nanocrystals

Thomas J. Kempa*[1,2], tkempa@jhu.edu. (1) Chemistry, Johns Hopkins University, Baltimore, Maryland, United States (2) Materials Science and Engineering, Johns Hopkins University, Baltimore, Maryland, United States*

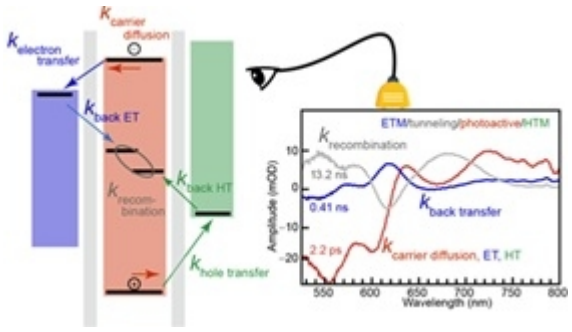
Two-dimensional (2D) transition metal dichalcogenide (TMD) crystals exhibit electronic, magnetic, and optical properties which can be manipulated through control of crystal dimensionality, edge character, and strain state. We recently introduced a rational chemical synthesis strategy, based on gas-phase growth of TMD crystals on designer surfaces, that substantially improves control over the dimensions, morphology, and crystalline edges of 2D TMDs without top-down fabrication. TMD nanoribbons prepared in this manner exhibit atomically sharp edges, readily controllable dimensions, and anomalous photoluminescence features. This talk will focus on our recent efforts to better understand some of these optical anomalies. A mixed-dimensional architecture comprised

of a 2D TMD crystal carefully interfaced with a Si nanowire enables the introduction of localized strain fields. Detailed structural and optical characterization of these architectures reveals unique edge- and strain-mediated photoluminescence that is localized and significantly red-shifted in energy. Our results highlight how rational design of low-dimensional materials can enable future optoelectronic and quantum device goals.

305. Photo-induced charge transfer dynamics and mechanisms in thin-films of Sb_2S_3

Elizabeth R. Young, *ery317@lehigh.edu. Chemistry, Lehigh University College of Arts and Sciences, Bethlehem, Pennsylvania, United States*

The prospect of widespread energy conversion from sunlight requires solar cells fabricated using stable, sustainable, non-toxic semiconductors based on earth-abundant elements. Materials comprising solar cells must be assembled in carefully designed stacks of light absorbing layers and hole and electron transporting materials creating thin film p-n or p-i-n devices. The electron transfer at these material heterointerfaces is the most important factor controlling the behavior of such electronic devices. As such, continually shrinking feature sizes in nanoelectronics and the drive for inexpensive solar energy conversion systems make fundamental understanding of photo-induced ET at interfaces essential to next generation devices. This talk will present our work on using transient absorption spectroscopy to *directly* observe carrier diffusion, electron transfer, hole transfer and charge recombination through uniform ultra-thin (< 3 nm) layers of insulating or transport materials deposited by atomic layer deposition (ALD) that are coupled to photo-active materials. Our work focuses on stibnite (Sb_2S_3) as the photo-active layer, which is of particular interest due to the suitable band gap of 1.7 eV and high absorption coefficient (1.8×10^5 cm^{-1} at 450 nm). Our results will be used to correlate the structure and function of material thickness and transport type to develop a fundamental, detailed, quantitative understanding of photo-induced ET dynamics through thin films of materials.



Using transient absorption spectroscopy to directly measure photo-induced charge transfer in thin films of photo-active materials.

306. Bidirectional excited-state charge-transfer and extended charge separation within covalently-tethered type-II CdSe/CdTe quantum dot heterostructures: Colloidal and multilayered systems

***Caitlin McGranahan**, crmcgran@buffalo.edu, Guy Wolfe II, David Watson. Chemistry, University at Buffalo, Buffalo, New York, United States*

Semiconductor quantum dots (QDs) are prime candidates as harvesters of light and donors of excited charge carriers for solar energy conversion. Our group's recent efforts have established the validity of utilizing carbodiimide-mediated coupling chemistry to selectively tether two QDs through the formation of an amide bond between the terminal functional groups of capping ligands. We previously reported on excited-state hole transfer in colloidal CdS/CdSe QD heterostructures, which exhibit quasi-type-I interfacial energetic offsets.

This presentation reports on our efforts to improve and expand upon our previous work in two ways. First, we synthesized and characterized covalently tethered colloidal CdSe/CdTe QD heterostructures via formation of amide bonds. These heterostructures exhibit type-II energetics that promote interfacial charge separation, irrespective of which constituent QD is initially excited, and afford enhanced control over the thermodynamic driving forces for charge transfer. Within these heterostructures, photogenerated electrons are transferred from CdTe to CdSe, and photogenerated holes are transferred from CdSe to CdTe, on timescales of 10^{-8} s. Second, we prepared ternary CdSe/CdTe heterostructures by immobilizing a covalently-linked bilayer of these QDs on a metal oxide substrate. When compared to colloidal heterostructures, thin films consisting of QDs adsorbed to a metal oxide substrate, introduce the possibility of an additional stepwise excited-state charge transfer process. We hypothesized that a stepwise process such as this should facilitate extended spatial separation of charge carriers and longer charge-separated state lifetimes, such that energy is harvested more efficiently and desirable processes can more effectively compete with recombination. Dynamic quenching of emission was observed in heterostructure-modified thin films, consistent with excited-state charge transfer. Rate constants for photoinduced electron and hole transfer between QDs are on the order of 10^{8} s^{-1} and 10^{7} s^{-1}, respectively.

The bidirectional interfacial charge transfer within these type-II QD heterostructures, both in dispersion and within films, further reveals the potential of this system for use in light harvesting and solar energy conversion. This presentation will highlight these recent results as well as our ongoing time-resolved spectroscopic characterization of photoinduced charge transfer in CdSe/CdTe QD heterostructures.

307. Fibrous phosphorus quantum dots for cell imaging

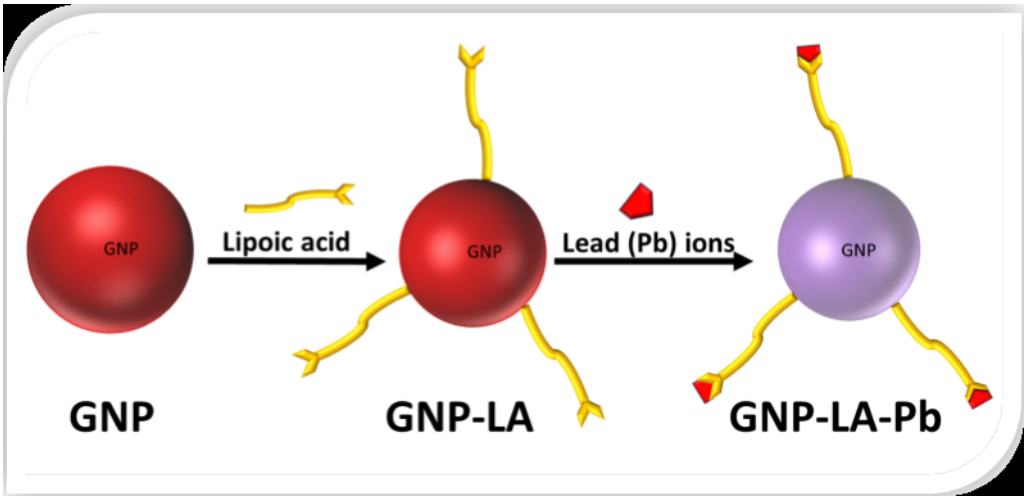
*Pedro Amaral[1], Donald C. Hall[2], Jarek Krol[1], Garth Ehrlich[2], **Haifeng Ji**[1], hj56@drexel.edu. (1) Dept of Chemistry, Drexel University, Philadelphia, Pennsylvania, United States (2) Chemistry, Drexel University, Delta, Pennsylvania, United States*

Fibrous phosphorus is a crystalline structure belonging to the extensive family of phosphorus allotropes. The material's structure consists of one-dimensional tubular layers held together by van der Waals forces and is a semiconductor with an optical band gap of 2.12 eV in its bulk form. We have developed a facile solution-based method for the fabrication of fibrous phosphorus quantum dots (FPQDs). The FPQDs were prepared by sonicating the material in N-methylpyrrolidone (NMP) and centrifuging to separate by size. The application of FPQDs as a fluorescent label in bioimaging of adenocarcinoma cells will be introduced. Some other applications of red and black phosphorus nanomaterials will also be discussed.

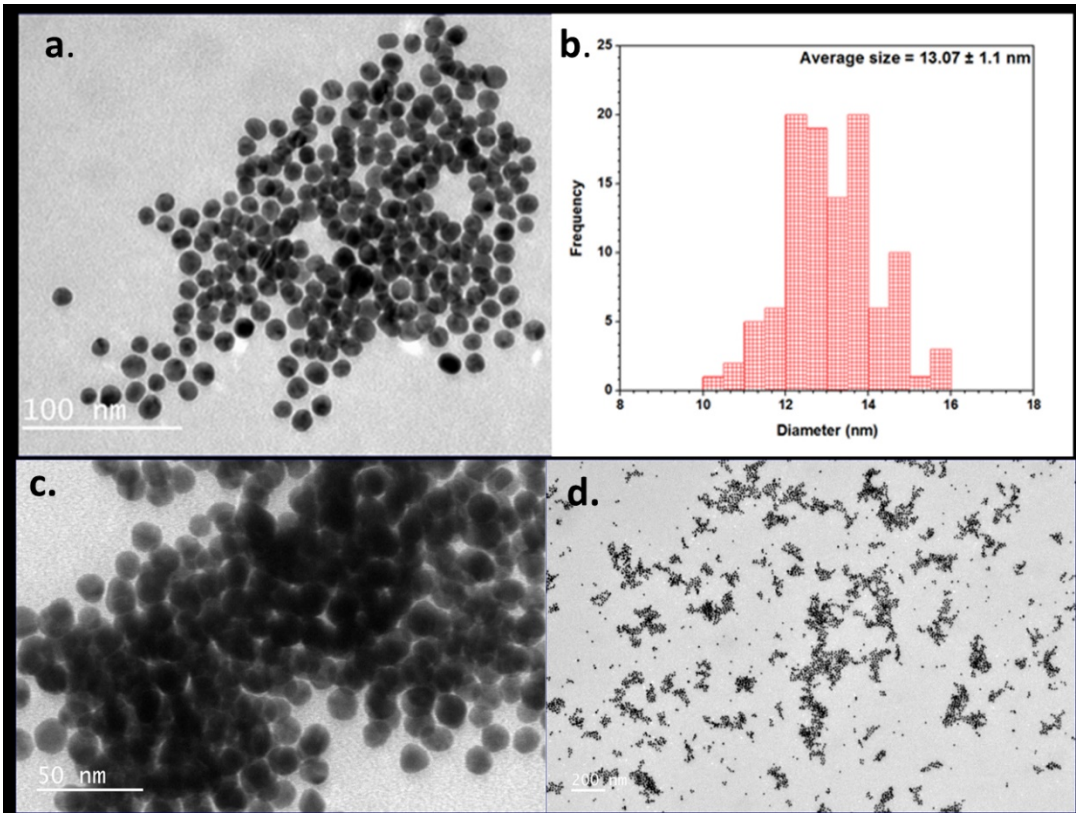
308. Lipoic acid decorated gold nanoparticles and their application in the detection of lead ions

***WILLIAM GHANN**, wghann1@umbc.edu, Tyler Harris, Jamal Uddin. Coppin State University, Baltimore, Maryland, United States*

The outcome of the interaction between gold nanoparticles and light is significantly influenced by the size, shape, and environment of the gold nanoparticles. Consequently, the color of the gold nanoparticle solution change when the particles aggregate or when their surfaces are modified. This phenomenon has been exploited extensively in biomedical and engineering research and applications. A simple colorimetric method was developed for the current detection of lead (Pb^{2+}) in water samples using lipoic acid-functionalized gold nanoparticles. The synthesized gold nanoparticles were characterized using UV-visible spectrometry, dynamic light scattering, and transmission electron microscope. The lipoic acid-functionalized gold nanoparticles were induced to aggregate in the presence of the Pb^{2+} which resulted in a change in the color of the functionalized gold nanoparticles. The change in color and the amount of Pb^{2+} producing the change could be monitored via UV-visible spectrophotometry. A good correlation coefficient of 0.9927 was obtained for the calibration curve of the colorimetric method. The method was applied in the determination of Pb^{2+} in water samples, and the results compared to that of measurement carried out with Atomic Absorption Spectroscopy.



Mechanism behind colorimetric detection of Lead ions



EM image of gold nanoparticles before and after conjugation with Pb ions. a) GNPTA; b) corresponding histogram of GNPTA-Pb; (c and d) GNPTA-Pb at different magnifications

309. Long chain hydrosilanes as phase transfer agents

*Bhanu P. Chauhan, **Elijah Cook**, cooke7@student.wpunj.edu, Qiaxian R. Johnson. Department of Chemistry, William Patterson University, Wayne, New Jersey, United States*

The synthesis of aqueous gold nanoparticles is a common procedure that is quite simple and a very effective means to produce various sizes and morphology. Nanoparticles prepared in organic solutions are useful for applications in catalysis as well as surface modifications with organic ligands. As there are many protocols for the synthesis of aqueous nanoparticle solutions, the development of a general procedure for the phase transfer of nanoparticles could be useful. This research presents a new approach to the dispersion and stabilization of gold nanoparticles from aqueous to organic solution through the use of alkylsilanes. The unique activity of poly(hydro)silanes inspired the investigation of monomeric hydrosilanes as transfer agents. This transfer method utilizes n-butylsilane to complete a ligand exchange, allowing the particles to flow into organic solution. The gold and silver nanoparticles transferred using this protocol maintained their size and shape throughout the reaction.

List of Authors