1. Enabling novel circular economy processes utilizing mass balance in chemical processes

***Thomas McKay**, thomas.mckay@basf.com. BASF Corp, Florham Park, New Jersey, United States*

Mass Balance (MB) is a proven chain of custody methodology that enables new or novell recycling processes to get started utilizing existing supply chains. This provides a relatively low risk, low barrier to entry pathway to start developing circular processes until economies of scale allow segregated supply chains to be justified.

Few know the details of how MB works, especially in highly complex value chains found in the chemical industry. This talk will cover the basics on what MB is, how it works, why it's used and the value it brings in developing circular pathways for end of life materials.

2. Microscopy supports on circular economy in BASF North America

***Keqing Fa**, keqing.fa@basf.com. BASF, Wyandotte, Michigan, United States*

BASF has set up aggressive goals on sustainability. Analytical North America (ANA) is the key component of global efforts on Circular Economy, and biodegradation & microplastics center of excellence. Feedstocks, R&D samples, and commercialized materials are frequently needed to be characterized and tested for assuring materials quality, facilitating formulation/processing development, and meeting regulatory requirements. In this presentation, microscopy technologies used in characterizing samples in CE are discussed and application examples are demonstrated to show the importance of analytical supports.

3. Evolving industrial analytics for the plastics circular economy

***Jeanne Hankett**, jeanne.hankett@basf.com. Analytical & Material Science North America, BASF Corporation, Wyandotte, Michigan, United States*

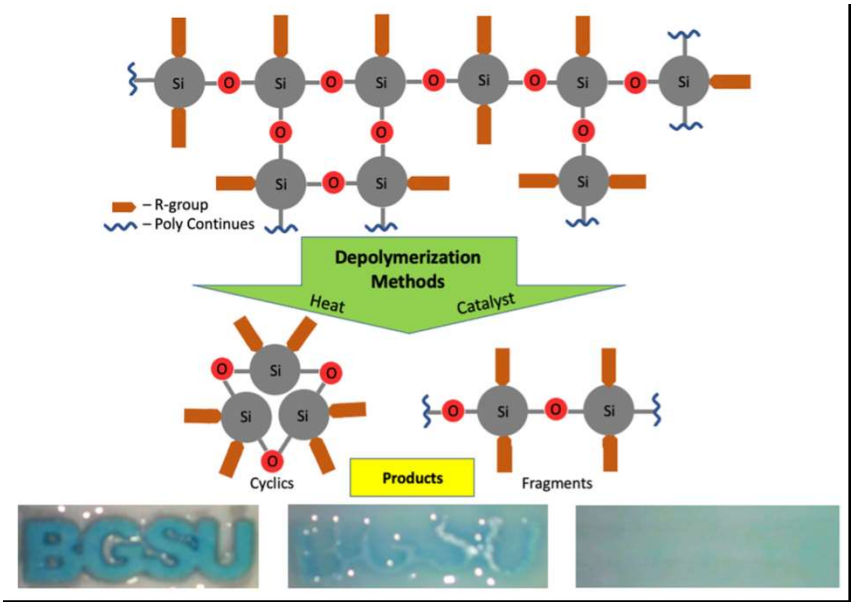
Industrial innovations to generate a plastics circular economy, a cradle-to-cradle model for polymers that prevents the generation of plastic waste and improves carbon footprint, are developing at a fast pace. As a result, new categories of chemical and physical analytics must continuously grow and evolve in industry to support these emerging needs. From evaluation of biodegradable polymeric products, to understanding chemical recycling and improved mechanical recyclability, analytical methods must generate reliable, robust results for increasingly complex chemistries. This seminar will focus on emerging and growing analytics for biodegradable chemistries, microplastics, chemical recycling, and odor analysis as relevant to the chemical industry. It will also include an overview of the new Analytical Center for Microplastics & Biodegradation at BASF’s Corporate Analytical & Material Science North America and provide a window into how industry tackles complex challenges in developing a polymeric circular economy.

4. Circular upcycling approach to sustainable silicone polymers

***Joseph C. Furgal**, furgalj@bgsu.edu, Kalani D. Edirisinghe, Herenia Espitia Armenta, Ethan Chandler, Cory B. Sims, Buddhima Rupasinghe. Chemistry, Bowling Green State University, Bowling Green, Ohio, United States*

This presentation will showcase our recent work on the development of circular methodologies for siloxane-based elastomers and resins to demonstrate the potential industrial feasibility of silicone recycling/upcycling. We have developed an efficient methodology to depolymerize polysiloxanes of various forms and cross-link densities to cyclic siloxanes of D_4, D_5, and D_6

with an emphasis towards D_4 development and then demonstrate their repolymerization back to polysiloxane structures. The depolymerization processes are conducted using a cocktail of fluoride ions from tetrabutylammonium fluoride or from photoreleasable flourides from phenacyl photocages in THF or MEK and other intermediate high swell solvents. The reactions are highly efficient with conversion to cyclomers taking place in as little as 30 min through an equilibration process, with quenching by $CaCl_2$ to remove active fluoride ions and lock the cyclic structures. The conversion to cyclomers are verified by ^{29}Si NMR and GCMS spectroscopic techniques. Traditional methods such as triflic acid initiated polymerization have shown effective repolymerization to polysiloxanes containing M_w up to 8600 Da. We also demonstrate methods for the mechanochemical transformation of siloxane polymers to cyclic compounds and also the conversion of siloxanes directly to alkoxysilanes via catalytic processes. Lastly, we will show how the incorporation of light responsive cross-linkers into siloxane systems can enable dynamic re-processible polymeric systems by losing and then restoring mechanical properties for adhesives and self-healable materials.



5. Sense of belonging of students from historically excluded groups in general chemistry courses

Nicole M. Karn*, karn.38@osu.edu, Jennifer Collins, Luka Medvedovic, Makda Berhe, Sarah Ogrin-Cotarlan. Chemistry and Biochemistry, The Ohio State University, Columbus, Ohio, United States*

Students with a strong sense of course belonging tend to have higher course level academic achievement and persist in STEM. Systemic racism and sexism in STEM fields may lead to a lower sense of belonging and higher belonging uncertainty in students from historically excluded groups. A survey on sense of belonging was conducted in all general chemistry courses during autumn 2022 at a large research institution in the Midwest. From this survey, we will examine students' sense of belonging and belonging uncertainty with respect to course progress. Data on sense of belonging will be disaggregated by self-reported demographic information. The role of intersectionality will be examined. The ways in which various course aspects such as recitation, lab, homework, and exams relate to sense of belonging will be explored.

6. Implementation of a vertical and interdisciplinary curriculum-based research experience in organic chemistry courses

Marwa Abdel Latif[1], *abdellmk@udmercy.edu,* ***Mara Livezey***[1], *livezemr@udmercy.edu,* ***Steven Scribner***[1,2], *scribnsl@udmercy.edu, Eleni Geragosian*[1], *Maryam Yousif*[1], *Courtney Profley*[1]*. (1) Chemistry and Biochemistry, University of Detroit Mercy, Detroit, Michigan, United States (2) University of Michigan Dearborn Office of Metropolitan Impact, Dearborn, Michigan, United States*

Creating opportunities for learners to explore research projects in their undergraduate curriculum is critical to 1) enhance problem solving skills, 2) master laboratory skills in synthesis, and 3) become creative in designing future research. More importantly, this approach can assist in creating a more equitable experience for non-traditional learners. A team of faculty members at University of Detroit Mercy has been designing a module of vertical research projects to incorporate the synthesis and characterization of organometallic ferrocene hybrids using a combination of experimental conditions and coupling reagents. The project is also aimed to incorporate biochemical and electrochemical investigations to simulate interdisciplinary work in chemistry. Through a set of laboratory courses, the faculty members expanded on the implementation and modifications of ferrocene syntheses and worked to create a community of learners who contribute to a common goal of expanding knowledge about successful syntheses. This presentation will address the design and implementation of a two-year vertical CURE and will include students' perspectives of their learning experiences. Faculty members are interested in assessing students' responses to determine whether multi-module exposures enhanced their attitudes towards research and to identify challenges in implementing vertical CUREs in chemistry. Additional modifications and examples of students facing resources will be shared.

7. Navigating the hidden curriculum of academia: Critical approach to understanding the racial and science identity formation of Latine undergraduate students

Danielle N. Maxwell[1], *maxweldn@umich.edu, Jorge L. Rivera-Colon*[2], *Kathryn Hosbein*[3], *Paulette Vincent-Ruz*[4], *Ginger V. Szymczak Shultz*[1]*. (1) University of Michigan, Ann Arbor, Michigan, United States(2) University of Wisconsin-Madison, Madison, Wisconsin, United States(3) Middle Tennessee State University, Murfreesboro, Tennessee, United States(4) New Mexico State University, Las Cruces, New Mexico, United States*

The narrative that science is objective, value-free, acultural, and rooted within a system of meritocracy constrains the representation and advancement of minoritized groups in science. Although there are initiatives to improve the representation of non-majority groups in STEM, much of this effort focuses on achieving racial or ethnic diversity rather than recognizing students' diverse worldviews and identities in the classroom. To understand how students learn science, we need to understand how students engage with science and how this influences their personal and science identities. This study aims to understand how Latine undergraduate students at Hispanic-Serving Institutions (HSIs) develop science identities and how racialized experiences may influence this formation. In this study we use multiple theories of identity, a critical epistemological perspective, and qualitative research methods to build a conceptual framework and describe the salient experiences of our participants. We interviewed 18 Latine third- and fourth-year undergraduate students at three HSIs in the southwestern United States. Our analysis indicates that Latine students use a variety of racialized identity resources to negotiate the formation of their science identities. Positive or negative experiences with these resources can greatly influence their science identity formation.

Specifically, Latine students have complex access and interactions with relational and material resources that influence their sense of belonging and science identity formation. The results of this study provide insights into how Latine students engage with the culture of science and advance our understanding of how to best support Latine students throughout their undergraduate science education. Furthermore, this study demonstrates the need for more Latine instructors and culturally responsive curriculum development in higher education.

8. Student perspectives to transform the general chemistry learning environment at predominantly white institutions

***Jennifer Collins**, collins.1711@osu.edu, Nicole M. Karn, Makda Berhe, Sarah Ogrin-Cotarlan, Luka Medvedovic. Department of Chemistry and Biochemistry, The Ohio State University, Columbus, Ohio, United States*

The general chemistry course, especially at Predominantly White Institutions (PWI), is confirmed to be a gatekeeper to science and engineering degrees. Acknowledging this reality, research focused on understanding student perceptions of the learning environment and the barriers to success in general chemistry is extremely critical to shape efforts to advance systemic change in chemistry education. Student perceptions is especially critical as they are arguably the most critical stakeholders of higher education. Given this, this research study qualitatively and quantitatively examines student perspectives on the general chemistry environment with respect teaching practices, faculty and teaching assistant interactions, curriculum, and courses policies. Students in the study are enrolled at a research intensive PWI, and a research-based survey was administered to gather student perspectives in Autumn 2022. Preliminary results from 1637 general chemistry course 1 students indicate complex and multidimensional perceptions largely related to course difficulty, fast pace of the course, and unsupportive instructional behaviors and practices. Findings imply systemic change efforts should place considerable attention to course structural and curriculum reform, to ultimately advance student success and racial equity in general chemistry.

9. Utilizing student-generated Mathematica demonstrations in general chemistry courses

***Heidi P. Hendrickson**[1], hendrihe@lafayette.edu, Theresa Chua[1], Vedit Venkatesh[1], Tracie Addy[2]. (1) Chemistry, Lafayette College, Easton, Pennsylvania, United States(2) Center for the Integration of Teaching, Learning, and Scholarship, Lafayette College, Easton, Pennsylvania, United States*

The Compute-to-Learn (C2L) Pedagogy is a semester-long, project-based learning experience in which students collaborate within a peer-led studio environment to code Mathematica demonstrations of abstract course concepts that can be illuminated by dynamic computation. During this experience, students learn key programming skills that they apply within the context of physical chemistry. At the end of the semester, the student demonstrations undergo external peer-review and are published on the Wolfram Demonstrations Project website.

The C2L pedagogy was originally designed for introductory physical chemistry courses at a large midwestern research university. However, parameters for pedagogy design and implementation vary across different types of institutions. The strategies and solutions for implementing the C2L pedagogy in both advanced and introductory courses at an undergraduate liberal arts college are described here. In particular, the effect of utilizing student demonstrations created by upper-level physical chemistry students is investigated within a general chemistry course.

10. Utilizing the 'Student Interaction Discourse Moves' (SIDM) framework to characterize student discourse in a chemistry POGIL session

***Archer Harrold**, Aharrold@umich.edu, Danielle N. Maxwell. Chemistry, University of Michigan, Ann Arbor, Michigan, United States*

It is important to understand how students' interact with scientific literature and chemistry that is relevant to their lives. Process oriented guided-inquiry learning (POGIL) sessions are one way to have students' interact with new knowledge in group discursive settings. Herein, a POGIL sessions was implemented into a general chemistry course at the University of Michigan. The POGIL activity was created based on scientific literature and involved data relevant to students' perceptions of the Arctic. As part of the data collection, audio recordings of groups' dialogue was collected. This presentation seeks to utilize the Student Interaction Discourse moves (SIDM) framework to analyze these audio recordings. Our goal is to implement this framework and characterize students' discourse moves in a chemistry POGIL activity. As part of this analysis, we aim to investigate the nuances associated with the structure of POGIL activities, and instructor facilitation on students collaborative discourse.

11. Development and assessing the impact of student-generated videos, infographics, and open education resources related to sustainability and green chemistry

***Alexey Leontyev**, alexey.leontyev@ndsu.edu, Krystal D. Grieger. Chemistry, North Dakota State University, Fargo, North Dakota, United States*

Scaffolded semester-long projects were organized into phases and designed to promote the goals of teaching students about green chemistry and sustainability concepts while simultaneously creating case study videos, infographics, and open educational resources for future students. Learning objectives for these activities are two-fold. The first includes students connecting organic chemistry topics, green chemistry principles, planetary boundaries, and the UN sustainable development goals. The second refers to professional skills such as information literacy, communication, and peer review. Thorough evaluation of the impact of these curriculum innovations on student learning was conducted using high-quality assessment techniques, including sets of multiple-choice questions, student assessment of learning gains, open-ended questions that asked students to explain their reasoning about “greener” chemical reactions, and questionnaires. Overall, positive learning gains on chemistry knowledge and skills were observed and students viewed the projects favorably, with most indicating a desire for similar assignments in future courses.

12. Undergraduate research and green chemistry: Exploring applications within analytical chemistry

***Matthew J. Fhaner**, fhaner@umich.edu. Natural Sciences, University of Michigan-Flint, Flint, Michigan, United States*

Often times, the concept of green chemistry is associated with the synthesis of new compounds or the toxicological and environmental impacts of chemical processes. This can leave easily accessible opportunities for green chemistry to be integrated into other areas of chemistry. As chemistry programs across the nation look to introduce their students to more sustainable and green material, one option that remains an exciting opportunity is through undergraduate research. This presentation will focus on the use of electrochemical methods and their application to assessing the quality of frying oils for restaurants and snack-food manufactures. In order to move these techniques to industry, a greener solvent system needed to be identified. The tenants and current outcomes of this research, in addition to how this

project provides a platform for introducing undergraduate students to green chemistry will be presented.

13. Using environmental justice to explore scientific ethics, chemical literature, and presentation skills in a seminar course

***Jessica L. Tischler**, jtisch@umich.edu. Natural Science, University of Michigan-Flint, Flint, Michigan, United States*

In 2017 UM-Flint became the 38th signer of the Green Chemistry Commitment. Part of that pledge is the incorporation of Green Chemistry principles across the curriculum. This talk will describe a poster assignment in our Junior Seminar course that asks students to explain a green chemistry solution to an environmental injustice. This assignment seeks to teach scientific ethics by exploring the social impacts of chemistry with the social responsibility we have as scientists.

14. What do our students need to know about green and sustainable chemistry?: Panel discussion with industrial chemists

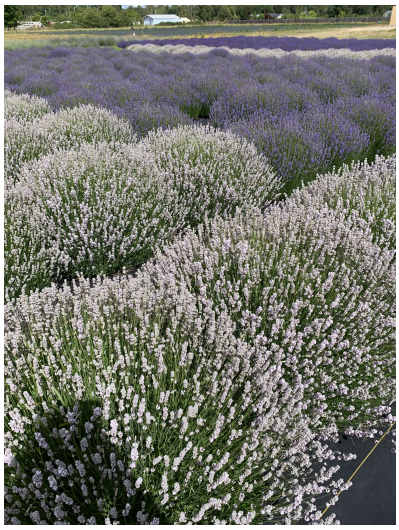
***Jessica L. Tischler**, jtisch@umich.edu. Department of Natural Sciences, University of Michigan-Flint, Flint, Michigan, United States*

In this session, we will host a panel discussion with speakers from BASF and Dow to discuss the incorporation of green and sustainable chemistry into industrial practices and corporate vision. We will explore how we as educators can better prepare our students to meet the challenges of today's industrial careers and their companies' sustainability goals.

15. Seed to oil, bench and beyond: Medicinal and aromatic plant course

***Marilee A. Benore**, marilee@umich.edu, Simona Marincean. Natural Sciences, University of Michigan-Dearborn, Dearborn, Michigan, United States*

Aromatic plants have bioactive components which contribute to their therapeutic, aesthetic, and medicinal uses. Due to increasing interest, use and commercial promise of natural products, we created a novel course on isolation and characterization of natural products, with a focus on essential oils. The course attracts students interested in integrative medicine, cannabis, small business, medical anthropology and pharmacognosy research. In Medicinal and Aromatic Plants BCHM 413, advanced students couple their knowledge of biochemistry with biology, analytical and organic techniques and skills in applied projects. Students chose





specific aromatic plants to study and extract oils or other plant products. Purification and characterization methods included solvent extraction and distillation (glass and copper alembics), while products and standards were compared using UV/Vis analysis, Gas Chromatography/Mass Spectrometry (GC/MS) and bacterial testing (contamination and resistance). Each student created a prototype product after researching the plant, selecting a type of consumer product, choosing an appropriate method to create a safe and chemically stable product, and designing the product literature.

16. Controlling the kinetics of oxidation of Eu^{II} relevant to imaging hypoxia in vivo with magnetic resonance imaging

*Md Mamunur Rashid[1], Andrea Batchev[1], Md Abul Hassan Samee[2], Robia Pautler[2], **Matthew J. Allen**[1], mallen@chem.wayne.edu. (1) Wayne State University, Detroit, Michigan, United States(2) Baylor College of Medicine, Houston, Texas, United States*

Divalent europium is isoelectronic with trivalent gadolinium, which is used in clinical settings as a contrast agent for magnetic resonance imaging. The divalent oxidation state of europium changes to the trivalent state in normoxic conditions, completely changing the ability of the ion to enhance contrast. Because of the stark change in contrast enhancing ability in response to oxidation, the europium ion is an outstanding candidate for use in imaging of hypoxia. However, control of the switch in oxidation state is the key challenge to the use of europium for responsive imaging of hypoxia. I will share efforts to use chemistry to slow the rate of oxidation of Eu^{II}. I will also share in-vivo examples of the use of the ion to delineate hypoxic and normoxic regions of tissue using magnetic resonance imaging.

17. Investigating the influence of alkyl substituents on the ability of β-carbonylphopshine oxide compounds to sensitize lanthanide luminescence

***Shannon M. Biros**, biross@gvsu.edu. Chemistry, Grand Valley State University, Allendale, Michigan, United States*

Our group has been studying the ability of ligands containing the β-carbonylphopshine oxide group to sensitize the luminescence of lanthanide(III) metals. This presentation will describe systematic variations to the aromatic groups on these ligands, and how the changes affect metal binding in solution. We will also discuss the characterization of these ligands' complexes with Eu^{3+}, Tb^{3+}, Dy^{3+} and Sm^{3+} with regard to their luminescence lifetimes, quantum yields and triplet state energies.

18. Density functional study of binding mechanism of rare-earth elements with Bis(ethylhexyl)amido diethylenetriaminepentaacetic acid

***Timothy Quainoo**, gw3083@wayne.edu, Zhenfei Liu. Chemistry, Wayne State University College of Liberal Arts and Sciences, Detroit, Michigan, United States*

Bis(ethylhexyl)amido diethylenetriaminepentaacetic acid, denoted as modified DTPA here, has recently emerged as an outstanding ligand for extracting rare-earth elements on a solid-phase media, while the microscopic mechanism for the binding between rare-earth elements and the modified DTPA is still unknown. In this work, we fill this knowledge gap by employing first-principles density functional theory to study the binding mechanism of rare-earth elements with the modified DTPA at different pH values. We first compute the pKa values of the modified DTPA and study the binding between hydrated cations of rare-earth elements and the

dominating modified DTPA species at different pH values. Our calculations of the Gibbs free energy explain the qualitative trends observed experimentally in the extraction of rare-earth elements. Our study provides insight into the thermodynamics of binding and separation of rare-earth elements using such materials and guides the future design of ligands for the extraction of rare-earth elements.

19. MR responsive and theranostic probes: Where are we headed?

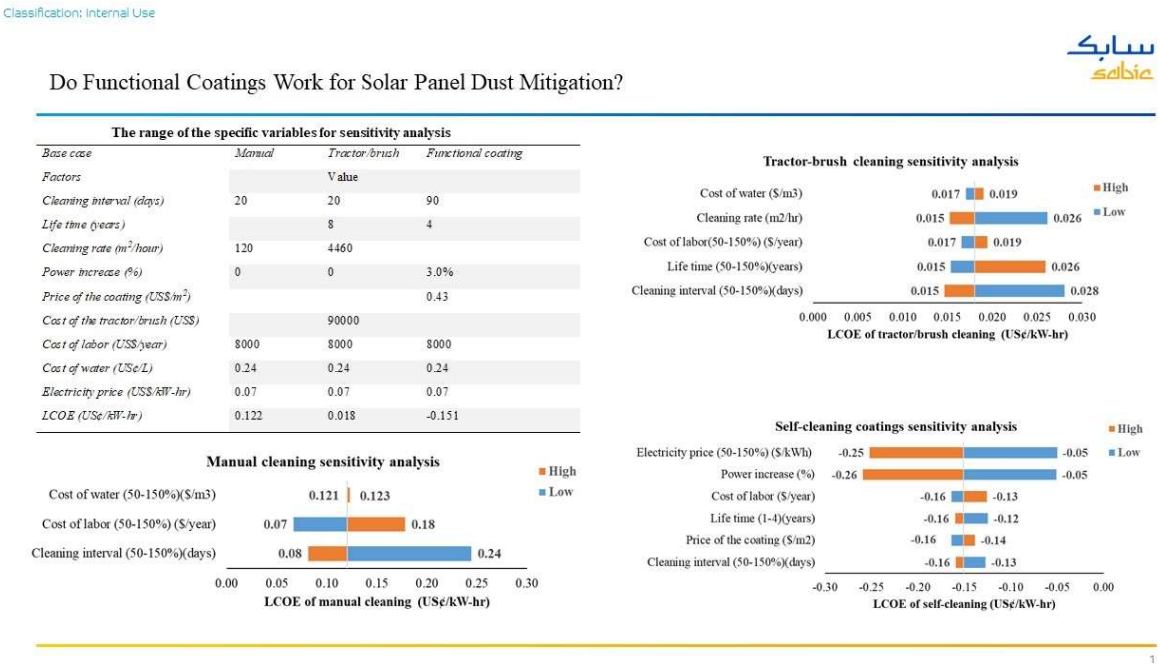
***Thomas J. Meade**, tmeade@northwestern.edu. Departments of Chemistry, Northwestern University, Evanston, Illinois, United States*

We report a new series of MR contrast agents for tracking gene therapy in vivo and to ultimately treat monogenic diseases. With mean survival rate of 5 years (and most cases are fatal) lysomal storage diseases (LSD) are among the most dismal of prognosis in all of medicine. LSD's represent a large number of monogenetic diseases and while rare the prevalence is to hemophilia. As monogenetic diseases with clearly defined genotype-phenotype relations, lysosomal storage diseases are excellent candidates for gene therapy. The transformative results documented in an adeno-associated virus (AAV) gene therapy clinical trial in infants affected by spinal muscular atrophy demonstrated unequivocally the potential of in vivo gene transfer to treat monogenic neurological disorders. To date there is a lack of non- invasive ways to determine biodistribution or activity levels of these AAV therapies in patients. This is a significant hinderance, leaving investigators guessing which organs or structures are effectively treated and, due to the lag time associated with clinical disease progression, this limitation ultimately impacts the evolution of treatment modalities. In order to overcome these limitations, we have developed a new class of bioresponsive MR imaging agents to track enzymatic activity in any organ, peripheral nervous system (PNS), or central nervous system (CNS) over time. MR imaging is an ideal technique for the study of neurological disorders.

20. Do functional coatings work for solar panel dust mitigation?

***Tayirjan T. Isimjan**, Tayiris@gmail.com, David West. Saudi Basic Industries Corp, Riyadh, Saudi Arabia*

As one of the sustainable energy sources, solar energy is the ultimate replacement for fossil fuels. More than 3% of worldwide electricity demand is satisfied by solar photovoltaic (PV) and the number keeps increasing. However, apart from the inherent low efficiency, environmental factors such as hail, humidity, dust, and temperature have a significant influence on the effectiveness and practicality of the PV module. Where the weather is dry and sandy, in the Middle East for instance, mitigating against the effects of high temperature and dust are the main issues. Although some type of functional-coating-based, self-cleaning technology is proposed as the most effective approach towards dust mitigation (DM) in the literature, no report on a cost analysis comparing the practicality of such technologies with conventional methods such as manual cleaning and tractor-mounted brush cleaning has been undertaken. For this work, we performed a detailed techno-economic analysis on three different DM approaches using the outdoor testing data generated at installations in Rumah, Saudi Arabia, and Inner Mongolia, China, respectively. The results reveal that a durable superhydrophilic transparent coating is the most economical way of cleaning solar panels due to the 3% increase in annual generated power compared to an uncoated, regularly-cleaned solar farm. Moreover, the return on investment is 15 months at the PV electricity-selling price of 0.07 $/kW-hr.



21. Laser-induced graphene interdigitated electrodes modified with gold nanoparticles for non-faradaic impedimetric detection of cortisol

***Kyle Duke**, kcduke@student.ysu.edu, Prakrit i Dhungana, Kyle Preusser, Byung-Wook Park. Youngstown State University, Youngstown, Ohio, United States*

Wearable biosensors have received a lot of attention for their promising applications in personalized medicine. Cortisol is a biomarker for various diseases and plays an important role in metabolism, blood pressure regulation, and glucose levels. In this study, we fabricated laser-induced graphene interdigitated electrodes (LIG-IDE) for the non-faradaic impedimetric detection of cortisol in sweat. A direct laser writing technique was used to produce the LIG-IDE. Gold nanoparticles (AuNPs) were electrochemically deposited onto the surface to enhance impedance response. A self-assembled monolayer (SAM) was formed with on the AuNPs via MPA thiol chemistry. The carboxylic acid (-COOH) groups of the MPA were activated using EDC/NHS chemistry. Following activation, anti-cortisol antibodies were immobilized on the surface. Lastly, the IDE-LIG was incubated in the blocking agent bovine serum albumin (BSA) to avoid unwanted detection. Surface characterization of the LIG was performed at each step of modification by Electrochemical impedance spectroscopy (EIS) in a phosphate buffered saline (PBS) solution containing a 5 mM $[Fe(CN)_6]^{3-/4-}$ (1:1) redox couple. Further characterization of the modified LIG electrode was achieved through Fourier transform infrared (FTIR) spectroscopy, surface-enhanced Raman spectroscopy (SERS), and X-ray diffraction (XRD). The detection experiment using EIS was carried out in increasing concentrations in cortisol (0.1 pM-100 nM) in PBS. A decrease in Z_{Mod} was found for increasing cortisol concentrations, verifying its ability to detect cortisol. The performance of the LIG-IDE were further examined by selectivity, reproducibility, and sensitivity experiments. The developed immunosensor shows excellent performance such as lower limit of detection, high selectivity, and good stability, and has great potential for development in point-of-care diagnostics in the future.

22. Ligand-associated adsorbents for selective recovery/extraction of rare-earth elements: Role of solid supports

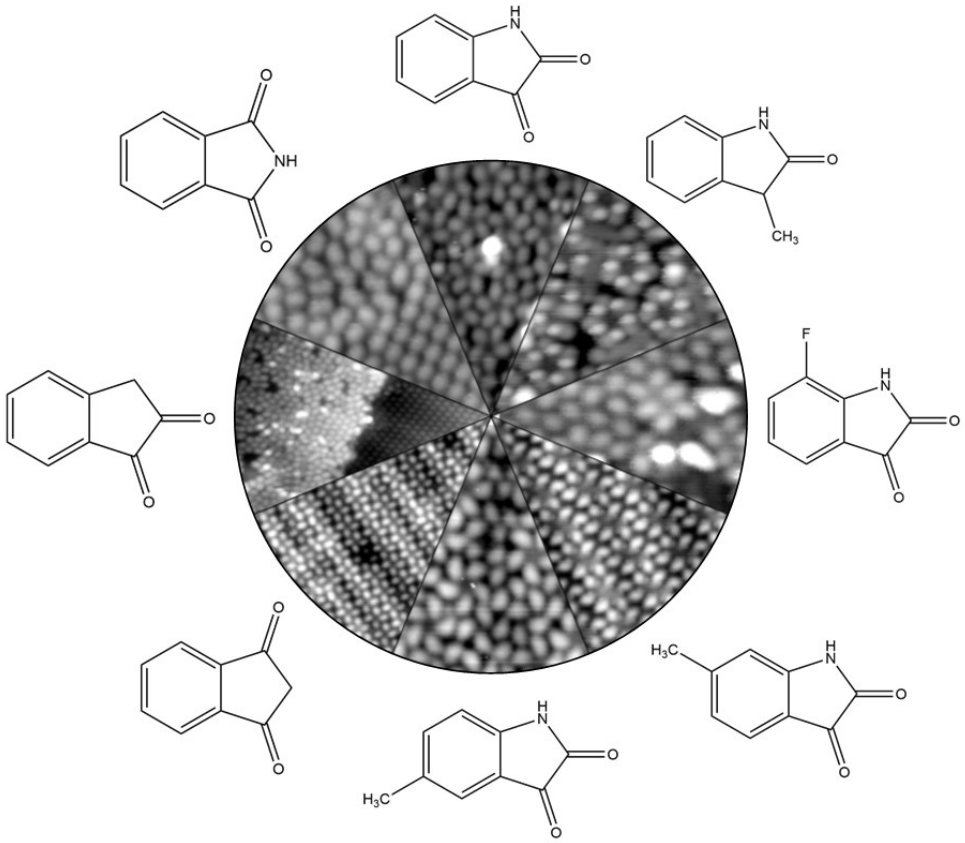
***Sai Praneeth**[1], hl9199@wayne.edu, Preetom K.Roy[1], Mohammed Dardona[1], Ahmed K.Sakr[1], Chandra Mouli Tummala[1], Matthew J. Allen[2], Timothy M. Dittrich[1]. (1) Civil and Environmental Engineering, Wayne State University, Detroit, Michigan, United States(2) Department of Chemistry, Wayne State University, Detroit, Michigan, United States*

Rare-earth elements (REE) have been used in increasing quantities for applications ranging from automobile parts to satellites in recent years. It is estimated that demand for REE usage will grow by 7 times by 2040. It is also expected that the supply-demand gap will further accelerate with current geo-political tensions, which will increase focus on REE recovery and extraction from wastes for domestic sources. There have been various techniques used for REE recovery/separation such as precipitation, liquid-liquid extraction, and ion exchange resins as sorbent/ solid supports for solid-liquid extraction of REE. Due to the high cost of making resins, the need for more economic sorbents or solid supports has been explored recently. In this study, the diethylenetriaminepentaacetic acid (DTPA) ligand was modified by attaching hydrophobic chains and grafted on commercially available solid supports, including organosilica (O), sol-gel activated/synthesized organosilica (D), pyrolyzed coconut shell (C) and Amberlite resin (A). The resultant media were used in absorption studies to see the selectivity and recovery of 17 elements (REE + Sc+ Y+ Th) under various conditions such as pH, dosage, kinetics, and isotherms. O-DTPA media showed the highest sorption capacity (22 mg/g) and strong selectivity toward Sc and Th between pH 3 and 4. Sorption of REEs onto coconut-based media indicates the DTPA ligand is not attached to the solid support (coconut shell carbon), possibly indicating the insufficient presence of key functional groups. There was no significant selectivity and recovery of REEs onto A-DTPA (13 mg/g) at pH 2.

23. Self-assembly controlled at the level of individual functional groups

***Benjamin Heiner**, benheiner7@gmail.com, S. Alex Kandel, Alexander M. Pittsford. Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana, United States*

Molecular self-assembly is a process that occurs when component molecules spontaneously organize into a specific arrangement due to the intermolecular interactions between them. These interactions are influenced by the functional groups present on the component molecules. By understanding the effects that different functional groups have on the self-assembly process, we can predict and control it. To do this, we study "families" of molecules that have a common backbone but differ in the functional groups they possess. We use a combination of experimental techniques, such as pulse deposition for scanning tunneling microscopy (STM), and a variety of computational methods to investigate the changes in self-assembly behavior that result from small modifications to the functional groups. In this talk/poster, I will present our work on a family of molecules with an indole backbone, including indol carboxylic acids, multiple isatin derivatives, and proline. By studying these molecules, we are able to gain a deeper understanding of the various intermolecular interactions that drive self-assembly in these systems.



Functional groups drive self-assembly.

24. Iron-coated waste nutshells to recycle the lost phosphate and its potential application as a slow-release fertilizer for agriculture

Chandra Mouli Tummala[1]*, gs4273@wayne.edu, Sanjay K. Mohanty*[2]*, Timothy M. Dittrich*[1]*. (1) Civil and Environmental Engineering, Wayne State University College of Engineering, Detroit, Michigan, United States(2) Civil and Environmental Engineering, University of California Los Angeles, Los Angeles, California, United States*

Direct application of phosphate fertilizer in agricultural fields can lead to >15% loss of total phosphate via agriculture runoff. Runoff containing excess phosphate fertilizer can create eutrophication in receiving waters, which has been linked to low dissolved oxygen, toxic compounds, and other problems. Slow-release phosphate fertilizers can be a potential solution to prevent this loss. In this study we have coated iron onto the surface of waste pistachio and walnut shells to synthesize biowaste adsorbent material, which has been shown to recover the phosphates from the water system. We have conducted laboratory scale experiments to understand the phosphate uptake capacity, kinetics and demonstrate its potential slow-release application as an agricultural fertilizer. XRD analysis have shown the iron coating process led to the formation of hematite particles on the surface of the waste nutshells. Batch studies have shown both iron coated shells follow pseudo second order kinetics and agree with the Freundlich isotherm model. Column studies have shown that the maximum uptake capacity of the iron coated pistachio and walnut shells is 12.63 mg/g and 9.25 mg/g, respectively. Experiments to validate the slow release of phosphorus under soil-relevant conditions are in progress to determine if this biodegradable waste material can be used as potential slow-release fertilizers in the agricultural fields

25. STM investigations into the role of chirality on molecular self-assembly

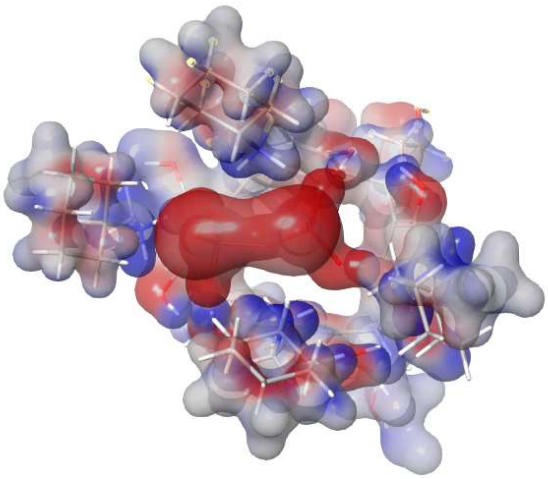
***Alexander Pittsford**, apittsfo@nd.edu, Benjamin R. Heiner, Alexandra L. Walter, Kaitlyn Handy, Jewel Soucek. University of Notre Dame, Notre Dame, Indiana, United States*

The study of chiral molecular self-assembly is key for many fields, such as enantioselective heterogeneous catalysis and 2D chiral crystal engineering. However, the fundamental role of chirality in crystal formation is not well understood. This study aims to investigate the role that molecular chirality plays in the 2D crystallization, using scanning tunneling microscopy (STM) to study the self-assembly of enantiopure molecules and compare them to achiral analogues. Clusters of the chiral molecule S-indoline-2-carboxylic acid (S-ICA) are extremely similar to clusters of its achiral analogue, indole-2-carboxylic acid. Both molecules form chiral pinwheel pentamers that are present on the surface in a racemic mixture. These results suggest that the molecular chiral center of S-ICA does not drive the chirality of crystallization.

26. Macrocyclic resorcinarene salts as sensors for bioanalytes

***Ngong K. Beyeh**, beyeh@oakland.edu. Chemistry, Oakland University, Rochester, Michigan, United States*

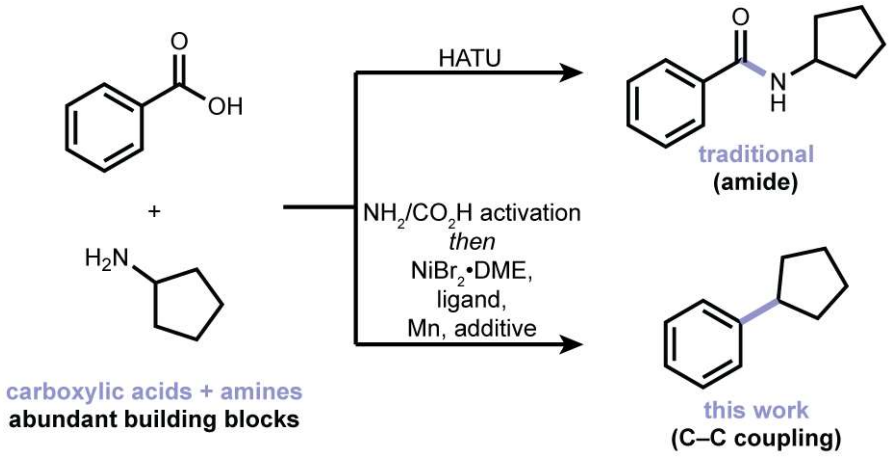
Synthetic materials that interact with biological target molecules are of paramount importance for the development of various biotechnological applications. Cyclophanes are macrocyclic supramolecular hosts famous for their ability to bind atomic or molecular guests via noncovalent interactions within their well-defined cavities. In this talk, I will present recent results on the design, formation, and host-guest properties of cationic macrocyclic resorcinarenes receptors and biological anions (chloride and pyrophosphate), and kynurenic acid, a bio-relevant analyte.



27. Formal cross-coupling of amines and carboxylic acids to form sp3–sp2 carbon–carbon bonds

***James L. Douthwaite**[1], jdouth@umich.edu, Ruheng Zhao[1], Eunjae Shim[2], Babak A. Mahjour[1], Paul M. Zimmerman[2], Tim Cernak[1,2]. (1) Department of Medicinal Chemistry, University of Michigan, Ann Arbor, Michigan, United States(2) Department of Chemistry, University of Michigan, Ann Arbor, Michigan, United States*

Amines and carboxylic acids are abundant synthetic building blocks that are classically united to form an amide bond. To access new pockets of chemical space we are interested in the development of amine–acid coupling reactions that complement the amide coupling. In particular, the formation of carbon–carbon bonds by formal deamination and decarboxylation would be an impactful addition to the synthesis toolbox. Here we report a formal cross-coupling of alkyl amines and aryl carboxylic acids to form C(sp3)–C(sp2) bonds following pre-activation of the amine–acid building blocks as a pyridinium salt and N-acyl-glutarimide respectively. Under nickel-catalyzed reductive cross-coupling conditions, a diversity of simple and complex substrates are united in good to excellent yield, and numerous pharmaceuticals are successfully diversified. High-throughput experimentation was leveraged in the development of the reaction, and to the discovery of performance-enhancing additives such as phthalimide, RuCl3 and GaCl3. Computational and experimental mechanistic investigations suggest phthalimide may play a role in stabilizing productive Ni complexes rather than being involved in oxidative addition of the N-acyl-imide and that RuCl3 supports the decarbonylation event, improving reaction selectivity.



28. Carbenes and carbazoles: Elucidating solution-state behavior with non-traditional hydrogen bonding

***Zacharias Kinney**, kinney@oakland.edu. Chemistry, Oakland University, Rochester, Michigan, United States*

Since the discovery of isolable singlet carbenes there has been a concerted effort to probe these unique molecules across a range of chemistry disciplines. Two of the most well-developed classes of isolable carbenes, *N*-heterocyclic carbenes (NHCs) and cyclic (alkyl)(amino)carbenes (CAACs), have been of interest due to their contrasting reactivities. NHCs are generally considered to be both weak nucleophiles and bases; while CAACs exhibit both increased nucleophilicity and basicity in comparison to NHCs. While studies on metal–carbene complexes, from both a photophysical and structural perspective, are well known, examples employing metal-free systems are still relatively unexplored.

Our research efforts have been to modulate the properties, both photophysical and structural, of *NH*-containing fluorophores. The focus of this seminar is to look at the interactions of NHCs and carbazoles, wherein we find the emission of the fluorophore is quenched at elevated concentrate, but returns to its emissive state upon dilution. Further investigation reveals the defining characteristic of these products is a non-traditional hydrogen bond between the

carbazole *NH* and the carbenic carbon of the NHC. With this as our foundation, we posit that oligomeric carbazoles can form hydrogen bonded adducts with NHCs, ultimately imparting geometric constraints on these disordered foldamers.

29. New developments in interrupted carbonyl-olefin metathesis reactions

***Sean Burns**, seanbur@umich.edu. University of Michigan, Ann Arbor, Michigan, United States*

Carbonyl and olefin functionalities can undergo carbon-carbon bond-forming reactions through carbonyl-ene or Prins pathways upon activation with Lewis or Brønsted acids. Both pathways are accessible from similar substrates, depending on the choice of catalyst and conditions. Carbonyl-ene reactions result in the formation of homoallylic alcohols upon addition of an electrophilic carbonyl to an alkene with concomitant transfer of an allylic hydrogen atom. In comparison, the Prins reaction proceeds through an intermediate carbocation that is subsequently captured by an exogenous nucleophile to result in the corresponding alcohols. Our recently reported catalytic carbonyl-olefin metathesis reaction represents a third reactivity mode between carbonyl and alkene functionalities that proceeds via intermediate oxetanes and results in cyclic alkene products. As part of our efforts in developing new cycloaddition reactions between carbonyls and olefins, we discovered a fourth reactivity mode between these two functional groups that similarly proceeds under Brønsted or Lewis acid-catalysis. This transformation resembles the carbonyl-olefin metathesis reaction in that it also relies on intermediate oxetanes, however the ultimate products formed are tetrahydrofluorenes. We herein report new developments in this area of interrupted carbonyl-olefin metathesis reactions relying on aliphatic ketones as substrates to form valuable carbocyclic building blocks in a single transformation.

30. Kinetics of chlorine reactions with RNA: A step toward predicting viral inactivation during water treatment

***Alex Szczuka**, aszczuka@umich.edu. Civil and Environmental Engineering, University of Michigan, Ann Arbor, Michigan, United States*

Chlorine treatment is commonly used to inactivate viruses. Chlorine inactivates viruses by reacting with their biomolecules, including their genomes. Understanding viral genome reaction mechanisms, and identifying the biological significance of reaction products, can help us predict the fate of newly emerging viruses during treatment. However, reaction mechanisms and reaction products of viral genomes with chlorine are poorly characterized. Further, genome inactivation kinetics have been predominantly measured using polymerase chain reaction (PCR)-based assays, which can underestimate degradation rates, and bias observed reaction kinetics. To address this, we exposed the genome of bacteriophage MS2, a commonly used surrogate for viruses in water treatment scenarios to chlorine. After exposure, we digested the genome enzymatically into individual nucleosides, and measured decay and product formation using an Orbitrap ion mass analyzer. We found that reaction kinetics of nucleosides incorporated in the MS2 genome differed from those observed for unincorporated nucleosides, and the reaction kinetics of the MS2 genome measured using the Orbitrap ion mass analyzer differed compared to reaction kinetics measured using PCR based assays. The results of this study will help us predict the fate of emerging viruses during treatment, and help us identify the biological significance of viral genome disinfection products.

31. Alkene aminoarylation via N-centered radical reactivity of sulfinamides

***Mark Glossbrenner**, mglossbr@umich.edu. Chemistry, University of Michigan, Ann Arbor, Michigan, United States*

Reported is an alternative strategy for accessing arylethylamines from ubiquitous starting materials. Careful modulation of the pKa properties of the N-H bonds found in sulfinamides allows for single electron transfer (SET) pathways to be exploited under photocatalytic conditions to participate in Smiles-Truce rearrangement with arylsulfinamides and unactivated alkenes. Our group has successfully established a system wherein generation of arylsulfinamide radicals can be achieved under basic conditions and can be adjoined with alkenes to make new C-N bonds yielding intermediate carbon centered radicals that undergo Smiles-Truce rearrangement. Using this method, we have shown that pharmaceutically relevant building blocks can be accessed and with high regio- and diasterocontrol. The nature of these rearrangements lends itself not only to 1,2-aminoarylation, but also as a viable methodology to access nitrogen-centered radicals (NCRs). More work to explore use of these NCRs is currently underway in our group.

32. Chemists with disabilities and inclusion: ACS efforts and resources

***Jim Landis**, jlandis@home.msen.com. Detroit Local Section, American Chemical Society, Detroit, Michigan, United States*

The American Chemical Society has been working to include people with disabilities into the chemical enterprise for many years. A brief history of these efforts will be described, followed by a discussion of the resources currently available to the chemistry community as a whole with reference to issues concerning the education and employment of individuals with disabilities.

33. Investing in the bigger picture: Importance of incorporating diversity, equity, and inclusion into research

***Brianna Simms**, briana.simms@duke.edu. Departments of Chemistry, University of Cincinnati, Cincinnati, Ohio, United States*

As scientists, we often address questions from a bottom-up or top-down approach. Whichever way you attack questions or challenges in science, the bigger picture is always in view. We can approach diversity, equity, and inclusion in research (DEIR) efforts in this way too. When we invest in improving DEIR, we see positive results at the local level (student/trainee, department, institution) and in the broader community (chemistry, the scientific field, and outside of the scientific world). In this talk, we will discuss what makes up a valuable investment in DEIR, and how you and your department can work towards making this investment. Then we will talk about the overall potential outcomes of making this investment and how everyone wins when DEIR is a conscious and active component of the field.

34. Understanding diversity, equity, and inclusion in chemistry through National Diversity Equity Workshops (NDEWs)

***Vartike Chandra Saman**, vsaman1@jhu.edu. Departments of Chemistry, Johns Hopkins University, Baltimore, Maryland, United States*

The culture in every discipline exhibits important differences emerging from the differentiated modalities required to practice and advance a given discipline and its ontological development. Thus, it is critical to characterize and analyze how multiple systems intersect to produce inequalities within a discipline over a period. Our project ‘Open Chemistry Collaborative in

Diversity Equity (OXIDE)' by organizing biennial workshops- National Diversity Equity Workshops (NDEWs) tries to articulate and contextualize solutions regarding DEIR driven by the top-down hypothesis where we argue that holding department chairs accountable and providing them with appropriate tools will lead to DEIR. The National Diversity Equity Workshops represents is a biennial series of diversity workshops designed for chairs of leading research intensive (RI) chemistry departments to discuss methods and policies in order to reduce inequities that have historically led to disproportionate diversity representation on academic chemistry faculties by helping to change the infrastructure from the top down. The findings have been analyzed and reinterpreted contextually in order to understand how people learn the concepts, practices, and ways of thinking within chemistry departments and a significant portion of the faculty have been driven to advance these efforts either because of social justice or the business case.

35. Fostering diversity, equity, inclusion, and respect across the chemistry enterprise

***Reni Joseph**, rjoseph15@stlcc.edu. Departments of Chemistry, St. Louis Community College, St. Louis, Missouri, United States*

The talk will highlight the work being done by the Committee on Minority Affairs (CMA), American Chemical Society (ACS) to engage and promote Diversity, Equity, Inclusion and Respect across the chemical enterprise. The Committee on Minority Affairs was established in 1993 by the American Chemical Society to address the racial and ethnic underrepresentation in ACS membership. Learn how CMA approaches this opportunity through our mission, vision and strategic goals developed to help accomplish inclusivity and respect within the chemistry enterprise.

36. Identifying the relevance of organic chemistry through writing

***Safron Milne**[2], milne066@morris.umn.edu, Solaire Finkenstaedt-Quinn[2], Nicholas Garza[2], Steven C. Zimmerman[1], Ginger V. Szymczak Shultz[2]. (1) Chemistry, University of Illinois Urbana-Champaign, Urbana, Illinois, United States(2) Chemistry, University of Michigan, Ann Arbor, Michigan, United States*

Students in organic chemistry, a historically difficult subject, often exhibit decreasing motivation through the course of the semesters. Therefore, educators seek ways to support students' motivation for learning. Appealing to students' interests in academic settings or demonstrating chemistry's relevance to their life have been suggested as mechanisms to support self-motivated learning. To support students in making their own connections, we implemented an open-ended writing assignment in an introductory level organic chemistry course where students were tasked with choosing an organic molecule and writing about why they found it important to their life. Utilizing a relevance framework, this study investigates the types of connections that students made with their chosen organic compound on personal, societal, and vocational levels. Through qualitative analysis of the writing assignments and interviews with a subset of students, we found that students were identifying the relevance of a variety of organic molecules throughout various times in their life. Personal relevance, rather than societal or vocational relevance, dictated the choice of many of the students' molecules. Additionally, the students were motivated to study their molecule as shown by the level of detail provided in their assignments. Our study indicates that incorporating short writing tasks that support students in identifying the relevance of chemistry to their own lives may reinforce their comprehension and appreciation of chemistry as it may support their motivation to learn.

37. Polymer and organometallic systems thinking activities for second semester organic chemistry

Amelia Anderson-Wile[1], *a-anderson.4@onu.edu, Sara Madsen*[2]*. (1) Chemistry and Biochemistry, Ohio Northern University Getty College of Arts and Sciences, Ada, Ohio, United States(2) South Dakota State University, Brookings, South Dakota, United States*

Two modules related to polymer and organometallic chemistry have been developed and piloted for second semester organic chemistry lecture courses. The modules focus on incorporating introductory systems thinking concepts using the ideas of green chemistry and the United Nations Sustainable Development Goals (UNSDGs) to help students relate chemistry concepts to real world applications. Each module is broken up into multiple activities which could be incorporated into either a traditional lecture as homework assignments or an active learning classroom as group activities. In addition to the UNSDGs, students are introduced to concepts such as atom economy, E-factor, and solvent intensity. Students are challenged to develop Systems-Orientated Concept Map Extensions (SOCME) to illustrate the relationships between chemical principles and big picture ideas. Summative assessments along with the evaluation of SOCMEs provide insight into student learning outcomes for this project.

38. Eliciting student understanding of the relationship between energy and interactions in the context of effects of solvation in organic reactions by engaging them in causal mechanistic reasoning

Kriti Seth[1], *sethkrit@msu.edu, Elizabeth L. Day*[2]*, Melanie Cooper*[1,3]*. (1) Chemistry, Michigan State University, East Lansing, Michigan, United States(2) Chemistry & Biochemistry, The University of Texas at El Paso, El Paso, Texas, United States(3) CREATE for STEM, Michigan State University, East Lansing, Michigan, United States*

Causal mechanistic reasoning is a powerful explanatory and predictive tool that involves unpacking behaviors and entities at a scalar level below and connecting the lower-level behaviors back to the target phenomenon. Thus, one way to support students as they make sense of complex, multifaceted phenomena is to help them engage in causal mechanistic reasoning by constructing explanations in the context of formative tasks. We have used evidence centered design to construct a set of scaffolded formative tasks, that are intended to elicit student understanding of how and why a particular solvent would change the rate of a given organic reaction. We have collected written responses from about 250 students enrolled in a transformed organic chemistry curriculum and have conducted think-aloud interviews with a subset of 10 students. We found that students struggled to “keep the thread” of explanation going in our pilot activity for this phenomenon, which requires them to retrieve and coherently connect a long chain of inferences. The relationship between strength of the solvent-solute interaction and energy (and stability and reactivity) was one such causal link that students especially struggled with, but that is integral to many chemical phenomena. Using resources framework as our theory of cognition, we have characterized the resources leveraged by students in their responses, the type of reasoning they used, and the type as well as number of causal linkages established between ideas. Using this data, we were also able to identify areas which are specifically troublesome where they need more scaffolding and/or instructional support. This work can inform us on how to best design curriculum and assessment materials to support students in constructing causal mechanistic explanations to reason through other complex phenomena.

39. Case study on post-secondary chemistry instructors' resources for planning instruction

***Rebecca Fantone**, rfantone@umich.edu, Ginger V. Szymczak Shultz. University of Michigan, Ann Arbor, Michigan, United States*

This study draws inspiration from mathematics education research that explores how K-12 mathematics teachers develop resources (e.g., in-class problems, homework sets, learning management systems, etc.) as part of their teaching work. This research emphasizes the importance of teachers sharing resources. To understand this work in post-secondary chemistry instruction, we used a case-study approach to examine how three post-secondary instructors with varying levels of experience develop resources for teaching chemistry. We qualitatively analyzed multiple interviews and observations collected over multiple semesters. We capture what resources the instructors adopted, how they were developed over time, and examine the broad resource systems developed for their work. We will present how the three instructors developed resources for their contexts and what contextual factors, especially their social interactions, influence their work, providing an alternative perspective to understanding post-secondary chemistry instruction.

40. Analysis of silylated polyphenols found in banana peels

***Barry Miburo**, bmiburo1@gmail.com. Sciences and Mathematics, Abraham Baldwin Agricultural College, Tifton, Georgia, United States*

Polyhenols have been found to have beneficial properties of interest to human health. They have been detected in a large variey vegetable sources. Banana peels, which are a usually discarded by-product of banana foods processing, are an important source of polyphenols. That enhances their value as a potential source of medically valuable substances. Polyphenols from banana peels have been studied by chemical and spectroscopic methods such as HPLC-UV and HPLC-MS. Their study by GCMS is limited by the fact that their boiling points are beyond the ranges of the instruments. Transformation of the polyphenols to derivatives with lower boiling points is one way to overcome that challenge. In this study, banana peels were extracted and derivatized by silylation and the derivatives were studied by GCMS. The results will be presented at the CERM.

41. Investigating how organic chemistry faculty structure their knowledge and their beliefs about student learning

***Sewwandi Abeywardana**, abeyward@msu.edu, Melanie Cooper. Chemistry, Michigan State University, East Lansing, Michigan, United States*

Previous literature on how people learn suggest that disciplinary experts organize their knowledge differently than the beginners. Studies from a wide range of fields such as physics, computer science, and chess show that experts in a discipline tend to organize their knowledge around overarching ideas which help them access and use that knowledge in new contexts, whereas beginning students tend to focus on disconnected surface features. In chemistry, such studies have been limited to reaction card sorting tasks and to our knowledge there are no investigations on how organic chemistry faculty structure their knowledge as a whole. In this study, in a semi-structed interview setting, we explore how organic chemistry faculty (n=8) structure their knowledge and faculty beliefs about student learning using a Grounded Theory approach to analyze interview data. Initial themes that emerged from interviews suggest faculty tend to organize their knowledge around overarching ideas such as structure and properties relationships, energy and bonding and interactions. Furthermore,

these themes tend not to align with the ideas faculty believe are important for students to learn. We propose that findings from this study can expand the literature base on how organic chemistry experts structure their knowledge as well as how faculty may support students to think and organize knowledge. Additionally, by explicitly eliciting the disconnect between faculty knowledge structures and how teaching and learning are enacted in their courses, it may be possible develop faculty support structures that help them better align these their beliefs with what we know about the development of expertise.

42. Analysis of the ashes of the peels of bananas grown in South Georgia

***Barry Miburo**, bmiburo1@gmail.com. Sciences and Mathematics, Abraham Baldwin Agricultural College, Tifton, Georgia, United States*

The peels of bananas grown in South Georgia were incinerated and extracted with water. The soluble bases contained in the ashes were titrated with hydrochloric acid. The extracts that were found to contain hydroxides were treated with barium chloride to precipitate the carbonates and the hydroxides were titrated separately. The elements contained in the extracts, the extraction residues and the total ashes were analyzed by ICP atomic absorption spectroscopy. The results will be presented in the 2023 CERM.

43. Ligand-Associated Sorbents and Extraction Systems for Rare-Earth Element Recovery from Coal Fly Ash

***Timothy Dittrich**, timothy.dittrich@wayne.edu. Civil & Environmental Engineering, Wayne State University, Detroit, Michigan, United States*

Rare-earth elements (lanthanide series plus scandium and yttrium) have many critical uses in advanced technology and the lack of a reliable domestic supply has been identified as a vulnerability to US economic security. Commercial sources of rare-earth elements (REEs) include ion exchange clays and bastnaesite, monazite, and xenotime minerals; however, the processing of these materials to extract and recover the rare-earth elements is challenging and resource intensive. In addition to these traditional ores, waste materials such as coal fly ash, acid mine drainage solids, and mine tailings have shown to be potentially viable alternative sources. Our interdisciplinary team has developed two new classes of ligand-associated separation media using DTPA-analog and glycolipid molecules and designed a process to produce rare-earth oxide concentrates and individually separated elements from coal fly ash. Bench-scale testing has produced >10 wt% rare-earth oxide powders from coal fly ash leachates. We have also produced high-purity (>90% pure) Sc and Th in one pass through a packed-bed column with mixed element REE solutions, while producing significant separation among the remaining 15 naturally occurring REEs. The process allows for the separation of mixed light REEs from heavy REEs in a single pass through a column, with further separation occurring with subsequent passes through a sequential column separation scheme. These new sorbents could be used in an environmentally-friendly process that leads to lower costs than are currently provided by state-of-the art organic solvent extraction and requires significantly less hazardous waste disposal.

44. Employing radicals and bismuth in lanthanide single-molecule magnet design

***Selvan Demir**, sdemir@chemistry.msu.edu. Departments of Chemistry, Michigan State University, East Lansing, Michigan, United States*

Molecules that possess an energy barrier to spin inversion have intriguing potential applications in areas such as magnetic refrigeration, molecular spintronics and high-density

information storage. For these applications, however, key performance characteristics such as large spin-relaxation barriers (Ueff) and high magnetic blocking temperatures (TB) are required. Lanthanides have been proven to be particularly well-suited for the design of single-molecule magnets owing to their large magnetic moments and magnetic anisotropy that stem from strong spin-orbit coupling of the 4f orbitals. By using lanthanide ions such as Tb3+, Dy3+, and Er3+ which possess intrinsically large orbital angular momentum, significantly higher Ueff and TB can be achieved. A general methodology to improve TB in multinuclear single-molecule magnets is to generate strong magnetic exchange between lanthanide centers through the employment of radical bridging ligands with diffuse spin orbitals that can penetrate the core electron density of the lanthanide ions where the 4f spin orbitals lie buried. Another successful approach to strong coupling targets the use of heavy p-block elements since their diffuse valence orbitals facilitate better penetration of the core electron density of the lanthanide ions relative to diamagnetic ligands comprising lighter p-block elements. Here, we will present the synthesis of multiple lanthanide single-molecule magnets that contain radical ligands and bismuth clusters, respectively.

45. Cadmium Schiff base complexes that glow: Unexpected structures and room temp phosphorescence

*Morgan Deal[1], Matthias Zeller[2], **Evan R. Trivedi**[1], trivedi@oakland.edu. (1) Oakland University, Rochester, Michigan, United States(2) Purdue University, West Lafayette, Indiana, United States*

Exploratory work with respect to the title complexes has been surprising and exciting. We will present our structural findings by an analysis of single crystal X-ray and other spectroscopic techniques. These complexes have Ci symmetry and remarkable room temperature phosphorescence with lifetimes on the millisecond scale. Synthesis, structural characterization, and photophyscial characterization will be discussed for these fascinating cadmium schiff base complexes.

46. Coordination chemistry studies for ion flotation to selectively remove nickel(II) and cobalt(III) using amine-based ligands

***Eva Mwakazi**, evamwakazi@wayne.edu. Chemistry, Wayne State University College of Liberal Arts and Sciences, Detroit, Michigan, United States*

Ion flotation is a surfactant-based separation process used to concentrate metal ions present in dilute aqueous solutions using surfactants with an opposite charge to that of the metal ion. Due to the emerging electric vehicle (EV) industry and plans to reduce carbon emissions by fuel operated vehicles, nickel, and cobalt have found an increased demand in manufacture of EV batteries. In this research we propose extracting nickel and cobalt from fly ash a byproduct of coal mining rich in 3d and 4d metals using ion flotation providing an alternative source to the fast-depleting natural reserves present. Ligand field theory and coordination chemistry gives insight to the preferred geometries of these metal complexes; cobalt (III) d6 low spin is octahedral geometry and nickel (II) d8 low spin is square planar geometry. We hypothesize that we can have selective removal of cobalt and nickel by using strong field ligands that promote these geometries. In this research we will use sodium dodecyl sulfate as the anionic collector surfactant and sequestriant ligands are: triethylenetetramine, ethylenediamine, cyclen, 1,2-Bis(3-aminopropylamino) ethane (3,2,3) and N,N′-Bis(3-aminopropyl)-1,3-propanediamine (3,3,3). The parameters to be studied include molar ratio of coordination complexes of ligand to metal, optimum concentrations of surfactant and the pH. They will be studied using coordination chemistry experiments with subsequent analysis using UV-visible

followed up by TD-DFT calculations, mass spectrometry and ICP-MS. Data obtained shows highest amount of nickel removal occurs at basic pH with ethylenediamine and triethylenetetramine showing 98% nickel recovery. In a mixture of gadolinium and nickel using 333 and 323 selective recoveries for nickel occurred at pH 11 with 99% recovery and gadolinium at pH 8 at with 80% recovery. Coordination chemistry studies and a preliminary crystal structure shows nickel coordinates in 2:3, 1:3 with triethylenetetramine, ethylenediamine respectively suggesting an octahedral structure of the complexes.

47. Multi-electron redox chemistry with thorium(IV) iminoquinone complexes

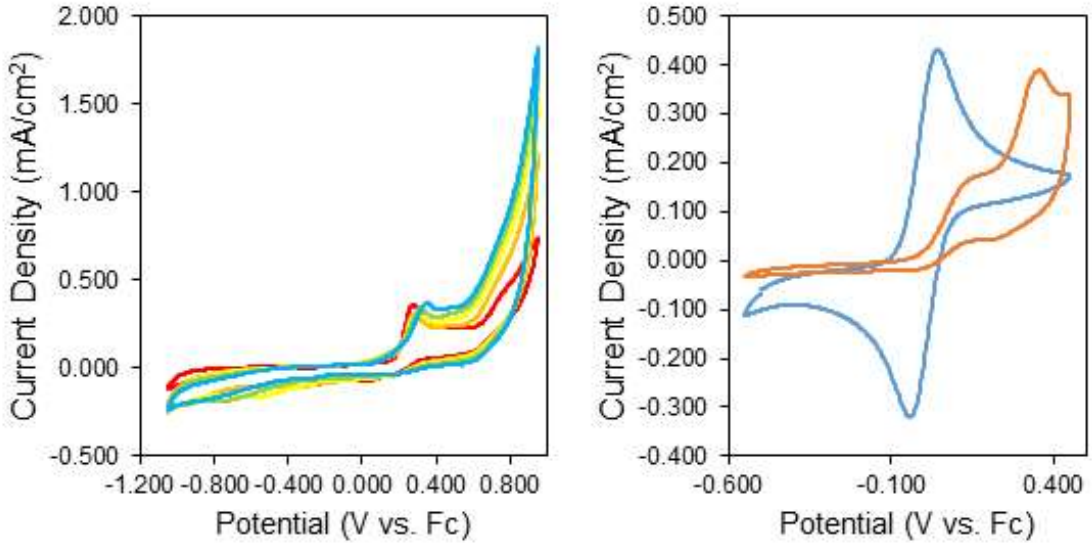
***Suzanne C. Bart**, sbart@purdue.edu. Department of Chemistry,, Purdue University System, West Lafayette, Indiana, United States*

Thorium complexes primarily exist in the thermodynamically stable (IV) oxidation state, with limited examples of low-valent thorium(III) complexes known. As a result, redox chemistry with thorium is challenging without carefully designed ligand environments. This redox-restricted nature of thorium(IV) makes redox-active ligands an attractive option to facilitate multi-electron redox chemistry. In this work, a series of thorium(IV) complexes featuring the redox-active iminoquinone ligand and its derivatives, including the iminosemiquinone and amidophenolate species, were synthesized and isolated. Oxidation chemistry resulted in formation of a terminal oxo species, which is rare for thorium species. Spectroscopic and structural characterization of each derivative established the +4 oxidation state for thorium with redox chemistry occurring on the ligand. Magnetic and EPR studies confirmed the formation of new thorium species featuring multiple ligand radicals as well.

48. Electropolymerization of organometallic cyclopentadienyl pyridazines for advanced electronics

*Valeria Mattern Mondragon[1], **Daniel J. Little**[1], danlittle1010@hotmail.com, Nathan C. Tice[2], Seth T. King[3]. (1) Mathematics, Computer, and Natural Sciences, Ohio Dominican University, Columbus, Ohio, United States(2) Department of Physical Sciences, University of Findlay, Findlay, Ohio, United States(3) Department of Physics, University of Wisconsin-La Crosse, La Crosse, Wisconsin, United States*

Heterocycles and their derivatives have been of great interest in organic electronic applications, such as organic light-emitting diodes, (OLEDs) and organic photovoltaics (OPVs). Here we report the formation of a cyclopentadienyl pyridazine organometallic complex that incorporates metal atoms directly into a thin-film electropolymer. Electropolymerization allows for convenient pathways for tuning band structure, as well as other chemical and physical properties. The electrochemical properties and structural characterization will be discussed, as well as insights into the mechanism of polymerization.



49. Morphology-controlled vapor-phase nanowire growth with Ruddlesden-Popper Lead Bromide Perovskite

***Pushpender Yadav**, yadavpus@msu.edu, Kyeongdeuk Moon, Anupam Biswas, Seokhyoung Kim. Chemistry, Michigan State University, East Lansing, Michigan, United States*

Two-dimensional (2D) Ruddlesden-Popper (RP) halide perovskite has attracted significant attention as a promising candidate for high-efficiency light sources. RP perovskites, when synthesized into well-defined nanowires (NW), have the potential to serve as nanoscale coherent light sources by incorporating optical cavity effects with their light emission behaviors. However, RP perovskites tend to grow in macroscopic thin sheets as opposed to relevant NW structures due to the layered nature of the crystal lattice, which necessitates a new way of controlling nanoscale morphologies. Here, we achieve NWs of RP BA_2PbBr_4 (BA= butylammonium), for the first time, using chemical vapor deposition (CVD) by systematically navigating a wide range of growth conditions and constructing growth regimes of distinct morphologies. Of the two particular regimes that produce well-formed nanostructures, we find that RP BA_2PbBr_4 grows into energetically-favored thin nanoplatelets (NPLs) at high temperatures whereas intermediate temperatures allow it to first grow into 3D pyramidal nuclei and then get elongated into NWs upon continued growth. We propose temperature-dependent diffusion of surface species as a deciding factor of our morphological control. We present crystallographic and elemental analyses to confirm that our NWs have appropriate lattice structures and chemical stoichiometry of BA_2PbBr_4. Static and time-resolved optical measurements show quantized absorption and emission features at 400 and 406 nm, respectively, with a radiative decay time of 1.7 ns which is much quicker than the 8.7 ns decay time of prototypical 3D $CsPbBr_3$ perovskite. The RP NWs exhibit a strong exciton binding energy of 276 meV, which can be understood by the reduced dimensionality of BA_2PbBr_4. The strong absorption and radiative emission characteristics suggest that the RP BA_2PbBr_4 NWs are good candidates as bright, ultrasmall light sources for nanophotonic and optical communication applications.

50. Ultrafast excited-state interactions between carbon dots and luminescent materials

***Sukanya Saha**, sukanya.saha@wmich.edu. Chemistry, Western Michigan University, Kalamazoo, Michigan, United States*

Carbon-based-nanoarchitectures have been in the forefront of research for last three decades with applications in interdisciplinary areas of science and engineering. In recent years, a new class of Carbon-nanoarchitectures have emerged called Carbon dots with absorption in the UV to visible region and variable photoluminescence. Electrostatic-interaction or covalent-binding of organic-chromophores or semiconductor-nanomaterials to Carbon Dots can be achieved to develop hybrid optical-materials with interfacial-energy/charge-transfer interactions. In this study, we have designed and developed a novel photoactive-nanomaterial obtained by the spontaneous electrostatic coupling of negatively charged carbon nanodots (multi-colored N-doped and without-doped) with a dye, 3,3′-dihexyloxacarbocyanine iodide($DiOC_6$). We have also probed the interaction between different bandgap perovskites with the carbon dots. Using steady-state, time-resolved absorption, and photoluminescence experiments, we have investigated the excited-state-interactions in the CD^-/dye and CD^-/perovskites hybrid assembly. PL studies revealed enhancement of the dye emission (75% to 122%) upon addition of CD^- (without vs doped), which supports the fact, there is an electrostatic and hydrophobic-interaction which causes the enhancement. On the other hand, PL studies shows quenching of perovskites emission upon addition of CD^-. Ultrafast transient absorption measurements confirmed there are two different processes going on in two hybrid systems. The PL enhancement in CD^-/dye is because of the reduced non-radiative deactivation due to energy-transfer from CD^- to dye, achieved by coupling $DiOC_6$ and Carbon dots, produced a long-lived species. On the other hand, CD^-/perovskites showed interfacial-charge-transfer process.

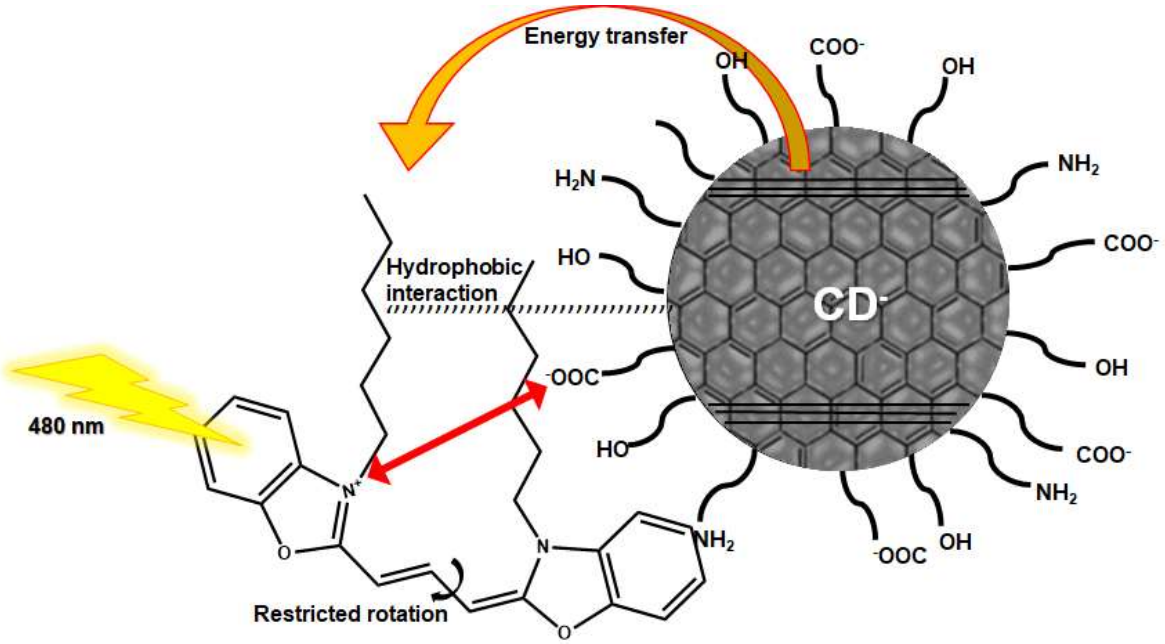


Figure 1. Schematic of the interaction between $DiOC_6$ and CD^-s in toluene.

51. CdS ultrasmall quantum dots: Synthesis and gelation kinetics

***Isa Ahmed**, isaahmed41@gmail.com, Vinicius Alevato Neves, Stephanie L. Brock. Chemistry, Wayne State University College of Liberal Arts and Sciences, Detroit, Michigan, United States*

The generation of environmentally friendly fuels like H2 from renewable energy sources is a critical component of efforts to combat the energy crisis and climate change. CdS is a visible light-absorbing semiconductor often used for photocatalytic water splitting to generate H2 gas. Using CdS quantum dots (QDs), materials with 0D dimensionality, have benefits over bulk materials such as increased surface area and light absorption, in addition to the ability to tune

the light absorption wavelength by controlling quantum dots' size. However, QDs tend to aggregate with time, decreasing their efficiency. Forming QD assemblies prevents their aggregation, and our group already showed that the oxidative assembly of QDs into aerogels (AGs) improves their photocatalytic efficiency by enabling multiple photogenerated electrons to be driven towards catalytic sites, besides keeping high surface areas.

To obtain a better comprehension of the energy transfer processes involved in the photocatalytic application of CdS QDs and AGs, better computational models are needed to more precisely calculated the band energies and overall electronic structure of the materials, especially concerning interparticle bonding. The development of more advanced models is hindered not only by the lack of data regarding CdS QDs band energies, but also by the lack of good and reproducible synthesis protocols for CdS QDs with sizes below 2.0 nm. The synthesis of these ultrasmall quantum dots with precise size control is a challenging task, and can be considered the bottleneck for the further modeling strategy that starts with smaller QDs sizes, going to bigger sizes and then to the aerogel frameworks.

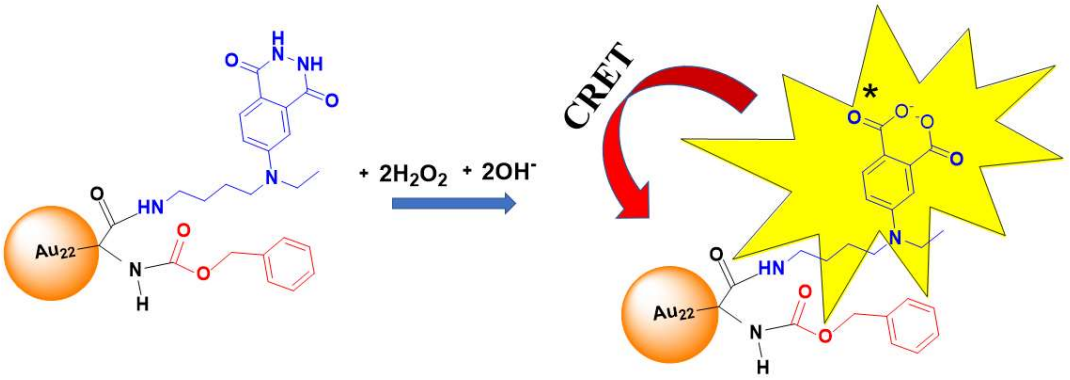
Herein, we will demonstrate a controlled synthesis method for CdS quantum dots ranging in diameter from 1.5-3.2 nm, and their oxidative assembly to from gels, and aerogels. Finally, we will provide spectroscopic data for the CdS ultrasmall quantum dots and discuss our goals for the future characterization of the QDs and AGs with respect to electronic structure and computational modeling.

52. Photoluminescence enhancement of quantum-sized gold nanoclusters by Chemiluminescence-resonance-energy-transfer

***Shivi Saxena**, shivi.saxena@wmich.edu, Atheer Alharbi, Rama Krishna Guda. Chemistry, Western Michigan University, Kalamazoo, Michigan, United States*

Over the past few decades, quantum-sized gold clusters have emerged as ultra-small nanomaterials with intriguing photophysical characteristics such as good photostability, long-luminescent lifetimes, and large two-photon cross sections. This has paved the way for their applications including bio-imaging, energy harvesting, and optical sensing. However, their relatively low Photoluminescence Quantum Yield (PLQY) when compared to organic dyes, quantum dots, and luminescent polymers is limiting their use. The all-chromophore conjugation of clusters is one promising strategy leading to manifold PL enhancement in clusters. However, the greater extent of conjugation leading to chromophore aggregation is one drawback of this strategy. One lesser-utilized strategy for PL enhancement in clusters is by energy transfer from a covalently bonded chemiluminescent (CL) Reagent to the gold cluster. The CL reagent acts as a donor and generates a high-energy state leading to energy release after the reaction. This photonic energy can be accepted by the conjugated cluster like other 'signal-on' acceptors such as fluorescent dyes, polymers, and quantum dots. The main objective of this study is to enhance PLQY in gold clusters by the avenue of resonance energy transfer by a CL reagent, N- (4-aminobutyl)-N-ethylisoluminol (ABEI). The clusters $Au_{25}(SG)_{18}^-$, $Au_{22}(SG)_{18,}$ and $Au_{18}(SG)_{14}$ are synthesized by altering the ratios of Au with Glutathione and $NaBH_4$ under different reaction conditions. The ABEI-conjugated clusters are synthesized by known EDC/NHS coupling reaction. The covalently bonded cluster with ABEI is probed for photoluminescence enhancement by the CRET mechanism. The effect of non-covalent interactions between ABEI and clusters is also utilized for enhanced PL in gold clusters. The CL intensity of ABEI is also probed for enhancement upon binding with clusters. ^1H NMR and ESI-MS revealed the number of ABEI conjugated to the clusters. The CL and PL counts are

observed in the microplate reader. The CL-spectra profile of ABEI and ABEI-Cluster system along with PL curves confirmed the energy-transfer events.



Schematic: CRET in ABEI- conjugated $Au_{22}(SG)_{18}$

53. Riboflavin binding protein: Vitamin interactions in the binding pocket

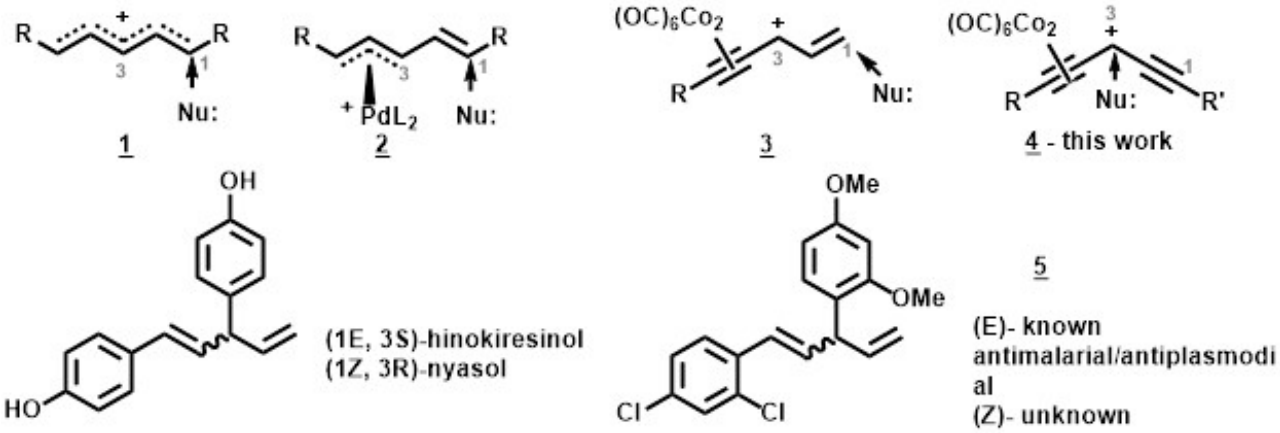
***Simona Marincean**, simonam@umich.edu, Diana Nichols, Marilee Benore. Department of Natural Sciences, University of Michigan - Dearborn, Dearborn, Michigan, United States*

Riboflavin, a B family vitamin that is characterized by an isoalloxazine ring connected to a ribityl moiety via a C-N bond, is the precursor of two coenzymes, flavin mononucleotide (FMN) and flavin adenine dinucleotide (FAD). These two cofactors are involved in many electron and proton transfer reactions, DNA repair, protein folding, fatty acid and amino acid oxidation, and other metabolic processes. Humans have lost the ability to synthesize riboflavin which is provided through diet and transported in cells by carrier proteins. Recently, Riboflavin receptors have been reported as overexpressed in several types of cancer. Thus, the nature and specificity of the vitamin-carrier protein interactions are critical. We have synthesized and characterized a series of Riboflavin derivatives selectively modified in the ribityl region to address the structure-activity relationships. The individual and combined effects of these structural modifications on protein binding of the derivatives have been examined through fluorescence studies.

54. Reliable C-3 substitution in pentadiynyl Nicholas reactions and the preparation of dichlorodimethoxy analogues of hinokiresinol and nyasol

***Brent St. Onge**, stongeb@uwindsor.ca, Marcus Muresan, James R. Green. Chemistry, University of Windsor, Windsor, Ontario, Canada*

The application of pentadienyl cations **1** and their pentadienylmetal and pentenylmetal equivalents (**2**, **3**) towards skipped diene synthesis is a challenge, due to the dominance of C-1 over C-3 nucleophilic attack. The reaction of the pentadiynyldicobalt cation complexes **4** with nucleophiles feature the dominance of their C-3 reactivity, and they will be discussed, along with the scope of their nucleophilic partners and limits in their regioselection. The application of these reactions in the synthesis of both (Z)- and (E)- isomers of antimalarial hinokiresinol/nyasol analogue **5** also will be presented.



55. New developments in visible light-mediated aza Paternò-Büchi reactions

***Seren Parikh**, sgparikh@umich.edu. University of Michigan, Ann Arbor, Michigan, United States*

Azetidines are four-membered nitrogen-containing heterocycles that represent powerful synthetic building blocks in the design of bioactive molecules. The azetidine system is most-commonly accessed via intramolecular nucleophilic substitution or by the reduction of beta-lactams, but these methods are limited in scope. A [2+2]-cycloaddition between an imine and alkene, referred to as the aza Paternò-Büchi reaction, is arguably a more direct and efficient transformation to access azetidines. We have recently developed a new design principle for aza Paternò-Büchi reactions relying on the activation of activated alkenes or functionalized imines with a suitable photosensitizer and visible light. We herein report new developments in this class of transformations that overcome existing limitations in inter- and intramolecular [2+2]-cycloadditions to give rise to previously inaccessible azetidines in a single synthetic transformation.

56. Photo and catalytic desulfurizations: Application to organic molecules, peptides and proteins

***Venneti Naresh Murty**, nareshmurty@gmail.com, Ganesh Samala, Rana Morsy, Lawrence Mendoza, Jennifer L. Stockdill. Chemistry, Wayne State University, Detroit, Michigan, United States*

A high yielding photodesulfurization of cysteine containing peptides reported with minimum equivalents use of the phosphine reagents. This facile desulfurization method doesn't demand the use of radical initiator or photocatalyst or exogenous thiols or other H-atom donors. It has wide applicability in organic and aqueous solvent conditions. This method was successfully examined with unprotected and protected peptides with different combinations of amino acids. The applicability of this method was implemented with synthesis of polypeptides and proteins. In addition, a catalytic thiyl-radical mediated desulfurization method was developed, and this method utilizes a catalytic phosphite reagent and thermal initiator with stoichiometric silane as a hydrogen donor. This method was applicable to organic molecules and small peptides.

57. Investigating coupling reagents for the synthesis of ferrocene hybrids from ferrocenecarboxylic acid in organic laboratories

***Marwa Abdel Latif**[1], abdellmk@udmercy.edu, **Steven Scribner**[1,2], scribnsl@udmercy.edu, **Mara Livezey**[1], livezemr@udmercy.edu, **Eleni Geragosian**[1], geragoek@udmercy.edu. (1)*

University of Detroit Mercy, Detroit, Michigan, United States(2) University of Michigan Dearborn Office of Metropolitan Impact, Dearborn, Michigan, United States

Synthesis of ferrocene hybrids for anti-cancer studies in primarily undergraduate institutions has been challenging due to the limited availability of starting materials and the lack of stability of recommended synthetic pathways. This project is focused on exploring multiple synthetic pathways of a selection of ferrocene hybrides with ferrocenecarboxylic acid and a set of anilines with various substituents. A combination of coupling reagents such as dicyclohexyl carbodiimide (DCC) with hydroxy-benzotriazole (HO-Bt) were investigated for these syntheses under atmospheric conditions. The work was designed for an undergraduate organic chemistry laboratory series and modifications were implemented through multiple sections to evaluate potential combinations for each of the anilines used for these studies. This presentation will address the synthetic approach, challenges, and product yields for various coupling combinations.

58. Effect of PRIMA-1^{MET} and vitamin D on triple negative breast cancer cell lines

***Shadi Kotob**, skotob@umich.edu, **Ashlyn Savoie**, asavoie@umich.edu, **Jessica Kelts**, jkelts@umich.edu. University of Michigan-Flint, Flint, Michigan, United States*

Triple Negative Breast cancer (TNBC) affects many worldwide and is more difficult to treat than other types of breast cancer due to its lack of hormone receptors. We previously sought to determine the effect of vitamin D on TNBC cell lines and found that TNBC cells were either resistant to vitamin D or it caused them to grow more. In MCF-7 cells and many other cell types, vitamin D slows cell proliferation. It was theorized that lack of p53 activity caused the lack of typical response to vitamin D in the TNBC cell lines MDA-MB-468 and MDA-MB-231. In this work, we seek to determine if the vitamin D analogs calcipotriol and EB1089 also demonstrate this same phenomenon and if the use of the compound PRIMA-1MET (APR-246) allows vitamin D and analogs to cause growth inhibition of TNBC cell lines. PRIMA-1MET is a small molecule reported to restore p53 protein function in cells with mutated p53. Future analysis of western blots and PCR gene expression will be performed to determine p53 restoration in MCF-7, MDA-MB-468, and MDA-MB-231 cell lines. We also plan to assess cell viability with PRIMA-1MET while using ferroptosis inhibitors to help determine the mechanism of PRIMA-1MET in these cells.

59. Characterization of an exact electron correlation symmetry in AHCs using MO Theory at the single CI level of approximation

***Christina A. Farwick**, christinafarwick@outlook.com, Mark Masthay. Chemistry, University of Dayton, Dayton, Ohio, United States*

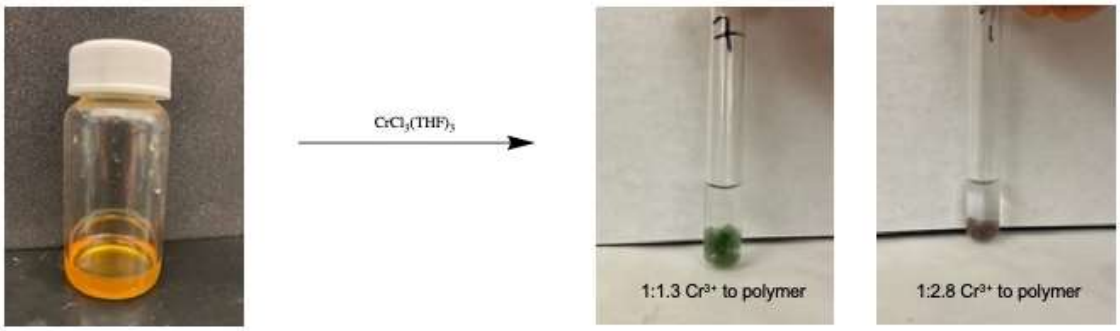
Electron-electron repulsion in a quantum system facilitates the correlated motion of electrons, or electron correlation. The extent to which the movement of an electron is influenced by surrounding electrons is proportional to the correlation energy. This project explores unique electron correlation characteristics manifested in the excited singlet states of alternant hydrocarbons (AHCs) – specifically, butadiene and hexatriene. Data was generated using the semiempirical Pariser-Parr-Pople Method, which combines molecular orbital (MO) theory approximation techniques and configuration interaction (CI) calculations. Slater determinants are used to derive configurational wavefunctions that account for all possible single-electron excitations. Each electronic state Ψ can then be expressed as a linear combination of the singly-excited configurations, with coefficients and corresponding transition energies calculated using the CI method. The results indicate that certain wavefunctions – referred to as plus and

minus states – are solely comprised of paired configurations (in equal magnitude), and all other coefficients are zero. The identical wavefunctions of the paired configurations allow for exact electron correlation symmetries to be demonstrated, yielding uncorrelated plus states ($\Psi^+ > 0 \rightarrow$ alternancy heap) and correlated minus states ($\Psi^- = 0 \rightarrow$ alternancy hole). Analysis of each electronic state transition energy as a function of the range of electron-electron repulsion shows that at short ranges, the plus state energy increases due to the presence of alternancy heaps, while the minus state decreases because of alternancy holes. These results are consistent with the exact symmetries derived for the excited singlet states of AHCs.

60. Photo-responsive Cr(III)-supramolecular siloxane polymers with self-healing potential

***Herenia Espitia Armenta**, hespit@bgsu.edu, Joseph C. Furgal. Chemistry, Bowling Green State University, Bowling Green, Ohio, United States*

Over the years there has been a surge of interest in developing supramolecular polymers because of the reversibility and tunability of incorporable metal-organic ligand interactions within them. These systems have been used to develop materials with intrinsic healing, which can be induced by internal or external stimuli such as heat, pH, and light. The polymers healing ability is attributed to changes in viscoelastic properties resulting from the temporary demetallation of the metal-ligand complex. Cr^{3+} supramolecular polymers have shown characteristics desirable for self-healing materials using light stimulus, with favorable excited state de-coordination when irradiated. Siloxanes used in high performance coating and biomedical applications can take advantage of this self-healablity. We have exploited this unique photochemical and photophysical property of Cr^{3+} ligation in the development of polymeric siloxane systems to imbue stimuli-responsive self-healing capabilities. This investigation entailed the synthesis of siloxane polymers containing photodynamic metal coordination sites ($Cr3^+$-imidazole) and characterizing their photoresponsive behavior for applications in light induced healability.



Scheme 1. Method used for the metalation of siloxane polymer and Cr(III).

61. Single-molecule human nucleosome spontaneously ruptures under the stress of compressive force: New perspective on gene stability and epigenetic pathways

***Lalita Shahu**, shahulalita46@gmail.com. Chemistry, Bowling Green State University College of Arts and Sciences, Bowling Green, Ohio, United States*

Force manipulation on the biological entities from living cells to protein molecules has revealed many mechanical details of cell biology from resolving folding and unfolding pathways to finding molecular interaction forces. A nucleosome is the basic repeating unit of chromatin where the histone octamer is wrapped by DNA, important for gene stability and regulation.

How the inner side of the DNA gets accessed by other DNA binding molecules has been a puzzle that has been intensively studied and debated, important to epigenetics, gene stability, and regulations. Here we report our observation of spontaneous ruptures of human nucleosomes under pico-Newton (pN) compressive force applied by Atomic Force Microscopy (AFM). The amplitude of the compressive force, a squeezing rather than pulling force, involved in our experiment is tens of pN, which can be thermally available by biological force fluctuation at room temperature and under physiological conditions. This kind of structural rupture can loosen up the DNA around the histone, which in turn makes the DNA accessible to transcription and epigenetic modifications.

62. Synthesis and characterization of cadmium valen complexes with tunable room temperature phosphorescence

*Morgan Deal[1], Matthias Zeller[2], **Evan R. Trivedi**[1], trivedi@oakland.edu. (1) Chemistry, Oakland University, Rochester, Michigan, United States(2) Chemistry, Purdue University, West Lafayette, Indiana, United States*

The ‘valen’ Schiff base ligand has been studied for its ability to form bimetallic complexes. We have recently discovered that valen type complexes of Cd^{2+} form as a dimer when bridged by sodium acetate. Varying the aromaticity of the organic portion of the valen ligand allows the electronic absorption, and therefore color of phosphorescence, to be tuned. Herein we report a series of valen Cd^{2+} complexes with either an aliphatic (***cyclohexavalen***) or aromatic (***valphen***) backbone and varying peripheral R-groups (***R = H, Br, Ph***). Increasing aromaticity (*valphen* vs. *cyclohexavalen*) red-shifts the electronic absorption by *ca.* 41 nm and a similar red-shift is observed with increasing electron density/size of the peripheral R-group. Each of these complexes is room temperature phosphorescent on the microsecond scale; the lowest energy phosphorescence is observed from the complex with the most aromaticity.

63. CO_2 deprivation and oxidative stress delay the production of cyanophages and lysis of infected cyanobacteria

***Syed Badshah**, sbadshah@asu.edu. Civil and Environmental Engineering, The University of Toledo, Toledo, Ohio, United States*

The phototrophic organisms fix the carbon dioxide for making sugar in the Calvin cycle. It has been proposed that the cyanophages block the Calvin cycle of the host cyanobacteria to fulfill their requirements for nucelotides and other metabolomic necessities. During this process, the ATP and NADPH produced in the light reaction are utilized for the nucleotides biosynthesis of the cyanophages. Several studies showed that an intrinsically disordered small protein CP12 is produced in higher plants, algae and also expressed by cyanophages to block the Calvin cycle. The CP12 binds with phosphoribulokinase and glyceralsehyde 3-phosphate dehydrogenase of the Calvin cycle and inhibits the CO_2 fixation. The cyanophages used the CP12 to inhibit the Calvin cycle so that the ATP and NADPH produced in the light reaction are utilized for its nucleotide biosynthesis. To elucidate the effect of inhibition of CO_2 fixation in Calvin cycle on cyanophage production and ultimate host cell lysis we inhibited the phosphooribulokinase using glycolaldeyde. It was observed that inhibition of the Calvin cycle delayed the maturation of cyanophages and host cell lysis. The cyanophages independently control the host cell metabolic processes for the prouction of new cyanophage particles. Thus, a healty host cyanobacterial cell is always important for the cyanophage infection and production of its particles. During the CO_2 starvation of the host cell, the cyanophage delay the lytic cycle till the full maturation of its particles and this delay depends upon the extent of host cell starvation of CO_2. For the first time this work showed that contiuous supply of all nutrients

and their consumption in host cell metabolic pathways for biosynthesis of cyanophage particles is important for full phage production.

64. Modulation of multiple signaling pathways by spinosyn A induces anti-tumorigenic effects on ERα-positive breast cancer cells sensitive to progesterone: Evidence from RNA sequencing analysis

*Besa Xhabija, **Anthony Kaniski**, kaniskia@umich.edu, Darena Matti. University of Michigan Dearborn Office of Metropolitan Impact, Dearborn, Michigan, United States*

Breast cancer is a significant public health concern in the United States, with women over the age of 50 being the most affected group. While various factors, including family history, genetic mutations, and exposure to estrogen, have been implicated in the disease's development, current therapeutic interventions, such as surgery, chemotherapy, and hormone therapy, have their limitations. Therefore, alternative approaches that can offer better efficacy and lower toxicity are needed. Natural products, including spinosyn A, a compound derived from the soil bacterium Saccharopolyspora spinosa, have shown promise as potential anti-cancer agents. In this study, we aim to investigate the effect of spinosyn A on breast cancer cells and explore its potential mechanism of action via cytotoxicity studies, migration and proliferation assays, and transcriptomics analysis. This study's findings could provide valuable insights into spinosyn A's therapeutic potential as a novel anti-cancer agent for breast cancer.

65. Targeting multiple signaling pathways, baicalein suppresses tumorigenesis in ERα-positive breast cancer cells

*Besa Xhabija, **Aidan J. McLaughlin**, sirflash@umich.edu, **Elisabeta Ujeniuc**, eliuje@umich.edu. Department of Natural Sciences, University of Michigan College of Literature Science and the Arts, Dearborn, Michigan, United States*

Although baicalein has been shown to possess anti-tumor capabilities, its potential anti-cancer effects in ERα positive breast cancer cell lines have not been extensively studied. To address this, we investigated the cytotoxicity of baicalein in T47-D and MCF-7 cells using cell viability and colony formation assays. Furthermore, we evaluated the impact of baicalein on various anti-cancer properties, including cell migration, proliferation, and cell cycle profiles, using wound healing assays and flow cytometry. Our findings demonstrate that baicalein can significantly reduce cell viability, proliferation, and migration in a dose-dependent manner through multiple signaling pathways.

66. Disrupting bacterial homeostasis: Stealth manganese carrier for killing multidrug-resistant *Staphylococcus aureus*

***Khalil Mudarmah**[1,2], kmudarma@kent.edu, Songping Huang[1]. (1) Chemistry and Biochemistry, Kent State University, Kent, Ohio, United States(2) Chemistry, Jazan University, Jazan, Saudi Arabia*

The growing prevalence of antibiotic resistance in *Staphylococcus aureus* necessitates the development of novel approaches for antimicrobial therapy. Manganese is essential for bacterial growth and survival, but excess amounts can disrupt metabolism and cause cellular toxicity. Bacteria employ various mechanisms to regulate intracellular manganese levels to ensure optimal growth and survival. Recent studies have demonstrated that small lipophilic molecules, including 8-hydroxyquinoline and its derivatives, possess the ability to bind to manganese and transport it across lipid membranes. This inspired us to synthesize, characterize, and investigate the potential of the Mn[(5,7-dichloro-2-methyl-8-

hydroxyquinoline)(DMSO)]$_2$ complex (**1**) as a stealth manganese carrier. This complex has the ability to evade manganese trafficking regulation in bacterial cells, representing a promising strategy for disrupting manganese homeostasis and killing pathogenic bacteria. To evaluate its efficacy as an antimicrobial agent, we assessed the antimicrobial potential of **1** in vitro using multidrug-sensitive and multidrug-resistant strains of *Staphylococcus aureus.*

67. Chemical tools to identify substrate motifs of a kinase enzyme for characterization of cell signaling

***Hannah Bremer**, gx8437@wayne.edu, Mary Kay Pflum. Chemistry, Wayne State University, Detroit, Michigan, United States*

Phosphorylation is a reversible post-translational modification that changes the function of proteins and controls certain biological events, such as cell signaling and growth. The addition of a phosphoryl group onto a serine, threonine, or tyrosine residue of a substrate protein is catalyzed by kinase enzymes. Kinase activity must be highly regulated for normal cell function. When uncontrolled phosphorylation due to aberrant kinase activity alters cell signaling pathways, pathologies such as cancers and neurodegenerative diseases can arise, making kinases attractive drug targets. Because of the impact on cell signaling and disease, methods must be developed to study kinase activity, particularly to monitor kinase-substrate relationships. A popular method for prediction of substrates is based on the preference each kinase maintains for amino acid sequences surrounding the serine, threonine, or tyrosine phosphosite, called the substrate motif. If a phosphoprotein is identified without a known kinase, the amino acid sequence surrounding the phosphosite can guide kinase predictions. While substrate motifs can predict kinases, distal binding interactors and associated proteins of the full length phosphoproteins also influence kinase substrate binding, which is not considered the substrate motif alone. New methods that identify substrates using full length proteins are needed to improve kinase-substrate pair prediction beyond the substrate motif.

To study kinase-substrate pairs, the Pflum lab has taken a chemical approach by modifying the universal cosubstrate of kinase-mediated phosphorylation, adenosine 5’-triphosphate (ATP) with a functional tag. Several γ-phosphoryl modified ATP analogs collaborate with kinases to label phosphoproteins and covalently crosslink a kinase to its substrate during the phosphorylation event. Once the kinase-substrate complex is covalently stabilized, the kinase can be isolated and the substrate identified via gel or mass spectrometry analysis. Past ATP analogs successfully identified novel kinase-substrate pairs, but were unable to identify the specific site of phosphorylation. In this poster, a method is presented to identify kinase phosphosites using full length proteins in a complex lysate mixture. The method will inform future kinase-substrate pair studies, expanding known kinase biology and increasing cell signaling pathway characterization.

68. Application of nanosecond excitation in light-induced cellular processes

***Josephine Leone**, joleone@umich.edu. Chemistry, University of Michigan, Ann Arbor, Michigan, United States*

Astrocytes are specialized glial cells used in the central nervous system. Due to their significance in the regulation of neural signaling, they are used to study cellular communication. Live astrocyte cells were extracted from mice and incubated with Fluo-4 AM, a fluorescent Ca2+ indicator, in order to determine the response to classical infrared pulses. Using a nanosecond excitation microscope, pulses were delivered to the cells and recorded for analysis. Given that the change in Ca+2 concentration is proportional to the change in

fluorescence intensity, cell communication was measured by the change in fluorescence in cells before and after laser exposure. By tracking the fluorescence over time, signaling pathways between astrocytes indicate their prolonged response to nanosecond excitation. Along with Fluo-4 AM, cells were also incubated with inhibitors in order to determine the mechanism of their response. Here we found that only a fraction of TRP channels are involved in the cellular process, while others are uninvolved. Given that TRP channels are located on the cellular membrane, as opposed to within organelles, it is found that laser excitation triggers a response outside the cell.

69. Investigating novel structural and functional binding interactions of UHRF2 with H3

Jennifer R. Kean[1]*, jkean@emich.edu, Raymond C. Trievel*[2]*, Brittany Albaugh*[1]*. (1) Chemistry, Eastern Michigan University, Ypsilanti, Michigan, United States(2) Biological Chemistry, University of Michigan, Ann Arbor, Michigan, United States*

Ubiquitin-like containing plant homeodomain and ring finger (UHRF)2 is an epigenetic reader protein with roles in regulating DNA maintenance, methylation, gene repression, cell cycle and proteasomal degradation. UHRF2 has been overexpressed in some cancers (colon/gastric) and it has been lost/reduced in some cancers (lung, leukemias). UHRF2 contains two reader domains, TTD and PHD, that engage H3 that is trimethylated on lysine 9. Recently, we solved the crystal structure of UHRF2 TTD-PHD in complex with histone H3. From this structure, we identified novel interactions between the histone binding domains of UHRF2 and H3. To test these interactions, we created mutants and measured the binding interactions of UHRF2 and the H3K9me3 peptide complex. By studying these novel interactions, it will allow us to identify new pathways for potential drug inhibition of UHRF2.

70. Use of entangled two photon microscopy for imaging of brain tissue

Paloma R. Johnson*, palomaj@umich.edu, Oleg Varnavski, Tiecheng Liu, Christopher Fields, Dinesh Pal, George Ashour, Theodore G. Goodson. University of Michigan, Ann Arbor, Michigan, United States*

There are many benefits of using entangled photons for biological imaging. For example the lower intensity needed for experiment with entangled photons is safer for biological systems and has less of a potential to interfere with biological mechanisms. For the results that will be presented, we utilized an entangled two-photon microscope to image selectively stained brain tissue slices. In our experiments the brain tissue slices were stained with typical (classical) two-photon chromophores. The samples were imaged with both classical and entangled two-photon microscope techniques for a comparison study. The results of these experiments will be discussed in this poster.

71. Cellular investigation of UHRF1 interactions with a novel histone modification

Panida Khuansanguan*, spaemai@gmail.com. Chemistry, Eastern Michigan University, Ypsilanti, Michigan, United States*

UHRF1 is a multi-domain epigenetic protein that plays an essential role in regulating gene expression by binding histones and methylated DNA. The binding of UHRF1 to histone H3 tri-methylated at lysine 9 (H3K9me3) is well characterized, however, we have recently discovered that UHRF1 also interacts with a novel histone modification. To better understand the importance of this interaction, we have utilized pull-down assays and Western blots to show whether this interaction occurs in cells.

72. $Cu_xFe_yP_z$ nanoparticles synthesis and characterization for overall water splitting reaction

***Faria Sultana**, fariasultana3208@gmail.com. Chemistry, Wayne State University, Detroit, Michigan, United States*

Approximately 80% of the world's current energy supply is solely reliant on fossil fuels, the combustion of which is attributed as the most significant contributor to global warming, therefore, finding renewable alternatives to fossil fuels with “zero” CO_2 emissions is required to address this issue. For the future energy portfolio, electrocatalytic water splitting is one of the most promising sources of renewable energy as it produces hydrogen gas as the fuel with oxygen gas as the reaction byproduct. Electrocatalytic water splitting reaction takes place by passing a renewable resource-derived electric current through water for cleaving H-O-H bonds in H_2O, which is facilitated with the utilization of a catalyst. Some precious group metals or their oxides, for example, IrO_2, RuO_2, and Pt show extremely good catalytic activity toward water-splitting reaction. However, the need for large-scale production of H_2 necessitates the search for inexpensive and widely available materials. In terms of availability, the first-row transition metals are abundant in addition to being cheap. Their catalytic properties can be fine-tuned by incorporating a nonmetal into their crystal structure, such as phosphorus, which is more electronegative than metals and can draw more electrons from the transition metals while efficiently trapping positively charged protons during the electrochemical hydrogen evolution reaction. Availability of catalytic sites can be increased by producing materials on the nanoscale. Recent studies on different binary metal phosphide nanoparticles (NPs) including copper phosphide ($Cu_{3-x}P$) demonstrate their potential as good water splitting catalysts.

We and others have found that the bimetallic, ternary metal phosphide system is more catalytically active than the monometallic, binary phases towards water splitting. Therefore, in this study, our material of interest will be copper phosphide nanoparticles as the template, which will be cation exchanged with other first row transition metal ions starting with Fe^{3+}. Here, we will prepare a series of $Cu_xFe_yP_z$ bimetallic, ternary phases and evaluate their structure-property relationship and their activity towards water electrolysis. Our initial effort on $Cu_{3-x}P$ synthesis and cation exchange with Fe^{3+} will be presented.

73. *Cannabis sativa* may play a role in the phytoremediation of PFAS: Hemp seedlings can take up PFAS from a hydroponic solution and from soil

***Elisabeth F. Wells**, eliwells@nmu.edu, **Kevin Schick**, kschick@nmu.edu, Dominick Dotson, Lesley J. Putman. Chemistry, Northern Michigan University, Marquette, Michigan, United States*

Hemp (Cannabis sativa) seedlings grown hydroponically in a solution containing 5 µg/L PFBA (perfluorobutanoic acid) took up PFBA into their stems and leaves. After 35 days, the leaves contained 450 ng of PFBA per g of dried leaf. Although some PFBA was found in the stems, 90% of the PFBA was concentrated in the leaves. Hemp seedlings were also grown in soil and watered with a solution containing 5 µg/L PFBA for 10 weeks. As with the hydroponic system the leaves accumulated most of the PFBA with a final amount of 480 ng PFBA per gram of dried leaf. These experiments were repeated using PFOS (perfluorooctane sulfonate) with quite different results. In a hydroponic system where the seedlings were exposed to 5 µg/L PFOS for 42 days, most of the PFOS was found in the roots: 390 ng PFOS per g dried root compared to 28 ng PFOS per g dried leaf. When hemp seedlings were grown in soil containing PFOS, small amounts of PFOS were detected in the aerial portions of the plant after 4 weeks.

Hemp seedlings are more effective at taking up PFBA than PFOS, but they may be able to hold PFOS in their roots to prevent movement of the contaminant into groundwater.

74. Investigating the ground and several excited states of late 3D and 4D transition metals through multireference calculations

***Mahboubeh Khorrami**, khorram4@msu.edu, Nuno Almeida, Angela K. Wilson. Chemistry, Michigan State University, East Lansing, Michigan, United States*

Transition metals are one of the most researched elemental groups in different fields such as chemistry, physics, materials science, and catalysis. The theoretical study of transition metals is crucial in understanding their electronic properties, reactivity, and behavior for the development of novel materials, or prediction of new potential catalysts. However, accurately describing these systems using *ab initio* electronic structure theory is a significant challenge. Achieving accurate ground and excited state spectroscopic data in transition metal requires the use of advanced methodologies and multireference approaches. Here, late 3d and 4d transition metal spectroscopic data is determined and the findings are compared to experimental results. This approach paves the way for a better understanding of transition metal spectroscopy.

75. Characterizing the energy levels of early 3d and 4d transition metals by multireference techniques

***Ebtisam M. Telb**, telbebti@msu.edu, Nuno Almeida, Angela K. Wilson. Chemistry department, Michigan State University, East Lansing, Michigan, United States*

Transition metals-containing molecules are of great importance in various areas of chemistry, physics, engineering, and material science. For example, they are a popular choice as catalysts in chemical reactions, allowing for more efficient and selective chemical transformations. The accurate description of the electronic structure of transition metal atoms is crucial in advancing our understanding of atomic structure, predicting spectra, improving experimental data, and designing new materials. Due to narrow energetic gaps and high density of states, reliable computational routes are fundamental in characterizing the excited states of atomic transition metals. High level multireference calculations allow for a correct description of the system's static and dynamic correlation, for not only the ground state, but several excited states, as is demonstrated in this work. The findings are analyzed and compared to the experimental results, paving the way for understanding computationally the atomic and molecular properties of transition metal containing species.

76. Effect of PFAS on proteins: Computational investigation

***Rana Massoud**, massoudr@msu.edu. Chemistry, Michigan State University, East Lansing, Michigan, United States*

Per- and polyfluoroalkyl substances (PFASs) are a broad family of more than 4,000 synthetic aliphatic compounds with at least one carbon-fluorine (C-F) bond. PFASs are very hard to degrade in nature due to their high stability; hence called "*forever chemicals*". PFASs are immensely utilized in industry, military, and other commercial applications due to their desirable properties, such as thermal resistance and stability, oil, and water repellency. Via ingestion and bioaccumulation, PFASs can be transmitted and accumulate in humans and animals.

Recent investigations on the effects of PFAS on the environment and humans have shown that PFASs can result in adverse health impacts such as carcinogenic effects, developmental toxicities, and endocrine-disrupting activities. In addition, PFAS can accumulate in animals and cause a series of health issues. In this study, the binding affinity and stability of selected PFASs and proteins in animals was investigated by *in silico* modeling. Root mean square deviations and fluctuations, and residue decomposition were measured and analyzed. Molecular mechanics with Poisson−Boltzmann surface area (MM-PBSA) and molecular mechanics with a modified general born solvation model (MM-GBSA) methods were used to calculate the free energies of the binding of the PFASs to the investigated proteins.

77. Making and adjusting Galinstan in the teaching laboratory: An example of some fascinating, low-melting alloys

Phebi Lee, Andrew Fei, Mac Golden, Hadi Obeid, Heather Rice, Liliana Romeo, Maryan Yousef, Omar Ammoun, Juliana Jakubczak, ***Mark A. Benvenuto****, benvenma@udmercy.edu. Chemistry & Biochemistry, University of Detroit Mercy College of Engineering and Science, Detroit, Michigan, United States*

Galinstan is an alloy made from gallium, indium, and tin (hence its name). We have found that not only can galinstan be made in the teaching laboratory, but that its composition can be adjusted in favor of gallium or in favor of tin, resulting in alloys with significantly higher melting points. Since galinstan melts at -19^{o}C and gallium melts at 30^{o}C, we set a goal of finding some composition which melted between 0^{o}C and 30^{o}C. Our results will be presented.

78. Boiling and freezing point adjustment experiments for the general chemistry laboratory: Elevating the boiling point and depressing the freezing point of water to extremes, using high molality salt solutions

Bianca Gheorghila*, gheorgbi@udmercy.edu, Zoe Arrington, Katrina Yeldo, Sara Arment, Joseph Crandall, Leza Jeki, Philomena Anton, Chloe Cole, Genevieve Crocker, Josefina Kusiak, Evelyn Rihacek, Chloe Spitzer, Candice Tayler, Omar Ammoun, Juliana Jakubczak, Ndeye Ka, Mark A. Benvenuto. Chemistry & Biochemistry, University of Detroit Mercy College of Engineering and Science, Detroit, Michigan, United States*

The boiling point elevation and freezing point depression equations found in most freshmen chemistry textbooks are usually given no more than a passing mention by faculty. We have found that in the laboratory, when large amounts of salts are added to boiling water, or water cooled with dry ice, that remarkably large temperature elevations or depressions occur. Our recent findings will be presented.

79. Regulation of the amyloid precursor protein (APP) by acetylcholinesterase and brain-derived neurotrophic factor in lung cancer cells

Hind Al Khashali*, halkhash@emich.edu, Ravel Ray, Kai-ling Coleman, Ben Haddad, Ban Darweesh, Jeffrey Guthrie, Deborah Heyl-Clegg, Hedeel Evans. Eastern Michigan University, Ypsilanti, Michigan, United States*

Amyloid beta (Aβ) and the nicotinic acetylcholine receptor (nAChR) have been implicated in both Alzheimer's disease (AD) and cancer. In comparing two human lung cancer cells, we found lower levels of acetylcholinesterase (AChE) and intact amyloid-β40/42 (Aβ), and higher levels of mature brain-derived neurotrophic factor (mBDNF) in the media of H1299 cells as compared to A549 cell media. Knockdown of AChE led to increased soluble amyloid precursor protein α (sAPPα) levels and correlated with decreased levels of intact Aβ40/42 in A549 cell

media. Treatment with AChE decreased sAPPα levels and simultaneously increased the levels of intact Aβ40/42 suggesting a role of the protein in shifting APP processing away from the non-amyloidogenic pathway and toward the amyloidogenic pathway, whereas treatment with mBDNF led to opposite effects on those levels.

80. Modeling the elusive element astatine

***Vincent Casetti**, vincentcasetti@oakland.edu, James MacLean, Alexander Rusakov. Chemistry, Oakland University, Rochester, Michigan, United States*

Astatine shows encouraging properties in targeted radiotherapy treatments for cancer patients. However, it requires a cyclotron to produce, significantly limiting its accessibility to the majority of experimentalists. This leaves it up to computational models to provide the vital insights researchers need. Since astatine is the heaviest halogen, its chemistry is subject to an array of relativistic and electron-correlation effects that must be taken into account to produce accurate information. Even for diatomic molecules, it takes sophisticated quantum-chemical approaches whose execution is extremely computationally demanding. For cheaper methods such as relativistic density functional theory (RDFT), there are no consistently reliable exchange-correlation functionals, and suitable basis sets for accurate calculations remain underdeveloped. In our previously completed work, we use relativistic coupled-cluster approaches to establish reference data and assess the behavior of RDFT on small molecules such as At_2, HAt, AuAt, and AtO^+. These results inform our study of more complex molecules, such as astatine multivalent halides, and the development of high-quality basis sets for RDFT approaches.

81. Exploring the signaling pathways involved in controlling the levels of soluble Amyloid Precursor Protein α (sAPPα) levels in lung cancer cell culture media

*Hind Al Khashali, Ravel Ray, **Kai-ling E. Coleman**, kcolem24@emich.edu, Ben Haddad, **Ban Darweesh**, bdarwees@emich.edu, Jeffrey Guthrie, Deborah Heyl-Clegg, Hedeel Evans. Chemistry, Eastern Michigan University, Ypsilanti, Michigan, United States*

Amyloid precursor protein (APP) is a glycoprotein located on the membrane that is mainly known for its role in the pathogenesis of Alzheimer's disease and neuronal function. However, APP is also expressed widely by both neuronal and non-neuronal cells and has been reported to be overexpressed in various cancers, including lung, prostate, colon, breast, glioblastoma, and pancreatic cancer, leading to cancer cell growth. Our investigation focused on two non-small cell lung carcinoma (NSCLC) cells, A549 and H1299, which showed different levels of soluble amyloid precursor protein α (sAPPα) in the cell culture media. Previous research has revealed that sAPPα levels are regulated by various signaling pathways, such as protein kinase C (PKC), extracellular signal-regulated kinase (ERK)1/2, and phosphoinositide 3-Kinase (PI3K), in other cell types. Our study found that the levels of sAPPα in A549 and H1299 cell media are controlled by PKC, ERK1/2, and PI3K signaling pathways but not by protein kinase A (PKA).

82. Exploring the magnetic properties of coupled di-blatter radicals

***Gerard Flores**, gerardf@umich.edu, Daniel B. Lawson, Christos P. Constantinides. University of Michigan-Dearborn, Dearborn, Michigan, United States*

A stable high-spin ground state organic radical is the holy grail of lightweight, inexpensive magnetic materials. Radicals, organic molecules with unpaired electrons, have many applications in various scientific disciplines such as spintronics and energy storage. 1,2,4-

benzotriazin-4-yl radical, also known as the Blatter radical is one of the first stable organic radicals synthesized and first observed in 1968, however, challenges its synthesis as well as limitations. As a result of the extensive delocalization of the spin on the arene and the endocyclic nitrogens, Blatter radicals possess many unique electronic and magnetic properties. Optimizing systems based on the Blatter radical to enhance the stability and magnetic properties is vital to developing useful applications. Our approach is to consider interconnecting Blatter molecules, coupled di-Blatter radicals, through aromatic linkages and interchanging substituents to facilitate a range of behaviors. In this work we use density functional theory to demonstrate various planarized analogues of the Blatter radicals have the potential to tune electronic and magnetic properties of the radical.

83. Design and synthesis of the lanthanide-based host-guest systems

***Mahsasadat Boraghi**, mb957018@ohio.edu. Ohio University, Athens, Ohio, United States*

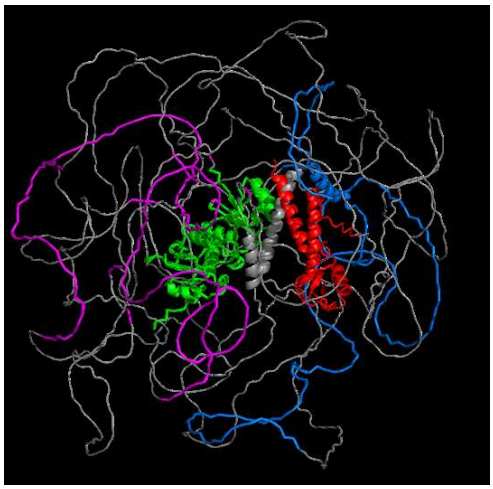
Supramolecular Coordination Complexes (SCCs) with the general formula M_mL_n (where M and L are metallic cations and ligands, respectively) are very desirable assemblies with distinctive chemical and photophysical properties. These SCCs assemblies have the ability to encapsulate small guest components due to the internal cavity incorporated in these complexes. Most SCCs have been based on main group ions and transition metals. However, due to the increasing demand for luminescent materials, lanthanide ions (Ln(III)) are attracting growing attention. Water-soluble Ln(III)-based SCCs are scarce, and the arrangement of water molecules inside the cavity, as well as the recognition properties of the latter, are mostly unknown. This project seeks to address this void.

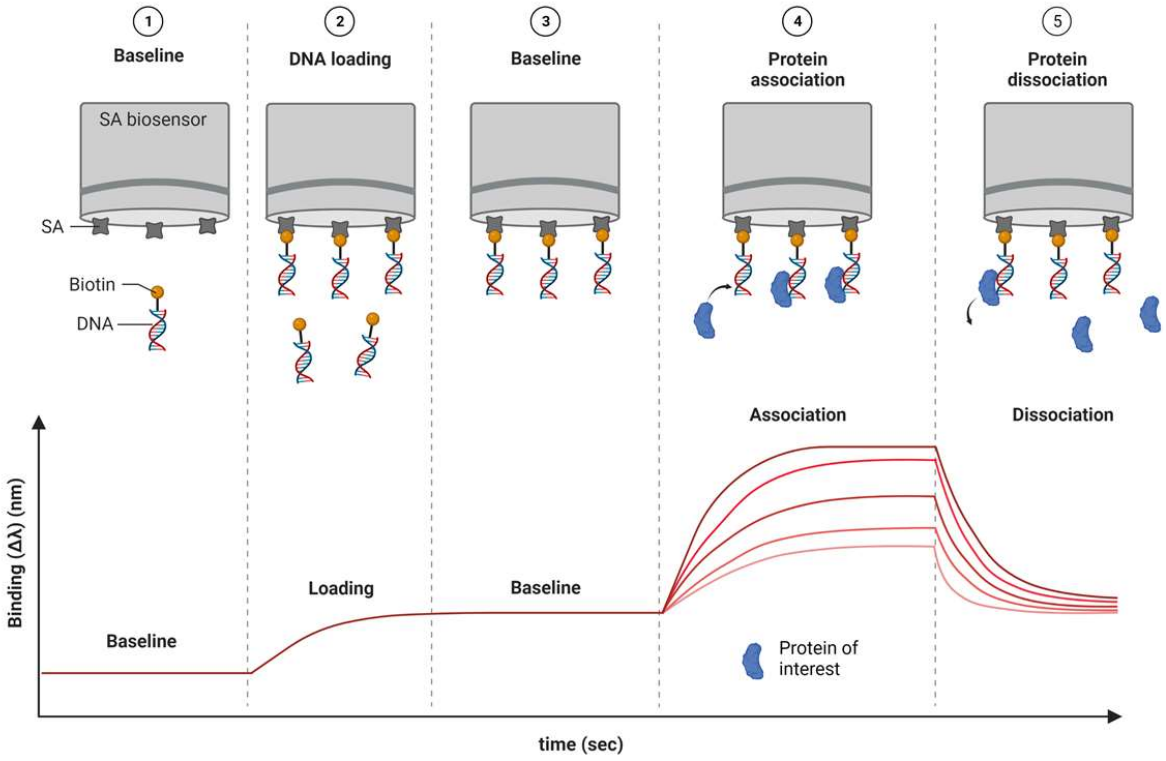
84. Effects of mutated DBD2 on BRCA1 function

***Vereena Salib**, vcsalib@oakland.edu, Colin Wu, Kaitlin Lowran. Chemistry, Oakland University, Rochester, Michigan, United States*

DBD2 is a domain within the DNA repair protein, BRCA1, that directly binds to DNA to correct errors made during replication. While the protein coded by wild type BRCA1 is known to act in this manner, it is not known how this mechanism is altered when mutations occur within DBD2. Mutations may cause changes in the structure of the BRCA1 protein as well as its ability to bind to and repair damaged DNA. Within DBD2, several alterations exist as both cancerous and unclassified variants. It is predicted that these variants will alter binding affinities in DNA repair and will allow us to relate DNA damage to cell toxicity. The goal of this project is to quantitatively identify which mutations within DBD2 have the largest impact on DNA binding interactions. Following mutagenesis and protein purification, biolayer interferometry (BLI) will be used to measure the affinities of the mutated BRCA1 proteins to different types of DNA.

This image is a representation of the folded structure of BRCA1. DBD2, shown in purple, is largely made up of an irregular arrangement called random coils. Blue shows DBD1, green depicts BRCT Domains, and red represents the RING domain.





This image is a representation of the stages of Bio-layer Interferometry and the resulting graph when testing differing protein concentrations against a type of DNA. These protein solutions are made by performaing a serial dilution. I will be focusing on the dissociation section of the curve to measure binding affinity.

85. BioBricks® platform for engineering of diverse anthracyclinone core scaffolds

***Nora E. Schwartz**, schwarn3@ferris.edu, Jacob Hecht, Eric Nybo. Pharmaceutical Sciences, Ferris State University, Big Rapids, Michigan, United States*

Anthracyclines are aromatic polyketides, or a class of natural products derived from precursor molecules consisting of a chain of alternating ketones and are produced by streptomyces. Anthracyclines are known to be potent therapeutics used for the treatment of human cancers. As a result of toxic side effects, engineering new analogues could decrease toxicity and

increase potency allowing safer use. Our approach is to genetically engineer streptomyces to produce these analogues as they are native producers of polyketides. Using these bacteria, we can use enzymes to create the stereocenters needed to produce these compounds.

Anthracyclines are biosynthesized through a multistep enzymatic pathway, which includes a tricyclic intermediate. The biosynthetic route for the transformation of the tricyclic intermediates nogalonic acid or aklanonic acid into tetracyclic anthracyclinones, requires three enzymes. First, nogalonic acid/aklanonic acid undergo O-methylation at the carboxylic acid functionality via nogalonic acid O-methyltranferase to form nogalonic acid methyl ester (NAME) or aklanonic acid methyl ester (AAME), respectively. Second, NAME/AAME undergoes a fourth ring cyclization to form tetracyclic anthracyclinones. Lastly, the anthracyclinone is reduced at C-7 to form nogalamycinone. In this work, we engineered S. coelicolor M1152matAB strains with different combinations of anthracyclinone biosynthetic genes to produce a comprehensive library of tetracyclic anthracyclinone core scaffolds that are useful for the elaboration of potent anticancer agents.

86. Theoretical interpretations of ESi-MS experiments of melamine and cyanuric acid

***Kaitlyn M. Handy**, Khandy2000@gmail.com, Alex L. Walter, Benjamin Heiner, S. Alex Kandel. Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana, United States*

Electrospray ionization mass spectrometry (ESI-MS), as a “soft” ionization technique, is able to observe clusters of molecules that form in solution. ESI-MS experiments on a mixture of cyanuric acid and melamine showed that multiple homogeneous and heterogeneous clusters are formed after electrospray from aqueous solution. There are several different clusters that were shown to form in high volumes. Density functional theory (DFT) calculations were used to model possible structures of the clusters. Heterogeneous clusters with one molecule of 1:1 proportionality arrange in a lattice structure, while no such structure is observed with there is a greater imbalance between the two molecules. The lattice structure is additionally associated with a greater cluster binding energy for proportionate structures.

87. ESI investigation of melamine and cyanuric acid for future pulse-deposited STM studies

***Alexandra L. Walter**, awalter7@nd.edu, Kaitlyn M. Handy, Jewel Soucek, Alexander M. Pittsford, Benjamin Heiner, S. Alex Kandel. Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana, United States*

Pulse deposition, a novel sample deposition technique for scanning tunneling microscopy (STM), sprays molecules onto a surface through a process that forces non-equilibrium, high-energy structures. Electrospray ionization mass spectrometry (ESI-MS) is a “soft” ionization method; molecules of interest do not fully fragment, but instead can be observed whole, as can dimers, trimers, and other supramolecular structures, which is often seen as a limitation. However, this clustering of molecules allows for a “screening” of sorts for pulse-deposited STM experiments, which are significantly more time-intensive. ESI-MS and pulse deposition have similar sample delivery methods, and thus can be compared to each other and used to study molecules in tandem. For example, melamine and cyanuric acid together form highly toxic complexes in the body, but the precise crystallization and intermolecular forces that drive the creation of the toxic clusters is unknown. Using the ESI-MS as a precursor to investigation with pulse deposited STM imaging, we observed several stable noncovalent clusters of melamine and cyanuric acid, ranging from mixed dimers to mixed nonamers (four melamines and five cyanuric acids). In this presentation, I will discuss the results of our ESI-MS experiments on

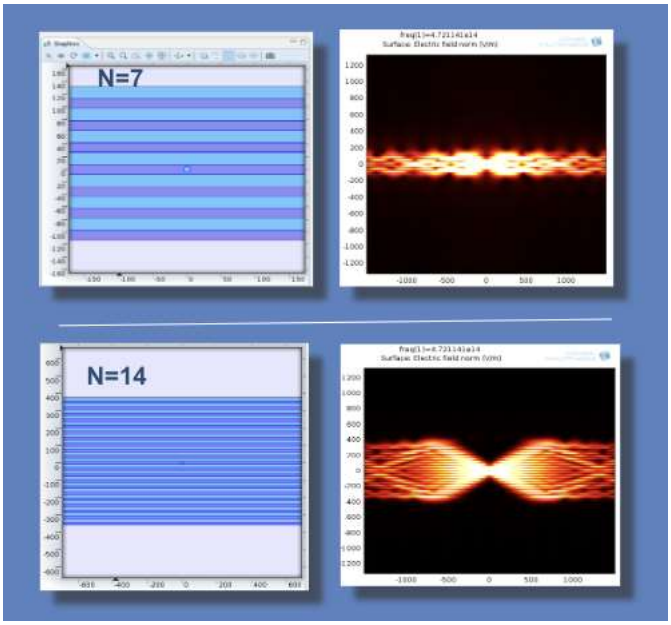
melamine and cyanuric acid as well as comment on the future study of this system, including STM experiments of different solution ratios and how ESI-MS and STM results can be jointly interpreted.

88. Study of electric fields in conductor and dielectric layers and surface plasmon resonances using theoretical calculation and computational simulations

***Richard Kyung**, nycrick@gmail.com, Haniel Jing. CRG-NJ, Cresskill, New Jersey, United States*

Surface Plasmon Resonance has been extensively studied and exploited for various applications, including biosensing, materials science, and nanophotonics. This oscillation results in the absorption and scattering of light at a specific wavelength, which is determined by the properties of the metal and the dielectric medium in contact with the metal surface. In this paper, Surface Plasmon Resonance in nano-scaled metamaterial units with metals and dielectric nonmetal compounds was studied. Both theoretical calculation and computer simulations were employed to find the optimum incident angle and reflection while the absorption of the light energy in the unit occurred. The SPR effect was observed for specific units while changing the optical variables and geometrical conditions. For example, Among the 47 metals(conductors) combined dielectrics tested, Beryllium, Iron, Germanium, Silicon, and Tungsten with oxides combination(period) produced few optimum angles.

One-period, two-period, and multi-period of metamaterials were analyzed on COMSOL. The reflection Coefficient vs. Angle and Reflection Coefficient vs. Effective Index (kx/k0) were also found and analyzed.



Electrical Fields yielding different resolutions with different T

89. Establishing histone deacetylase 7 as an epigenetic reader

***Ishadi Kodikara**, ishadi@wayne.edu, Mary Kay Pflum. Chemistry, Wayne State University, Detroit, Michigan, United States*

Histone Deacetylase (HDAC) enzymes remove acetyl groups from acetyl-lysine containing substrate proteins to regulate numerous cellular events, such as cell cycle progression, apoptosis, and cell proliferation. The clear role of HDAC proteins in cancer led in the

development of HDAC inhibitors as anticancer therapeutics. Among the eleven-metal dependent HDACs, class IIa HDACs (HDAC4, 5, 7, and 9) are enzymatically inactive in deacetylation reactions due to mutation of a catalytic Tyr to His. Hence, class IIa HDACs are hypothesized to be “reader” proteins that bind to acetylated lysine residues on target proteins to cause a downstream biological function. However, the roles of HDAC4, 5, 7, and 9 as readers are yet to be established. The long-term goal of this project is to provide evidence for the possible reader function of HDAC7. Based on prior work characterizing the reader function of HDAC7 with the hormone receptor Androgen receptor in the Pflum lab, we hypothesize that additional hormone receptors also mediate transcriptional activation through HDAC7. In this poster, the reader function of HDAC7 with several hormone receptors are explored. Based on the importance of HDAC7 as a drug target in numerous diseases, such as neurodegenerative diseases and cardiac hypertrophy, this project will uncover roles of HDAC7 in cell biology to apprise pharmaceutical drug designs.

90. Photoactivatable glycolipid probes for identifying outer membrane proteins in mycobacteria

Kyle Biegas[1], *biega1kj@cmich.edu, Herbert W. Kavunja*[2], *Nicholas Banahene*[1], *Benjamin M. Swarts*[1]*. (1) Chemistry and Biochemistry, Central Michigan University, Mount Pleasant, Michigan, United States(2) Michigan State University, East Lansing, Michigan, United States*

Mycobacterium tuberculosis, the causative agent of tuberculosis, is the deadliest bacterial pathogen worldwide, estimated to cause 10 million cases of active *Mtb* and 1.5 million deaths each year. Mycobacteria are characterized by a unique, glycolipid-rich barrier that is critical for cell protection and an important target for tuberculosis drug development. Despite the importance of this barrier, termed the mycomembrane, proteins associated with membrane construction, recycling and host interactions remain poorly understood. Here, we describe photoactivatable trehalose analogues to metabolically label outer membrane proteins, enabling *in vivo* photo-crosslinking and click-chemistry mediated capture and analysis. When deployed into *Mycobacterium smegmatis* in conjunction with quantitative proteomics this strategy enriched and identified over 100 candidate outer membrane proteins. Further application of this strategy helped identify a previously uncharacterized protein, PgfA, and demonstrated its role in trehalose glycolipid transport.

91. Targeting mycobacterial persistence: Trehalosamines inhibit the trehalose catalytic shift in *Mycobacterium tuberculosis*

Karishma Kalera[1,2], *kaler1k@cmich.edu, Jae Jin Lee*[3], *Daniel H. Swanson*[1], *Ulysses Johnson*[1,2], *Alicyn Stothard*[1], *Anne W. Poston*[1], *Hyungjin Eoh*[3], *Benjamin M. Swarts*[1]*. (1) Chemistry and Biochemistry, Central Michigan University, Mount Pleasant, Michigan, United States(2) BCMB program, Central Michigan University, Mount Pleasant, Michigan, United States(3) Keck School of Medicine, Molecular Microbiology & Immunology, University of Southern California, Los Angeles, California, United States*

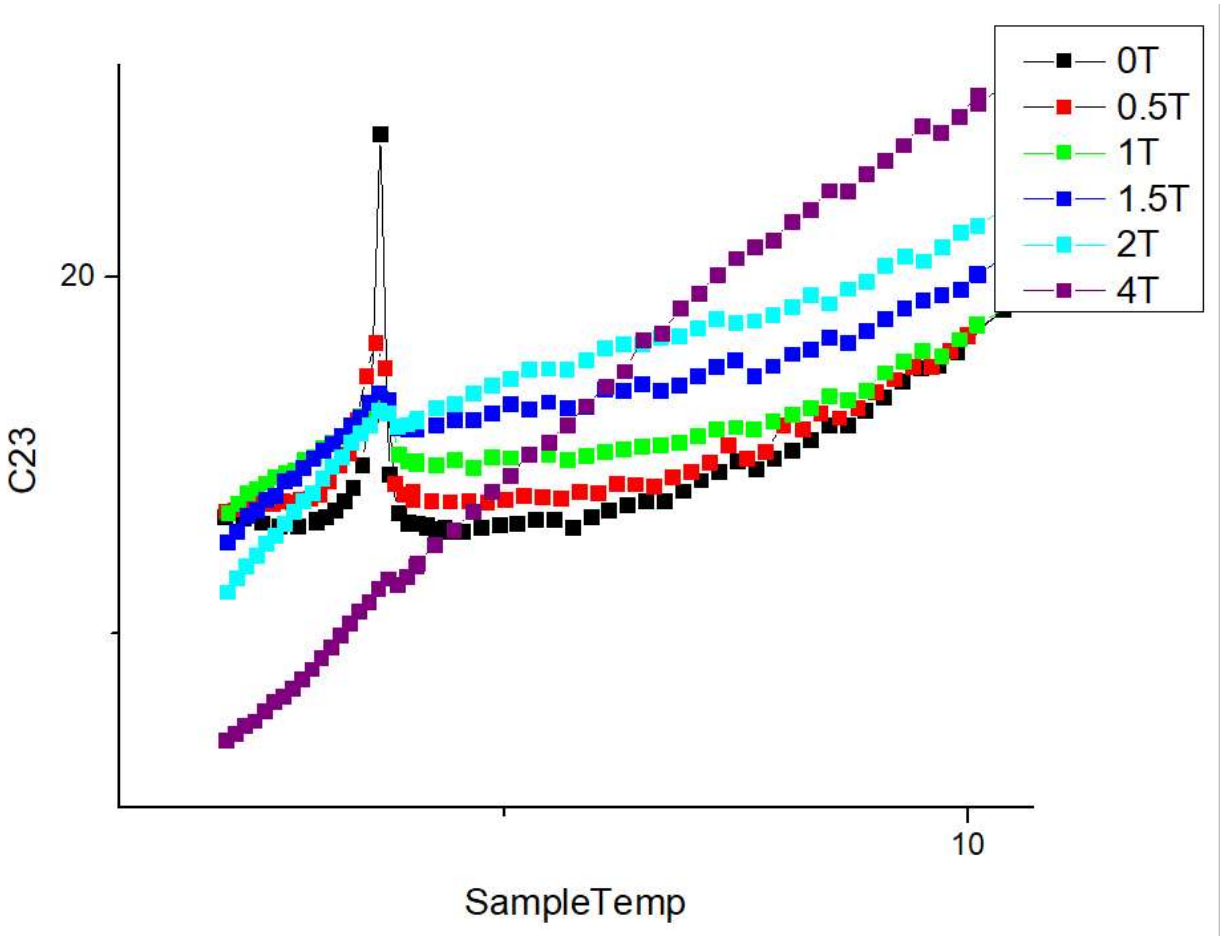
Trehalose, a non-mammalian disaccharide consisting of two glucose molecules joined by a 1,1-a,a-glycosidic bond, is a major component of cell wall-associated glycolipids in *Mycobacterium tuberculosis* (*Mtb*). Trehalose also plays a significant role in biogenesis and remodeling of the mycobacterial outer membrane. The metabolic pathways associated with trehalose-mediated mycolic acid transfer are conserved in mycobacteria and essential for viability, and thus represent promising targets for drug development. In a recent collaborative study, we discovered that 6-azido-6-deoxy-D-trehalose (6-TreAz) (i) selectively inhibits *Mtb* biofilm formation by disruption of TreS-mediated trehalose metabolic remodeling; and (ii)

sensitizes drug-tolerant *Mtb* to the existing anti-TB compound bedaquiline. Thus, 6-TreAz and related trehalose analogues, though difficult to synthesize, can potentially serve as valuable tools for understanding mycobacterial trehalose metabolic remodeling and exploiting it to develop novel adjunctive therapeutics for TB. Here, we report the synthesis of a panel of azido and amino-trehalose analogues and evaluation of these compounds as inhibitors of *Mtb* growth and biofilm formation. To further expand the panel and enable structure-activity relationship (SAR) studies in *Mtb* we designed and synthesized epimers of azido and amino trehalose analogues. Given the challenges of chemical synthesis of trehalose analogues, we enlisted the glycosyltransferase enzyme TreT to chemoenzymatically synthesize most of the target compounds in high yield. From the compound panel, multiple analogues were shown to selectively inhibit *Mtb* biofilm formation with better potency than 6-TreAz, and mechanism of action was investigated using knock-out mutants and metabolomics. These compounds can serve as tools to investigate mycobacterial trehalose metabolism and potentially serve as lead compounds in antibiotic development.

92. Synthesis and study of frustrated magnet KHoSe2

***Matthew Boswell**, boswel20@msu.edu, Haozhe Wang, Weiwei Xie. Chemistry, Michigan State University, East Lansing, Michigan, United States*

In this presentation we report the synthesis, phase identification, and heat capacity study of frustrated magnet KHoSe2. In condescend matter science frustrated magnets are highly sought after due to their unique properties and high potential in quantum computing and communication. Frustrated magnetism can lead to interesting magnetic ordering phases such as quantum spin liquids and quantum spin glasses. Frustrated magnetism occurs when favorable ordering of magnetic states is disrupted and causes the material to not reach a favorable low energy ordering. In recent years, a system of $ARECh_2$ (A= alkali earth metals, RE =Rare Earth metals, Ch = Chalcogens) has been proposed to exhibit frustrated magnetism and potential quantum spin liquids. KHoSe2 has been successfully synthesized and found to form in R-3m lattice structure. KHoSe2 is believed to be antiferromagnetic a magnetic susceptibility experiment will be run soon. The heat capacity study has shown that KHoSe2 has long range ordering without an external magnetic field. However, when a magnetic field is introduced, the entropy is reduced but not shifted. Furthermore, when induced to a 4 Tesla magnetic field the entropy peak is further reduced but also shifted. This heat capacity data is unusual for similar compounds and indicates that KHoSe2 may be a novel quantum spin glass.



93. Synthesis and characterization of lipid-based cubosomes loaded with siRNA

Mir M. Hossain *[1], m.m.hossain39@vikes.csuohio.edu, Mekki Bayachou[1,2]. (1) Chemistry, Cleveland State University, Cleveland, Ohio, United States(2) Department of Inflammation & Immunity, Lerner Research Institute, Cleveland Clinic, Cleveland, Ohio, United States*

One category of self-assembled lipid-based nanoparticles are known as cubosomes because of their facets' shapes. These entities have been used as drugs delivery devices and as biomolecules (siRNA, miRNA, etc.) carriers. They are bi-continuous cubic phase liquid crystals capable of encapsulating hydrophilic, lipophilic and amphiphilic drugs as required. Cubosomes have many potential properties that make them a promising alternative in the development of on-demand and controlled release systems. Effective drug delivery to the specific organs and tissues is one of the most important goals of pharmaceutical industry and cubosome nanoparticles seem to be amenable to targeted and on-demand drug delivery. In this work, cubosomal nanoparticles are prepared in phosphate buffer saline (PBS) system using a lipid building block monoolein (MO) and a pluronic F-127 polymer as a stabilizer. All the freshly synthesized formulations were in nano size ranges and showed exactly the typical morphology of cubosomes. The prepared samples were characterized using various unique methods such as dynamic light scattering (DLS), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and cryo-transmission electron microscopy (Cryo-TEM).

We have evaluated the anti-proliferation effect (IC_{50} value) of blank cubosomes compared to cubosomes encapsulating small interfering RNA (siRNA) on adequate cell lines. We tested the anti-proliferation on SK-Hep1 (hepatic adenocarcinoma) and on PC3 cells (prostate cancer

cells) compared to blanks and adequate controls. We will compare and contrast various preparation methodologies and how they affect the level and kinetics of siRNA release.

94. Synthesis of mycolic acid analogue for probing mycolic acid recycling pathways in mycobacteria

***Andy Kruskamp**, krusk1ad@cmich.edu, Kingsley Agu, Nicholas Banahene, Benjamin M. Swarts. Central Michigan University, Mount Pleasant, Michigan, United States*

Mycobacterium tuberculosis has plagued humanity for thousands of years, claiming a *billion* lives in the last 200 years alone. Far from being an obsolete pathogen, it still claims over a million lives a year, with over a quarter of the world's population being latently infected. Emergence of drug-resistant strains has galvanized research investigating pathways offering candidates for novel drug targets. Principal among these are recycling pathways. Mtb owes much of its success to its mycomembrane, a thick layer characterized by a unique fatty acid: mycolic acid. Mycolic acids present a unique architecture: the alpha carbon anchors a tributary alkyl chain, the beta carbon bears a hydroxy group, and further embellishments occur along the main chain (including methoxy, ketone, cyclopropyl, and methyl groups). This unique architecture plays a critical role in membrane structure and pathogenesis, and also serves as a template for probe development. Due to its unique structure, it can be inferred that mycolic acid must be chaperoned by proteins that are unique to mycobacteria and have the ability to discriminate between these and more generic straight-chain fatty acids that are more ubiquitous to life. A native mycolic acid analogue was synthesized and decorated with a fluorophore. It is hoped that this mycolic acid probe can be fed to mycobacteria and its movement tracked with the fluorescent handle. Tracking probe may elucidate mycolate recycling pathways and uncover novel drug targets.

95. Facile approach for preparing clickable platinum-based anticancer agents

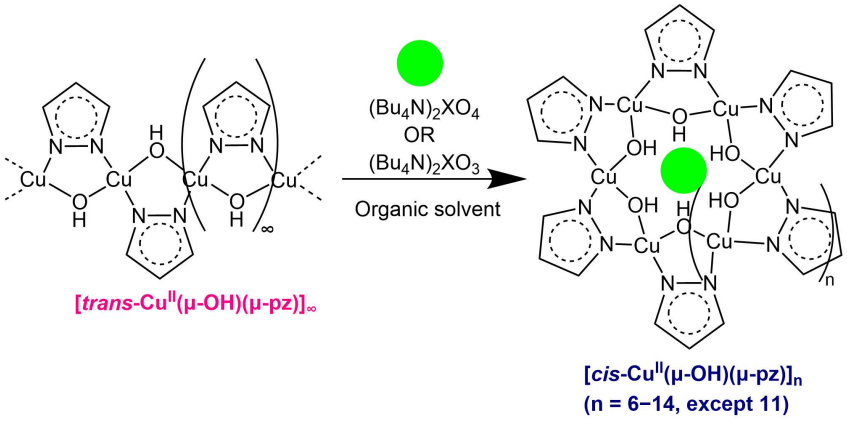
***Wjdan Jogadi**, wjogadi@kent.edu, Yaorong Zheng. Chemistry and Biochemistry, Kent State University, Kent, Ohio, United States*

In this study, we demonstrated a facile synthetic approach for designing a novel platform of Clickable Pt (IV) based anticancer agents via click chemistry. The click reaction approach is a powerful approach that has been used in drug development, which can be used as a simple way to develop the synthetic design and introduce multiple functions to the Pt (IV) center in a single step. The ability to rationally design and build a platform to develop new platinum (IV) prodrugs from a single precursor while utilizing a well-defined synthetic approach can be beneficial for discovering new therapies. However, complex syntheses can often hinder drug discovery efforts. To address this problem, we have synthesized Pt (IV) prodrug with two functional groups (hydroxyl and an azide) on its two ends using a two-step process. Then, the azide group can readily react with DBCO via click reaction and the DBCO group was functioned to increase the lipophilic properties of the prodrug. In addition, The Pt (IV) complexes demonstrated high cytotoxicity due to the accumulation of the complex in cellular and mitochondria uptake in ovarian cancer cells. Moreover, leading to induced Mitochondria and DNA damage and triggered cell death, as evidence by flow cytometric analysis and live-Dead imaging. These results suggest that the developed platform could potentially be used to overcome drug resistance in ovarian cancer. Overall, by utilizing a click chemistry approach, we have developed a novel platform to functionalize the Pt (IV) center and facilitate synthetic methods that could pave the way for researchers to explore new therapeutic agents.

96. Synthesis of carbonate-free nanojars by depolymerization of copper(II)-hydroxide/pyrazolate polymers

***Pooja Singh**, pooja.singh@wmich.edu, Gellert Mezei. Chemistry, Western Michigan University, Kalamazoo, Michigan, United States*

Nanojars are an emerging class of anion binding and extraction agents. These supramolecular coordination complexes (2 nm wide) exhibit exceptional anion binding strength which indicate their possible application in the recovery of toxic or valuable anions from water bodies. Nanojars of the formula $(TBA)_2[XO_{3/4}^{2-}\{Cu^{II}(\mu\text{-OH})(\mu\text{-pyrazolate})\}_n]$ (TBA = tetrabutyl ammonium cation, $XO_{3/4}^{2-}$ = anion, n = 26 – 36) are synthesized from Cu^{2+}, OH^-, pyrazolate ions and the TBA salts of various anions. Nanojars possess hydrophobic exteriors with an array of pyrazole ligands and hydrophilic interiors with a sequence of hydroxide functional groups which make them perfect incarcerating agents for anions with large hydration energy such as SO_4^{2-}, SeO_4^{2-}, CrO_4^{2-}, MoO_4^{2-}, WO_4^{2-}, HPO_4^{2-}, $HAsO_4^{2-}$, HVO_4^{2-}, SeO_3^{2-} and TeO_3^{2-}. One of the challenges in the study of nanojars is the competitive formation of CO_3^{2-}-incarcerating nanojars due to the carbonate impurities in the reagents when subjected to highly basic condition. Using the polymer $[Cu(OH)(pyrazolate)]_\infty$ with base (OH^- molecule) in it eliminates the need for additional base during nanojar synthesis, thus reducing the CO_3^{2-} impurities. Depolymerization of the [*trans*-Cu(OH)(pyrazolate)]$_\infty$ polymer into [*cis*-Cu(OH)(pyrazolate)]$_n$ (n = 27 – 32) in the presence of the TBA salt of different anions generates nanojars with no or minimal amounts of CO_3^{2-} impurities. Characterization was done by electrospray-ionization mass spectrometry, variable-temperature ^{1}H NMR spectroscopy and X-ray crystallography.



97. Electron and energy transfer dynamics in 2D PbS nanomaterials

***Adam J. Roach**, ajroach@bgsu.edu. Physics, Bowling Green State University, Bowling Green, Ohio, United States*

Lead sulfide nanomaterials are of interest in use in infrared devices such as photovoltaics and photocatalysis. Lead sulfide nanomaterials were attached to titanium dioxide and investigated via lifetime and photoluminescence. Sub-nanosecond electron transfer rates were seen in both PbS QDs and PbS nanoribbons via lifetime and spectral quenching. PbS QDs' faster electron transfer rate was attributed to prepping the QDs via ethanol wash. Further investigation of the reorganization energy and binding of the titanium dioxide will provide valuable insight into the system for utilization in devices. Further exploration of different nanomaterial energy will elucidate the nature of the electron transfer.

Resonance energy transfer was explored for use in infrared devices such as LEDs. The need for IR devices is becoming more prevalent as our society relies more heavily on information

infrastructure. Higher energy PbS QDs were mixed with lower energy PbS nanoribbons and exhibited FRET via photoluminescence ratio of donor and acceptor from solution to solid-state up to 25x change. Furthermore, the quenching of the donor and enhancement of the acceptor's lifetimes is consistent with energy transfer. PbS nanoribbons to nanoribbons showed a 13x change in donor-to-acceptor ratio. FRET in PbS nanomaterials show promise as an energy-transferring mechanism.

98. PFAS adsorption and transport in soils

***Christina E. Schumm**, schummch@msu.edu, Narasimhan Loganathan, Angela K. Wilson. Chemistry, Michigan State University, East Lansing, Michigan, United States*

Per- and polyfluoroalkyl substances (PFAS) are among the most prevalent contaminants of this day, due in part to their widespread use and persistence in the environment. Though long-valued for their non-stick and water-repellent commercial properties, many PFAS compounds have been linked to significant health concerns. Among one of the most problematic PFAS compounds is perfluorooctanoic acid (PFOA), which for a number of applications, has been replaced with GenX. However, studies from our group, as well as other groups, have shown that GenX has similar toxicological behavior as to legacy PFAS. Due to the critical role of sediments and soils in the movement of PFAS in the environment, the impact of the adsorption and transport of GenX has been examined in representative clay mineral constituents. This is one of the first studies to provide molecular-level insight about GenX in soil systems.

99. Metal hydride hydrogen compression

***Ketan Karkare**, kkarkare@mtu.edu. Mechanical, Michigan Technological University, Houghton, Michigan, United States*

Hydrogen is a light, clean, and renewable energy carrier, becoming an increasingly important substitute for fossil fuels in various industrial fields. One of the major application areas of hydrogen is the automotive application from small passenger vehicles ton heavy-duty trucks where hydrogen gases are stored on onboard storage at 70 MPa and consumed in the fuel cells to generate electric power. However, the production and storage of the high-pressure hydrogen at the hydrogen station is still an issue to overcome since the efficient compression methods of hydrogen to a high pressure of >70 MPa are not identified. Metal Hydride Hydrogen Compressor (MHHC) is a type of hydrogen compressor that utilizes a reversible chemical reaction involving a metal hydride. It exhibits various advantages over conventional mechanical compressors, such as safety, no pollution, no vibration, no noise, and lower cost. However, there is still no MHHC system that can efficiently utilize heat, improve system efficiency, and provide a higher compression ratio. Our study focuses on designing an efficient metal hydride storage system for hydrogen compression.

100. Investigation of the impact of PFAS on nuclear receptors via computational methods

***Deepak James**, jamesdee@msu.edu, Nuno Almeida, Semiha Kevser Bali, Cong Wang, Angela K. Wilson. Chemistry, Michigan State University, East Lansing, Michigan, United States*

Per- and poly-fluoroalkyl substances (PFAS) are a group of highly persistent, man-made chemicals that have been used in numerous industrial and consumer applications for several decades. There are thousands of PFAS compounds, with perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS), being the most common. Despite the utility of PFAS compounds, these species are persistent in the environment, and have been linked to health

issues including developmental effects, immune system dysfunctions, thyroid conditions, and a range of cancers. To better understand PFAS linkages to different diseases, the interactions of proteins with several PFAS species are examined. In this investigation, the interactions of PFAS with nuclear receptors (NRs), a class of proteins that play a broad range of roles in cell differentiation/development, proliferation, and metabolism, and, unfortunately, disease, are investigation. Computational chemistry methodologies including molecular dynamics, molecular dynamics, and binding free energy calculations have been utilized.

101. Studies of bacillithiol transferases: Enzymes involved in cellular detoxification in gram-positive organisms

***Morgan Buchman**, morgan.b5858@gmail.com, Paul D. Cook. Grand Valley State University, Allendale, Michigan, United States*

Low-molecular-weight thiols are organosulfur molecules that carry out many functions in cells, including detoxification of harmful molecules, acting as cytoplasmic redox buffers, and protecting cysteine residues on proteins. Bacillithiol is the major low-molecular-weight thiol present in Firmicutes such as *Bacillus anthracis* and *Staphylococcus aureus*. Bacillithiol transferases are important enzymes involved in detoxifying the cell by transferring bacillithiol to various electrophilic toxic compounds. Eight different bacillithiol transferases are presently known, named BstA - BstH. Previous research has shown activity with the model electrophilic toxin monochlorobimane in some of the transferases, however, the exact substrates that these enzymes act upon have not been identified. Additional activity assays as well as structural studies are needed to characterize these enzymes. Here we present X-ray crystallographic structures of select Bst enzymes from *B. subtilis*. Whereas kinetic assays show that BstF and BstH have no activity with the model electrophilic substrate dinitrochlorobenzene (CDNB), BstC, BstD, and BstE are active against this molecule. Additionally, we report progress on our determination of which metal ions are utilized by these enzymes. A thorough understanding of the cellular detoxification processes in Firmicutes may provide avenues for therapies against pathogenic Gram-positive bacteria that are growing in resistance to antibiotics such as fosfomycin.

102. Purification and structural analysis of UHRF2 bound to H3K9me3

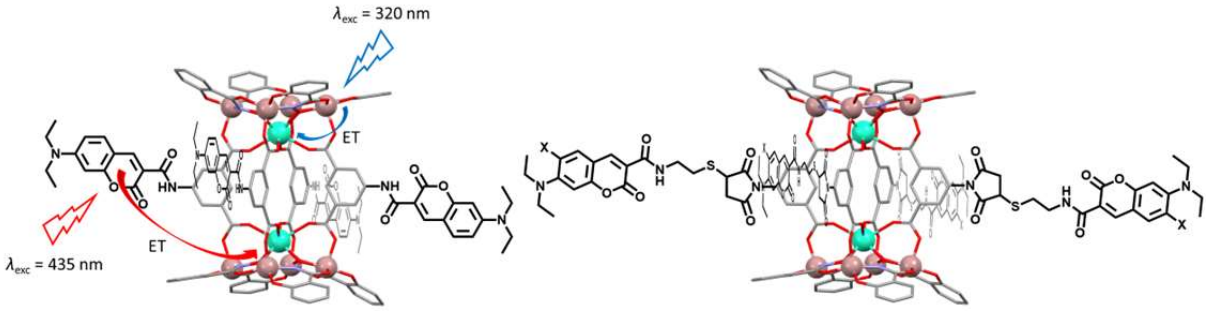
***William Jones**, wjones21@emich.edu. Chemistry, Eastern Michigan University, Ypsilanti, Michigan, United States*

UHRF2 is an epigenetic protein that regulates DNA methylation and histone modification. Previous studies have shown that the Tandem Tudor Domain (TTD) and the Plant Homeodomain (PHD) in UHRF2 bind to histone H3. X-ray crystallography data helps develop a three-dimensional “shadow” of the protein of interest, so that we may better understand its architecture. We crystallized UHRF2 in complex with H3 and solved a structural model using raw x-ray data and structural refinement software. Through X-ray crystallography, we gained structural insights into the histone-binding properties of UHRF2.

103. Coumarin-functionalized near infrared emitting metallacrowns for red-shifted excitation

***Timothe Lathion**[1], timothee.lathion@gmail.com, Svetlana Eliseeva[2], Matthias Zeller[3], Stephane Petoud[2], Vincent L.Pecoraro[1]. (1) Chemistry, University of Michigan, Ann Arbor, Michigan, United States(2) Centre de Biophysique Moleculaire, Orleans, Centre-Val de Loire, France(3) Chemistry, Purdue University, West Lafayette, Indiana, United States*

Metallacrowns (MCs) are a class of organometallic complexes that are like crown ethers. Instead of the repeating C-C-O motif, various *d* metals are used in the repeating N-O-M unit to form x-MCs-y of different sizes, such as 9-MC-3, 12-MC-4, or 15-MC-5, were x and y refer to the number of atoms forming the ring and the number of ligands, respectively. Ga^{III} was previously used in the N-O-M repeating unit along with salicylhydroxamic acid (shi) for the coordination of Ln^{III}, affording visible and near-infrared emitting metallacrowns such as $[LnGa_4(shi)_4(benzoate)_4]^-$ and their corresponding $[Ln_2Ga_8(shi)_8(ipa)_4]^{2-}$ dimers. While the Ga^{III}/shi scaffold allows for an efficient sensitization of Ln^{III} at λ_{exc} = 320 nm, red shifting that excitation wavelength is of interest for their potential use as imaging agents in biological media. For that purpose, various coumarin-based antennas were synthesized and incorporated to these Ln_2Ga_8 metallacrowns. The luminescence of the corresponding Nd^{III}, Er^{III} and Yb^{III} near-infrared emitting metallacrowns was studied both via excitation of the Ga^{III}/shi scaffold (λ_{exc} = 320 nm) and of the coumarin antennas (λ_{exc} = 390-435 nm).



Left: $[Ln_2Ga_8(shi)_8(C\text{-}ipa)_4]^{2-}$ metallacrown, where the coumarin antennas are attached through an amide bond to the isophthalic bridging ligands. Right: $[Ln_2Ga_8(shi)_8(C\text{-}mip)_4]^{2-}$ metallacrowns, where thiol-coumarin antennas are clicked onto maleimido groups via base mediated thiol-ene Michael addition.

104. Copper-mediated coupling of dodecaborates with phenols

Mackayla G. Pirie[1]*, pirie1mg@alma.edu, Joel A. Dopke*[1]*, Richard J. Staples*[2]*. (1) Alma College Department of Chemistry, Alma, Michigan, United States(2) Michigan State University, East Lansing, Michigan, United States*

The dodecaborate anion, $B_{12}H_{12}^{2-}$, and its derivatives have been of recent interest due to their high thermal and kintetic stabilities and low toxicities. These properties make the clusters attractive with regard to applications such as pollution remediation, cancer therapy and clean energy production. The iododododecaborate $B_{12}H_{11}I^{2-}$ readily reacts with phenols in the presence of a copper(I) catalyst and base to produce the phenolate-appended clusters, $B_{12}H_{11}(OAr)^-$ in moderate to high yields as evidenced by ^{11}B NMR. The reactions of interest were conducted in acetonitrile utilizing microwave heating, and the products were collected as colorless or light yellow solids as their quaternary ammonium salts following column chromatography. The products were characterized using ^{11}B, ^{1}H and ^{13}C NMR, and ESI-MS.

105. Heck couplings of aldehydes with dodecaborates

William J. Kidder[1]*, kidder1wj@alma.edu, Joel A. Dopke*[1]*, Richard J. Staples*[2]*. (1) Alma College, Alma, Michigan, United States(2) Michigan State University, East Lansing, Michigan, United States*

The modification of the dodecaborate anion $B_{12}H_{12}^{2-}$ provides the opportunity for the further incorporation of these species into a broad range of disciplines and applications such as

pollution remediation, cancer therapy and clean energy production. To that end, we investigated the palladium-catalyzed reaction of the iododododecaborate $B_{12}H_{11}I^{2-}$ with aldehydes in the presence of pyrrolidine to yield Zwitterionic products bearing both pendant cluster and pyrrolidinium moieties. Chromatography provided the product clusters in moderate yield as their colorless, quaternary ammonium salts. The identities of the products were established by ^{1}H, ^{13}C, and ^{11}B NMR spectroscopy, ESI-MS, and X-ray crystallography. The regiochemistry and potential mechanistic implications of the reactions will be discussed.

106. Experimental and computational approach to redox mediator design: Exploring the role of molecular structure in controlling bioelectrocatalysis

***Lincoln Mtemeri**, mtemeril@msu.edu. Chemical Engineering, Michigan State University, East Lansing, Michigan, United States*

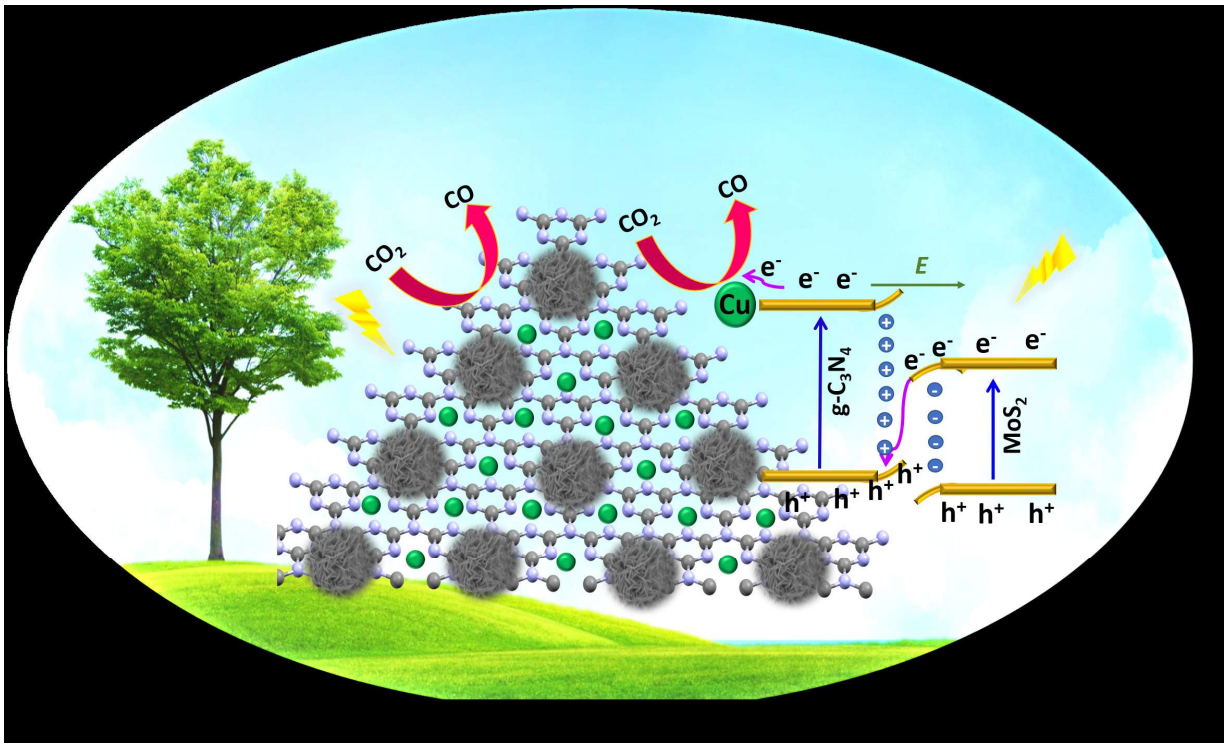
The global focus on a bio-based economy has led to the utilization of biological fuel cells for extracting energy from carbohydrates and biosensors for healthcare applications. These technologies rely on oxidoreductases such as glucose oxidase that have an active site that lies buried within the protein matrix of its structure, necessitating redox mediators to facilitate electron transfer from its FAD cofactor to the electrode interface. However, creating redox mediators for these enzymatic bioelectrode materials has proven to be a challenging task. Various redox-active molecular groups, such as ferrocene, quinone, and phenazine derivatives, are incorporated into biofuel cell electrodes to shuttle electrons from bioelectrocatalytic centers to electrode surfaces. Quinones have shown promise due to their low redox potentials, yielding low overpotentials when used as redox mediators. Previous studies have investigated how efficient redox mediators can be designed to regulate electron transfer rates between commercially relevant enzymes such as GOx, but the process is challenging and often relies on guess-and-check methods that only consider the redox potential of the mediator. The role of the mediator's structural features in altering enzyme-mediator kinetics is often ignored. Therefore, a comprehensive understanding of the relationship between mediator structure and homogeneous electron transfer rates is needed to design compatible redox species effectively. This work presents a combination of experimental and computational techniques to identify the parameters to be considered when designing redox mediators. The study uses supervised machine learning, molecular docking, and dynamics to provide fundamental insights into the design of next-generation bioelectrodes. These findings are critical in advancing the field of redox mediator design and in the development of efficient biofuel cells and biosensors.

107. Synergistic effect of cocatalyst and S-scheme heterojunction over 2D/2D g-C_3N_4/MoS_2 heterostructure coupled Cu nanoparticles for selective photocatalytic CO_2 reduction to CO

***Mohammed Al-Ghorbani**, mghorbani@taibahu.edu.sa. Chemistry, Taibah University, Madinah, Al Madinah, Saudi Arabia*

Step-scheme (S-scheme) configuration and cocatalyst are potential strategies for improving the photocatalytic activity of a nanoheterostructure. Herein, Cu nanoparticles (Cu-NPs) coupled 2D/2D van der Waals heterojunction (g-C_3N_4/MoS_2) has been developed for CO_2 reduction under visible light irradiation. Several analytical techniques were conducted to confirm the composition, morphology, and band configuration of the g-C_3N_4/MoS_2/Cu heterostructure. XPS and EPR analyses confirm that the charge transfer during photocatalysis follows the S-scheme mechanism. 2D/2D morphology enables a large interfacial intimate contract, and Cu-NPs act as a cocatalyst, boosting catalytic activity, facilitating electron

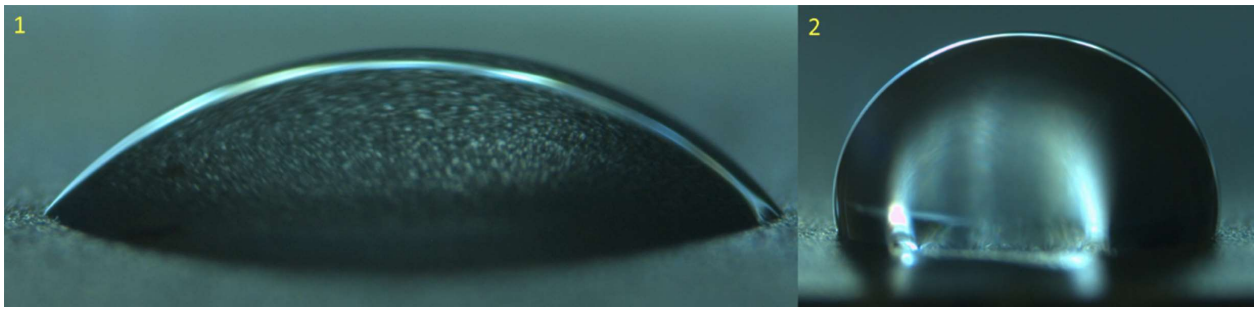
extraction, and tuning the product selectivity. As a result, the g-C_3N_4/MoS_2/Cu heterostructure achieved efficient photocatalytic CO_2 to CO reduction with a yield of 146.7 μmol g^{-1} h^{-1} and nearly 100% selectivity. This paper presents a systematic structural development strategy for controlling the different types of heterointerfaces, as well as facilitating a deep understanding of the mechanism of multi-junction photocatalysts.



108. Tri-cure hybrid organo-silicon coatings

***Cory B. Sims**, Cbsims@bgsu.edu, Chamika U. Lenora, Joseph C. Furgal. Chemistry, Bowling Green State University, Bowling Green, Ohio, United States*

A tri-cure coating system was created to shield stone, glass, metal, wood, and other architectural materials against environmental deterioration while also providing graffiti resistance on smooth surfaces. This technique employs three unique curing processes to provide a fast (30-minute) photo-initiated cure upon UV light exposure, followed by secondary amine-epoxy surface adhesion and sol-gel alkoxysilane crosslinking. Despite repeated use, the system's structure allows it to be stored as a one-pot solution for more than a year. Surfaces are made more hydrophobic, oxidative and flame resistant, anti-fouling, and chemical, photo, and thermal stable.



Water droplets and their static contact angles on the surface of raw steel 58.8 ° (1) and the coated surface 103.7 ° (2).

109. Regulation of Cisplatin resistance in lung cancer cells by Nicotine, BDNF, and adrenaline

***Ravel Ray**, rray9@emich.edu, Ben Haddad, Hind Al Khashali, Kai-ling Coleman, Jeffrey Guthrie, Deborah Heyl-Clegg, Hedeel Evans. Eastern Michigan University College of Arts and Sciences, Ypsilanti, Michigan, United States*

It is well-recognized that cigarette smoking is a primary risk factor in the development of non-small cell lung cancer (NSCLC), known to account for ~80% of all lung cancers with nicotine recognized as the major addictive component. In investigating the effect of nicotine, brain-derived neurotrophic factor (BDNF), and the β-adrenergic receptor blocker, propranolol, on sensitivity of NSCLC cell lines, A549 and H1299, to cisplatin, we found increased cell viability, and enhanced cisplatin resistance with nicotine and/or BDNF treatment while opposite effects were found upon treatment with propranolol.

110. Revving up a designed copper nitrite reductase using non-coded heterocycles

***Winston Pitts**, winstonpitts@live.com, Aniruddha Deb, James E. Penner-Hahn, VincentL. Pecoraro. Chemistry, University of Michigan, Ann Arbor, Michigan, United States*

De novo designed metalloproteins permit the investigation of the relationship between structure and function in metalloenzymes. Incorporating non-coded amino acids into proteins has provided a powerful way to probe fundamental questions involving metalloproteins and has contributed to our understanding of the subtle roles of amino acids/structure in their function. This offers unique opportunities to design novel active sites with novel ligands to explore small molecule activation in a protein environment. Synthetic methods were developed to introduce pyridine heterocycles within the hydrophobic core a three stranded coiled coil (3SCC) to generate a unique copper active site to explore NO_2^- reduction at novel copper centers in a protein environment. This is the first time a type 2 Cu center has been generated with 6-ring heterocycles inside of a protein which has resulted in the fastest homogenous CuNiR mimic in water including both homogenous and heterogenous small molecule mimics. Since we have full synthetic control of the ligands situated in the active site, we have changed the position of the nitrogen by incorporating either 4'-Pyridine or 3'-Pyridine side chains. Detailed steady state kinetics reveal that changing the position from the 4' to 3' position, alone, more than doubles the catalytic efficiency suggesting that the orientation of the nitrogen plays a criterial role in catalysis. Interestingly, we discovered that Cl^- competitively inhibits enzyme turnover by binding directly to the Cu(I) oxidation state with Cu^I-Cl distances between 2.25-2.30 Å. We used kinetic Cl^- titrations to demonstrate that NO_2^- binds directly to the Cu(I) active catalyst as opposed to the Cu(II) oxidation level, likely as the N-bound isomer. Incorporating pyridine side chains lowers the K_m by a factor of 5-fold as compared to histidine suggesting that the nitrite has a higher affinity to the pyridyl Cu(I) species. XANES/EXAFS analysis of the Cu(I) enzymes suggests that higher catalytic efficiency may be attributed to a preference to react at a 2-coordiate Cu(I) verse a 3-coordiate Cu(I), giving us insights into nitrite reduction at two different coordination modes of Cu(I). Overall, the marriage between *de novo* design proteins and inorganic coordination chemistry has proven useful in the design of the fastest homogenous CuNiR mimic to date all in a non-native fold that contains novel coordinative ligands in the protein active site.

111. Determination of tautomerase product profile via structural feature elucidation

***Katelyn Silva**, Kate LSilva@aol.com, Amaya Sirinimal, James Geiger, Karen Draths. Chemistry, Michigan State University, East Lansing, Michigan, United States*

There is a common goal to reduce the potent one carbon chemicals, methane (CH_4) and carbon dioxide (CO_2) from the atmosphere while maintaining their reduction. Acetylenecarboxylic acid (ACA) is a feedstock that is derived from CH_4 and CO_2 that can be further converted to high value chemicals such as 3- hydroxypropionic acid and malonic acid. In this study, we evaluate the tautomerases, *cis*-CaaD and Cg10062, in the production of malonate semialdehyde (MSA), a common pathway intermediate for these enzymes. *cis*-CaaD and Cg10062 have 53% similarity, identical active site amino acid residues, a homologous β-α-β structure, a catalytic proline at the *N*-terminal, and require no cofactor or metal for catalysis. *cis*-CaaD catalyzes the formation of MSA as the only observable product, while Cg10062 provides acetaldehyde (ACH, 81% product formation) as the major product with low amounts of MSA (19% product formation). In addition, Cg10062 is a more efficient enzyme with a *Km* of 66 μM in comparison to *cis*-CaaD (*Km* 1160 μM). We aim to evaluate the structural reasoning for the different product profile of these corresponding enzymes. Site-directed and error prone mutagenesis were preformed to improve the rate and efficiency of exclusive MSA production. Here we present kinetic and atomic resolution structural parameters to detail the differences between these two wild type enzymes as well as newly characterized variants. These finding provide insight into the mechanism of major product formation for the specified tautomerases. We show how one carbon derived ACA can be used as a feedstock in the biocatalysts of commodity chemicals while maintaining that these same one carbon derivatives are not reproduced mechanistically through this bioconversion.

112. Finding the perfect prodrug: Modifying platinum (IV) prodrug ligands to exploit cisplatin-resistant ovarian cancer mutations

***May Cheline**, mcheline@kent.edu, Yaorong Zheng. Chemistry and Biochemistry, Kent State University, Kent, Ohio, United States*

Ovarian cancer has proven a formidable challenge for traditional platinum-based chemotherapy due to its ineffectiveness at treating ovarian tumors. The main source of this drug resistance has been rooted in the upregulation of the transmembrane protein CD36, which is used to bring fatty acids into the cell for lipid metabolism. Although these upregulations have weakened the effects of platinum chemotherapeutic agents, novel developments have turned this upregulation of CD36 from a problem into a solution. The CD36 protein has susceptibility to compounds that have comparable properties to fatty acids. Fatty acids have a nonpolar organic carbon-chain at one end, and a polar carboxylic acid or “head group” at the other end. The addition of an axial carbon-chain tail and a polar head group have effectively increased the uptake of platinum-based drugs into the cell. Evidence has shown that these platinum (IV) compounds have higher uptake in drug-resistant ovarian cancer cells compared to traditional chemotherapeutic platinum drugs; however, these platinum (IV) compounds have differing levels of uptake comparatively. The synthesis of varied platinum (IV) molecules using head groups with differing polarities was used to find the most effective polarity. The results were able to clearly correlate the polarity of the head group with the efficacy of the compound. These findings have the potential to be used to make more effective chemotherapeutic options for ovarian cancer patients.

113. Chemical remodelling of the mycomembrane with chain-truncated lipids sensitizes mycobacteria to antibiotics

***Izzy Gaidhane**[1], gaidh1iv@cmich.edu, Kyle Biegas[1,2], Benjamin Swarts[1,2]. (1) Chemistry/Biochemistry, Central Michigan University, Mount Pleasant, Michigan, United*

States(2) Biochemistry and Molecular Biology, Central Michigan University, Mount Pleasant, Michigan, United States

Mycobacterium tuberculosis, the causative agent of tuberculosis, causes over 1.4 million deaths worldwide per year. Mycobacteria possess a highly protective outer membrane, which plays a key role in the bacterium's innate drug tolerance. It consists of large (up to C_{90}) hydrophobic lipids, notably the major mycolic acid conjugates arabinogalactan-linked mycolate (AGM) and trehalose dimycolate (TDM). Both AGM and TDM are synthesized from the precursor trehalose monomycolate (TMM), whose mycoloyl group is transferred by Ag85 mycoloyltransferase enzymes onto acceptor glycans to build AGM and TDM. Our lab has previously shown that TMM analogues with unnatural acyl chains can incorporate into AGM and TDM via Ag85. In this project, we synthesized a panel of truncated TMM derivatives to test the effect of shortening of acyl chain lengths (C_6, C_{14}, and C_{22}) on cell envelope permeability. These compounds, notably the C_6-TMM, were tested in various permeability and antibiotic cotreatment assays with *Mycobacterium smegmatis*. We found that the C6-TMM increases permeability of the mycobacterial outer membrane to larger, more impermeable drugs such as rifampicin, increasing the bacterium's drug susceptibility by up to 67%.

114. Characterization of trehalose analogues' hydrolytic resistance and their potential use as inhibitors of trehalose utilization in microorganisms

***Ulysses Johnson**, johns1ug@cmich.edu, Benjamin Swarts. Chemistry and Biochemistry, Central Michigan University, Mount Pleasant, Michigan, United States*

Metabolism of the non-mammalian disaccharide trehalose is essential for survival and virulence in many bacterial and fungal pathogens. While trehalose analogues have proven to be highly-effective tools for investigating *Mycobacterium tuberculosis*, these tools have been little explored in other microorganisms. Here, we used a combination of chemical and chemoenzymatic synthesis to generate a panel of single-position modified trehalose analogues and investigated their hydrolytic resistance to recombinant bacterial and mammalian trehalases. All modifications afforded some degree of resistance to hydrolysis, whereas modification in the 2 and 4 position showed complete resistance. The resistant character of these analogues is being further studied in live cultures of *Escherichia coli, Bacillus subtilis, and Mycobacterium smegmatis* to evaluate whether they support bacterial growth and whether they inhibit utilization of native trehalose.

115. Analysis of cell-surface associated biomolecules of *Pseudomonas aeruginosa* planktonic and biofilm cell subpopulations using MALDI-TOF MS

***Chase N. Morse**[1], cnmor1097@gmail.com, Taylor A. Dodson[1], Nathan Wamer[1], Eric A. Carlson[1], Jennifer Gadient[2], Erin G. Prestwich[1]. (1) The University of Toledo College of Pharmacy and Pharmaceutical Sciences, Toledo, Ohio, United States(2) The University of Toledo College of Natural Sciences and Mathematics, Toledo, Ohio, United States*

Pseudomonas aeruginosa is an opportunist, gram-negative bacterium capable of producing prolific biofilms leading to chronic infection. *P. aeruginosa* excretes a variety of small molecules during its growth and biofilm development. Many of these small molecules are part of quorum sensing (QS) systems that aid cells in communicating and forming biofilms. Our lab previously developed methods to isolate and characterize three distinct biofilm cell subpopulations. To understand which molecules are on the outside of each subpopulation, we utilized matrix assisted laser desorption ionization time of flight mass spectrometry (MALDI-TOF MS). Many cell-surface associated molecules were identified using collision-induced

dissociation (CID) and were found to belong to the following molecular classes: quinolones, lactones, rhamnolipids, and phenazines. Several molecules were unique to each specific cell subpopulation. The localization of the different subpopulations within a biofilm were mapped using MALDI imaging combined with colocalization analysis of specific selected ions. Another study analyzed cell-surface associated molecules in planktonic cells and MALDI matrices. Six different matrices were utilized to analyze three major molecular classes: quinolones, rhamnolipids, and phospholipids. The ionization of the molecular classes and their subclasses differed based on the matrix used. Thus, the matrix selection heavily influences the classes of molecules that are observed in MALDI analysis. Our studies allowed us to understand more about planktonic and biofilm subpopulations of cells in *P. aeruginosa* and the small molecules that they produce.

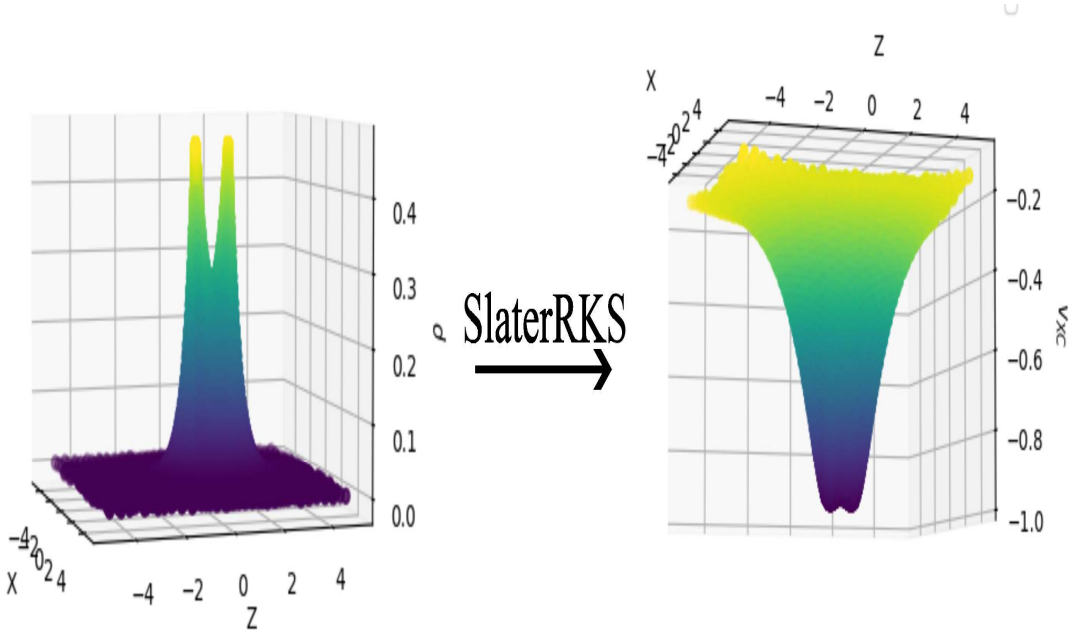
116. SlaterRKS method: Exchange correlation potential from slater FCI densities

Soumi Tribedi[1,2]*, stribedi@umich.edu. (1) Chemistry, University of Michigan, Ann Arbor, Michigan, United States(2) Institute for Data Science, University of Michigan, Ann Arbor, Michigan, United States*

Density functional theory (DFT) is the predominant method for estimating properties of molecules and materials, owing to the balance of accuracy and cost. Affordability stems from the Hohenberg-Kohn theorem that the ground state of a system can be expressed in terms of the electron density (ρ). All quantities required to get the ground state energy are analytically known except for the exchange correlation (XC) energy. In practice, various approximations have been used for the XC term in different functionals aiming at obtaining correct energies for a particular problem of interest, often overlooking the resulting incorrect densities and potentials. Current shortcomings of DFT such as self-interaction, delocalization errors and strong correlation can be addressed with the knowledge of the XC potential (v_{XC}). The Ryabinkin-Kohut-Staroverov (RKS) method is one of the more numerically robust strategies to obtain the v_{XC} from a wavefunction density. So far, RKS has been employed using Gaussian basis sets which have inaccurate nuclear cusps and long-range decay. Slater basis functions on the other hand are more suitable choice as they display correct nuclear cusp and long range behaviour. Starting from the Slater basis Full Configuration Interaction (FCI) densities, which are exact in that basis set, we employ the RKS method to calculate the corresponding exchange correlation potential

(v_{XC}). The use of physically correct basis functions along with availability of full correlation through GPU accelerated FCI calculations create a robust method for obtaining accurate exchange correlation potentials in moderately sized basis sets without any unphysical artifacts.

Some examples of weakly and strongly correlated molecules are chosen for demonstration.



117. Multiconfiguration pair-density functional theory beyond single-point calculations

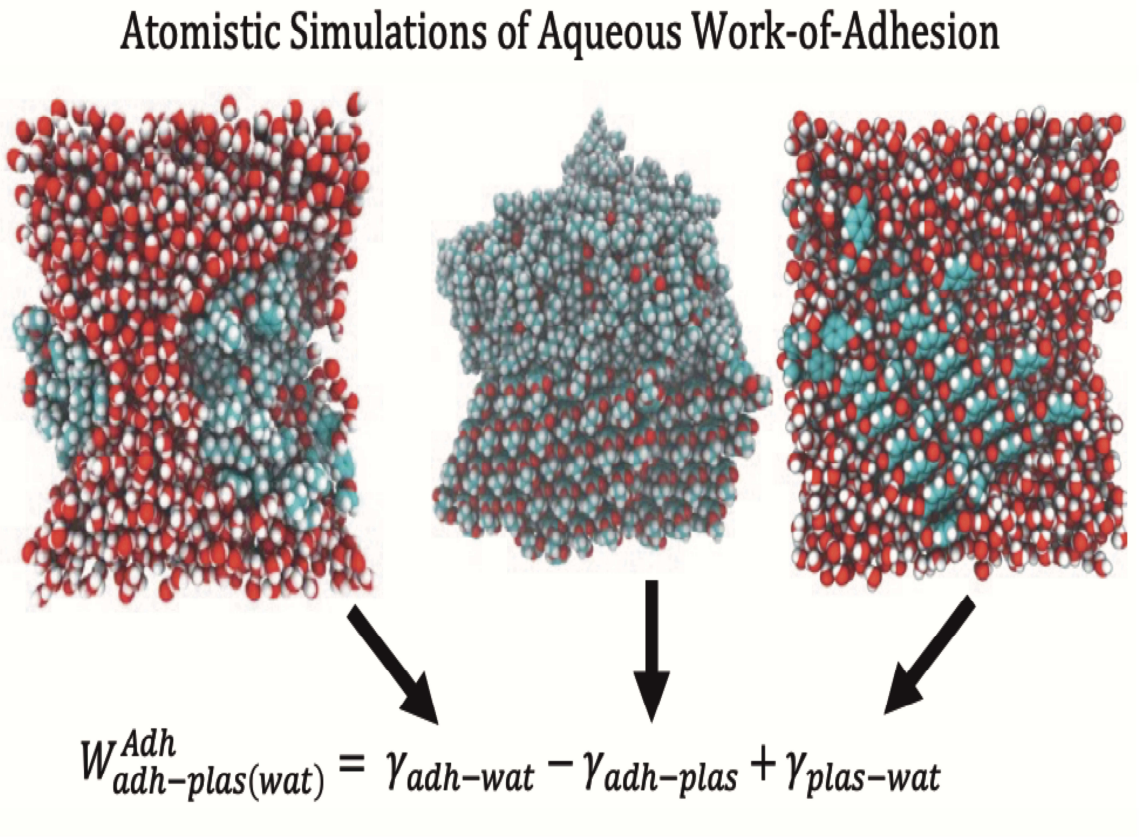
Paul B. Calio[1], *pcalio@uchicago.edu, Matthew Hermes*[1], *Jie Bao*[2], *Ignacio F. Galván*[3], *Roland Lindh*[3], *Donald G. Truhlar*[2], *Laura Gagliardi*[1]. *(1) Chemistry, University of Chicago Division of the Physical Sciences, Chicago, Illinois, United States(2) Chemistry, University of Minnesota Twin Cities, Minneapolis, Minnesota, United States(3) Chemistry-BMC, Uppsala Universitet, Uppsala, Sweden*

Multiconfiguration pair-density functional theory (MC-PDFT) is a multireference electronic structure method that predicts reaction energies and excitation energies as accurately as complete active space second-order perturbation theory (CASPT2), but MC-PDFT has the advantage of being significantly computationally cheaper. Furthermore, analytical nuclear gradients have been developed for MC-PDFT, and this presentation will describe our work towards making MC-PDFT an electronic structure method for nonadiabatic molecular dynamics (NAMD) simulations. The beginning of this talk will show the first application of MC-PDFT NAMD simulations by describing the intersystem crossing dynamics within thioformaldehyde. Our findings show MC-PDFT results that are comparable to multistate CASPT2 but at a more affordable cost. The second part of this talk will focus on making MC-PDFT a method for internal conversion processes. Specifically, this talk will show the development of nonadiabatic coupling vectors for compressed multistate (CMS)-PDFT, and show that we can optimize structures at the minimum energy conical intersection. Taken together, the two parts of this presentation will describe the progress towards making MC-PDFT a method that can be applied to understand photodynamic properties in systems that were previously considered too large for accurate multireference calculations.

118. Developing novel adhesives for microplastic remediation: How composition and environment impact selectivity

Erasmus M. Jugovic, *tim.jugovic@hotmail.com, Paul M. Zimmerman. Chemistry, University of Michigan, Ann Arbor, Michigan, United States*

Microplastics (MPs) are a growing class of environmental pollutants with profound impacts on the health of organisms that ingest them. Adhesive-coated substrates have been used to non-selectively capture microplastics (MPs) in water, and if made selective represent potential solution to remediation of MPs. Polyacrylates are a broad category of adhesives containing many different possible co-polymers and auxiliary monomers that have the potential to achieve the desired selectivity. However, the chemical space of possible novel co-polymers is enormous. Our lab has designed an algorithm that can rapidly generate many large polyacrylate polymers with a specific ratio of a desired co-polymer or auxiliary monomer. GPU accelerated CHARMM molecular dynamic simulations are then used to determine the relative adhesive ability (called Work-of-Adhesion (WoA)) to a specific type of MPs. Investigations were able to enhance the selectivity toward polystyrene by increasing %tridecafluorooctyl acrylate (TDO) relative to 2-ethylhexyl acrylate. This is the first time that thermodynamic selectivity between plastics has been enhanced simply by manipulating polyacrylate composition. Predictions were used to guide polyacrylate synthesis targets in work done by the McNeil Group at University of Michigan. Experimental probe-tack measurements of aqueous adhesion confirmed the computational models' ability to predict trends of strength and specificity. Models were then developed to incorporate common dissolved salts and surfactants that are found in real extraction environments such as laundry effluents. The effect of dissolved molecules on adhesive selectivity can be both profoundly negative and positive. This presentation will discuss how computational methods have been used in the development of highly selective adhesives for MP remediation from waste streams.



119. Monte Carlo framework for molecularly doped organic semiconductors

Archana Verma[1]*, archana.x.verma@gmail.com, Nicholas Jackson*[2]*. (1) Chemical Engineering, University of Illinois Urbana-Champaign, Urbana, Illinois, United States(2) Chemistry, University of Illinois Urbana-Champaign, Urbana, Illinois, United States*

Organic semiconductors (OSCs) enable a new technological paradigm of solution-processable, lightweight, flexible, and low-cost optoelectronic devices. Analogous to silicon microelectronics, the addition of electronic dopants is a ubiquitous performance augmentation strategy in OSCs that improves conductivity. Although the importance of optimizing OSC/dopant interactions is well-recognized, challenges arise from experimental structure-function relationships being subject to the sensitivity of doping to processing conditions and film morphology. Computational modelling for OSC/dopant design is potentially more systematic but requires simultaneous treatment of molecular electronic structure and mesoscale morphology. This confluence necessitates using both coarse-grained and electronic structure prediction models to obtain detailed quantum mechanical predictions at mesoscopic spatiotemporal scales. To step towards coupling quantum chemical changes in electronic state to morphology, we present a Monte Carlo model that samples the morphologies of molecularly doped OSCs. These generated morphologies are subsequently characterized to clarify how equilibrium doping configurations vary with local energetics. Addressing these phenomena will elucidate the inherently multi-scale nature of doping and elucidate fundamental relationships between morphology, electronic structure, and conductivity. Success of this effort, more broadly, will facilitate curating design rules for OSC/dopant systems and prepare OSCs for application in flexible electronic devices across industries.

120. Application of the semi-stochastic CC(*P*;*Q*) approach for electronic excitations in molecules and singlet–triplet gaps in biradicals

Arnab Chakraborty[1], *arnabc3792@gmail.com, Stephen H. Yuwono*[1], *J. Emiliano Deustua*[1], *Jun Shen*[1], *Piotr Piecuch*[1,2]. *(1) Department of Chemistry, Michigan State University, East Lansing, Michigan, United States(2) Department of Physics and Astronomy, Michigan State University, East Lansing, Michigan, United States*

It is well established that the exponential wave function ansatz of coupled-cluster (CC) theory and its equation-of-motion (EOM) extension to excited states are among the most appealing ways to describe the electronic structure of molecules. One of the key challenges in the development of the CC and EOMCC methodologies is the incorporation of many-electron correlation effects due to higher–than–two-body components of the cluster and EOM excitation operators, needed to achieve a quantitative description, without running into prohibitive computational costs of the full CCSDT/EOMCCSDT, full CCSDTQ/EOMCCSDTQ, etc. schemes and without resorting to perturbative ideas that fail in multireference situations, such as bond breaking and excited states dominated by two-electron transitions. One of the most promising approaches in this area is the semi-stochastic CC(*P*;*Q*) methodology that identifies the most important higher–than–doubly excited determinants needed in the high-level CC/EOMCC calculations with the help of the stochastic configuration interaction (CI) Quantum Monte Carlo (QMC) wave function propagations. In this presentation, I will discuss our recent work on extending the semi-stochastic, CIQMC-driven, CC(*P*;*Q*) framework to excited electronic states and open-shell systems. We investigate the performance of the resulting methods by examining their ability to recover the high-level CCSDT/EOMCCSDT energetics in calculations of the electronic excitation spectra of the CH^+, CH, and CNC molecules and singlet–triplet gaps in a few biradical systems, including cyclobutadiene, cyclopentadienyl cation, and trimethylenemethane. We demonstrate that the semi-stochastic CC(*P*;*Q*) calculations are capable of generating results of the CCSDT/EOMCCSDT-quality, out of the early stages of the CIQMC wave function propagations.

121. From atoms to proteins and quantum mechanics to molecular dynamics

***Nuno Almeida**, almeidan@msu.edu, Sasha C. North, Timothé Melin, Semiha Kevser Bali, Angela K. Wilson. Chemistry, Michigan State University, East Lansing, Michigan, United States*

Computational chemistry is a powerful field, offering a panoply of methodologies to aid in solving complex problems such as those for which the solutions may be hindered due to safety, short atomic lifespan, extraordinarily complicated electronic manifolds, or complex *in vivo* interactions. However, the computational routes chosen must be carefully selected to accurately reproduce physical and chemical properties. In this presentation, the tremendous utility of computational methodologies, from quantum mechanics to molecular dynamics towards applications from the smallest of heavy element species to the impact of environmental contaminants upon human proteins are overviewed.

Quantum chemistry is often utilized for smaller systems (up to only a few hundred atoms), and computationally demanding *ab initio* approaches are often necessary for detailing transition and heavy metal species. Due to the presence of many excited states, spin multiplicities, and relativistic effects in these species, high-level *ab initio* approaches are often needed to predict reliable thermochemical or spectroscopic properties. In this work, the ground and excited state properties of lanthanide and actinide oxides and fluorides are provided as examples of the utility of rigorous computational methods in state-of-the-art predictions for heavy elements.

Furthermore, when faced with larger systems such as proteins, molecular dynamics can be very useful. For example, Nuclear Receptors (NR) are often the focus of many drug targets, due to their role as the fundamental building blocks of gene expression, and molecular dynamics provides the best computational route in detailing these proteins. Many human NR have been negatively impacted by per- and polyfluoroalkyl substances (PFAS) resulting in severe health conditions in humans. Herein, the potential binding between common PFAS and NR was determined to gain insight about the impact of these species and consider possible routes that can help to alleviate the effects of these “forever chemicals”.

122 Grading gets in the way of my students’ learning: Alternative grading strategies

***Matthew J. Mio**, miomj@udmercy.edu. Chemistry and Biochemistry, University of Detroit Mercy, Detroit, Michigan, United States*

The Covid-19 pandemic has accelerated pedagogical research in the area of alternative grading strategies (AGS). Traditional grading, via points and/or letters, is neither ancient nor helpful: the literature now characterizes it as **ineffective** for both instructor and student, **harmful** to learning, and patently **unjust**. The benefits of AGS are plentiful, including decreased anxiety and cheating, and emphasis on student-regulated learning. Multiple, specific examples of AGS will be given in this talk, both at the lesson and course level. The main aim of the talk will be to convince the audience that dysfuncational illusions of academic rigor have pervaded the academy and that the evidence that AGS are more effective than traditional methods is so strong that the burden has shifted.

123. Storytelling in chemical education

***Sibrina N. Collins**[1], sibrina.collins@gmail.com, Michelle Nelson[1], Tiffany Steele[2]. (1) College Arts and Sciences, Lawrence Technological University, Southfield, Michigan, United States(2) Department of Educational Leadership, University of Rochester, Rochester, New York, United States*

Storytelling in chemistry as a pedagogical tool provides an alternative learning format for students to discover more about the people behind STEM (Science, Technology, Engineering

and Mathematics) innovations that impact our society. Four narrative films celebrating the significant contributions of chemists Alice Augusta Ball, Dr. Saint Elmo Brady, Dr. Percy Lavon Julian, and Dr. Bettye Washington Greene were screened in a social science seminar course with the theme “Equity and History of Science.” Our study suggests the films had a positive impact on all the students in the course. We will also discuss a practical example of how chemistry faculty can use strategies that leverage popular films such as Marvel Studios’ *Black Panther*, where the fictional element vibranium (Vb) is an important protagonist for student engagement in chemistry.

124. Investigating the use of ChatGPT with chemistry exam questions

***Ted M. Clark**, clark.789@osu.edu. Chemistry and Biochemistry, The Ohio State University, Columbus, Ohio, United States*

The artificial intelligence chatbot ChatGPT was used to answer questions from final exams administered in two general chemistry courses, including questions with multiple-choice format and with open-response format. Reponses were coded based on concept identification, problem-solving strategy, and execution to reach the final solution. For multiple-choice questions ChatGPT was very capable at identifying the concept even when the question included a great deal of chemical symbolism. However, ChatGPT’s success at solving problems was only 44%, a value well below the class average of 69%. Similarly, on open-response questions, ChatGPT’s ability to identify the concept surpassed its ability to provide responses of an average student. Incorrect responses and flawed explanations were often logically sound and would be persuasive to a novice. The chatbot is currently ill-equipped to provide reliable feedback to students for representative exam questions, but could be used to create assignments in which students analyze and improve ChatGPT’s responses.

125. Isolation of microplastics and student perceptions of their environmental footprint

***Kelly Hall**, k-hall.6@onu.edu, Amelia Anderson-Wile. Ohio Northern University, Ada, Ohio, United States*

It is commonly known what microplastics are and where they come from; however, it can be difficult to connect one’s own use of plastic materials to broader environmental impacts. In an effort to improve student engagement, several microplastic related activities have been implemented into organic and polymer chemistry courses. Students have worked on isolation of microplastics in soil and sea salt samples while being challenged to connect a small sample isolation to the larger environmental picture and their own personal use of plastics. Upon completion of isolation students then submitted a community outreach project focused on how they could impact plastic usage in their own community. Examples of these projects included infographics, podcasts, and memos to community leaders. The students were then surveyed about perceptions of their own plastic waste footprint and changes they would make as a result of what they learned during the experiment.

126. Organic chemistry students’ engagement in mechanistic reasoning about the role of adenosine triphosphate (ATP) in reaction coupling

***Clare G. Franovic**, carls500@msu.edu, **Dani Losinski**, losins10@msu.edu, Keenan Noyes, Melanie Cooper. Michigan State University, East Lansing, Michigan, United States*

In science education research, there is consensus that building interdisciplinary connections and reasoning mechanistically about phenomena are valued ways of thinking. Our work aims to support students in building connections between their chemistry and biology courses by

engaging them in mechanistic reasoning (i.e., how and why things happen) about phenomena that carry relevance in both disciplines. Little work has been done to investigate how organic chemistry students apply their understanding of reactivity and energy to phenomena relevant in biology, such as reaction coupling. In the work presented here, we designed and administered a scaffolded activity with the goal of supporting students' mechanistic explanations for the role of ATP in a coupled reaction. While this phenomenon is more frequently taught in biology courses, we designed the activity so that students in both organic chemistry and molecular biology (and more senior level) courses could construct reasonable explanations using ideas relevant to their courses or prior knowledge. The activity focuses on the ATP-driven formation of glutamine from glutamate and ammonium, with an emphasis on helping students identify and use important chemical and biological ideas such as reactivity and energy transfer. We collected responses in Fall 2022 from 230 first semester organic chemistry students and analyzed their explanations for how ATP drives this unfavorable reaction using a previously developed coding scheme. Several organic chemistry students leveraged productive ideas from both the activity and their prior knowledge to construct mechanistic explanations; however, some students used explanatory black boxes or invoked prior knowledge about ATP that was not relevant to the phenomenon. We provide access to the full activity and invite discussion regarding how it might be implemented in chemistry courses to better support students as they transfer ideas to biological/biochemical contexts.

127. "Mostly I just copy what my chemist colleagues tell me": An investigation of molecular biology instructors' experiences teaching about adenosine triphosphate (ATP) and chemical bond energy

Clare G. Franovic[1]*, carls500@msu.edu, Keenan Noyes*[1]*, Nicholas R. Williams*[1]*, Michael Klymkowsky*[2]*, Melanie Cooper*[1]*. (1) Michigan State University, East Lansing, Michigan, United States(2) University of Colorado Boulder, Boulder, Colorado, United States*

Within the chemistry education literature there exists a well-documented, and persistent misconception that breaking a chemical bond results in a release of energy. This misconception is exacerbated by relatively common depictions and language concerning the use of the critically important biological molecule adenosine triphosphate (ATP), often referred to as the "energy currency of the cell." In 1941, Lippman introduced the term "high-energy bond" when he elucidated the excessive heat accompanied by hydrolysis of ATP. The idea that breaking off a phosphate group from ATP results in energy release became commonplace in the biology classroom and remains so today. In more recent publications in chemistry and physics education, there has been a push to focus on the mechanism by which ATP hydrolysis is coupled to the release of energy via the formation of more stable bonds, as well as the recognition that there is a discrepancy between how different disciplines discuss these ideas. However, discussing ATP hydrolysis in terms of bond energies may prove problematic for biology instructors who have several additional complex themes to cover in a short period of time. Additionally, in biological systems ATP rarely hydrolyzes and never does so when used in reaction coupling. Rather, the terminal phosphoryl group is often transferred to a substrate creating a high-energy intermediate that reacts to produce the intended product. In this talk, I will share results from a larger study involving interviews with several chemistry, biology, and biochemistry faculty about the role of ATP and energy in their courses. While several ideas emerged regarding this theme, here we present the emotions, including dissatisfaction and frustration, that three introductory molecular biology instructors shared concerning their experiences with teaching about ATP.

128. New developments in catalytic carbonyl-olefin metathesis

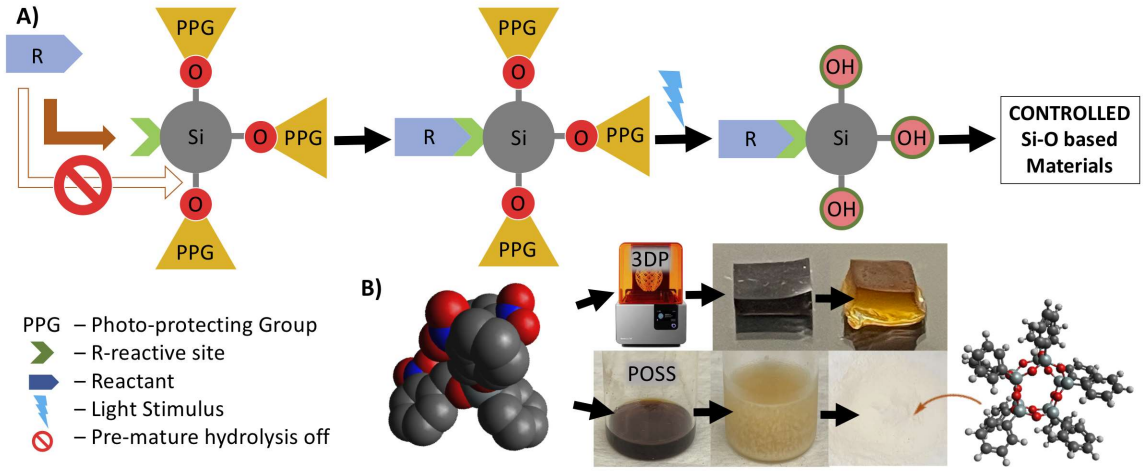
***Timothy McClure**, mccluret@umich.edu. University of Michigan, Ann Arbor, Michigan, United States*

The olefin-olefin metathesis reaction is a revolutionary industrial process that utilizes precious metal complexes to enable direct carbon-carbon bond formation from simple olefin starting materials. The carbonyl-olefin metathesis reaction similarly enables the construction of carbon-carbon bonds and has the potential to have an analogous impact on synthetic strategy. However, currently available synthetic procedures are significantly less advanced. Our research laboratory has developed Lewis acid-catalyzed carbonyl olefin metathesis that represents a new reactivity mode between carbonyl and olefin functionalities. Our design principle fundamentally differs from stoichiometric carbonyl-olefin metathesis protocols proceeding via intermediate oxametallacycles. It is instead based on the in situ formation of oxetanes as reactive intermediates via an asynchronous, concerted [2+2]-cycloaddition of a carbonyl and an olefin upon activation with a Lewis acid catalyst. This distinct reactive intermediate no longer limits the process to precious metals, enables catalytic turnover, and prevents the formation of stoichiometric waste. While this new design principle for carbonyl-olefin metathesis enabled important advances for ring-closing, ring-opening, cross, and transannular carbonyl-olefin metathesis reactions, limitations remain that require a deep understanding of the controlling features of this transformation. We herein report new developments focused on mechanistic investigations and catalyst design that overcome current challenges.

129. Photocaged R-alkoxysilanes for on-demand functionalization and polymerization control

***Mahmud R. Rashed**, rashedm@bgsu.edu, Joseph C. Furgal. Chemistry, Bowling Green State University, Bowling Green, Ohio, United States*

R-alkoxysilanes are the monomer workhorses of silicon-based sol-gel chemistry and are used as the building blocks for materials from silicas to silicones. However, uncontrolled hydrolysis, premature condensation, and overall polymerization control have plagued the sol-gel and siloxanes communities since their inception. This study was to develop new silicon sol-gel chemistry methodologies that utilize photo protected R-alkoxysilanes (PPGs) to control the synthesis of unique silicon-based materials. We have started our investigation with the synthesis and characterization of 2-nitrobenzyloxy based PPG systems from ethyl and phenyl (R_x-(alkoxy)$_y$silanes, with x=0-3 and y=1-4). With these systems, we have explored the photochemical response for PPG removal including kinetics and removal efficiency, and the tin catalyzed coupling of deprotected products to form polymers. We have found that reasonable removal of the photoprotecting groups was achieved giving a new avenue to generate silicon-based polymeric materials. Furthermore, a crude study has found that it is possible to directly 3D print with these materials.



130. Insights into the mechanism of Boyland-Sims oxidation reaction

***Jojo Joseph**, jojo.joseph@fairmontstate.edu. Fairmont State University, Fairmont, West Virginia, United States*

The Boyland-Sims oxidation is the reaction between peroxydisulfate ions and arylamines to form the aryl amine *ortho* sulfate with small amounts of the *para* isomer. The long-standing mechanism involves a nucleophilic attack by the amine on peroxide oxygen to form arylhydroxylamine-O-sulfonate intermediate, which then rearranges to the arylamine *o*-sulfate. The long-standing mechanism has been questioned by Marjanović *et al*. who have proposed a nitrenium ion intermediate as the reactive species rather than the uncharged amine. The nitrenium ion proposal was based on relatively low-level calculations. It has been challenged by a variety of experimental observations previously. We present here new computations at a high-level of density functional theory (B3LYP/6-311++G**) to model both arylhydroxylamine-O-sulfonate and nitrenium ion pathways in a series of aromatic amines. In this study, the energetics of reaction intermediates in both mechanisms are computed for aniline, 2,4-dinitroaniline, N,N-dimethylaniline, and a series of alkyl-substituted aromatic amines. To further support the pathways of the reaction, the calculations were performed to find the transition states involved in both mechanisms. The transition state calculations revealed two possible energetically feasible pathways for the rearrangement of arylhydroxylamine-O-sulfonate to arylamine *o*-sulfate. Our results indicate that the Boyland-Sims oxidation reactions proceed via arylhydroxylamine-O-sulfonate intermediate as predicted earlier, which makes doubtful the importance of a nitrenium ion in this process.

131. Acetylene dicarboxylic acid: C4 bridge between C1 feedstocks and commodity chemicals

*Bismarck Amaniampong, Hadi Nayebi Gavgani, Amaya Mathes Hewage, **Karen Draths**, draths@chemistry.msu.edu. Chemistry, Michigan State University, East Lansing, Michigan, United States*

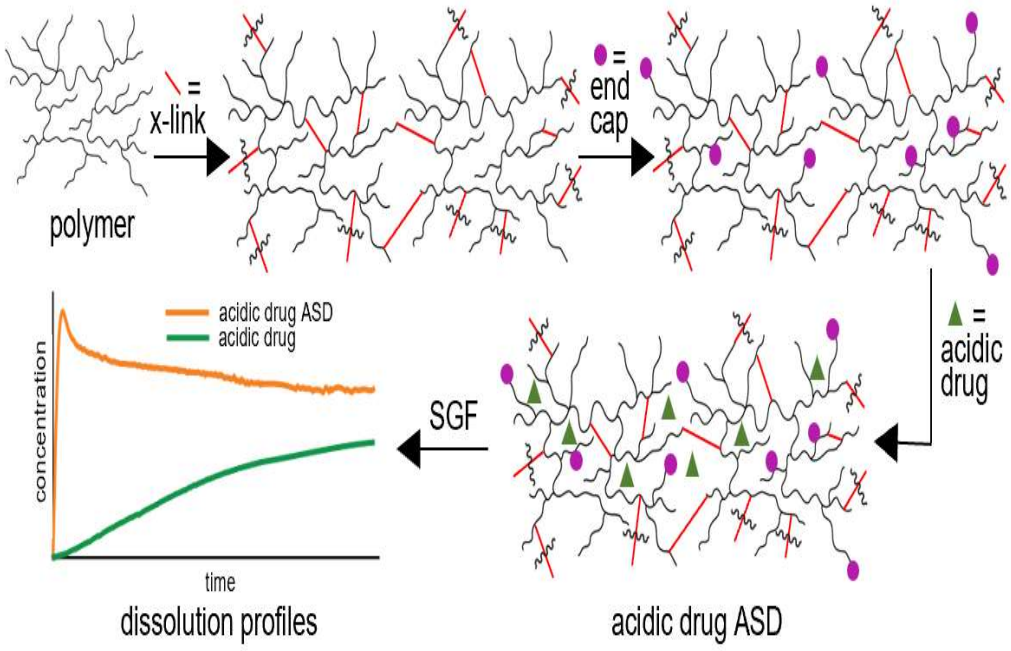
Recent years have seen a dramatic increase in exploration of commodity chemical production that relies on the C1 feedstocks methane and carbon dioxide. The U.S. dual priorities of a globally competitive chemical industry and satisfying decarbonization goals warrant investigation of a multitude of approaches for chemical production. We offer here a strategy that relies on chemical and biological catalysis. Chemical catalysis enables transformation of methane and carbon dioxide into acetylene dicarboxylic acid, which is then transformed via

biological catalysis into chemical commodities of interest. At the outset of the project, we wondered if acetylene dicarboxylate could mimic natural dicarboxylates to function as a viable carbon source for bacterial growth. Our findings following adaptive laboratory evolution of *Escherichia coli* to grow on acetylene dicarboxylate will be described including transcriptome analysis, metabolite profiling, and comparative genomics to elucidate the mechanism and regulation of carbon substrate assimilation. The genetic basis for improved growth on an unnatural carbon source will be discussed. As proof-of-concept for the strategy, synthesis of lactic acid from acetylene dicarboxylate will also be described.

132. Crosslinked polyethylenimine: Novel drug delivery system for acidic drugs

Kristen N. Kelsall[1,2]*, kkelsall@umich.edu, Leila M. Foroughi*[2]*, Derek S. Frank*[3]*, Luke Schenck*[3]*, Anthony La Buda*[2]*, Adam J. Matzger*[2,1]*. (1) Macromolecular Science and Engineering, University of Michigan, Ann Arbor, Michigan, United States(2) Chemistry, University of Michigan, Ann Arbor, Michigan, United States(3) Particle Engineering Lab, Process Research & Development, Merck & Co Inc, Rahway, New Jersey, United States*

Poor solubility limits oral bioavailability for many pharmaceuticals. Crystalline drugs with low solubility have the potential to benefit from delivery in the amorphous form; however, poor physical stability of amorphous forms is a persistent problem. Amorphous solid dispersions (ASDs), in which polymeric excipients are mixed with an active pharmaceutical ingredient (API) to inhibit crystallization, overcome this problem though the number of FDA-approved polymeric excipients is low. In this work, crosslinked polyethylenimine (cPEI) is investigated for delivery of an acidic biopharmaceutical classification system (BCS) class II drug; cPEI was chosen for its potential for high API loading due to the abundance of basic nitrogen functionality. Amine group capping is employed to increase hydrophobicity of the crosslinked materials. In order to develop PEI, commonly used for gene delivery, as a drug delivery vehicle, this work shows novel cPEI design and optimization, ASD formation with a BCS class II drug, the identity of the drug species at different drug loadings, improved dissolution rate and solubility relative to crystalline drug, and promising physical stability data. The development of strong intermolecular interactions between the drug and polymer are expected to lead to physically stable dispersions. These findings motivate the broadening of polymer classes employed in ASD formation to allow tunability for drug acidity and enable loadings not readily achieved with existing polymers.



133. Michigan drug discovery: Partnering a portfolio of projects

***Peter L. Toogood**, toogood@umich.edu. Michigan Drug Discovery, University of Michigan, Ann Arbor, Michigan, United States*

Michigan Drug Discovery is a campus-spanning program to foster, enhance and support drug discovery projects at the University of Michigan (U-M). In this presentation, I will describe how Michigan Drug Discovery works to provide opportunities and guidance for faculty and trainees. I will briefly introduce the capabilities of our research core facilities that contribute much of key expertise and training for advancing our projects, and I will describe how these facilities can be accessed by researchers outside of U-M. Finally, I will provide examples of projects that illustrate U-M's rich drug discovery environment.

134. Design, synthesis, and biological evaluation of PF543 analogs as two pore channel blockers

***Ali Hamzah**[1], Ali.Hamzah@rockets.utoledo.edu, Giselle A. Soares[1], Timothy F. Walseth[2], Katherine A. Wall[1], James T. Slama[1]. (1) Department of Medicinal and Biological Chemistry, The University of Toledo, Toledo, Ohio, United States(2) Department of Pharmacology, University of Minnesota Twin Cities, Minneapolis, Minnesota, United States*

Two-pore channels (TPCs) are Ca^{2+}-permeable endolysosomal ion channels responsible for calcium release from acidic stores in response to activation by the second messenger nicotinic acid adenine dinucleotide phosphate (NAADP). Recently, TPCs have emerged as a promising drug target in severe human diseases such as viral translocation, bacterial infections, and cancers. Recently published work in (Cell Calcium **75** (2018) 42-52) identified the sphingosine kinase inhibitor PF-543 as a TPC blocker that abolished NAADP-mediated Ca^{2+} release in sea urchin egg homogenates and cultured human cells. In the hope of increasing the potency and specificity of PF-543 as a TPC blocker, we synthesized 95 analogs of PF-543 introducing different chemical moieties in their structure. We used sea urchin egg homogenates to evaluate the potency of the TPC blocker and subsequent DO-11-10 cells to validate the inhibition of NAADP-evoked Ca^{2+} release. PF-543 contains three aromatic rings and a hydroxymethyl pyrrolidine linked together using a sulfoxide methylene linker and oxymethylene

linker. We explored the effects of introducing different substituents in each ring. Sulfoxide phenyl is essential for TPCs antagonist activity. Hydroxymethyl pyrrolidine substitution with imidazole increased the activity of the PF-543 analogs along with the presence of central methyl and para hydrogen, methyl, and methoxy substitution on the phenyl sulfoxide ring. Sulfoxide spacer linker replacement with methylene, alkyne, or amide linkage will decrease the TPCs blocking activity significantly.

135. Structure-based drug design of novel therapeutics against an inflammatory cytokine

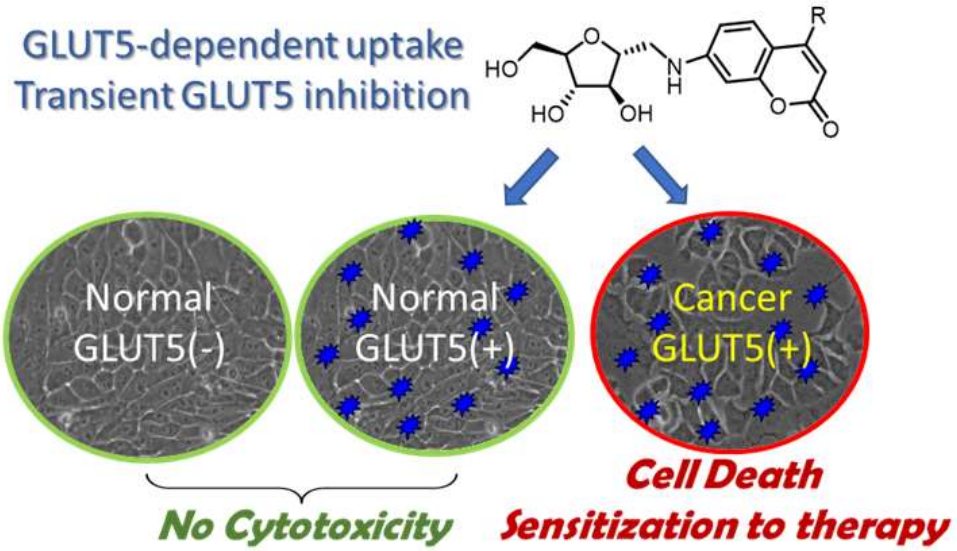
***Don L. Warner**, dwarner@boisestate.edu. Chemistry and Biochemistry, Boise State University, Boise, Idaho, United States*

An IL-6 family inflammatory cytokine (IC) has been implicated in a number of notable diseases, most notably it is associated with decreased survival in breast cancer patients. The IC stimulates metastasis by promoting survival, proliferation, angiogenesis, and an epithelial to mesenchymal transition in cancer cells. As such, the IC is an attractive therapeutic target. We recently reported a first-in-class small molecule inhibitor of the IC that displayed low micromolar binding affinity. This presentation will describe our efforts to characterize the binding of the small molecule to the cytokine using computational docking experiments, fluorescence quenching assays, and nuclear magnetic resonance chemical shift perturbation experiments in order to inform structural optimization. Our synthetic efforts, cell culture inhibitory activity assays, and preliminary in vivo experiments to evaluate activity in living systems will also be presented.

136. Revealing weak sports in cancer viability through GLUT-targeting molecular probes

***Marina Tanasova**, mtanasov@mtu.edu. Chemistry, Michigan Technological University, Houghton, Michigan, United States*

Enhanced sugar uptake and metabolism have long been identified as a hallmark of cancer, providing a basis for new strategies to target and impact cancer cells. The identified links between the expression of fructose-specific transporter GLUT5 and cancer development and progression prompted exploring inhibition of GLUT5 activity to affect GLUT5 and fructose-dependent cancer cells. Here, using fluorescently labeled fructose mimetics as high-affinity GLUT5-specific uptake probes, we demonstrate a proof of concept for achieving cancer-selective cytotoxicity through competitive inhibition of GLUT5 activity. GLUT5-specific activity probes (ManCous) induce cytotoxicity in breast cancer cells. At the same conditions, no cytotoxicity is observed in normal cells regardless of GLUT5 levels. The cytotoxic effects arise from probe-induced oxidative stress in response to diminishing GLUT5 activity. The outcomes reveal the intriguing difference in cytotoxicity-related mechanisms between the early-stage MCF7 cells and triple-negative MDA-MB-231 cells, with the latter exhibiting higher levels of cell death due to probe-induced senescence. The reported findings present a targeted approach to impact breast cancer cells through competitive inhibition of GLUT5 and lay the foundation for targeted cancer cell sensitization towards establishing more effective regiments for triple-negative cancers.



137. Dynamics and energetics of the transport cycle for small multidrug resistance transporters

Daipayan Sarkar[1]*, sarkarda@msu.edu, Jessica L. Egleston*[2]*, Josh V. Vermaas*[1,2]*. (1) DOE Plant Research Laboratory, Michigan State University, East Lansing, Michigan, United States(2) Michigan State University Department of Biochemistry and Molecular Biology, East Lansing, Michigan, United States*

Antibiotics have significantly improved human health around the globe. However, evolution has increased antibiotic resistance among bacteria, creating a critical public health concern. Thus, it is important to understand antibiotic resistance mechanisms bacteria. Members of the small multidrug resistance (SMR) protein family confer resistance to antibiotics by leveraging an established proton gradient. SMR proteins are small homodimers and are broadly classfied into Qac and Gdx sub-families based on selective substrate transport across the membrane. Using molecular dynamics (MD) simulations in explicit lipid and solvent environment, we compare members of the two subfamilies to evaluate the similarities and differences at the molecular scale. Starting from recent crystallographic and NMR structures, we compare EmrE against Gdx-Clo from the Qac and Gdx sub-families respectively. Earlier work on EmrE revealed the presence of an electrostatic lock based on the protonation of glutamate residue (E14), while Gdx-Clo has a similar protonation site one residue earlier (E13). To evaluate the impact for glutamate protonation, 40 microseconds (μs) aggregated simulation time was compared depending on the four possible protonation states for both EmrE and Gdx-Clo. The simulations suggest a similar mechanism for coupling protonation to conformational change, relying on a hydrogen bond between glutamate and a nearby tyrosine to regulate the transport cycle. However, root-mean square deviation analysis suggests Gdx-Clo has lower root-mean square deviation compared to EmrE for all different protonation states by approximately 2 Å. We also find that even in the absence of substrate, the number of water molecules within the lumen is greater for EmrE than it is for Gdx-Clo. Combing results from all-atom molecular simulations and estimating relative binding free energy using alchemical perturbation, we provide a plausible explanation towards substrate selectivity between these two protein macromolecules belonging to the SMR family. The larger EmrE lumen is allows large cationic substrates such as tetraphenylphosphonium, while Gdx-Clo favors smaller cations such as guanidinium. These results help understand the selective substrate transport in SMR family of transporters.

138. Chemistry challenges in the automotive industry: OEM perspective

***Mark Nichols**, mnichols@ford.com. Ford Motor Company, Dearborn, Michigan, United States*

Many of the most difficult challenges facing the automotive industry are fundamentally chemistry related. Some of the challenges are new, such as the urgent need to improve electric vehicle (EV) range, charging speed, cost, and safety. Other challenges are receding. The long-standing need for a better understanding of combustion and abatement chemistry, and the resultant effects on atmospheric chemistry are less important as internal combustion engines (ICE) are de-emphasized. Ongoing challenges remain in the realm of materials chemistry for improved appearance, durability, sustainability, and performance. This talk will explore some of these challenges and hopefully provide some inspiration for new solutions and avenues of research to address the automotive industry's needs.

139. Developing structural natural fiber parts using Spray Transfer Molding (STM) process for automotive applications

***Elias Shakour**, elias.shakour@basf.com. Performance Materials, BASF Corp, Florham, New Jersey, United States*

This development will emphasize in utilizing new process technology named Spray Transfer Molding (STM) where the fabric is impregnated locally outside the mold using high pressure spray process then molding it in a compression press.

The process works as follows, a blank of dry fiber is held by a programed robot that has an optimized and controlled spray pattern, once sprayed using a high-pressure nozzle head that atomized the spray polyurethane, the robot will lay down the impregnated blank into the tool to be fully molded and cured. The cycle time from part to part for such a process will be completed in 90 seconds.

In this study technology will be using a state-of-the-art several natural fiber random fabric matts , such as hemp, jute, flax, banana and hybrid mix that will be laid on top and bottom of honeycomb to make a honeycomb sandwich part.

The study will show the performance of gibers and how can they be a good replacement to glass fiber due to its high mechanical performance that can be equal if not more than the Glass fiber.

Finally, a simulation of seatback part will be presented with its mechanical performance for interior applications.

140. Sustainable solutions for automotive OEM coatings

***Karel Hartlieb**, karel.hartlieb@gmail.com. BASF Corp, Southfield, Michigan, United States*

Automotive OEMs have created ambitious manufacturing sustainability goals for the next 25 years, with many aiming for carbon neutrality by 2050. Up to 70% of the energy in an OEM assembly plant is consumed in the paint shop, therefore, achieving these sustainability goals will require innovations in both paint formulation and application technologies. This presentation will cover the evolution of paint chemistry, formulating and application, the key drivers of this being the introduction of the Clean Air Act in 1970, which established Volatile Organic Compound (VOC) emission standards, as well as the need to maintain paint quality and achieving the appearance and durability demands of customers. Some of the important developments in paint chemistry include the transition from low solids to high solids formulations and from solventborne to waterborne technologies. Innovations to the technology

surrounding the application of paint to vehicles are another way in which sustainability continues to be improved, some examples of which include moving from hand-spray to high-transfer efficiency electrostatic application, reducing the number of baking steps required for each layer in the coating system, and recent developments in overspray free application.

141. Modeling solid electrolyte interphase formation and growth in Li-ion batteries using reactive molecular dynamics simulations

***Avinesh Ojha**, aojha@ford.com. Ford Motor Company, Dearborn, Michigan, United States*

Formation is the most time-consuming and expensive step in battery manufacturing process. Understanding solid electrolyte interphase (SEI) formation is therefore critically important for designing high performance Li-ion batteries, and to reduce the overall material and energy cost. However, the details of how SEI builds up into a nanometer-thick layer from molecular level reactions on anode are still unclear. In the current work, we propose to develop and apply reactive molecular dynamics simulations and density functional theory calculations to track the evolution of SEI composition and to obtain key kinetic parameters governing SEI formation and growth. These parameters serve as inputs to an integrated atomistic-mesoscale model for SEI-growth at experimental relevant time & length scales. Such an approach could accelerate the discovery of new low-cost battery chemistries with reduced formation time.

142. Understanding PFAS toxicity through computational approaches

***Semiha Kevser Bali**, balisem1@msu.edu, Nuno Almeida, Deepak James, Cong Wang, Rebecca Martin, Kyleen Hall, Arohi Nair, Angela K. Wilson. Michigan State University College of Natural Science, East Lansing, Michigan, United States*

Per- and poly-fluoroalkyl substances (PFAS) are environmental pollutants that are garnering significant attention due to their harmful effects on both humans and the environment. Although PFASs have been utilized in a wide variety of industrial processes due to their water and oil-repellent properties, it is now known that exposure to PFASs is linked to disruption of fatty acid and insulin metabolism, changes in thyroid hormone levels, and a higher occurrence of certain types of cancers. This broad range of impacts of PFASs on human health necessitates a more detailed understanding of the mechanisms associated with these species. Computational methodologies have proven to be essential approaches in uncovering the molecular mechanisms and the atomistic-level insight into the toxic effects of PFAS. By investigating the specific proteins associated with PFASs, better strategies for mitigating the toxicities can be developed.

143. From the astatine's quantum chemistry to the development of new heavy-element computational infrastructure

***Alexander Rusakov**, rusakov@oakland.edu. Chemistry, Oakland University College of Arts and Sciences, Rochester, Michigan, United States*

Besides tennessine, astatine is the least-studied element in the halogen group. On the fundamental level, its elusive chemistry limits our understanding of periodic trends at the periodic table's bottom. In practical applications, it impedes the successful design of At-211-based radiopharmaceuticals. Significant experimental complications of working with astatine make quantitative quantum-chemical modeling indispensable on both levels. Suitable computational approaches require the simultaneous treatment of electronic correlations and the effects of relativity, including massive spin-orbit interaction. Quantitative "gold-standard" relativistic coupled-cluster calculations are tremendously demanding already for diatomic

species, such as At_2 or AtO^+. Cheaper relativistic DFT simulations suffer from unpredictable behavior of available exchange-correlation functionals developed primarily for light-element chemistry. Furthermore, the shortcomings of relativistic DFT tend to conflate with those of commonly used basis sets, making the sources of error untraceable. Using astatine chemistry as a case in point, we suggest feasible computational approaches to the quantitative modeling of heavy elements and superheavy elements' chemistry and outline recent development of basis sets, exchange-correlation functionals, and force fields for heavy elements using machine learning approaches.

144. Computational insights to sulfate sensing in mNeonGreen via flexible loop engineering

Vishaka Pathiranage[1], *hh5639@wayne.edu, Ke Ji*[2], *Whitney S. Ong*[2], *Sheel Dodani*[2], *Alice Walker*[1]. *(1) Department of Chemistry, Wayne State University, Detroit, Michigan, United States(2) Department of Chemistry and Biochemistry, The University of Texas at Dallas, Richardson, Texas, United States*

Fluorescent proteins are well known for their excellent ability to act as biosensors which helps to investigate biochemistry of living cells and organisms. mNeonGreen(mNG) is one of the brightest green fluorescent proteins which has been identified as a turn on fluorescent protein sensor for chloride with a resolved x-ray crystallographic data for bound chloride. However, experimental data has shown that mNG shows a turn off response for sulphate at physiological pH. Our main goal was to envision the mechanisms involved and how mutations on flexible loops located close to the chromophore could help to further engineer this biosensor. We applied constant pH molecular dynamic simulations and ran production for wild type, two single mutated systems and a double mutated system (2G) at pH 7. Through simulations we were able to observe a random diffusion of sulphate ion into the beta barrel of mNG where the location and orientation of entry residues acted as the limiting factor for the entry of ions. Specially the gating motion shown by W138 had a major effect on the entry of sulphate ions into the beta barrel. Among the mutated systems 2G has the best experimental results and computational studies shows that 2G has the highest opening of the entry point when sulphate is unbound and once bound the inner binding pocket rearranges accordingly locking the sulphate in place. Further root mean square deviation also decreases substantially once sulphate is bound to 2G making the system more stable. Upon binding of sulphate, a change in the chromophore conformation was also observed in all the systems. As a summary we were able to identify likely binding pathway for sulphate for mNG and found a consisting binding site for all the systems. Also, we were able to determine key binding residues which were consistent with the mutated systems and the atomic level details for these mutations. Future studies involve identifying the effect on the biosensor by mutating basic residues located near entry points and to carry out quantum mechanical studies to help explain the quenching mechanism.

145. Computational insights into *minima remodeling* using myoglobin in organic solvents for pharmaceutical applications

Hannah Palomino[1], *hlpalo@umich.edu, Sophia Liu*[1], *Mark A. Hix*[2], *Alice Walker*[2], *Nicolai Lehnert*[1]. *(1) University of Michigan Department of Chemistry, Ann Arbor, Michigan, United States(2) Wayne State University Department of Chemistry, Detroit, Michigan, United States*

The pharmaceutical industry demands high stereoselectivity in drug synthesis, which traditional chemical catalysts struggle to achieve. Enzymes offer an elegant solution, naturally achieving stereo-purity without protection or purification steps. Myoglobin has been engineered

as a biocatalyst to perform challenging transformations with high selectivity in aqueous media, but its industrial application is limited by stability, cost, and ultimately organic solvent incompatibility. We have developed a novel method called *minima remodeling* which we use to engineer myoglobin for efficient -NH insertion, cyclopropanation and epoxidation transformations in various anhydrous organic solvents, yielding unparalleled reactivity, selectivity, stability, and reusability. We have used molecular dynamics to help elucidate the structural changes in the minima remodeling preparation of myoglobin and reaction conditions in order to aid in reactivity optimization. This advancement in protein engineering offers a significant step forward in biocatalyst design and industrial capabilities for stereoselective pharmaceutical synthesis and discovery.

146. Potential energy curves and the singlet-triplet gap of cyclobutadiene: CIPSI-driven CC(*P*;*Q*) study

Swati Snigdha Priyadarsini[1]*, priyada2@msu.edu, Karthik Gururangan*[1]*, Jun Shen*[1]*, Piotr Piecuch*[1,2]*. (1) Chemistry, Michigan State University, East Lansing, Michigan, United States(2) Physics and Astronomy, Michigan State University, East Lansing, Michigan, United States*

Obtaining the correct value of the singlet-triplet gap in cyclobutadiene remains a challenging test for modern high-level *ab initio* methods in quantum chemistry because one has to balance the nondynamical correlation effects needed for an accurate description of the low-spin singlet state, which is a multi-configurational mixture between two quasi-degenerate closed-shell determinants, with the dynamical correlations of the high-spin triplet state, which has a predominantly single-reference character. It has been shown that high-level coupled-cluster (CC) approaches, specifically, the CC method with full treatment of singles, doubles, and triples (CCSDT), provides an accurate description of the singlet-triplet gap in cyclobutadiene, however, the routine application of this method is hindered by its high computational cost. Therefore, our group has recently developed a practical alternative to converging the high-level CCSDT energetics at a fraction of the computational cost in a black-box manner by merging the CC(*P*;*Q*) moment expansion formalism with selected configuration interaction (CI). By tailoring the expansion of the cluster operator using information extracted from the compact selected CI wave functions computed by the approach abbreviated as CIPSI, and subsequently correcting for the missing many-electron correlation effects of interest using the non-iterative and non-perturbative moment expansions, we show that one can recover the CCSDT energetics for the lowest-lying singlet and triplet states of cyclobutadiene along the automerization coordinate, as well as the gap between them, using a minuscule fraction of triply excited cluster amplitudes.

147. Advances in time-dependent spin-orbit configuration interaction: Spin-flip and pulse optimization

Ben Peyton*, bgpeyton@gmail.com, Angela K. Wilson. Chemistry, Michigan State University, East Lansing, Michigan, United States*

Real-time electronic structure methods describe the direct response of a quantum mechanical system to a time-dependent perturbation without the usual constraints of time-dependent pertur- bation theory (i.e. response theory). Such approaches enable the investigation of strong-field dynamics and ultrafast spectroscopy directly in the time domain. Time-dependent configuration interaction algorithms in particular can be readily modified to include heuristic ionization models, spin-orbit coupling, and multiconfigurational reference wave functions. Relativistic effects in small molecules, such as spin-flip processes relevant to spin-trapping and metal-ligand charge transfer, are probed using these methods.

148. How the analysis of publication practices during the Coronavirus pandemic informs teaching the information literacy in chemistry

***Yulia Sevryugina**, yulias@umich.edu. University of Michigan, Ann Arbor, Michigan, United States*

Choosing where to publish and understanding the different options for publishing can be confusing. In teaching information literacy in Chemistry, an author regularly conducts workshops on navigating the publishing landscape in chemical and biomedical fields. Among the topics discussed are different types of publishing venues, pros and cons of open access avenues, and tips for things to look for when selecting an appropriate journal for publishing research. Data science analysis of publication practices provides evidence-based support for describing trends and providing recommendations to next generation of young scientists. Specifically, this data science research project used peer-reviewed journal and review articles indexed in PubMed and their associated preprints posted on bioRxiv and medRxiv servers in regard to the SARS-CoV-2 research. The author will show how the analysis of publication practices during the coronavirus pandemic informs the information literacy curriculum and aids students in developing knowledge and skills necessary for presenting and communicating their research.

149. Active learning in the general chemistry lab using the 5E Instructional Model

***Julius Nagy**, julius.c.nagy@gmail.com. Chemistry, Siena Heights University, Adrian, Michigan, United States*

General chemistry labs used to be done by handing students a printed handout and, after some instruction as to methods, watching and guiding the students through the instructions until they turned in a data sheet or brief lab report. Active learning requires hands-on activities that are built on the previous experiences of the students, followed by the sharing of new knowledge. The 5E Instructional Model was used to design an experiment that led to the burning of magnesium into magnesium oxide after exploration of fire fundamentals, the observation of burning candles, and an internet search of burning metal. Student learning via this process far surpassed the learning obtained from the traditional hand out-driven method of doing the lab.

150. Can the organic chemistry laboratory be green ?

***Mengqi Zhang**[1], zhan1962@msu.edu, Elizabeth L. Day[2], Steven Petritis[1], Hunter Mcfall-Boegeman[3], Melanie Cooper[1]. (1) Chemistry, Michigan State University, East Lansing, Michigan, United States(2) Department of Chemistry & Biochemistry, University of Texas at El Paso University Research Institute, El Paso, Texas, United States(3) Division of Science and Mathematics, University of Minnesota Morris, Morris, Minnesota, United States*

The large-enrollment undergraduate introductory organic chemistry laboratory course at Michigan State University has been redesigned to emphasize green and sustainable chemistry and to incorporate evidence-based instructional approaches. Principles of green and sustainable chemistry are introduced in the lab projects and case studies, where students investigate a variety of approaches and discuss the relative merits of different approaches from a range of perspectives including efficiency, environmental impact, and cost. This presentation will focus on the design and implementation of the new curriculum from an instructor's perspective.

151. Framing our teaching: Exploring graduate teaching assistants' enactment of a collaborative activity in an organic chemistry laboratory

***Daisy Haas**, dahaas@umich.edu, Ina Zaimi, Ginger V. Szymczak Shultz. Chemistry, University of Michigan, Ann Arbor, Michigan, United States*

Graduate teaching assistants (GTAs) hold a unique positionality as a near-peer instructor to students, research mentee to faculty members, and an employee to the institution. With limited pedagogical training and resources, the enactment of planned teaching activities and resources may be influenced by how GTAs conceptualize their teacher identity, role, and experiences. In this study, we explore how organic chemistry GTAs enact a collaborative active learning activity in a second-semester organic chemistry laboratory course. Through the lens of the Teacher Noticing framework, we conducted a case-study analysis of two GTAs which consisted of a pre-class interview, an in-class audio and visual observation, and a post-class retrospective interview featuring observation audio and visual data. We aim to qualitatively capture how GTAs' teacher beliefs, knowledge, and perceived role in the classroom influence the enactment of instructional materials and activities. Because chemistry GTAs serve as instructional facilitators in many undergraduate educational settings, understanding unique GTA framing may support both GTA and undergraduate learning experiences. Furthermore, our study will have implications for researchers who design organic chemistry learning resources to consider different ways GTAs may support student learning.

152. Is scientific reproducibility a fallacy, a misunderstanding or sign of poorly designed experiments?

***Andrew L. Ekstrom**, aekstrom@umich.edu. Oakland University, Rochester, Michigan, United States*

A past survey by Nature, asked readers if they ever had trouble reproducing results they found in a journal or results from their own experiments. Most of the respodents claimed they had issues doing both. In this talk, we will discuss methods for improving the reproducibility of experiments and look at better methods for determing if we should trust journal results.

153. Exploring how graduate teaching assistants enacted an active-, cooperative-learning activity in a second-semester organic chemistry course

***Ina Zaimi**, zaimina@umich.edu, Daisy Haas, Ginger V. Szymczak Shultz. Chemistry, University of Michigan, Ann Arbor, Michigan, United States*

Prior research has established that organic chemistry students' reasoning needs to be supported, and subsequent research has implemented and recommended activities. However, how instructors enact these activities is underexplored. We explore how graduate teaching assistants (GTAs) enacted an active-, cooperative-learning activity in a second-semester organic chemistry laboratory course. Our study is guided by the conceptual framework of teacher noticing. Teacher noticing – an instructor observing instructional moments and connecting their observations to theory and practice – is a part of developing instructional responses rooted in students' reasoning. Pairing this framework with a case study methodology, we recruited two GTAs, and we conducted a pre-interview, two observations, and a post-interview. We analyzed GTAs' teacher noticing – what they observed and interpreted as well as how they responded. We found that GTAs not only observed students' questions but also created instructional moments (e.g., asking a series of probing questions) that elicited them. Furthermore, we found that students' questions shaped GTAs' interpretations and instructional responses. These findings reveal the importance of instructors

asking students questions, instead of waiting for students to ask them questions, in facilitating students' reasoning.

154. Characterizing resources students use to understand chemical equilibrium via mathematical thinking and mechanistic reasoning

***Veeda Scammahorn**, scammaho@msu.edu, Melanie Cooper. Chemistry, Michigan State University, East Lansing, Michigan, United States*

It has been shown that the study of chemical equilibrium is fraught with difficulties for students. Much of the earlier work in this area focused on the identification of misconceptions about equilibrium concepts. For example, the idea that a reaction stops when it is at equilibrium, or that the reaction has equal concentrations of products and reactants at equilibrium have all been noted. However, more recent work often applies a different lens to student understanding where student ideas take the form of conceptual and epistemic resources. Using this approach, the role of the instructor is not to focus on "overcoming misconceptions", but rather to support students as they weave together productive resources to produce coherent understanding. The focus of this work is to elicit and understand the resources that students use to think about chemical equilibrium phenomena.

155. OrganicERs: Active learning workshops to build a community of practice for organic chemistry instructors

***Alexey Leontyev**, alexey.leontyev@ndsu.edu. North Dakota State University, Fargo, North Dakota, United States*

This project aims to increase faculty awareness of evidence-based instructional practices through Active Learning in Organic Chemistry workshops, assisting faculty with implementation, expanding the community of practice, and fostering the development of educational resources. The project team and workshop participants are generating active learning materials and posting them on the Organic Education Resources website (https://www.organicers.org/), so they can be used by anyone, including organic chemistry instructors. To keep momentum after the workshops, online Faculty Learning Communities (FLCs) will be implemented. We used Roger's Diffusion of Innovation Theory and the Theory of Planned Behavior to investigate projects' effectiveness.

156. Design of transition metal phosphide nanoparticles for energy conversion: Electrocatalytic water splitting

***Stephanie L. Brock**, sbrock@chem.wayne.edu. Chemistry, Wayne State University, Detroit, Michigan, United States*

Renewable energy resources, such as solar energy and wind, suffer from intermittency; i.e., electricity is not generated at night or when the wind is not blowing, and more electricity is generated at times when demand does not keep up. One mechanism to address this challenge (either on the grid, or off) is to store excess electrical energy in a battery, or by converting it to a fuel that can generate electricity on-demand when needed (via fuel cell). Transition metal phosphides have been shown to be excellent electrocatalysts for the electrolysis of water to produce hydrogen as a fuel. However, the functionality of the phosphide is sensitively dependent on composition, structure and particle size. In order to better understand the roles of structure, electronics, and surface chemistry on catalytic activity and stability, synthetic methods that enable composition, structure, and size to be targeted, and that yield low-polydispersity samples, are needed. In this presentation, the synthesis of bimetallic phosphide

nanoparticles will be described and their composition-dependent activity for electrocatalytic water splitting presented. The role of structure, site occupancy, and electronic considerations on functionality will be discussed in the context of designing more active and stable electrocatalysts for fuel generation.

157. Additive carbon dots nanocrystals for enhancement of the efficiency of dye-sensitized solar cells in energy applications technology

***Getachew Kumak. Watiro**, getachewkuma2020@gmail.com. Institute of Applied science and Technology, National Taiwan University of Science and Technology, Taipei, Taipei city, Taiwan*

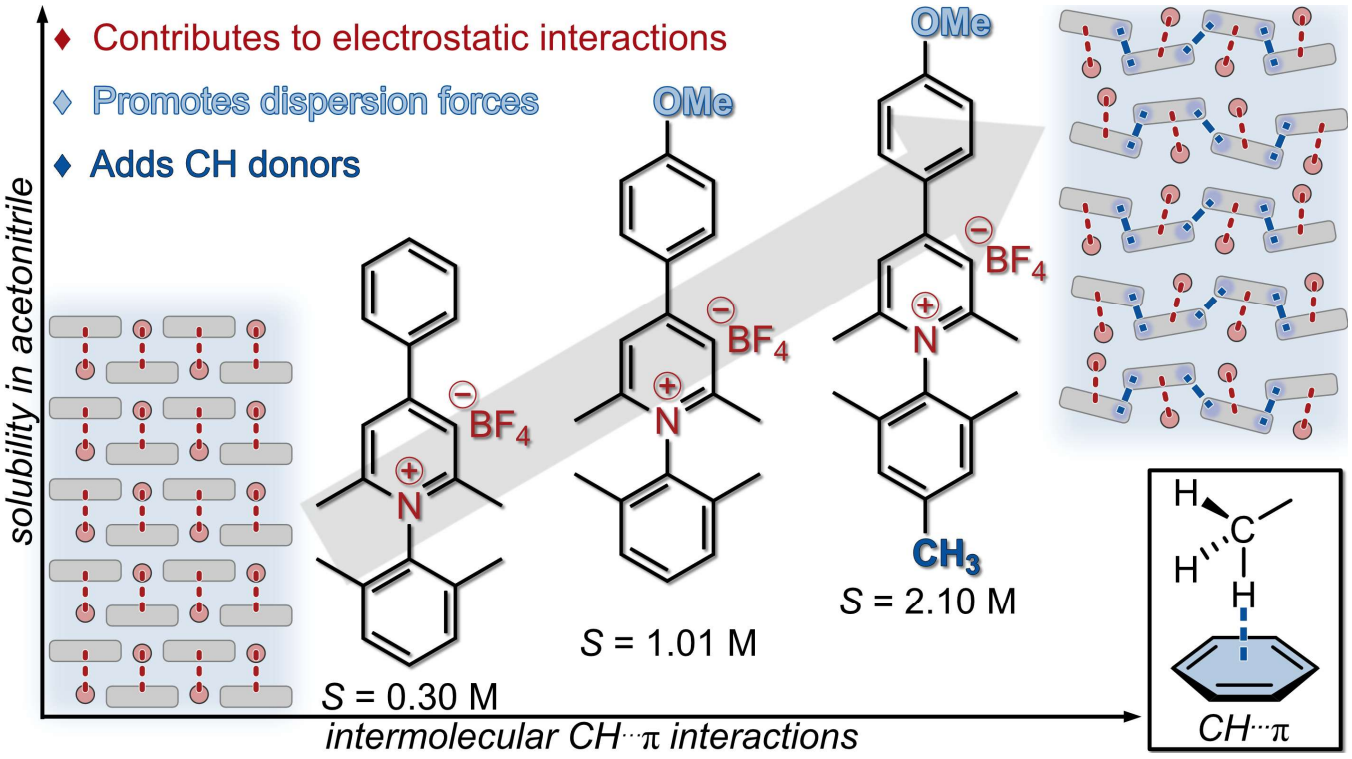
The need for solar energy is constantly increasing and it is widely available on the earth's surface. Photovoltaic technology is one of the most capable of all viable energy technologies, a promising approach to the control era as it is readily available, and has zero carbon emissions. Furthermore, inexpensive and versatile solar cells have achieved the conversion efficiency and long lifetime of dye-sensitized solar cells, improving the conversion efficiency from the sun to electricity. DSSCs have received a lot of attention for Various potential commercial uses such as mobile devices and portable electronic devices, as well as integrated solar cell modules. The systematic reviews were used to show the critical impact of additive C-dots in the Dye Sensitized solar cell for energy application technology. This research focuses on the following methods to synthesize nanoparticles such as a polyol, calcination, and hydrothermal technique. In addition to these, additives C-dots by the Hydrothermal method. This study deals with the progressive development of DSSC in photovoltaic technology. The photoconversion efficiency of. The applications of single and heterojunction devices were used (ZnO, NiO, and NiO/ZnO/N719), and employing C-dots additives on ZnO, and NiO (ZnO/C-dots /N719, NiO/C-dots/N719, and ZnO/NiO/C-dots/N719) and its effects were reviewed. More than all, the technology of DSSC with C-dots enhances efficiency. Finally, recommendations have been made for future research on the application of DSSC with the use of this additive.

158. Solubility trends in pyridinium salts for non-aqueous organic redox flow batteries

***Sharmila Samaroo**[1], samaroos@msu.edu, Charley Hengesbach[1], Chase Bruggeman[1], Nunzio G. Carducci[1], Lincoln Mtemeri[1], Richard J. Staples[2], Thomas F. Guarr[1], David P. Hickey[1]. (1) Chemical Engineering and Material Science, Michigan State University, East Lansing, Michigan, United States(2) Chemistry, Michigan State University, East Lansing, Michigan, United States*

Redox flow batteries (RFBs) are a grid-scale energy storage technology designed to promote the implementation of renewable energy sources, such as wind and solar. They convert electrical energy to chemical energy using a solution of charged redox active molecules (ROMs). For energy storage applications, desirable ROMs undergo charge-discharge cycling at high and low potentials, with minimal chemical decomposition, and are highly soluble. Notably, high solubility is a critical physicochemical property because ROM concentration is directly proportional to volumetric energy density. RFBs with high energy densities can deliver equivalent energy capacities with a reduced land footprint. Pyridiniums have been identified as a class of ROMS that demonstrate high persistence at multiple charge states while exhibiting exceptionally low redox potentials. However, relationships between structural variation and pyridinium solubility have not been explored, and practical molecular design techniques to improve ROM solubility are extremely limited. Herein, we establish a pyridinium synthesis, evaluate solubility, investigate computational and experimental solubility parameters, and establish a linear correlation between CH-pi interactions and pyridinium solubility. The

established pyridinium library enabled probing of distinct relationships between molecular structure and solubility. CH-pi interactions, discrete interactions between a H (of a C-H bond) and the pi-system (of an aromatic ring) were identified in pyridinium crystal structures. The number of these CH-pi interactions resulted in a direct, linear correlation with pyridinium solubility (R^2 = 0.93). This work highlights how weak dispersion forces (CH-pi interactions) can disrupt strong electrostatic intermolecular interactions and result in dramatically different solvation behavior between structurally similar pyridinium derivatives.



The trend identified in this work highlights how weak dispersion forces (CH-pi interactions) can disrupt strong electrostatic intermolecular interactions and result in dramatically different solvation behavior between structurally similar pyridinium derivatives.

159. Fundamental insights to the motional narrowing of organic exciton polaritons

Sachithra T. Wanasinghe, *gw7915@wayne.edu, Aaron Rury. Chemistry, Wayne State University, Detroit, Michigan, United States*

Enhancing the spatial coherence between molecular exciton constituents is crucial for the next generation optical and optoelectronic devices for energy technologies. However, ultra-short lifetimes due to significant energetic disorder and strong interactions between electronic excitations reduces the coherence of these systems and their real-world applicability. On the other hand, photons weakly interact with each other and with their environment. We are trying to understand how polariton (hybrid light-matter states) formation from these molecular materials suppresses exciton disorder and enhances the coherence. Polaritons form when one embeds light-absorbing molecules in a Fabry-Perot (FP) cavity tuned to the molecular exciton energy. Under the strong coupling between the cavity photon and the molecular excitons, one creates new eigenstates called lower polariton (LP) and upper polariton (UP). Porphyrins are a class of organic molecules used in natural and artificial photosynthetic systems. High transition dipole moment values make these molecules ideal for polariton formation. We fabricated a few cavity polariton samples using the weakly coupled porphyrin dimer 4,4'-bis[zinc(II)-5,10,15-

pentaflorophenyl-20-porphinyl]diphenylocetylene ($F_{30}Zn_2U$). We carried out angular-dependent transmission measurements for the fabricated samples and fit the spectra to asymmetric Lorentzian functions to obtain full-width half maximum (FWHM) of the LP peak. The FWHM of the LP peak is inversely proportional to the lifetime of this state. In this study, we observed the width of the LP was suppressed near the exciton-photon resonance condition. We expect the suppression of FWHM of LP is due to the reduction of exciton disorder, in other words the motional narrowing effect. Furthermore, we observed that increasing the concentration of molecules inside the FP cavity further suppress the exciton disorder of $F_{30}Zn_2U$ molecules. We modeled the narrowing of the LP branch of polariton samples using the simple model described in the Whittaker et al 1996. Our results demonstrate how researchers can design coherence into hybrid molecular material systems using polariton formation to improve their suitability for next-generation energy technologies.

160. 1-(2-Ethoxyphenyl)-3-phenyl-1,4-dihydrobenzo[e][1,2,4]triazin-4-yl as a spin source in organic spintronic devices

***Christos P. Constantinides**, cconst@umich.edu. Natural Sciences, University of Michigan - Dearborn, Dearborn, Michigan, United States*

Organic radicals have long been suggested as candidates for organic magnets and components in organic spintronic devices. Herein, we demonstrate a novel spin current emission from an organic radical film via spin pumping at room temperature. We present, the synthesis and the thin film preparation of 1-(2-ethoxyphenyl)-3-phenyl-1,4-dihydrobenzo[e][1,2,4]triazin-4-yl, a Blatter-type radical with outstanding stability and low roughness. These features enable the fabrication of a radical/ferromagnet bilayer in which the spin current emission from the organic radical layer can be reversibly reduced when the ferromagnetic film is brought into simultaneous resonance with the radical. The results provide an experimental demonstration of a metal-free organic radical layer operating as a spin source, opening a new avenue for the development of purely organic spintronic devices and bridging the gap between potential and real applications.

161. Towards molecular alloys: Computational and experimental studies on *p*-NCC_6F_4CNEEN (E = S/Se)

***Asli Wehelie**[1], weheliea@uwindsor.ca, Lara Watanabe[1], Bin Zhang[2], Sahar Nikoo[1]. (1) Chemistry&Biochemistry, University of Windsor Faculty of Science, Windsor, Ontario, Canada(2) Zhengzhou University, Zhengzhou, Henan, China*

The *β*-phase of the dithiadiazolyl (DTDA) radical, *β*-*p*-NCC_6F_4CNSSN (**1β**) is known to exhibit long range magnetic order below 36 K at ambient pressure.[1] In contrast, the corresponding diselenadiazolyl (DSDA) radical *p*-$NCC_6F_4CNSeSeN$ (**2**) has been reported to form a dimer, $(\mathbf{2})_2$, in which spin-pairing occurs quenching the paramagnetism.[2] The present study describes theoretical studies on **2** which reveal it exhibits a similar shape, size and charge distribution to **1**, suggesting it may be possible to incorporate **2** into the host lattice of **1β**. In addition, incorporation of **2** into **1β** is computed to enhance magnetic communication between DTDA and DSDA radicals in relation to pure **1β** which should favour an enhancement in the magnetic ordering temperature. Approaches to experimentally incorporate **2** into the framework of **1β** at dopant levels < 10% are explored through cocrystallization from solution and cosublimation *in vacuo*.

162. Synthesis, characterization, and reactivity of paramagnetic (PNNP)Co complexes

***Justin Miller**, miller.8533@osu.edu, Christine M. Thomas. Chemistry and Biochemistry, The Ohio State University, Columbus, Ohio, United States*

Square planar cobalt(II) complexes based on a tetradentate bis(phosphine) bis(amino) ligand, $[PNNP]^{2-}$, have been synthesized. The parent $(PNCH_2CH_2NP)Co$ complex exhibits a paramagnetic ^1H NMR spectrum and has been characterized through electron paramagnetic resonance (EPR), cyclic voltammetry (CV), and single crystal X-ray diffraction. An analogous (PNCHCHNP)Co complex has been synthesized through hydrogen atom abstraction from the ethylene backbone increasing the conjugation of the ligand framework. The cyclic voltammogram for this hydrogen atom abstraction complex exhibits three reversible redox processes in the CV due to the increased conjugation. Characterization data and investigations into the reactivity of these complexes will be discussed.

163. Synthesis and magnetic properties of large Fe^{III} based coordination clusters

***Daniel J. Cutler**[1,2,3], dcutler@uwindsor.ca, Euan K. Brechin[2], Jürgen Schnack[4], Hiroyuki Nojiri[3]. (1) Chemistry and Biochemistry, University of Windsor, Windsor, Ontario, Canada(2) EaStChem,School of Chemistry, The University of Edinburgh, Edinburgh, Edinburgh, United Kingdom(3) Tohoku Daigaku, Sendai, Miyagi, Japan(4) Universitat Bielefeld, Bielefeld, Nordrhein-Westfalen, Germany*

Historically, polynuclear Fe^{III}-O clusters have been at the heart of the study of molecular magnetism. One particularly interesting aspect of Fe^{III} clusters is their potential to grant access to large ground state spins. Molecules with such properties include the $[Fe_{17}/_{19}]$ twin clusters and the $[Fe_{17}]$ “molecular mineral” species. The discovery of such clusters using relatively simple organic ligands has prompted us to speculate that new Fe^{III}-O clusters may be synthesised that can display larger spin ground states and that new topologies may be reachable. Here we present a variety of such clusters including an expansion of the iron oxide based “molecular mineral” family with clusters ranging in size from $[Fe_8]$ to $[Fe_{34}]$ The importance of iron oxides in the modern world cannot be understated with uses in multiple industries. Often these oxides are used in the form of mineral products such as magnetite, or as nanoparticles. The three new clusters are reported - $[Fe_{34}]$, $[Fe_{30}]$ and $[Fe_8]$ (Figure 1)- are prepared from simple one pot reactions involving monodentate pyridine-type ligands. Another simple organic ligand explored is triethanolamine, here we present a further three iron-based clusters an $[Fe_{15}]$ cluster with an uncommon tetrakis hexahedron topology and two new Fe^{III} based rings, a rare odd numbered $[Fe_{11}]$ ring and it’s even numbered analogue $[Fe_{12}]$. High field magnetisation measurements performed at Tohoku University reveal stepped behaviours indicative of a cross over of excited spin states with the ground state (Figure 2).

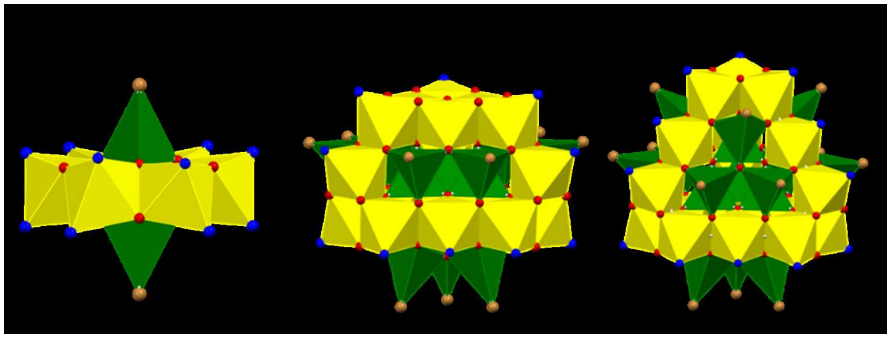


Figure 1: Polynuclear represetations of $[Fe_8]$, $[Fe_{30}]$ and $[Fe_{34}]$. Colour code: $Fe_{octahedral}$, yellow; $Fe_{tetrahedral}$, green.

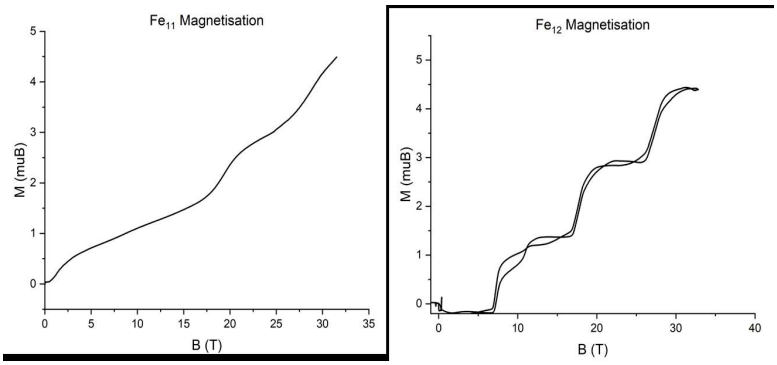


Figure 2: Magnetisation plots for [Fe_{11}] (left) and [Fe_{12}] (right)

164. Exploring the cluster chemistry of pyridyl alkoxide ligands for the discovery of 3d/4f single molecule magnets

***Gabriele Delle Monache**, gd13so@brocku.ca, Melanie Pilkington. Brock University, Saint Catharines, Ontario, Canada*

Single molecule magnets (SMMs) are discrete coordination complexes typically comprised of transition metal and/or lanthanide ions that can be magnetized in the presence of an applied magnetic field and below their blocking temperatures, remain magnetized when that field is subsequently removed[1]. There is currently intense worldwide interest in SMMs given their potential applications for high-density information storage, magnetic qubits and spintronic devices[2]. In recent years the Pilkington group investigated the *3d* cluster chemistry of pyridyl alkoxide ligands which has afforded new interesting clusters that includes a unique {Mn_{31}} SMM[3]. We have now extended this approach to target the discovery of novel heteronuclear *3d/4f* clusters since it enables us to combine the ground spin states of *3d* metal ions, together with the large magnetic anisotropy of the *4f* ions.

Three pyridyl alkoxide ligands $bhpH_2$ (**1**), mpmH (**2**) and dmpmH (**3**) have been recently prepared and together with auxiliary carboxylate ligands their cluster chemistry has been explored for the preparation of heterometallic *3d/4f* clusters. This strategy has afforded several new complexes with [Cu_2Ln_2], [Cu_6Ln_5], and [Cu_4Ln_2] cores, (where Ln(III) = Gd, Tb and Dy). The syntheses, structural and magnetic properties of these heterometallic clusters will be presented, highlighting how by carefully fine tuning their molecular structures it is possible to suppress quantum tunneling mechanisms (QTM) and switch on their SMM properties.

165. Strong coupling and magnetic blocking in organometallic Lanthanide single-molecule magnets

***Selvan Demir**, sdemir@chemistry.msu.edu. Department of Chemistry, Michigan State University, East Lansing, Michigan, United States*

A general approach to high blocking temperatures, T_B, in multinuclear single-molecule magnets is to generate strong magnetic exchange between lanthanide centers. This is particularly effective by using radical bridging ligands with diffuse spin orbitals that can penetrate the core electron density of the lanthanide ions. Here, we will present several new radical-bridged organometallic lanthanide singlemolecule magnets.

166. Building sustainable cathode material production in North America and globally

***William Mays**, william.mays@basf.com. Battery Materials North America, BASF, Wyandotte, Michigan, United States*

BASF implementation of advanced 21st century battery cathode material manufacturing utilizes a global footprint, closed loop recycling and sustainable metal supply. BASF is providing high performance CAM in a sustainable manner to the auto industry which is helping to make electric vehicles a success.

167. Mitigating the hazards of battery thermal runaway events

***Craig Gorin**, cgorin@dow.com. Dow Performance Silicones R&D, Dow, Midland, Michigan, United States*

The mobility industry is heavily investing in new battery pack designs as the adoption rate of electric vehicles accelerates. Safety has become a major concern with the increasingly large amount of energy stored in a battery pack for a marketable range per charge. A key focus in the industry has been on the significant challenges of thermal runaway and propagation prevention, as extreme hazards are present when even a single battery cell goes into thermal runaway. Material and chemistry based-approaches for mitigation of an event are required.

First, a technical analysis was completed of hazards generated from thermal runaway; including flame, heat, hazardous smoke, flammable gas, electrical shorting and high-speed molten particle generation. Next, various mitigation approaches were evaluated, with a focus on battery pack assembly materials that provide passive protection. Potential materials include coatings, molded goods, extruded form factors, or pre-formed sheets. These materials can be leveraged throughout the entirety of a battery pack, providing beneficial properties in normal use and more importantly, during and after a thermal event. Finally, advantages and disadvantages of different mitigation strategies were determined based on new application-focused high temperature testing capabilities and analytical techniques that have been developed.

168. eMobility Material Analysis solutions Platform (e-MAP) in BASF

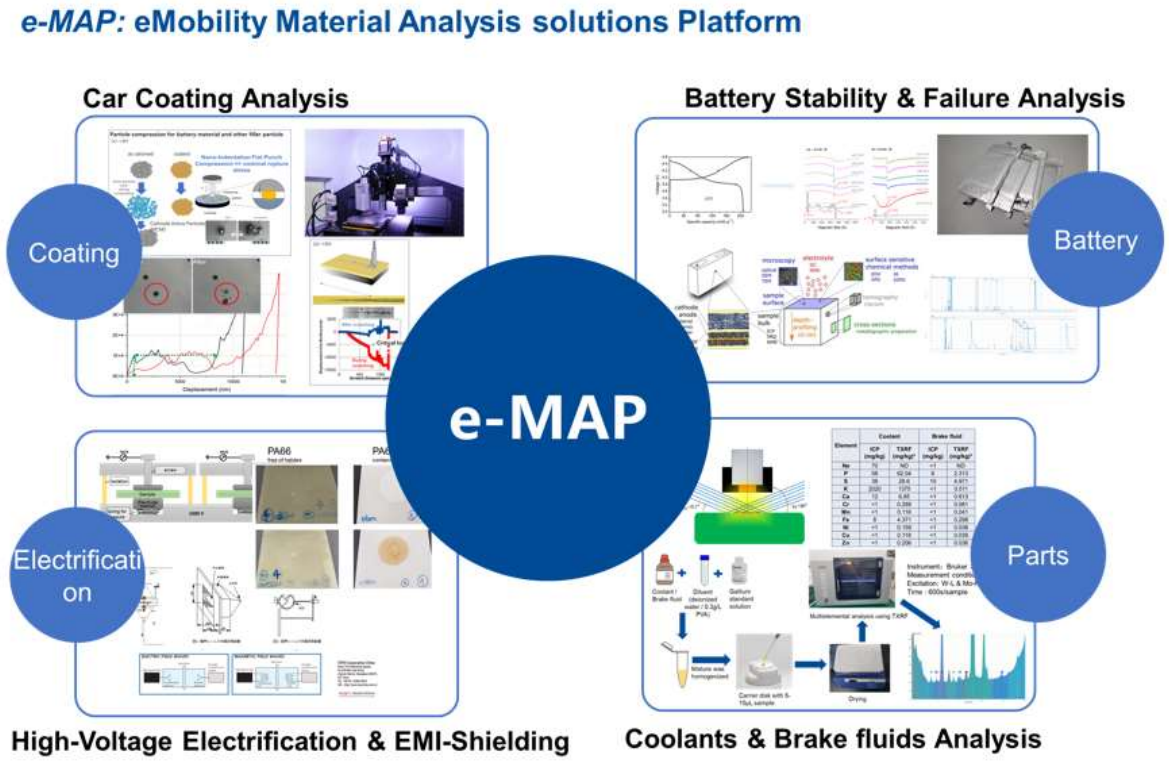
***Yunzhi Zhang**, yun-zhi.zhang@basf.com. Research Group, BASF Corp, Wyandotte, Michigan, United States*

As an important part of sustainability, the development path of automobiles is gradually tilting from traditional gas vehicles to new energy vehicles, such as the fast-growing electric vehicles. Out of the world’s top 20 vehicle manufacturers, which represented around 90% of new car registrations in 2020, 18 have stated plans to widen their portfolio of electric vehicle models. Current e-Mobility industry’s fast-changing requirements and regulations require high-performance material solutions. BASF, as a global chemical company, has built a material analysis platform to empower e-Mobility materials research and development globally.

e-MAP is a BASF e-Mobility material analysis platform that leverages BASF’s analytical testing capabilities globally. e-MAP enabling the development and application of e-mobility materials with accurate analysis and quick response in various applications. In e-MAP, customers and BASF experts will work together and find solutions in many directions, such as increasing the durability and functionality of car coating display; designing lighter, longer-lasting batteries; improving the reliability of advanced driver assistance systems and making a longer-lasting EV coolant.

Our advanced analytical technologies and expertise from around the world are aligned in this platform, integrating global resources to serve our local EV customers and meet the needs of customized materials. The future-proof material analysis technologies and proven expertise

provided by e-MAP help optimize the latest chemical analytical technologies, certify BASF reliable and efficient products and fulfill regional e-Mobility market needs.



169. Considerations for developing a greener chromatographic method

Bonnie A. Alden, Kenneth D. Berthelette, Kimberly Haynes, ***Nicholas Santiago****, Nicholas_Santiago@waters.com. Waters Corporation, Milford, Massachusetts, United States*

Method development for reversed-phase high-performance liquid chromatography (HPLC) separations has traditionally been conducted using acetonitrile-water or methanol-water gradients. Although both organic solvents have certain advantages and disadvantages, they provide different selectivities. For this reason, screening both solvents is valuable during method development. Acetonitrile is often preferred because of its ability to dissolve a wide range of solutes, its low UV cutoff, compatibility with mass spectrometry detection, and lower viscosity. However, it is also designated as usable, yet problematic. Reducing the use of acetonitrile could be one of the options to consider when developing greener LC methods. HPLC columns with 4.6 mm internal diameters can be replaced by narrower ID columns containing smaller particles. Higher viscosity alternatives to acetonitrile such as isopropanol or ethanol can be evaluated with the utilization of high-pressure LC instrumentation.

In recent years, the maximum operating pressure of LC instrumentation has increased to 15,000 psi or higher, and modern stationary phase technologies such as superficially porous particles have been shown to produce lower backpressures than fully porous particles of similar size. In this poster we have explored whether greener solvents such as ethanol or isopropanol could replace acetonitrile in some instances. Chromatographic separations achieved using alternative solvents, solvent reduction, and solid-core particle technology will be shown.

170. Efficient synthesis of the *N*-Boc-Adda amino acid

***Mahesh Yadab**, mahesh1yadav85@gmail.com, Jennifer L. Stockdill. Chemistry, Wayne State University, Detroit, Michigan, United States*

The unnatural amino acid (2*S*,3*S*,4*E*,6*E*,8S,9*S*)-3-amino-9-methoxy-2,6,8- trimethyl-10-phenyldeca-4,6-dienoic acid (Adda) is a crucial component of cyclic hepatotoxic heptapeptides Microcystins, as well as pentapeptides nodularin and motuporin. Several naturally occurring Protein phosphatases (PPIs) possess the “ADDA” residue, which has been shown to be crucial for their inhibitory activity.

The Adda amino acid is a structurally complex, stereochemically dense amino acid for which several synthetic approaches have been reported. These synthetic achievements notwithstanding, samples of *N*-Boc-Adda-OH are not available for purchase, and one must synthesize it to access all MC congeners. The shortest linear approach of Adda synthesis involves 15 steps and contains several non-atom-economical steps such as sequential Wittig/Horner-Emmons reactions. We recently completed the *N*-Boc-Adda-OH synthesis that shortens the route by 3 steps and eliminates multiple high waste operations in favor of stereoselective catalytic reactions. The synthetic route involves enantioselective hydrohydroxyalkylation and the Aldol condensation to furnish *syn* chirality between the methyl and hydroxyl groups, an olefin Cross-Metathesis and Horner-Emmons Wodsworth to afford *E* selectivity, and Intramolecular Mitsunobu reaction to invert the chirality.

171. Towards a polyethylene terephthalate (PET) degradation scheme

***Evan Grim**, elg5357@psu.edu. Chemistry, The Pennsylvania State University, University Park, Pennsylvania, United States*

Polyethylene terephthalate (PET) is a thermoplastic polymer that is widely used to create fabric, bottles, and other packaging. Due to its resilience to high temperatures and mechanical stress, much of it remains intact in the environment after disposal, presenting hazards to wildlife and long-term health risks to humans in the form of microplastics. This work aims to evaluate the efficiency and reliability of the degradation of PET through a method using dimethyl sulfoxide (DMSO) as a solvent and hydrotalcite as a catalyst. This scheme provides a sustainable way to recycle PET using the byproducts of industry and recycling the reagents used in the degradation. Several experimental conditions are considered, such as varying reaction times or levels of solvent. Through analysis and refinement of the experimental methods and products, a step toward efficient, sustainable recycling can be taken.

172. Dimerization kinetics of NAD^+ biomimetics: Alternating current voltammetry as an analytical tool

***Chase Bruggeman**, bruggemanchase@gmail.com, David P. Hickey. Chemical Engineering and Materials Science, Michigan State University, East Lansing, Michigan, United States*

We use alternating current voltammetry (ACV) to measure the dimerization rates and reduction potentials of a family of NAD^+ biomimetics (NAD = nicotinamide adenine dinucleotide). NAD^+ can undergo reversible hydride transfer to form NADH; both of these cofactors are used by about half of known oxidoreductase enzymes (~15% of all documented enzymes) for highly specific chemical transformations, including stereospecific alkene reductions and regiospecific aryl oxidations. An ability to regenerate NADH from NAD^+ would enable large-scale employment of these valuable reactions, with only a catalytic amount of the expensive cofactor. Electrochemistry holds special appeal as a way to regenerate NADH, by avoiding the need for stoichiometric amounts of reducing agent; however, electrochemical regeneration of NADH and its mimetics is intercepted by radical-radical dimerization. The rate of this reaction

is often too fast to measure with conventional electrochemistry techniques (k_D >> 10^7 $M^{-1}s^{-1}$). By applying ACV to a family of NAD^+ mimetics ($mNAD^+$) in acetonitrile, we show that the dimerization rates are at or above the theoretical diffusion limit (k_D >10^9 $M^{-1}s^{-1}$), although there appears to be no general trend relating dimerization rate to molecular structure. The reduction potential, however, drops by 6-18 mV when the mimetic counterion is switched from Br^- to Cl^-, and the reduction potential is more positive when sp^2 carbons rather than sp^3 carbons are located near the redox-active pyridinium site. The results shed light on the structure-function relationships governing NAD^+ mimetics, and they demonstrate the utility of ACV for investigating kinetically challenging systems.

173. Quinones as redox electrolytes in pH gradient flow batteries

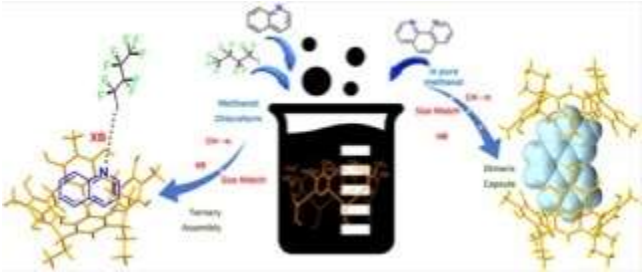
***Christina Jiang**, jiangy@mail.gvsu.edu, Andrew W. Lantz. Chemistry Department, Grand Valley State University, Allendale, Michigan, United States*

Redox flow batteries have gained attention recently as potential large-scale, low-cost energy storage systems for renewable energy sources (e.g. wind, solar, etc.). Recently, aqueous soluble organic redox species have been studied as alternative electrolytes to overcome the limitations of current vanadium chemistry, namely low energy density, moderate charge/discharge efficiency, cost, and toxicity. Quinones are a class of organic redox active compounds that are attractive electrolyte candidates due to their redox reversibility and high energy densities. In addition, the reduction potential of quinones may be easily altered through derivatization of their substituents or varying the solution conditions. Reduction potentials and electrochemical characteristics of several quinone derivatives were studied using cyclic voltammetry in acidic or basic solutions to evaluate the effect of electrolyte pH. Electrolyte pairs that show proper potentials and reversibility were tested in a small-scale battery cell to assess charge/discharge performance and pH stability.

174. 'Nitrogen effect': Complexation with macrocycles potentiates fused heterocycles to form halogen bonds in competitive solvents

***Frank B. Osei**[1], fosei@oakland.edu, Kwaku Twum[1], Sanaz Nadimi[2], Rakesh Puttreddy[3], Yvonne B. Ojong[1], John J. Hayward[3], Kari T. Rissanen[3], John Trant[2], Ngong K. Beyeh[1]. (1) Chemistry, Oakland University, Rochester, Michigan, United States(2) University of Windsor, Windsor, Ontario, Canada(3) Jyvaskylan yliopisto, Jyvaskyla, Keski-Suomi, Finland*

Weak intermolecular forces are difficult to observe in highly competitive polar protic solvents primarily due to the overwhelming quantity of competing solvents. It is more challenging in cases of ternary assemblies of pure organic compounds. Aromatic N-heterocycles are potent halogen-bond acceptors that interact with suitable halogen-bond donors. In this work, we overcome these complications by leveraging the binding of fused aromatic N-heterocycles in open resorcinarene cavities to template the formation of halogen-bonded ternary assemblies in a protic polar solvent.



175. Synthesis of a series of ligands, in the freshman chemistry laboratory, to be used as complexing agents

***Andrew Ivanciu**, ivanciac@udmercy.edu, George Brown, Michael Caruso, Yoona Park, Pahul Bedi, Roxana Nistor, Hazel Song, Marc Naddaf, Nawres Alkhareef, Farah Abdulrahim, Abdullah Al-Wakeel, Alzhra Alduis, Jasmine Fettohy, Naya Kheirbek, Fatima Siddique, Anna Mousaad, Rama Hamo, Roopum Virk, Evgenia Koneva, Gregorios Mihalopoulos, Zain Shouman, Renee Trotman, Leza Jeki, Joseph Crandall, Mark A. Benvenuto. Chemistry & Biochemistry, University of Detroit Mercy College of Engineering and Science, Detroit, Michigan, United States*

A series of bi-dentate ligands have been produced which have long, non-polar tails and relatively polar heads. The synthesis involves a Schiff's base condensation, and can often be run at room temperature. We will present results of these syntheses, as well as the results of initial trials in producing ligand-metal complexes using various metal salts.

176. Regioselective and functional divergent azidation of olefins for the preparation of biomolecular probes

***Jonathon Truong**, jonathontruong1@gmail.com, **Michelle Huynh**, 20mhuynh@gmail.com. The University of Toledo, Toledo, Ohio, United States*

Click chemistry facilitates the union of an azide and an alkyne with relatively mild reaction conditions to form a substituted triazole. This reaction provides an optimal avenue for probing living systems due to its rapid rate and minimal byproducts. The recent award of the Nobel Prize highlights the impact of click chemistry’s application with molecular probes in bioimaging systems. However, procedures describing the production of azides, especially those with additional functional groups, are limited. There are even fewer options for the di-substitution of alkenes with an azide group. Here, we provide a one-pot protocol that allows for regioselective functionalization of an azide and halide or an azide and alcohol across an alkene. Furthermore, this di-functionalization procedure occurs via divergent substitution mechanisms. Thus, we present a desirable and convenient strategy to introduce an azide alongside another functional group to further expand the growing use of click chemistry in biological systems.

177. Synthesis of bisphenol A analogs for reproductive toxicity testing: A search for safer plastics

*William S. Shall, Jessica Clore, **Shannon C. Timmons**, stimmons@ltu.edu. Department of Natural Sciences, Lawrence Technological University, Southfield, Michigan, United States*

Bisphenols are a well-known class of endocrine-disrupting chemicals that can adversely affect human health and the environment. Despite their association with a variety of health-related disorders, they are ubiquitous in everyday life and are found in many plastic products. Bisphenol A (BPA), for example, has been linked to developmental and reproductive abnormalities. Several analogs of BPA, including BPS and BPZ, have been evaluated in the search for safer bisphenols to potentially replace BPA in consumer products; however, numerous studies have shown that neither BPS nor BPZ are less toxic than BPA. In a course-based research experience at Lawrence Technological University, BPA analogs were synthesized for reproductive toxicity testing. Through a study of reaction variables, an effective synthetic methodology was developed by varying reaction time, temperature, and stoichiometry to prepare BPA analogs in higher yield than the low-yielding preparations typically described in the scientific literature. An efficient purification protocol was developed using a C18 reversed-phase column and an automated flash chromatography system. Using

this approach, a structurally diverse library of less-studied BPA analogs was successfully prepared and purified. Through reproductive toxicity testing, a structure-activity relationship will be established that will help further our understanding of how bisphenol structure relates to reproductive health.

178. Monitoring and quantitation of bacterial growth via capillary isotachophoresisi

***Joshua Gibbons**, gibbojos@mail.gvsu.edu, Andrew W. Lantz. Chemistry Department, Grand Valley State University, Allendale, Michigan, United States*

The quantitative analysis of bacterial cultures is essential for monitoring bacterial growth under varying conditions and in samples such as biological systems, water and food sources, and consumer products. Capillary electrophoresis has gained significant attention as a tool for the separation and detection of microorganisms due to its rapid analysis times, low cost, and method simplicity. Isotachophoresis is a mode of capillary electrophoresis that utilizes a heterogeneous buffer in the capillary to separate charged species by their electrophoretic mobilities. Recently, capillary isotachophoresis has been used to sort, focus, and quantify microorganisms based on their ranges of electrophoretic mobilities. Here, we evaluate this method for monitoring the growth of bacterial species under varying conditions and in mixed cell cultures. This work demonstrates that this capillary isotachophoresis method is capable of being used as a rapid cell quantitation tool.

179. Pi-stacking interactions between lumiflavin, tryptophane and tyrosine via density functional theory

***Moina Al-Modhafir**, mmalmodh@umich.edu, Daniel B. Lawson, Simona Marincean. University of Michigan-Dearborn, Dearborn, Michigan, United States*

This work computationally investigates the binding interaction of tryptophane and tyrosine with lumiflavin in the gas phase and in water. Geometry optimizations and vibrational frequencies were performed by density functional theory (DFT) using wb97xd/def2TZVP. Time-dependent density functional theory (TDDFT) was used to calculate the electronic transitions of the molecules using cam-b3lyp/def2TZVP, wb97xd/def2TZVP, and the b3lyp/def2TZVP with the wb97xd//def2TZVP geometry. Polarizable Continuum Model (PCM) is used for calculations in water. Total electronic energies, complexation energies, free energy differences, solvation energies, excitation wavelengths, and HOMO-LUMO energy gaps of complexes are evaluated and compared between gas phase and solvated.

180. Nuclear magnetic resonance spectroscopy as a tool for identification of varietal honey

***Taylor Mac**[1], tmac2@emich.edu, Justin Norris[1], Gregg Wilmes[1], Maria Goodrich[2], **Cory D. Emal**[1], cemal@emich.edu. (1) Chemistry, Eastern Michigan University, Ypsilanti, Michigan, United States(2) Biology, Eastern Michigan University, Ypsilanti, Michigan, United States*

In recent years there has been an increase in interest in specific varietal honeys, produced when honeybees forage from a dominant floral source. Certain varietals are prized for their particular organoleptic qualities, particularly by meadmakers, as the aromatic qualities present in honey typically translate to mead post-fermentation. Other varietals have found a market due to purported health benefits conveyed by specific chemicals found in those specimens. Because of these increased market pressures, the development of analytical methods to verify chemical fingerprints characteristic of specific botanical sources has become a high priority. Here we describe efforts towards the use of nuclear magnetic resonance spectroscopy (NMR)

to identify molecular markers specific to particular varietal honeys of interest. Our approach is to use a combination of NMR spectroscopy and multivariate analysis to identify the molecular 'fingerprints' of varietal honeys, with a particular focus on the minor components of the mixture.

181. Tracking bitterness units in beer throughout the brewing process using a streamlined spectroscopic method

***Kimgech Kean**, kkean2@emich.edu, **Cory D. Emal**, cemal@emich.edu. Chemistry, Eastern Michigan University, Ypsilanti, Michigan, United States*

Bitterness in beer is mainly caused by isoalpha acids derived from hops added during the brewing process prior to fermentation. The concentration of these compounds is commonly described as Bitterness Units (BU) and can be measured using a standard method that employs ultraviolet spectroscopy. We have developed a streamlined version of this standard method that circumvents some of the specialized equipment not typically present in a commercial brewery setting. Here we describe this adapted method and use it to track changes in BU throughout the brewing process, including fermentation. The ability to more easily measure and track these changes will allow brewers to make adjustments to their process in case the profile of a given fermentation falls out of range, giving them the opportunity to produce a more consistent product with their desired characteristics.

182. Diaminoanthracene dicarboxylic acid as a bis-aryne building block for polycyclic hydrocarbon synthesis

***Gabriel Rudebusch**, grudebus@emich.edu. Chemistry, Eastern Michigan University, Ypsilanti, Michigan, United States*

Carbon-rich polycyclic compounds have found application in organic semiconductors, memory storage and spin-transistor type devices. Some favorable properties of these compounds include narrow frontier orbital energy gaps, close π-π packing in the solid state and thermally accessible triplet spin states. The development of new synthetic methods and building blocks is necessary in accessing new scaffolds in this chemical space. To leverage the synthetic utility of aryne formation from 2-aminobenzoic acids, we set out to synthesize 2,6-diamino-anthracene-3,7-dicarboxylic acid (DDA). Synthesis of DDA is achieved in two steps from an easily accessed dibromoanthracene starting material. We will present the synthetic story towards DDA along with characterization and reactivity trends. DDA should prove to be a useful building block in the preparation of new polycyclic compounds with useful properties.

183. Self-assembly of pyridyl-coinage metallo-macrocycles: Synthesis and applications

***Calvin Goldsmith**, cgoldsmith@oakland.edu, Emmanuel Adusei, Zacharias Kinney. Chemistry, Oakland University College of Arts and Sciences, Rochester, Michigan, United States*

The use of weak noncovalent interactions, such as arene-arene stacking and metallophilic interactions, in tandem with directional ligand–metal coordination are known to work synergistically to assemble metallo-macrocycles with applications in organic electronics. These photoactive materials have been applied as nanofibers, organic light-emitting diodes (OLEDs), and organic semiconductors.1,2 Specifically of interest are pyridyl ligands and coinage metals, which form near linear N–M–N linkages. When combined with π-conjugated monomers, noncovalent interactions are primed to arrange metallo-macrocycles into bricklayer or columnar stacked structures with enhanced optoelectronic properties.1,2

Our research group recently developed streamlined synthetic routes to naphtho[2,1-b:3,4-b']dithiophene (Alpha NDT), a Pi-conjugated monomer with defined geometry. This monomer has been selected due to the versatile properties of thiophenes in organic electronics such as environmental stability, metal-like conductivity, ease of synthetic modification, and low production cost-effectiveness in contrast to its inorganic counterparts.3,4 The termini of our alpha NDT can be functionalized with 3-pyridyl groups (3-py), resulting in a structural analog to a 3-pyridyl end-capped meta-terphenyl. We have begun reacting these 3-py end-capped alpha NDTs with Ag(I), finding that these immediately form higher order structures, most likely being our target [2+2] metallo-macrocycles. The synthesis and structural analysis of these monomers and metallo-macrocycles will be discussed.

184. Flavor component profiling of American whiskeys by direct analysis in real time mass spectrometry

*Harriet A. Lindsay, Ruth Ann Armitage, **Jonathan Zhu**, jzhu@emich.edu. Chemistry, Eastern Michigan University, Ypsilanti, Michigan, United States*

Bourbon whiskey is considered a distinct product of the United States. It is produced under specific fermentation conditions using a combination of grains including at least 51% corn with the other 49% made up of grains such as barley, rye, wheat, or more corn. The high cost of bourbon along with its long maturation time has created a market for counterfeits, and with it a need to reliably identify these counterfeits. We propose using Direct Analysis in Real Time Mass Spectrometry (DART-MS) to analyze whiskey samples and compile flavor fingerprints unique to each. DART-MS would be a fast, inexpensive way to verify the integrity of bourbon samples while requiring minimal preparation compared to other methods. Here we report on the methodology for testing samples with DART-MS as well as identifying key fingerprints for the tested bourbon.

185. Synthesis and examination of the influence of a fluorine atom at various positions in the tail of alkoxy cyanobiphenyl mesogens

***Kiran Agrahari**, kagrahar@kent.edu. Chemistry and Biochemistry, Kent State University, Kent, Ohio, United States*

Alkoxy cyanobiphenyls are well known nematic liquid crystals. A study of the influence of the location of a fluorine atom in the tail of some alkoxycyanobiphenyls on their phase behavior was done. The new compounds pentyloxycyanobiphenyl with fluorine at the 4, 3 and 2 positions and butyloxycyanobiphenyl with fluorine at 3 and 2 positions have been synthesized for this study.

186. Assessment of seasonal variations of major chemical elements in water samples collected from Rouge River

*Yiwei Deng, **Slater Stanton**, stant@umich.edu, **Ashley Benson**, ashbenso@umich.edu. Natural Sciences, University of Michigan-Dearborn, Dearborn, Michigan, United States*

Rouge river is one of the most productive ecosystems which plays a very important role in the biogeochemical cycling of major and trace elements. Over the past three decades, much of efforts have been devoted to improving the water quality of Rouge River. However, information about seasonal variations of major elements (e.g., calcium, sodium, and chloride) is limited. The concentrations of the major elements in the river could be potentially amplified by human activities such as road salt spreading during winter season. The seasonal changes to the chemical composition of the river water could impact the ecology of Rouge River.

This work is undertaken to assess seasonal variations of calcium, sodium, and chloride species of Rouge River. The river samples were collected monthly. The concentrations of calcium and sodium were determined using flame atomic absorption spectroscopy (FAAS). The levels of chloride were analyzed using chloride ion selective electrode (ISE). In addition, the concentrations of calcium were also determined by potentiometric and complexometric titrations using auto-titrator coupled with calcium ion selective electrode. The preliminary result shows that the levels of calcium were lower in the fall, and higher toward the winter months. This may result from the extensive usage of salt for deicing roads in the winter season. The results collected from this study could help us better understand if human activities impact the seasonal variation of these elements, which in turn impact the overall water quality and ecosystem of Rouge River.

187. Diaryl selenides motifs as catalytic sites on electrode surface for peroxynitrite sensing

magdya. ibrahim[1]*, m.a.ibrahim@vikes.csuohio.edu,* ***Haitham Kalil***[1]*, h.kalil@vikes.csuohio.edu, Farid Fouad*[2]*, Mekki Bayachou*[1]*. (1) Chemistry, Cleveland State University, Cleveland, Ohio, United States(2) Chemistry& Biochemistry, Kent State University, Kent, Ohio, United States*

Peroxynitrite is a highly reactive species that is known to cause damage to cells, and it is challenging to measure its concentration accurately. Electrochemical methods for detecting peroxynitrite are limited, and there is ongoing research to develop effective electrochemical probes or catalytic materials that can serve as interfaces for efficient detection of peroxynitrite. In our previous work we developed and characterized a thin film material based on 4,4' diaminodiphenyl selenide grafted onto glassy carbon electrodes to create a functional interface for peroxynitrite detection. This selenide-based peroxynitrite sensors demonstrated remarkable sensitivity and a low limit of detection, and we postulated an electrocatalytic catalytic mechanism whereby the grafted selenide moieties act as electroactive mediators that ultimately lead to the catalytic oxidation of peroxynitrite. The positive charge developed on the selenium atom of the diarylselenide upon electrochemical oxidation is crucial for a such electrocatalytic mechanism. To test the validity of the postulated mechanism, we designed other other diarylselenides with different functional groups in the para position of the selenium atom. In this study, we decorated electrodes with diarylselenide moieties bearing various functional groups in the para position of the selenium atom of the diaryl selenide (See Scheme1; R=-H, -OMe, -CF_3).

We show that the electron-withdrawing -CF_3 group significantly improves the sensitivity of the corresponding electrode towards PON. The opposite is observed with the methoxy group, which almost abolishes the mediated electrocatalytic oxidation of PON. We will present the results and analyze these findings in light of the electron-donating or withdrawing ability of the substituents placed in the para position from the selenium atom in the context of the postulated electrocatalytic mechanism mediated by the selenide moiety.

188. Dynamic assembly of photoactive naphthodithiophene-based materials

Emmanuel B. Adusei[1]*, emmanueladusei@oakland.edu, Madison Caswell*[1]*, Calvin Goldsmith*[1]*, Lourdes Haddad*[1]*, Drecila Alinj*[1]*, Jimin Park*[2]*, Zacharias Kinney*[1]*. (1) Chemistry, Oakland University, Rochester, Michigan, United States(2) Troy High School, Troy, Michigan, United States*

To meet growing global energy demands, scientists have made a concerted effort to find renewable and sustainable energy solutions.[1] Central to the design, synthesis, and application of new organic electronic materials are π-conjugated organic molecules.[2] These molecules are known to be photoactive, and their absorption windows can be fine-tuned through strategic connectivity or substitution. Of particular interest are π-conjugated organic macrocycles, which offer extended π-conjugation and facile syntheses through dynamic covalent chemistry (DCC).[3] We believe that two isomeric naphthodithiophenes, naphtho[2,1-b:3,4-b']dithiophene (α-NDT) and naphtho[1,2-b:4,3-b']dithiophene (β-NDT), are an ideal platform for incorporation into complex architectures through DCC.[2,3] Imine condensation offers a pathway to the programmed assembly of rigid, π-conjugated materials with heteroatom-lined interior cavities.[4] The use of imines in this work has a two-fold effect. (1) Imines allow for error correction during the assembly process ultimately resulting in the thermodynamically preferred product.[4] (2) By strategically placing the imine nitrogen adjacent to the interior sulfur atoms, a four membered chalcogen bond is formed which works synergistically with the assembly process, both organizing and maximizing the rigidity of the products. [5]

Recently, our research group has found that indeed these processes work synergistically, wherein α-NDTs have successfully undergone imine condensation under facile reaction conditions. To expand the scope of this effort, we are moving beyond acyclic diimines with variable electronics towards multicomponent macrocyclic assembles with heteroatom-lined cavities.[3] The synthesis and structural analysis of these NDT-based assemblies, both acyclic and macrocyclic, will be discussed.

189. Synthesis of phenanthridine: Establishing a proof of concept for a new approach to the preparation of benzo[2,7]naphthyridines

***Samantha Dorn**, samantha.dorn@student.cuaa.edu, **Alex Martin**, martin.alex.d@gmail.com. Physical Sciences, Concordia University Ann Arbor, Ann Arbor, Michigan, United States*

Benzonaphthyridines are a major structural component of the class of biologically active compounds called pyridoacridine alkaloids. Derived from marine species, pyridoacridine alkaloids have been shown to be cytotoxic to tumor cells. Currently, these natural products are formed using long, linear processes. We have identified a new methodology to produce a similar heterocyclic compound, phenanthridine, where the only structural difference from the benzonaphthyridine is the nitrogen at the 2-position is replaced by a carbon. Our scheme utilizes a Suzuki reaction to join 2-bromobenzaldehyde and 2-nitrophenyl benzoic acid forming a new C-C bond, directly followed by a reductive cyclization which forms the middle ring producing phenanthridine in two telescoped steps. The products needed to synthesize benzo[2,7]naphthyridine are not currently commercially available to provide a straightforward path. By completing the synthesis of phenanthridine using our proposed chemistry, it is likely that this approach could be applied to the preparation of a wide range of benzo[2,7]naphthyridine compounds.

190. Atmospheric dry and wet deposition of total phosphorus to the Great Lakes

***Mary M. Lynam**, lynam@umich.edu, Lunia Oriol, Allison Steiner. University of Michigan, Ann Arbor, Michigan, United States*

In aquatic environments, excessive loadings of phosphorus can manifest as hypoxia, eutrophication, algal blooms, and dead zones. Quantification of total phosphorus (TP) loadings from the atmosphere to freshwater environments is essential to improved understanding of its fate and transport, and to mitigate the effects of excessive levels in aquatic ecosystems. For

dry deposition we use TP concentrations in fine particulate matter ($PM_{2.5}$) samples from fourteen land-based sites upwind of the Great Lakes to provide new fine particle dry deposition estimates. For wet deposition we use TP concentrations in wet-only precipitation samples collected at eleven land-based sites in the Great Lakes region.

Both dry and wet deposition exhibit seasonal cycles with higher concentrations in warmer and wetter months. There is an increasing gradient from north to south in wet deposition, likely driven by both higher precipitation and increased emissions near southern sites.

We estimate annual deposition of TP to Lakes Superior, Michigan, Huron, Erie and Ontario at 526, 702, 495, 212, and 185 metric tons per year, respectively, which is lower than prior estimates for Lakes Superior, Erie and Ontario, comparable for Lake Huron, and about two times greater for Lake Michigan. When considering only the contribution of fine particulate matter to the dry deposition, wet deposition dominated over dry at all lakes except for Lake Huron. However, prior global estimates suggest greater contributions from larger particles (PM_{10} and PM_{100}), yet observations to validate these estimates over the Great Lakes are not available. Our findings indicate that dry deposition of a range of particle sizes are needed to constrain the total atmospheric deposition of TP over the Great Lakes.

191. Investigating the effect of phenolic compound concentrations in staghorn sumac seeds on the winter foraging behaviors of birds

Joanna Hiebert[1]*, jhiebert@oswego.edu, Marcus Cleland*[1]*, Samuel Krebs*[2]*, Michael Schummer*[2]*, Vadoud Niri*[1]*. (1) Chemistry, State University of New York at Oswego, Oswego, New York, United States(2) Environmental Science and Forestry, SUNY College of Environmental Science and Forestry, Syracuse, New York, United States*

Staghorn sumac (*Rhus typhina*) is an early-successional shrub of old fields, hedgerows, and roadsides throughout the northeast and the upper mid-west United States and southeast Canada. Staghorn sumac contains many beneficial compounds, including phenolic compounds. These compounds are a defense mechanism to herbivory in plants and play a role in inhibiting seed germination. Specifically, when phenolic compounds decline, starches activate and respiratory activity increases, enabling seeds to germinate. It has been hypothesized that concentrations of phenolic compounds vary throughout the seasons, as an evolved mechanism to control the timing of seed dispersal by foragers and that freeze-thaw events transform and reduce phenolic compound concentrations.

The focus of this project was to determine if variation in foraging on sumac by birds was influenced by concentrations of the phenolic compounds commonly occurring in berries of this plant through the winter months. A solvent extraction method for extracting the phenolic compounds from seeds and an HPLC method for separating and quantifying these compounds were developed. The phenolic compounds under investigation were gallic acid and caffeic acid. The sumac seed samples were picked every other week from five different locations in central New York and analyzed for the concentrations of phenolic compounds. The results showed a decrease in the concentration from November to March.

192. Synthesis of diazirine all in one click NAADP for isolation and purification of the NAADP receptor in sea urchin egg homogeenates

Yuqing Zhang[2]*, zhangyuqing0710@gmail.com, Timothy F. Walseth*[1]*, James T. Slama*[2]*. (1) Department of Pharmacology, University of Minnesota Twin Cities, Minneapolis, Minnesota, United States(2) Department of Medicinal Chemistry, University of Toledo - Health Science Campus, Toledo, Ohio, United States*

Calcium ion is one of the most important intracellular 2nd messengers since it controls numerous cellular processes. Nicotinic acid adenine dinucleotide phosphate (NAADP) is a potent second messenger that mobilizes calcium from intracellular stores in both mammals and echinoderms. NAADP was shown to be crucial to cellular functions including fertilization, cell division, T-cell differentiation, and maturation. However, the NAADP binding protein in sea urchins has not yet been unambiguously identified. Previous work in our laboratory showed that a photosensitive probe, 5-azido-NAADP, was able to release calcium at low concentrations in sea urchin egg homogenates and specifically label NAADP binding proteins on irradiation. After that, our lab designed and synthesized AIOC-NAADP which was used to identify JPT2 as an NAADP-binding protein in human Jurkat cells. Based on this compound, we designed an NAADP analog that contains a similar chemical structure but a different photoactive group. The synthesis of NAADP analogs was achieved using a chemo-enzymatic approach. The bifunctional NAADP analogs will be tested for the ability to elicit NAADP-mediated calcium ion release from sea urchin egg homogenates and also will be tested for the ability to elicit NAADP-mediated calcium ion release from human Jurkat cells through microinjection. If it was recognized by NAADP binding receptors, we will try to use this newly synthesized bifunctional prob to specifically label NAADP binding proteins in sea urchin egg homogenates and try to identify the protein. Also, we will try to apply this compound on DO.11.10 cells to understand the post-translation modification of NAADP binding proteins.

193. Mid-Michigan technician group (MMTG)

Lacey J. Brissette[1,2]*, laceybrissette@hotmail.com. (1) Mid-Michigan Technician Group, Midland, Michigan, United States(2) Dow Chemical, Midland, Michigan, United States*

The Mid-Michigan Technologist Group (MMTG) is continuously trying to develop and strengthen a positive career attitude that can benefit technicians and their employers. We are a professional organization for technicians and technologists working in chemistry related industries, and for students actively pursuing a degree in the field of chemistry, in the Mid-Michigan area. We are affiliated with the Midland Section of the American Chemical Society (ACS). Our mission is to provide professional development opportunities to all individuals working with, or interested in, chemical technology.

194. Paramagnetic ionic liquids for extraction and forensic analysis of textile dyes

Joel Moss*, jemoss@bsu.edu,* ***David Bwambok****, dkbwambok@gmail.com. Ball State University, Muncie, Indiana, United States*

Textile dyes from fabrics can provide useful information for solving a crime by matching to the source of the dye. This requires nondestructive analytical methods to extract dyes from fibers while maintaining their chemical identity. The challenge is to find an extraction medium that is efficient on fibers and can dissolves the dyes for analysis with minimal sample preparation. Ionic liquids (ILs) are solvents that can be tailored to extract the organic dyes from fibers. This study evaluated the use of paramagnetic ionic liquids (PILs) for extraction, magnetic separation and analysis of textile dyes in a single step. The developed method was efficiently used for removal of various textile dyes from cotton fabrics using PILs. The PILs were synthesized using a tetraalkyl phosphonium cation that is paired with an anion containing a paramagnetic metal such as iron, manganese and holmium. Using the synthesized PILs, magnetic extraction was carried out for various dyes including malachite green, kiton red, acid yellow and acid red. Extraction of the dyes using an external magnet alleviates the use of volatile and toxic organic solvents for liquid-liquid extraction. In addition, the recycling of PILs for multiple extractions of dyes was explored.

195. Design and synthesis of platinum ligands for cancer treatment

***Klaus J. Friedrich**, friedrkj@udmercy.edu, **Margaret Iwu**, iwuma@udmercy.edu, **Jessica Sinani**, sinanijj@udmercy.edu, Dylan Nguyen, Selina Hakim, Hailey Kizy, Jacob Zdankowski. University of Detroit Mercy, Detroit, Michigan, United States*

Cisplatin and other platinum drugs are an essential part of combination chemotherapy to treat cancer. The compounds bind to and crosslink DNA, thus initiating apoptotic pathways in cancer cells. While many patients exhibit high initial responsiveness to treatment, numerous side effects lessen the therapeutic value of these metallodrugs.

When cancer cells grow at a high rate, they have an increased energy demand compared to non-cancerous cells; with that they need to facilitate an increased cellular uptake of energy sources, namely glucose, fructose, and galactose. Accordingly, many cancer cells overexpress hexose transporters, integral membrane proteins responsible for the transport of hexoses across cellular membranes. To focus the uptake of platinum drugs on fast-growing cells and by that to reduce deleterious side effects due to the interaction of the drugs with biomolecules other than DNA in cancer cells, hexose platinum conjugates that are potential substrates of hexose transporters are being synthesized. The conjugates consist of three domains, namely a transporter substrate, a spacer, and a chelant for platinum. A convergent synthetic approach makes it possible to independently vary these domains and to systematically study substrate-transporter and drug-DNA interactions. Several drug candidates are being synthesized.

196. Evaluation of antibacterial activity of compounds extracted from stem bark of *Alafia multiflora*

***Charles Kuedukey**, cnkuedukey@bsu.edu, **Davis Anum**, danum@bsu.edu, Julianna Borgia, John Mckillip, David Bwambok. Ball State University, Muncie, Indiana, United States*

Natural products are traditionally used for treatment of various ailments. Over the years, *Alafia multiflora* has been used for wound treatment in various communities, particularly in West Africa. Due to antimicrobial application of this plant extract, this study focused on isolation and characterization of compounds from *Alafia multiflora* and their activity guided fractionation against multidrug resistant bacteria. Extraction of crude compounds was carried out on dried, ground stem bark using polar and nonpolar solvents including hexane, ethyl acetate, dichloromethane and methanol and water. Results from the antimicrobial activity screening revealed that water/methanol (80/20) extract is active against various bacterial strains. For example, a minimal inhibitory concentration of 0.3 µg/mL was obtained against *Staphylococcus aureus, Klebsillae pneumonae, pseudomonas aeruginos*a strains. The active crude compounds were separated by column chromatography and characterized using nuclear magnetic resonance, infrared spectroscopy, UV-vis spectroscopy and liquid chromatography-mass spectrometry techniques for chemical identification of the active compounds.

197. Classification of biodegradable chemicals based on their structures and physicochemical properties using computational simulations

***Richard Kyung**[1], nycrick@gmail.com, Eunbin Cho[2]. (1) CRG-NJ, Cresskill, New Jersey, United States(2) Providence Christian Academy, Seoul, Korea (the Republic of)*

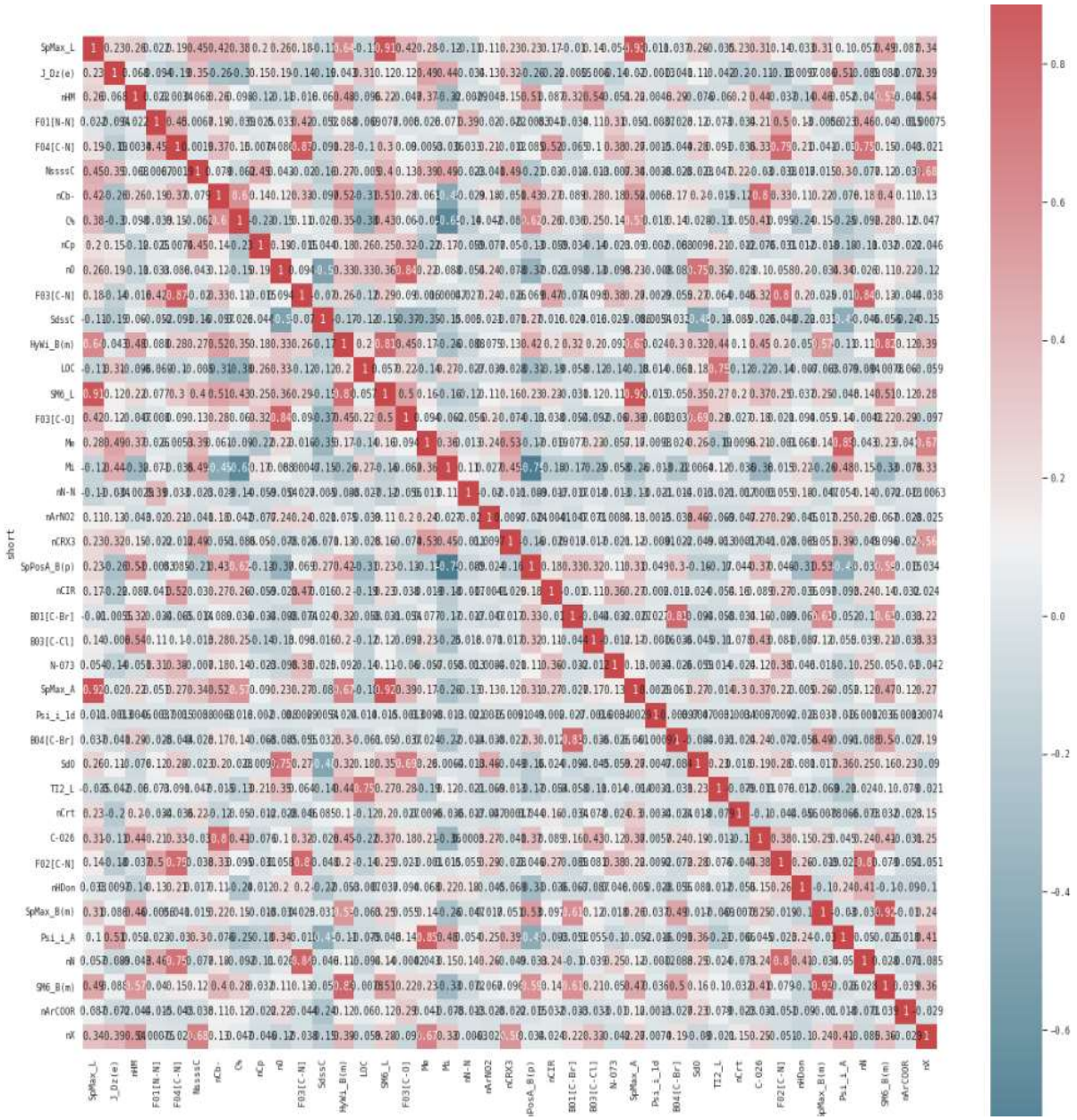
The development and validation of reliable models for biodegradation are essential for us to assess the environmental impact of chemicals and to prioritize the development of sustainable chemicals. The biodegradability of a chemical depends on its chemical structure and physicochemical properties, such as molecular weight, solubility, and hydrophobicity. In the

context of biodegradation, Quantitative structure-activity relationship (QSAR) models are used for this research to predict the biodegradability of chemicals based on their chemical structure and physicochemical properties. This prediction aids in the design of more environmentally friendly compounds.

In this paper, experimental values of 1055 chemicals were collected for the prediction. Forty-one molecular descriptors and one experimental class were used as attribute information. Explanatory Data Analysis (EDA) and data visualization were performed to identify the type and structure of the data and get the descriptive statistics.

The studied biodegradation model involves selecting a training set of compounds with known biodegradability and identifying relevant molecular descriptors, such as electronic, topological, and steric properties. These descriptors with machine learning are then used to develop a mathematical model that can predict the biodegradability of new compounds.

It showed that the accuracy and reliability of QSAR models depend on the quality and completeness of the training data and the relevance of the molecular descriptors used in the model.



198. Synthesis and characterization of a novel set of RM734-CN(2F) variant ferronematic liquid crystals

***Parikshit Guragain**, pguragai@kent.edu. Kent State University, Kent, Ohio, United States*

The recently discovered ferroelectric nematic phase (NF) is special in that their giant dielectricity, extreme sensitivity to the external stimulus like the electric field, and their fluidity are fused in one, making them really promising materials for cutting-edge liquid crystal-based electrooptic devices. Here, we report the synthesis of a new set of NF molecules, a variant of RM734-CN(2F), and their phase investigation. These molecules differ from entire RM734 materials in that they lack a previously believed essential component for achieving the NF phase in these kinds of materials—a substitution in the terminal position of the alkoxy substituted ring. Also, each one of them shows a direct isotropic to a ferronematic phase transition.

199. Functionalization of commercial hydrophilic-lipophilic balanced copolymer for automatic magnetic dispersive micro-solid phase extraction of surface water contaminants

***Celestine Vubangsi Gemuh**, gemuhc@faf.cuni.cz, Burkhard Horstkotte, Petr Solich. Analytical Chemistry, Univerzita Karlova Farmaceuticka fakulta v Hradci Kralove, Hradec Kralove, Hradec Králové, Czechia*

We present a simple approach to magnetic dispersive solid phase microextraction and its automation for the enrichment of water contaminants. Supel™-Select HLB (Hydrophilic modified styrene polymer) beads were made magnetically susceptible by introducing magnetite nanoparticles into the sorbent. The so-functionalized sorbent was used in a dispersive solid phase extraction methodology that was automated using the Lab-In-Syringe technique.

The methodology followed a previous study on using magnetic nanoparticles but enabling automated exchange of the sorbent, i.e. developing an in-syringe bead injection concept. In short, optimized volumes of sample and bead suspension were aspirated into the syringe void and dispersed by the aid of a magnetic stirring bar placed inside the syringe. By automatic activation and deactivation of magnetic stirring process, the analytes were retained on the dispersed sorbent, which was, when the stirring stopped, captured on the magnetic stirring bar. Afterwards, the sample solution was discarded, and beads were washed in-syringe with water. Thereafter, an optimized eluent was aspirated to strip the analytes from the anew dispersed sorbent.

The extraction system was coupled online to a liquid chromatograph for the determination of model analytes mebendazole, bisphenol A, benzyl 4-hydroxybenzoate, diclofenac, and irgasan. Essential parameters such as extraction time, elution time, sorbent suspension and eluent volume, as well as phase separation time were optimized. Limits of detection ranged from 1.2 µg/L to 6.5 µg/L with < 7 % RSD for all the analytes at 25 µg/L level. The method was linear over a tested range from 5 µg/L to 200 µg/L. The developed method was successfully implemented for the analysis of the chosen contaminants in surface water (lakes and rivers) with recoveries between 78.4 % and 105.6 %.

200. Computational insights on the structure of transition states and intermediates of the Boyland-Sims oxidation reaction

***Isaac Hall**[1], ihall4@students.fairmontstate.edu, Audrey L. Pumford[2], Edward J. Behrman[3], Jojo Joseph[1]. (1) Natural Sciences, Fairmont State University, Fairmont, West Virginia, United States(2) Chemistry, University of Cincinnati, Cincinnati, Ohio, United States(3) Biochemistry, The Ohio State University College of Arts and Sciences, Columbus, Ohio, United States*

The Boyland-Sims Oxidation reaction uses an alkaline solution of peroxydisulfate salt to convert arylamines to o-aminophenols. The long-standing mechanism involves a nucleophilic attack by the amine leading to the formation of an arylhydroxylamine-O-sulfonate intermediate, which then rearranges to the arylamine o-sulfate. The long-standing mechanism of a nucleophilic attack by the amine on peroxide oxygen has been questioned by Marjanović et al. who have proposed a nitrenium ion intermediate as the reactive species rather than the uncharged amine. It has been challenged by a variety of experimental observations. We present here new computations at a high-level of density functional theory (B3LYP/6-311++G**) to model both arylhydroxylamine-O-sulfonate and nitrenium ion pathways. In this study, the energetics of reaction intermediates in both mechanisms are computed for a series of aromatic amines such as aniline, 2,4-dinitroaniline, N,N-dimethylaniline. In addition to the

computational results, we will also report our synthetic effort to support the computational results. Our initial results suggest that the Boyland-Sims oxidation reactions proceed via the arylhydroxylamine-O-sulfonate intermediate as predicted earlier, which makes doubtful the importance of a nitrenium ion in this process.

201. To the rescue of our K-12 schools, please!

***Nada Saab**, saab1055@gmail.com. Detroit Public Schools, Detroit, Michigan, United States*

Several reports address the need to reform our K-12 schooling system and further compare it to other international systems. We can list:

“The Competition that Really Matters”, “ Report to the President, Prepare and Inspire: K-12 Education in Science, Technology, Engineering, and Math (STEM) for America’s Future”, “International Benchmarking”, and “Schools of the Future”.

Are we preparing our students well to compete nationally and internationally? Are we implementing the recommendations of experts in the field? Are we improving at the appropriate speed compared to other countries?. We have the best universities in the world and our schools are in need for their help before we loose the talents of our generation.

202. Is the NGSS curriculum sufficient to promote proficiency in high school chemistry?

***Lawrence H. Kolopajlo**, lkolopajl@emich.edu. Chemistry, Eastern Michigan University, Ypsilanti, Michigan, United States*

Although NGSS is thought of as a reform-based science curriculum, a close examination of its standards demsonstrates otherwise. For example, the word "chemistry" is nonexistent in its framework. Instead, "chemistry" has been removed from its venerable place as the central science, and replaced by "physical science", evoking vague general science courses, as often taught in 9th grade. In this paper, NGSS standards relating to chemistry will be evaluated, and compared to the National Science Education Standards released in 1994. Moreover, the NGSS curriculum will be compared to those used in China and European countries. As a measure of how well American students are doing in science, test scores from PISA (The Programme for International Student Assessment) will be presented.

203. Exploring the Tyndall Effect: Blending the chemistry and math with easy-to-use, inexpensive materials

***Bianca Gheorghila**, gheorgbi@udmercy.edu, Zoe Arrington, Katrina Yeldo, Sara Arment, Sabrina Cacanindin, Reina Seklauoi, Zahra Kanji, Lilian White, Evan Aeck, Angel Alexander, Luke Weisend, Dan Hamze, Jay McKenzie, Renee Kesto, Andreh Khosho, Aranza Ramirez, Albis Spahiu, Ahmad Naeem, Lobaid Murshed, Eryka Ely, Terika Johnson, Zoe Madden, Evgenia Koneva, Michael Caruso, George Brown, Yoona Park, Caliana Shouman, Josh Page, Lara Sabra, Zain Shouman, Renee Trotman, Evan DeVito, Xavier Sterling, Oriekaose Agholor, Andrew Bosah, Luke Adamczyk, Keara Moroz, Nudar Shabil, Zahra Albdair, Julia Kroha, Jamie Whitener, Katlynn Strnad, Joseph Crandall, Leza Jeki, Ndeye Ka, Mark A. Benvenuto. Chemistry & Biochemistry, University of Detroit Mercy College of Engineering and Science, Detroit, Michigan, United States*

The Tyndall Effect is often shown simply as a demonstration in a chemistry or other science class, in order to observe the phenomenon. We have found several ways in which it can be used as a starting point for a larger discussion of what materials are composed of, how light is scattered, and how the scattering can be quantified. We will present how to utilize the Tyndall

Effect as a teaching tool in chemistry and math, and how to do so with inexpensive, safe, easy-to-find materials.

204. Faculty beliefs on teaching and learning: Potential roadmap towards using evidence-based practices

***Jacob Starkie**, starkiej@msu.edu, Sewwandi Abeywardana, Veeda Scammahorn, Melanie Cooper. Chemistry, Michigan State University, East Lansing, Michigan, United States*

Improvement of postsecondary education requires a multifaceted approach, one that fundamentally must include the wide adoption of evidence-based practices in postsecondary classrooms. Efforts to support such adoption may include changing the current teacher evaluation model, emphasizing departmental responsibility for quality curriculum, and supporting ongoing professional development opportunities. Often attempts by researchers to support faculty in changing their teaching practices to align with evidence-based practices, by using the means previously stated, are met with heavy resistance. Past research, primarily conducted at the secondary level, has established a connection between faculty beliefs and educational decisions regarding the use of new or different teaching practices. The present study sought to fill in this gap in understanding by investigating postsecondary faculty teacher beliefs. This project investigated faculty's attitudes and opinions on teacher evaluation, learning objectives/assessments, and professional development using interviews and a department-wide survey. Understanding how faculty view critical components of education may give researchers predictive power on how any professional development materials or teaching evaluation models will interact with faculty's epistemological assumptions of what chemistry teaching and learning should look like at a large research-intensive university. Interviews with faculty members revealed beliefs about the connection between learning objectives and career goals, about departmental dedication to teaching as a profession, about the lack of support when changing teaching practices, and about gauging the effectiveness of their teaching. Specific attention is given to the differences in beliefs between relatively younger and older faculty members.

205. Green Organic Chemistry lab manual: What's new?

***Mengqi Zhang**[2], zhan1962@msu.edu, Elizabeth L. Day[1], Melanie Cooper[2]. (1) Department of Chemistry & Biochemistry, The University of Texas at El Paso, El Paso, Texas, United States(2) Chemistry, Michigan State University, East Lansing, Michigan, United States*

The large-enrollment undergraduate organic chemistry laboratory course at Michigan State University has been redesigned to emphasize green and sustainable chemistry and to incorporate evidence-based instructional approaches. The curriclum has been implemented successfully since 2021 fall semester to replace a traditional cookbook style lab curriculum. A new green organic chemistry lab manual will release soon that focuses on green and sustainable chemistry basics, green chemsitry metrics, lab safety, scientific communication and organic laboratory techniques.

206. Bridging the STEM gap in Appalachia: Engaging with students to iteratively improve faculty practices in support of student success

***Jojo Joseph**, jojo.joseph@fairmontstate.edu, Abby Chapman, Robert Niichel. Fairmont State University, Fairmont, West Virginia, United States*

The overall goal of this project is to increase enrollment, retention, and graduation of low-income, academically talented students in STEM programs. We offer robust curricular and co-

curricular support programs for our S-STEM students. Incoming S-STEM scholars attend an Immersion Week during the week before the beginning of classes in the fall semester. All scholars are invited to be part of a STEM Living and Learning Community (STEM LLC). S-STEM students will interact with their faculty and peer mentors regularly, especially during their first year of college. We envision active and ongoing professional development for faculty and peer mentors, coupled with a feedback mechanism for keeping the program student-focused and (in part) student-directed. We have established multiple agreements with local and regional industries to provide unique opportunities for our S-STEM scholars. We offer monthly STEM-specific colloquia featuring representatives from academia, industry, and other career areas matching the career interests of our S-STEM scholars. We have proposed an iterative model of program improvement, relying on a direct student/faculty inquiry and feedback system through our Faculty Mentor and Scholar Councils. These groups provide a grassroots-level accountability and stability to our program, allowing us to better optimize our program's efficiency and efficacy.

207. Process orientated guided inquiry learning in the physical chemistry laboratory

***Timothy R. Brewer**, tbrewer@emich.edu, Kyle DeVries. Chemistry, Eastern Michigan University, Ypsilanti, Michigan, United States*

POGIL (process oriented guided inquiry leanring) is a student-centered, group learning instructional strategy that has been shown to increase student success in courses. In a typical POGIL laboratory, students work in small teams to develop the methods to answer questions that are posed with the instructor acting as a facilitator. The student teams use specially designed activities that generally follow a learning cycle of introduction to the lab by researching basic concepts, designing an experiment to investigate the concept, thinking about the data and then designing experiments to probe deeper into the concepts being studied with data analysis involved to reach conclusions in the lab. We have used this method exclusively in the physical chemistry laboratory at Eastern Michigan Univesity to study various phenomena that have been studied in most classical physical chemistry textbooks. The experiments include freezing point depression, polymer viscosity, kinetics of a heterogeneous reaction, calorimetry of ionic compounds, vaporization of molecules, and absoprtion of conjugated dyes. The experiments are investigative and call for students to develop experiments to study probing questions. We will present the results of these experiments along with some results of students understanding of concepts and attitudes towards this type of learning.

208. Convenient method of esterification of fatty acids: Undergraduate organic lab experiment

***Pasquale R. DiRaddo**, diraddop@ferris.edu. Physical Sciences, Ferris State University College of Arts and Sciences, Big Rapids, Michigan, United States*

A common undergraduate organic experiment involves the acid or base catalyzed esterification of carboxylic acids. Nost often the reaction uses catalytic amounts of strong mineral acids under reflux conditions. Herein we describe an alternative method of ester formation that uses the inexpensive chlorotrimethylsilane (TMSCl), and alcohol, which acts as both reaction solvent and as the nucleophilic esterifying agent. The intermediate trimethylsiloxy compound serves as the electrophile of the second nucleophilic acyl substitution reaction. Various methyl and ethyl esters of saturated and unsaturated fatty acids were thusly made in excellent yields.

209. Biomimetic tridentate *cis, cis*-1,3,5-cyclohexane ligands and transition metal complexes

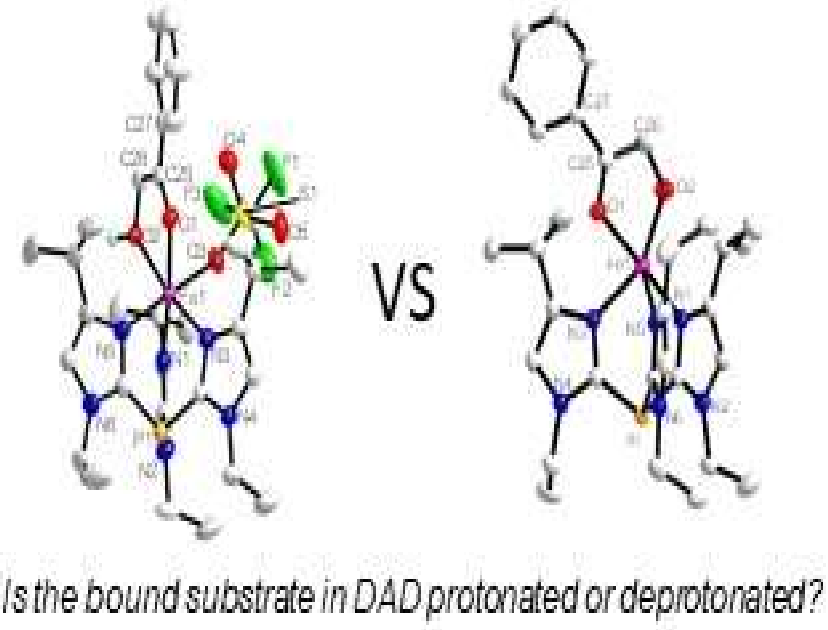
Alex Olivelli, Levi Wolff, Ryan Chafin, Sean Parkin, ***Aron Huckaba****, aron.huckaba@gmail.com. Chemistry, University of Kentucky, Lexington, Kentucky, United States*

Currently, the production of a wide range of chemical materials relies on the use of functionalized starting materials. By instead catalytically desaturating or oxygenating relatively inert hydrocarbon precursors through C-H functionalization, we could eliminate the cost of producing activated and otherwise functionalized starting materials while allowing access to underutilized feedstocks. With this in mind, we look to emulate the active site of various copper- and iron-centered enzymes found in nature that are known to catalyze the hydroxylation of various substrates. The active site of these enzymes, such as particulate methane monooxygenase or cysteine dioxygenase, feature a metal center bound by three histidine residues. Following this basic architecture, we have developed a small molecule ligand that uses azole chelating groups to facially coordinate a metal ion. The novel ligand was synthesized in one step and in good yield, chelated to a metal center, and then tested in catalytic reactions.

210. Probing the mechanism for 2,4'-dihydroxyacetophenone dioxygenase (DAD) using biomimetic iron complexes

Ferman A. Chavez*, chavez@oakland.edu. Chemistry, Oakland University, Rochester, Michigan, United States*

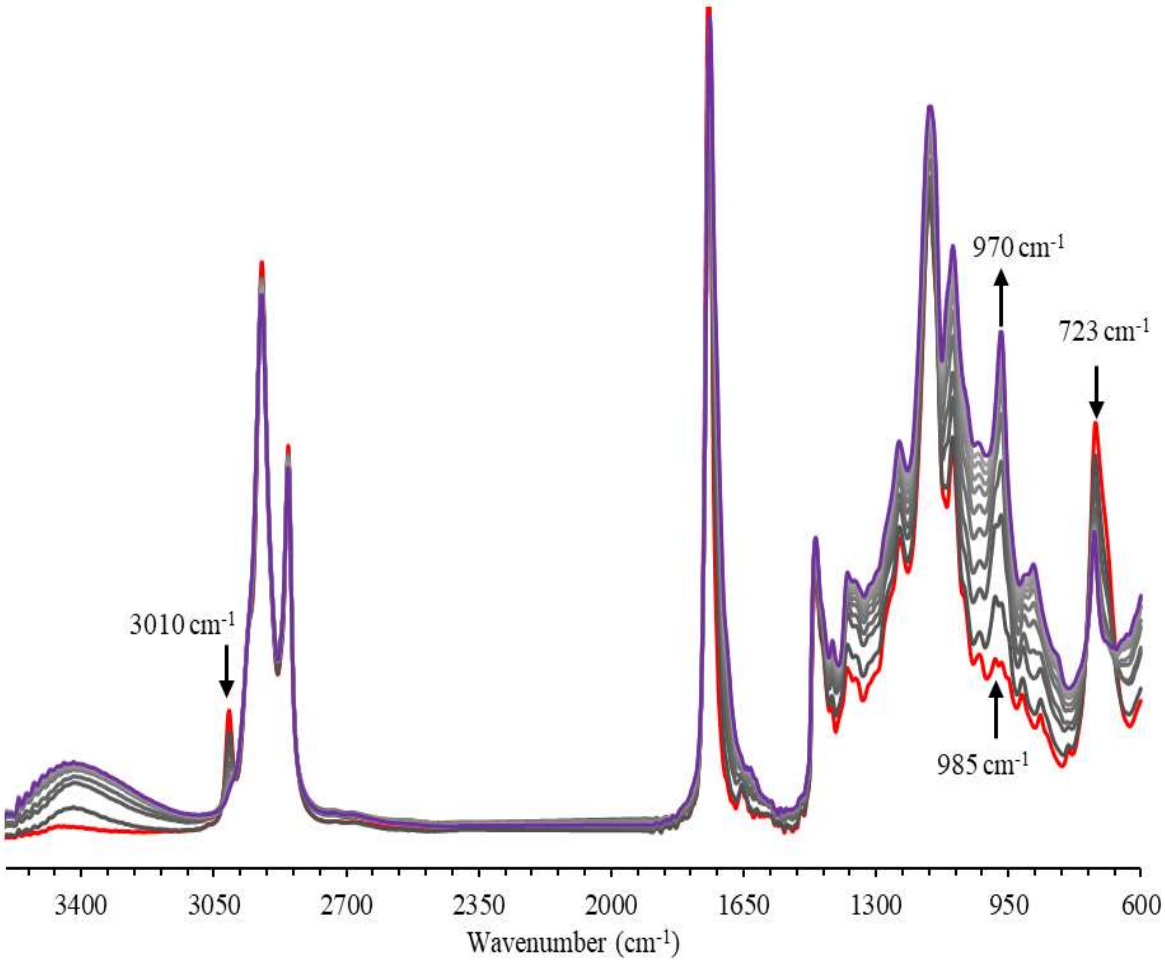
In this study we report the synthesis and characterization of [Fe(T1Et4iPrIP)(2-OH-AP)(OTf)](OTf) (**2**), [Fe(T1Et4iPrIP)(2-O-AP)](OTf) (**3**), and [Fe(T1Et4iPrIP)$(DMF)_3$]$(OTf)_3$ (**4**) (T1Et4iPrIP = tris(1-ethyl-4-isopropyl-imidazolyl)phosphine; 2-OH-AP = 2-hydroxyacetophenone, and 2-O-AP^- = monodeprotonated 2-hydroxyacetophenone). Both **2** and **3** serve as model complexes for the enzyme-substrate adduct for the nonheme enzyme 2,4¢-dihydroacetophenone (DHAP) dioxygenase or DAD while **4** serves as a model for the ferric form of DAD. Complexes **2**-**4** have been characterized by X-ray crystallography which reveals T1Et4iPrIP to bind iron in a tridentate fashion. Complex **2** additionally contains a bidentate 2-OH-AP ligand and a monodentate triflate ligand yielding distorted octahedral geometry while **3** possesses a bidentate 2-O-AP^- ligand and exhibits distorted trigonal bipyramidal geometry (t = 0.56). Complex **4** displays distorted octahedral geometry with 3 DMF ligands completing the ligand set. The UV-vis spectrum of **2** matches more closely to the DAD-substrate spectrum than **3** and therefore it is believed that the substrate for DAD is bound in the protonated form. TD-DFT studies indicate that visible absorption bands for **2** and **3** are due to MLCT bands. Complexes **2** and **3** are capable of oxidizing the coordinated substrate mimics in a stoichiometric and catalytic fashion in the presence of O_2. Complex **4** does not convert 2-OH-AP to products under the same catalytic conditions, however, it becomes anaerobically reduced in the presence of 2 equiv 2-OH-AP to **2**.



211. Oxygen gas as a sustainable oxidant for C-H bond activation and drying oil autoxidation

*Andrew Kalbach, **Alexander R. Parent**, alexander.parent@ndsu.edu. Chemistry and Biochemistry, North Dakota State University College of Science and Mathematics, Fargo, North Dakota, United States*

Oxidation by oxygen gas is one of the most common and important chemical reactions, responsible for everything from aerobic respiration, to the conversion of iron to rust, to the powering of the internal combustion engine. The Parent research group focuses on understanding and controlling the reactivity of oxygen gas using transition metal catalysts as redox mediators. Parent group's work synthesizing C-H bond oxidation catalysts capable of using O_2 as a sustainable oxidant will be described. Second, the group's efforts to understand and model the mechanisms of drier catalyzed autoxidation in drying oils will be presented. Implications of the autoxidation model developed will be discussed.



212. Iron(II)-alkoxide mediated carbene transfer to form cyclopropanes

Lakshani Wathsala Kulathungage[1]*, gw8543@wayne.edu, Sudheer Kurup*[2]*, Richard L. Lord*[3]*, Stanislav Groysman*[1]*. (1) Chemistry, Wayne State University, Detroit, Michigan, United States(3) Chemistry, Grand Valley State University, Allendale, Michigan, United States*

Cyclopropanes are three-membered rings undergoing facile ring opening owing to high ring strain. Therefore, they act as precursors and key intermediates in total synthesis of various organic compounds including pharmaceuticals. A common route towards cyclopropanes is via transition metal-mediated carbene transfer to olefins. However, most of the existing cyclopropanation catalysts are based on expensive and rare noble transition elements, such as Rh. Thus, there is a significant interest in developing efficient and sustainable catalysts which involve inexpensive 3d transition metals.

Our group focuses on the synthesis of middle and late transition metal catalysts featuring bulky alkoxide ligands, which exhibit nitrene and carbene-transfer reactivity. We have previously demonstrated that cobalt(II) bis(alkoxide) precursor $Co(OC^tBu_2Ph)_2(THF)_2$ formed a formally Co^{IV} carbene complex $Co(OR)_2(=CPh_2)$. While this complex exhibited carbene transfer to isocyanides (to form ketenimines) with various diazoalkanes/diazoesters as carbene sources, no cyclopropanation reactivity was observed. In contrast, the reaction of an iron(II) bis(alkoxide) complex $Fe(OC^tBu_2Ph)_2(THF)_2$ with diazoalkanes and diazoesters resulted in the reductive coupling of the diazo functionality through the terminal nitrogens; no carbene formation was observed. As an alternative approach towards a reactive carbene functionality,

we replaced the diazo carbene precursors with hypervalent iodine carbene precursors , of the general form $PhIC(COR)_2$. Herein we report that iodonium ylides lead to the efficient cyclopropanation catalysis under milder conditions using iron bis(alkoxide) precatalysts. The reactivity of three different iron bis(alkoxide)s was evaluated, including $Fe(OC^tBu_2Ph)_2(THF)_2$, slightly bulkier $Fe(OC^tBu_2\{3,5\text{-}Ph_2C_6H_3\})_2(THF)_2$, and chelating system $Fe[OO]^{Ph}(THF)_2$ ($H_2[OO]^{Ph}$ = [1,1':4',1"-terphenyl]-2,2"-diylbis(diphenylmethanol)). In this presentation, I will present a comparative reactivity of these catalysts in carbene transfer. I will also discuss possible reaction mechanism, which likely involves the O, O-coordination of the carbene precursor to the metal center.

213. Cobalt-catalyzed dimerization of terminal alkynes to 1,3-enynes

***Nathan A. Ward**, ward.1358@osu.edu, Joshua Prybil, Andrew Kollar, Casey R. Wade. Chemistry & Biochemistry, The Ohio State University, Columbus, Ohio, United States*

Enynes are valuable structural motifs owing to their utility as precursors to various natural products and biologically active compounds. Catalytic coupling of terminal alkynes provides a convenient and atom economical route to enynes. However, this transformation often requires expensive precious metals such as ruthenium, rhodium, or palladium. Thus, the ability to use inexpensive, abundant metals is highly desired. This presentation will describe our recent investigation of cobalt complexes supported by tetradentate $P^R{}_2N^{R'}{}_2$ (R = Cy, Ph; R' = Py, 4-MePy, *p*-Tol) ligands as pre-catalysts for rapid homo-dimerization of terminal alkynes to generate 1,3-enynes. The Co-$P^R{}_2N^{R'}{}_2$ pre-catalysts facilitate fast and quantitative dimerization of phenylacetylene at loadings of 1 mol% using only cobaltocene as an activator. The series of $P^R{}_2N^{R'}{}_2$ ligands have been evaluated for their relative activity as well as for their selectivity toward generation of the desired enyne versus trimer side product. Ongoing studies are focused on elucidating the mechanism of the Co-catalyzed dimerization as well as expanding the substrate scope of the transformation.

214. Exploring new approaches for Rh catalysis

***Michael Young**, michael.young8@utoledo.edu, Satheesh Vanaparthi, Indunil Alahakoon, Kendra K. Shrestha. Chemistry and Biochemistry, School of Green Chemistry and Engineering, The University of Toledo, Toledo, Ohio, United States*

Our group has a longstanding interest in expanding the utility of nitrene and carbene-transfer reactions through catalyst and methods development. In this presentation, we will discuss three different projects in the lab focused on using dirhodium-paddlewheel catalysts for hydrogen bond-directed alkene functionalization, carbohydrate couplings, as well as new heterogenized paddlewheels for improved sustainability.

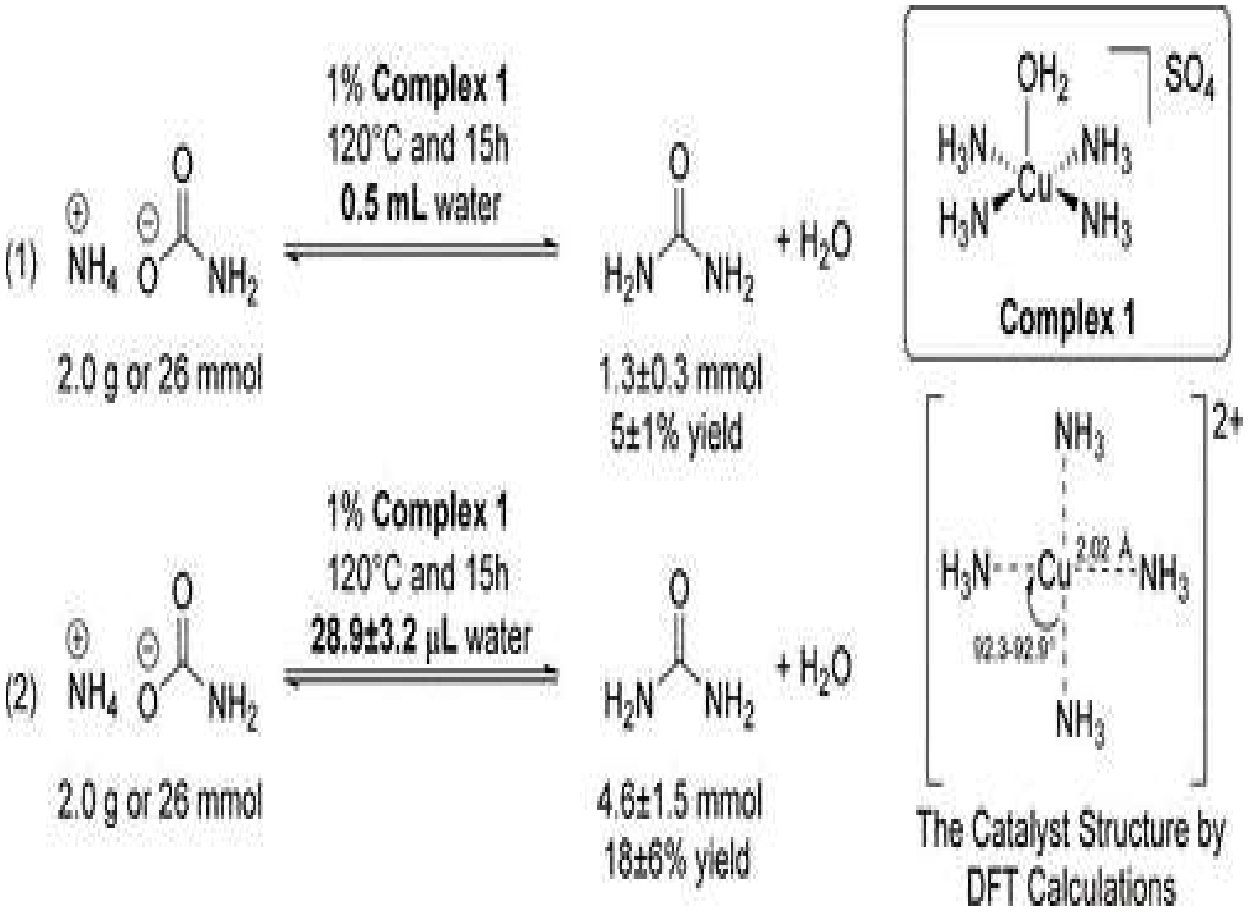
215. C-N bond formation from C1 feedstocks

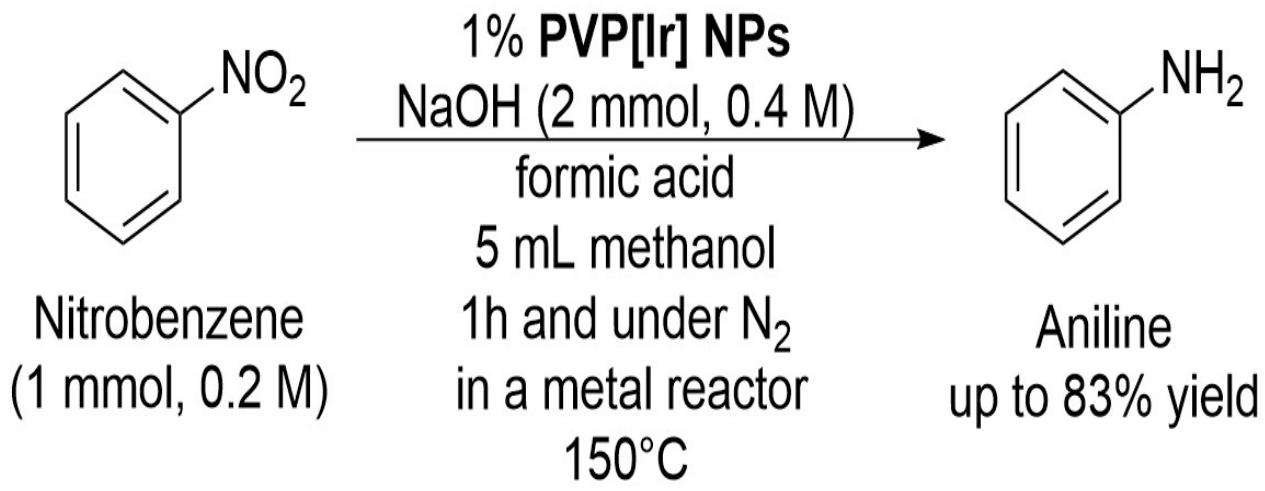
***Meng Zhou**[1], mzhou@ltu.edu, Dequan Xiao[2], Yigui Wang[2], Xinrui Zhou[1], Danielle Hanson[1], Erik Washburn[1], Merve Ekmekci[1], Donovan Dennis[1], Amay Paripati[1]. (1) Natural Sciences, Lawrence Technological University, Southfield, Michigan, United States(2) University of New Haven, West Haven, Connecticut, United States*

I will present our work on a water-soluble copper catalyst to produce urea fertilizer from CO_2 (Inorg. Chem. 2021, 60 (8), 5573-5589) and an iridium nanoparticle catalyst for the transfer hydrogenation of nitrobenzene using formic acid as the source of hydrogen (Chemistry 2020, 2(4), 960-968).

The synthesis of urea fertilizer is currently the largest CO_2 conversion process by volume in the industry. In this process, ammonium carbamate is an intermediate en route to urea formation. We determined that the tetraammineaquacopper(II) sulfate complex, $[Cu(NH_3)_4(OH_2)]SO_4$, catalyzed the formation of urea from ammonium carbamate in an aqueous solution. A urea yield of up to 18 ± 6% was obtained at 120 °C after 15 h and in a high-pressure metal reactor. No significant urea formed without the catalyst. A precipitation method using CO_2 was developed to recover and reuse 66 ± 3% of Cu(II). The catalysis mechanism was investigated by the density functional theory at the B3LYP/6-31G** level with an SMD continuum solvent model.

Catalytic nitrobenzene reduction is crucial for the synthesis of 4,4-methylene diphenyl diisocyanate, which is used to produce polyurethane foams, thermoplastic elastomers, and adhesives. We established the complete composition of 7.0 ± 1.1 nm iridium oxide nanoparticles that were stabilized by polyvinylpyrrolidone (PVP[Ir]). PVP[Ir] and its surface stabilizers were characterized. Using formic acid as the source of hydrogen, PVP[Ir] catalyzed the selective hydrogenation of nitrobenzene to give aniline as the only product in up to 83% yield at 160 °C in a high-pressure metal reactor.





216. Evaluation of multiple linear regression statistical methods to predict biodiesel spill composition

William H. Shirley[1]*, shirleyw@msu.edu, Megan Voisinet*[2]*, Victoria Mc Guffin*[1]*, Ruth Smith*[3,1]*. (1) Department of Chemistry, Michigan State University, East Lansing, Michigan, United States(2) School of Science and Medicine, Lake Superior State University, Sault Sainte Marie, Michigan, United States(3) Forensic Science Program, Michigan State University, East Lansing, Michigan, United States*

Biodiesel is a renewable fuel source that is growing in use around the world. Composed mostly of fatty acid esters synthesized from natural plant oils and animal fats (feedstocks), biodiesels are often mixed with petroleum diesel at different blend percentages. The increased use of biodiesel leads to potential environmental contamination due to spills during production, transportation, and use of the fuel. As subsequent cleanup procedures vary depending on the biodiesel feedstock and blend percentage, several researchers have developed partial least squares (PLS) regression models to predict feedstock and blend percentage. In the current work, an alternative method, principal component regression (PCR), was used to develop predictive models and the predictive performance was evaluated compared to more conventional PLS models.

Biodiesels were synthesized from four different feedstocks (corn, canola, soybean, and sunflower oils) and mixed with diesel to generate five biodiesel blends per feedstock. Biodiesels were analyzed by gas chromatography-mass spectrometry (GC-MS) and the chromatographic profiles were used to generate PLS and PCR models. In each case, feedstock-specific models as well as a comprehensive model was generated. A test set of biodiesels was also analyzed by GC-MS and used to evaluate the predictive performance of each model. Overall, the comprehensive models were the most accurate in predicting feedstock and blend percentage across the range of biodiesel blends with a root mean square error in prediction of 6.30 and 7.03 for the PCR and PLS models respectively. In this presentation, the development and performance of the models will be discussed in more detail, demonstrating the potential to accurately predict the blend percentage for a range of biodiesels.

217. Electrochemical analysis of Bovine exhaled breath condensate to detect biomarkers of respiratory disease using nanocarbon electrodes

***Aaron Jacobs**[1], jacobsaar98@gmail.com, Serban Peteu[1], Maiyara C. Prete[1,2], Andreas Lesch[3], Greg M. Swain[1]. (1) Department of Chemistry, Michigan State University, East Lansing, Michigan, United States(2) Department of Chemistry, Universidade Estadual de Londrina, Londrina, PR, Brazil(3) Department of Industrial Chemistry "Toso Montanari", Universita degli Studi di Bologna, Bologna, Emilia-Romagna, Italy*

Bovine respiratory disease (BRD) is a multi-factorial disease endemic in the North American dairy and feedlot cattle populations. Its presence in the United States is ubiquitous, with up to 97% of feedlots having positive BRD cases (1). BRD has a significant economic impact on U.S. bovine industries, costing $4.9 billion in revenue between 2015–2018 in the beef cattle industry alone (2). Considering that early diagnosis and subsequent treatment of BRD in cattle improves prognosis, there is economic importance to creating rapid, non-invasive, and inexpensive diagnostic technologies to detect BRD. Exhaled breath condensate (EBC) is a biospecimen that can be collected non-invasively and contains a host of potentially useful diagnostic targets that could indicate differences between the healthy and diseased states. Additionally, electrochemical sensors are advantageous due to their portability, rapid results, and inexpensive fabrication. This presentation outlines a facile EBC collection and analysis methodology utilizing flexible inkjet-printed carbon electrodes to detect electrochemically active species in bovine EBC and reports differences between the EBC of healthy and diseased animals. Once matured, this technology could be adapted into a multi-sensor screening platform to diagnose BRD and monitor treatment effectiveness.

218. Human serum albumin nanoparticles with near infrared ionic dye and chemotherapeutic drug for therapeutic applications

***Temitope Alonge**, temitope.alonge@bsu.edu, **David Bwambok**, dkbwambok@gmail.com. Ball State University, Muncie, Indiana, United States*

Drug delivery agents based on nanoparticles from human serum albumin (HSA) are have been approved by the Food and Drug Administration because they are biocompatible. This study focused on evaluation of HSA nanoparticles for encapsulation of both near-infrared ionic dye (IR 780) and hydrophobic chemotherapeutic drug for theranostics against cancer. IR 780 is a near-infrared dye has selective tumor toxicity based on the choice of anion. When illuminated with NIR laser, IR 780 dye emits in the near infrared diagnostic region of the spectrum. In this study, a desolvation method was used to prepare multifunctional HSA nanoparticles with a particle size in the range of ~ 150 nm using 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) as the crosslinker. The potential for improved therapeutic activity against tumor cells. The release of the therapeutic agents from these HSA nanoparticles is achieved by the enzymatic action of metalloproteinases that are overexpressed in tumor cells. This study reports the encapsulation efficiency and the enzymatic release of the NIR dye and chemotherapeutic drug from the HSA nanoparticles.

219. Application of electrochemical sensors to detect nitric oxide and acetylcholine release from mouse myenteric ganglia using an APP/PS1 mouse model

***Skye A. Henderson**[1], skyerussell13@gmail.com, James J. Galligan[2], Greg M. Swain[1]. (1) Chemistry, Michigan State University, East Lansing, Michigan, United States(2) Pharmacology & Toxicology, Michigan State University, East Lansing, Michigan, United States*

Alzheimer's disease (AD) is the most common cause of dementia and is hallmarked by the presence of amyloid beta (Aβ) plaques and neurofibrillary tangles which cause memory deficits and gradual cognitive decline. Studies looking at AD typically focus on central nervous system

dysfunction, however there has been an increasing number of studies that suggest the gut is involved in AD pathology. The enteric nervous system is a division of the autonomic nervous system that contains specific neural networks to control important gastrointestinal tract function such as digestion, motility, nutrient absorption, blood flow, and secretion. Intestinal motility is regulated through the synchronized activity of enteric neurons, interstitial cells of Cajal, and smooth muscle cells which lie within the musculature of the GI tract. Acetylcholine is released from excitatory motor neurons to contract smooth muscle while nitric oxide and ATP—or a similar purine—are released from inhibitory motor neurons to relax smooth muscle. Disruption in these signaling mechanisms which mediate the peristaltic reflex could lead to GI dysfunction in AD.

Electrochemical tools are incredibly useful for studying neurotransmission events owed to their spatial and temporal resolution. To determine if nitric oxide or acetylcholine release is altered in AD, we measured the real time release of nitric oxide and acetylcholine from mouse myenteric ganglia *in vitro* using electrochemical sensors and pharmacological tools. Nitric oxide was detected directly as oxidation current using continuous amperometry along with a boron-doped diamond (BDD) microelectrode modified with Pt nanoparticles and a Nafion coating. Acetylcholine was detected using an enzyme-based sensor which consisted of a platinized-Pt microelectrode modified with a permselective poly(*m*-phenylenediamine) coating and multienzyme film consisting of choline oxidase and acetylcholinesterase immobilized using inert protein bovine serum albumin and glutaraldehyde to cross-link the amino groups of the enzymes together. This presentation will focus on nitric oxide and acetylcholine sensor development and *in vitro* studies using an APP/PS1 transgenic mouse model, which mimics major AD pathology.

220. Environmental estrogens: An analytical challenge

Yuegang Zuo[1]*, yzuo@umassd.edu, Si Zhou*[1]*, Faten Albalawi*[1]*, Yiwei Deng*[2]*. (1) Department of Chemistry & Biochemistry, University of Massachusetts Dartmouth, Dartmouth, Massachusetts, United States(2) Natural Sciences, University of Michigan-Dearborn, Dearborn, Michigan, United States*

Estrogenic compounds, particularly the synthetic estrogenic steroids – ethinylestradiol (EE2) and mestranol(MeEE2) and natural hormone steroids – estrone(E1), estradiol(E2) and estriol(E3), have attracted a great deal of scientific and public attention during recent years due to their occurrence in surface waters and sewage treatment plant effluents and their potential adverse effects on the development and reproduction of fish, wildlife and even human beings. In this presentation, we will focus on our research on the occurrence, sources, and microbial and photochemical degradation of both synthetic and natural estrogenic steroids in fresh and marine aquatic environments and their effects on public health during the past decade. To face analytical challenges for determining trace amounts of estrogenic steroids in natural waters, GC-MS and HPLC analytical methods have been developed. The developed methods were applied to the water samples periodically collected from wastewater treatment plants, lakes, Acushnet River and Buzzards Bay. The interested compounds were detected in several of water samples in nano- to micro-gram per liter concentration range, in which can certainly cause fish feminization and may also contribute to the observed declines in American lobster population in Buzzards Bay [Zuo et al., Chemosphere 63 (2006) 1583; Zuo et al. Environ. Sci. Processes & Impacts 15 (2013 1529]. Microbial and photochemical degradation of E1, E2, E3, EE2 and MeEE2 have been also investigated in seawater as well as in waste, lake and river waters as a comparison. The microbial degradation of synthetic steroid estrogens is extremely slow with a half-life of longer than 70 days in seawater. However, the photodegradation of

these compounds are much faster with a half-life of 17 hours for EE2 and 19 hours for MeEE2. Humic and other dissolved organic substances significantly accelerate the sunlight-induced photodegradation of estrogenic steroids. Transition metal Fe(III), nitrate and nitrite can further catalyze the photochemical decomposition of these steroids.

221. The effect of added organic solvent on electron transfer kinetics and molecular diffusion in room temperature ionic liquids

Shashika Gunathilaka Sabaragam G. Ralahamilage*, sabaraga@msu.edu, Greg M. Swain. Chemistry, Michigan State University, East Lansing, Michigan, United States*

Room temperature ionic liquids (RTILs) have recently gained a significant attention from the scientific community because of their attractive physical and chemical properties, including low volatility, wide electrochemical working window and ability to dissolve polar as well as nonpolar compounds. Despite of these unique properties, high viscosity of these materials is a limitation with employing these solventless, liquid electrolytes in electrochemical systems, for example, electrochemical energy storage devices such as supercapacitors and batteries. Mixing of RTILs with organic solvents is offers a pathway to reducing the RTIL viscosity while maintaining a high operating potential window. In this work, we investigated the effect of acetonitrile and methanol addition into imidazolium based RTILs on electron transfer kinetics and diffusion of a model redox system, ferrocene. Binary systems were prepared by mixing the organic solvent with the ionic liquid at 0.1 to 0.4 molar fractions. The solution resistance and double layer capacitance at the open circuit potential were determined in the prepared mixtures by employing electrochemical impedance spectroscopy (EIS). The electron transfer kinetics in these binary systems were investigated by cyclic voltammetry (CV) using ferrocene as the analyte using a gold working electrode. The EIS results revealed a decrease in solution resistance and a slight increase in double layer capacitance upon the addition of organic solvents. The apparent heterogeneous electron-transfer rate constant increased by 5x when the organic molar fraction reached 0.4. The addition of the organic solvent progressively increased the diffusion coefficient of ferrocene in ionic liquids and altered the diffusion pathway, but in a non-linear manner. The presentation will review studies of the redox system behavior using cyclic voltammetry and chronoamperometry.

222. Excited state simulations of fluorescent proteins for rational design

Alice Walker*, arwalker@wayne.edu. Chemistry, Wayne State University, Detroit, Michigan, United States*

Fluorescent proteins are ubiquitous and powerful tools in chemical biology, imaging and sensing. Despite this, the underlying relationships between the electronic structure of the chromophore, the atomic-level details of the protein structure, and the final fluorescence output remain largely unclear. In this work, we apply dynamics calculations at various levels of theory, including classical molecular dynamics and combinations of multireference quantum mechanics and molecular mechanics, in order to investigate the underlying electronic-structure-function relationships of the chromophore to the protein environment. We apply this physical understanding to the development of new fluorescent protein sensors and improved rational design. We describe our approach for developing new anion detectors formulated from mNeonGreen in collaboration with experimental groups, tuning photodissociative pdDronpa dimers, and the effect of targeted mutations on the fluorescence quantum yield on FusionRed.

223. Understanding the role of JPT2 in NAADP-mediated calcium signaling in T cells

***Giselle A. Soares**, giselleamanda21@gmail.com, Shadia E. Nada, Katherine A. Wall. Department of Medicinal and Biological Chemistry, The University of Toledo, Toledo, Ohio, United States*

Nicotinic acid adenine dinucleotide phosphate (NAADP) is an important mediator of intracellular calcium (Ca^{2+}) signals in T cells and is essential for T cell activation, proliferation, differentiation, and cytokine secretion. However, the molecular mechanisms underlying NAADP-mediated calcium release are poorly understood. Recently, photolabeling studies revealed that NAADP binds to accessory proteins such as Lsm 12 and JPT2, following which Ca^{2+} release occurs via interactions with the two-pore channels (TPCs) located in the acidic endo-lysosomal compartments of cells.

In this study, we sought to identify the role of JPT2 in T cells. Using DO.11.10 cells, a T cell hybridoma that possesses the T cell receptor (TCR), we reveal that the knockdown of JPT2 resulted in a significant decrease in intracellular calcium levels following TCR stimulation. Moreover, we also report its significance in downstream processes pertaining to T cell-mediated immunity through its effect on proteins such as Lck and Zap70 and the NF-kB pathway. Our findings thus provide new insights into the molecular mechanisms of NAADP-mediated calcium signaling in T cells and highlight the importance of this accessory protein in regulating T cell activation and immune responses.

224. Molecular and structural characterization of the histone binding domains of the epigenetic regulator UHRF2

***Brittany Albaugh**[1], balbaug1@emich.edu, Shane Ginnard[1], Alyssa Winkler[1], Carlos Mellado-Fritz[1], Ray Kemmer[1], Tatum Bluhm[1], Nick Butkevich[1], Marisa Gilliam[1], Sara Abdrabbo[1], Bricker Kaitlyn[1], Deborah Heyl-Clegg[1], Raymond C. Trievel[2]. (1) Chemistry, Eastern Michigan University, Ypsilanti, Michigan, United States(2) Biological Chemistry, University of Michigan, Ann Arbor, Michigan, United States*

UHRF1 and UHRF2 are epigenetic proteins that regulate both histone and DNA methylation and appear to have associated functions in cancer development. Recently, there has been interest in identifying anti-cancer molecules that target these proteins. Both proteins contain TTD and PHD histone binding domains that interact with the H3 tail that is trimethylated on lysine 9 (H3K9me3). In this study, we performed a systematic investigation of the TTD and PHD domains of UHRF2, and compared those results with the histone binding properties of UHRF1. We also solved the crystal structure of UHRF2 in complex with the H3 tail. Together, we offer insights into the mechanistic differences within the TTD and PHD of UHRF1 and UHRF2, which may be potential avenues for identifying drugs that can selectively target these proteins.

225. Role of the dual specificity phosphatase hYVH1 in ribosome dynamics

***Panayiotis O. Vacratsis**, vacratsi@uwindsor.ca. Chemistry and Biochemistry, University of Windsor, Windsor, Ontario, Canada*

Human YVH1 (hYVH1, also known as DUSP12) is a dual specificity phosphatase ubiquitously expressed in human tissues. The YVH1 orthologues are extremely conserved throughout evolution and all possess a novel zinc binding domain in addition to their phosphatase domain. Our laboratory has demonstrated that hYVH1 is a novel cell survival factor preventing both thermal and oxidative stress induced cell death, with both phosphatase and zinc binding domains being required. In addition to the observation that hYVH1 expression protects cells from cellular insults, it has been shown that YVH1 orthologues are ribosome biogenesis factors

that function late in the 60S subunit maturation pathway. Moreover, we recently reported the results of a hYVH1-interactome study that discovered hYVH1 associates with additional ribonucleoprotein particles besides the 60S ribosome and functions as a novel stress granule disassembly factor. Interactome studies also provided preliminary evidence that the tyrosine kinase Src may regulate the activities of hYVH1. It has been confirmed that Src phosphorylates hYVH1 in cells and have used quantitative proteomics to demonstrate that co-expression of Src and hYVH1 positively affects translational fitness. We are now interested in thoroughly characterizing the functional significance of the Src-hYVH1 signaling pathway in terms of target identification and elucidating the proteome alterations necessary to restore translational fidelity during recovery from cellular stress.

226. Targeted protein degradation from the endoplasmic reticulum

Ryan Baldridge[1,2]*, ryanbald@med.umich.edu, Rachel Sharninghausen*[1]*, Jiwon Hwang*[1]*, Devon Dennison*[2]*. (1) Biological Chemistry, University of Michigan Michigan Medicine, Ann Arbor, Michigan, United States(2) Cellular and Molecular Biology, University of Michigan Michigan Medicine, Ann Arbor, Michigan, United States*

Degrons are the minimal features that target proteins for degradation and in most cases, degrons allow recognition by components of the cytosolic ubiquitin proteasome system. Currently, each degron that has been identified functions within the cytoplasm. Using *Saccharomyces cerevisiae*, we identified the first short linear sequences that function as degrons from the endoplasmic reticulum (ER) lumen. We show that when these degrons are transferred to proteins, they facilitate degradation through the endoplasmic reticulum associated degradation (ERAD) system at the cytosolic proteasome. These degrons enable degradation of both luminal and integral membrane ER proteins, expanding the types of proteins that can be targeted for degradation both in yeast and in mammalian tissue culture. We have functionalized the discovery of ER degrons and designed a framework to target proteins for degradation from the previously unreachable ER lumen and enabled novel therapeutic approaches that exploit the highly-conserved ERAD system.

227. Unicorn in the garden: Uracils in DNA

Ashok Bhagwat*, axb@chem.wayne.edu. Wayne State University, Detroit, Michigan, United States*

Uracil is a rare base in DNA occuring at a frequency of 1 in a million base pairs. It is generally introduced during replication as a result of utolization of dUTP and efficiently eliminated by the uracil-DNA glycosylase and the base excision repair machinary. However, the AID/APOBEC family of enzymes in vertebrates covert cytosines in DNA to uracils and this contributes to innate and adaptive immunity against viruses and other infectious agents. The expression of these deaminases is regulated by cytokines that are released by cells following an infection and expression of AID in B cells undergoing germinal center maturation results in somatic hypermutation (SHM) and class-switch recombination (CSR) in immunoglobulin (Ig) genes. The expression of APOBEC3 subfamily enzymes is responsible for the restriction of many human viruses including HIV-1, Hepatitis B and human papilloma virus. The processing of uracils in DNA by the base-excision repair (BER) and mismatch repair (MMR) pathways is essential for the immune functions of these enzymes and this causes mutations and strand breaks. Ectopic expression and misregulation of these enzymes is responsible for many of the mutations and chromosome translocations found in cancer cells. In this presentation, I will focus primarily on the action of AID in the switch regions of the immunoglobulin genes and how the uracils contribute to CSR.

228. Mitigating climate change: Atomistic simulations shed light on bromoform-membrane interactions

Kevin J. Cheng[1], *kjcheng2@illinois.edu, Jie Shi*[3,4], *TarasV. Pogorelov*[2,1], *Sara Capponi*[3,4]. *(1) Center for Biophysics and Quantitative Biology, University of Illinois Urbana-Champaign, Urbana, Illinois, United States(2) Department of Chemistry, University of Illinois Urbana-Champaign, Urbana, Illinois, United States(3) IBM Almaden Research Center, San Jose, California, United States(4) NSF Center for Cellular Construction, University of California San Francisco, San Francisco, California, United States*

Reducing ruminant methane emissions is crucial to mitigate global warming. Seaweed is a promising food additive due to its high bromoform concentration that can effectively inhibit methanogenesis. Increasing bromoform capacity in seaweed can be achieved through peroxisome organelle engineering; however, this feat requires a detailed understanding of how bromoform interacts with seaweed peroxisome membranes at the molecular level. We performed all-atom molecular dynamics simulations with new parameter and topology files in the CHARMM format to investigate these interactions. We simulated water and water-membrane systems with varying bromoform concentrations to understand how membranes affect bromoform behavior. Pure phosphatidylcholine (POPC) bilayers were employed since the peroxisome membrane composition is unknown. We validated the forcefield by comparing our results with published experimental data and determined that bromoform aggregates at high concentrations due to its hydrophobic character. Moreover, bromoform penetrates the membrane in nanoseconds at low concentrations with a diffusion coefficient comparable to common small organic molecules (~10^-6 cm^2/s). We also determined that bromoform increases the membrane thickness and is correlated with the number of molecules penetrating the membrane. Our findings provide insight into bromoform-membrane interactions and provide new testable hypotheses with the goal of peroxisome engineering.

229. Understanding carbonate formation in aqueous solutions at the atomic level via multi-level quantum mechanics/molecular dynamics simulations

Jan-Niklas Boyn, *jboyn@princeton.edu, Emily A. Carter. Mechanical and Aerospace Engineering, Princeton University, Princeton, New Jersey, United States*

Seawater based CO_2 capture provides a promising alternative to traditional air-based pathways by allowing for sequestration and storage in a single step. Carbonate minerals of Ca and Mg cations play a key role in this process by acting as long-term carbon sinks, however, while seawater is oversaturated with respect to the formation of both Ca and Mg carbonates, the former form much more readily than the latter. Here, we apply a recently developed multi-level quantum mechanics/molecular dynamics approach which combines embedded correlated wavefunction (ECW) theory with density functional theory (DFT) molecular dynamics (MD) to elucidate the atomic level processes involved in carbonate formation, allowing for the resolution of both structural dynamic effects and electron correlation with high accuracy. Our results reveal significant differences in the dehydration dynamics of the two cations and the mechanisms through which they form contact ion pairs with CO_3^{2-}. Importantly, calculations at varying pH values reveal an ability to modify the dehydration dynamics of $Mg(CO_3)$ via locally alkaline environments.

230. Computational study of quantum mechanical protein–ligand binding energies using the Molecules-In-Molecules (MIM) method

Sarah Maier[1]*, sarmaier@iu.edu, Bishnu Thapa*[2]*, Jon A. Erickson*[2]*, Krishnan Raghavachari*[1]*. (1) Chemistry, Indiana University, Bloomington, Indiana, United States(2) Eli Lilly and Company, Indianapolis, Indiana, United States*

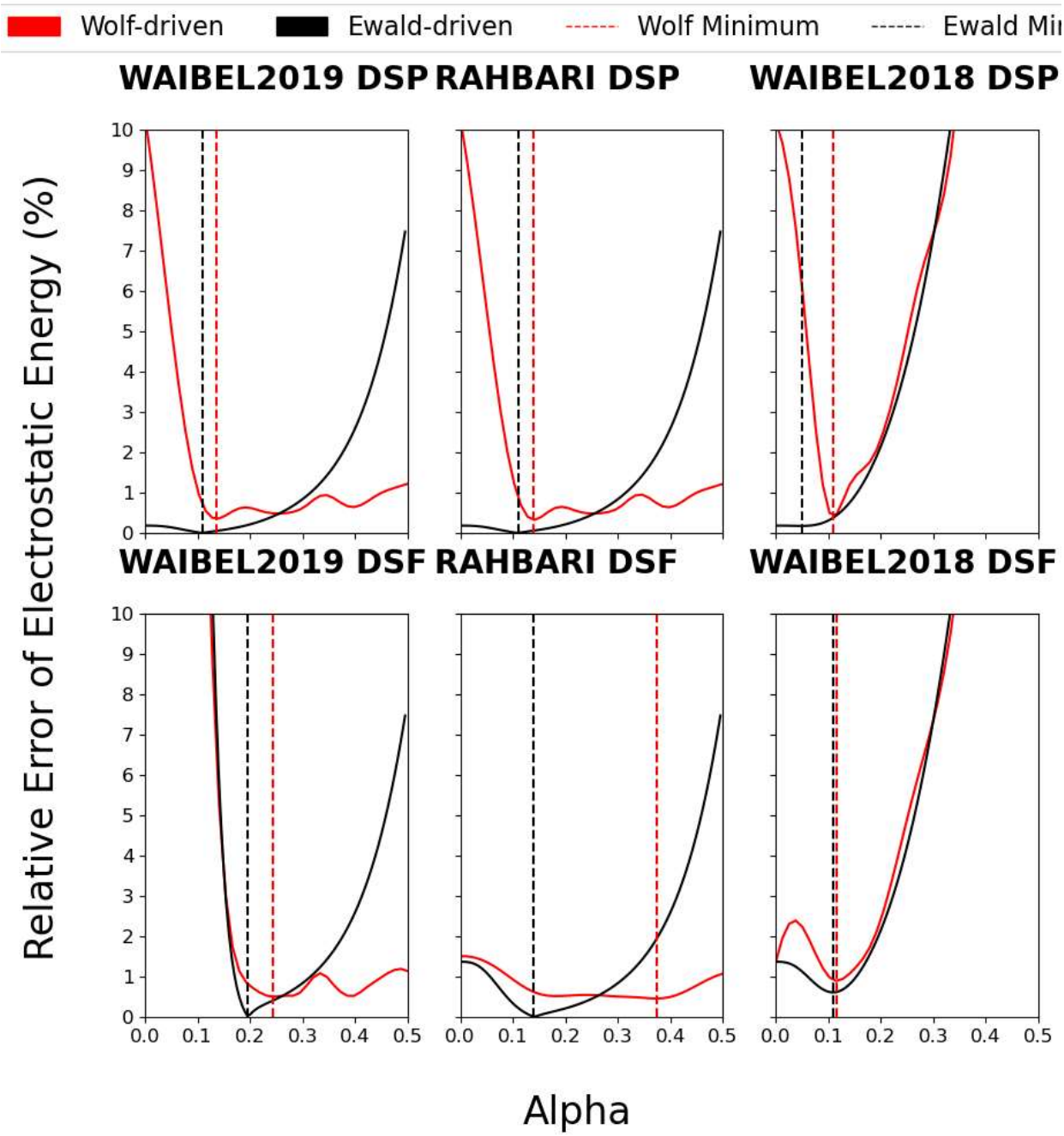
Computational methods which accurately predict protein–ligand binding energies are critical for drug discovery. In the last two decades, advances in chemical modelling have enabled steadily accelerating progress in the discovery and optimization of structure-based drug design. Most computational methods currently used in this context are based on molecular mechanics force fields that often have deficiencies in describing the quantum mechanical (QM) aspects of molecular binding.

Our project demonstrates the competitiveness of our QM-based Molecules-in-Molecules (MIM) fragmentation method for characterizing binding energy trends for several different datasets of protein–ligand complexes. By using molecular fragmentation, the MIM method allows for accelerated QM calculations. We demonstrate that for classes of structurally similar ligands bound to a common receptor, the MIM protocol provides excellent correlation to experiment, surpassing the more popular Molecular Mechanics Poisson-Boltzmann Surface Area and Molecular Mechanics Generalized Born Surface Area methods. The MIM method offers a relatively simple, well-defined protocol by which binding trends may be ascertained at the QM level and is suggested as a promising option for lead optimization in structure-based drug design. Additionally, we present recent progress towards a more complete picture of protein–ligand binding, considering solvation, thermostatistical contributions, and effects from multiple conformations.

231. Assessing electrostatic approximation of binding free energy by Wolf summation

Gregory Schwing[1]*, gregory.schwing@med.wayne.edu, Brad Crawford*[2]*, Mohammad Barhaghi*[3]*, Loren Schwiebert*[1]*, Jeffrey Potoff*[2]*. (1) Computer Science, Wayne State University, Detroit, Michigan, United States(2) Chemical Engineering, Wayne State University, Detroit, Michigan, United States(3) Theoretical and Computational Biophysics, University of Illinois Urbana-Champaign, Urbana, Illinois, United States*

Wolf Summation is an approximation of Ewald Summation for calculating electrostatic energy, only considering molecules within a spherical cutoff, thus reducing the time complexity from $O(n^2)$ to O(n). Wolf has been used to estimate the mixing enthalpy of liquid water-methanol, with the measurable cutoff artifacts having little to no effect on the thermodynamics of the system. However, these artifacts were shown to be magnified under confined systems such as the liquid-vapor interface of water, preventing accurate approximation of the electrostatic potential profile, dipole orientation function, and surface tension. The accuracy of the Wolf approximation is dependent on maintenance of a neutral charge environment surrounding each atom in the system through calibration of a damping parameter, α, and the cutoff length, R_c. The parameters used in the liquid-vapor interface calculations were obtained by selecting the α which best reproduces the instantaneous force of a configuration produced using Ewald Summation. This approach consistently underestimates the optimal α, as reported in Waibel et al., and we have demonstrated in Figure 1 for six different Wolf formulations. A ligand in a binding pocket is a confined system and should be subject to the same pitfalls as the liquid-vapor interface. By correctly identifying the optimal α parameter, the absolute binding free energy can be approximated within 1% relative error. We also demonstrate the performance benefit when treating with large proteins. These findings make Wolf Summation an attractive alternative to Ewald Summation for virtual ligand screening.



Calculating the mean relative error at different alpha values for Ewald-derived configurations (black) versus running short Wolf simulations with different alpha paramters (red) to obtain the ground truth relative error.

232. Quantum electron dynamics: Towards electron control

***Zachary Stewart**, stewa668@msu.edu, AngelaK. Wilson. Chemistry, Michigan State University, East Lansing, Michigan, United States*

With advances in ultrafast spectroscopy come the need to create methodologies to describe phenomena that occur in the relevant attosecond time scale. Quantum effects play a significant role in this regime, and full dynamic modeling of spin trapping can be important. Time-dependent configuration interaction provides a suitable approach to address quantum

effects, with a natural multireference framework and proper representation of spin. Our recent advances in the implementation and use of spin-orbit time-dependent configuration interaction (SO-TDCI) are highlighted.

233. Permeability, energetics and mean first passage time of photosynthetic for metabolite transport in synthetic carboxysomes

Daipayan Sarkar[1], *sarkarda@msu.edu, Christopher Maffeo*[2], *Markus Sutter*[3,4], *Aleksei Aksimentiev*[2,5], *Cheryl Kerfeld*[3,4], *JoshV. Vermaas*[1]*. (1) DOE Plant Research Laboratory, Michigan State University, East Lansing, Michigan, United States(2) Department of Physics, University of Illinois Urbana-Champaign, Urbana, Illinois, United States(3) Molecular Biophysics and Integrated Bioimaging Division, E O Lawrence Berkeley National Laboratory, Berkeley, California, United States(4) Environmental Genomics and Systems Biology Division, E O Lawrence Berkeley National Laboratory, Berkeley, California, United States(5) University of Illinois Urbana-Champaign Beckman Institute for Advanced Science and Technology, Urbana, Illinois, United States*

Carboxysomes are bacterial microcompartments (BMCs), found in cyanobacteria that locally concentrate carbon dioxide (CO_2) to improve the efficiency of the enzyme RuBisCO, a key step towards photosynthetic carbon fixation by the Calvin-Benson-Bassham cycle. The carboxysome shell encapsulates RuBisCO and carbonic anhydrase, where the latter converts water soluble bicarbonate to CO_2, increasing the local concentration of CO_2 for RuBisCO inside the carboxysome. In addition to CO_2, other metabolites such as oxygen, bicarbonate, 3-phosphoglyceric acid and ribulose-1,5-bisphosphate also need to permeate through the carboxysome shell to efficiently perform CO_2 fixation. Quantification of the permeability across the carboxysome currently remains a challenge and is a critical information towards the design of synthetic BMCs. Using a high resolution cryo-EM structure of a synthetic carboxysome shell and unbiased all-atom molecular simulations, we determine the metabolite permeability across the synthetic shell. Against popular belief, we find that the carboxysome itself is not selectively permeable to bicarbonate over carbon dioxide. Next, we calculate the change in free energy using enhanced sampling for metabolite transport across the carboxysome, which sheds light on the energetic cost required for such transport process to occur in photosynthetic bacteria. Finally, to understand how the carboxysome concentrate CO_2 to compensate for the inefficiencies of endogenous RuBisCO, specifically slow turnover rate, and photorespiration, we perform atomic-resolution Brownian Dynamics simulations, to estimate the mean first passage time for CO_2 diffusion in a crowded synthetic carboxysome. The first passage time calculated from ARBD simulations provide insights into the rate of diffusive CO_2 transport inside a RuBisCO packed carboxysome, where the CO_2 point particles interact with the RuBisCO protein. The results suggest that while CO_2 can leak from the carboxysome shell at 10^{-2} cm/s, there is a high propensity for the gas molecule to encounter a RuBisCO protein, before permeating out of the shell. The detailed mechanistic insights from molecular simulations enable us to build a metabolite flux model, based on permeability, change in free energy and first passage time kinetics for CO_2 interaction with RuBisCO inside a crowded environment. Such results would help design and engineer synthetic bacterial microcompartments for a wide range of sustainable energy applications.

234. Multiconfiguration electron-nuclear dynamics on open-shell molecules

Cong Wang[1], *wangcon9@msu.edu, Inga Ulusoy*[2], *Lucas Aebersold*[1], *Angela K. Wilson*[1]*. (1) Chemistry, Michigan State University, East Lansing, Michigan, United States(2) Institute for Scientific Computing, Universitat Heidelberg, Heidelberg, Baden-Württemberg, Germany*

Advances for multiconfiguration electron-nuclear dynamics (MCEND) are described for open-shell systems. Equilibrium distances, total energies, dipole moments, and absorption spectra are presented for diatomic molecules.

235. Halogen bonding and electron-transfer processes involving molecular iodine

***Emmanuel Adeniyi**, emmanuel.adeniyi@bsu.edu, Lauryn Snowden, Sergiy V. Rosokha. Chemistry, Ball State University College of Sciences and Humanities, Muncie, Indiana, United States*

Halogen bonds (HaB) are intermolecular attraction between electrophilic covalently-bonded halogen atoms (also known as HaB donor) and electron-rich species (HaB acceptors). As a result, small fraction of electron density is transferred from the primary Lewis site (electron donor, HaB acceptor) to an acidic Lewis site (electron acceptor, HaB donor). But a whole electron can be transferred from electron donor to electron acceptor in such systems as well. This work aims to study halogen bonds' role in electron-transfer processes between molecular iodine (I_2), and various anilines, and heterocyclic compounds. The UV-Vis measurement demonstrated that adding I_2 electrophiles to the solutions of various amines in dichloromethane resulted in a new absorption band in the range of ~350-480 nm showing complex formation. In acetonitrile, spectral measurements indicated formation of cation-radicals and/or triodide. These spectral features point out that redox reactions take place in acetonitrile. The quantum mechanical calculations were used to elucidate the binding modes and energetics of HaB complex formation and electron transfer reactions in the gas phase and in solutions. Computational data together with the study of kinetics of the redox processes suggested that halogen bonds significantly reduced the activation barriers for electron transfer. The rate constants of such (inner-sphere) processes can be evaluated from spectral, structural, and thermodynamic characteristics of the halogen-bonded associates.

236. Real-time electron dynamics under the influence of strong light-molecule coupling

***Jared Weidman**, weidma10@msu.edu, Angela K. Wilson. Michigan State University, East Lansing, Michigan, United States*

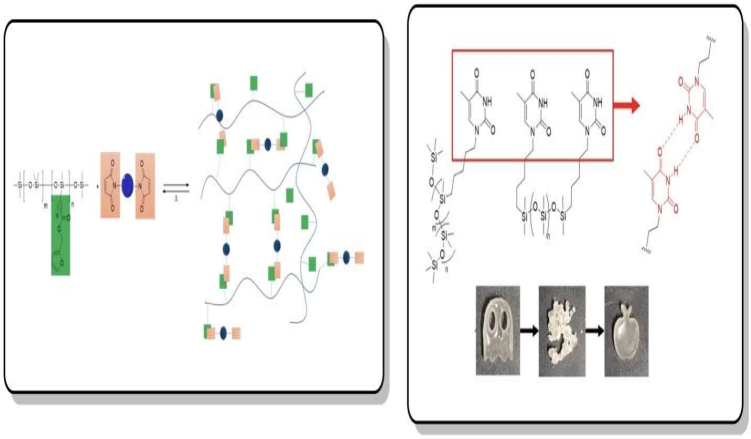
Polaritonic states, formed by resonances between a molecular excitation and a photonic mode of a cavity, have a number of useful properties that offer new routes to control chemical reactivity. In order to understand how these states affect the electron dynamics in molecules, we implement the effects of strong light-molecule coupling into the time-dependent configuration interaction (TDCI) method. The TDCI method is a real-time electronic structure method based on an expansion of the time-dependent wavefunction as a linear combination of time-independent CI eigenstates. The effects of a resonant cavity mode are introduced via a model Hamiltonian, and transitions between states are induced via an external electric field. This method is used to study charge transfer and dipole-switching dynamics in small polar molecules.

237. Increasing sustainability through self-healing and recycling: Extending the lifetime of silicone materials

*Laura J. Voigt[1], Paria Azadi Namin[1], Katie Tucker[1,2], Phoebe Booth[1,2], Julio Trevino[1], **Paul Zelisko**[1], pzelisko@brocku.ca. (1) Chemistry and Centre for Biotechnology, Brock University, St. Catharines, Ontario, Canada(2) Chemistry, Cardiff University, Cardiff, Cardiff, United Kingdom*

Solid silicone materials are typically manufactured by forming cross-links between the individual polymer strands. One method of cross-linking silicones includes using a two-component system, in either a room temperature vulcanization (RTV) process with a tin catalyst, or addition cure system using a platinum catalyst. Although quite effective at cross-linking silicones, both metals in these catalysts must be mined and are non-renewable; tin is also extremely neurotoxic. These metal-based systems are extremely effective at catalyzing the formation of cross-links in silicones, however, the toxic nature of tin and the scarcity and cost of platinum necessitate the need to develop modalities for forming cross-links in silicones that are more cost effective and environmentally benign. Another detriment of silicone materials cross-linked using RTV or addition cure methodologies is that the resulting materials are typically thermoset and cannot be readily remolded or recycled at the end of their useful lifetime. An ideal thermoplastic silicone material would be one that can be healed or undergo remolding with a minimal input of external energy, optimally at room temperature.

This presentation will discuss our recent efforts to synthesize more sustainable solid silicone materials. Our strategy has been to apply chemoenzymatic approaches to produce silicone materials via the Diels-Alder reaction, ideally ones that can cure at room temperature, and to incorporate bio-inspired approaches to cross-linking utilizing DNA bases. The synthetic methodologies to produce these materials, their physical properties, and their capacities for healing and remolding will be discussed.



238. Stereolithography with lignin and cellulose: Designing chemistry for 3D printed continuous and aligned fiber composites that mimic plants

Stephen C. Chmely*, sc411@psu.edu, Evan Battisto, Mostafa Rohi, Aditi Arya, Jeffrey M. Catchmark. Agricultural and Biological Engineering, The Pennsylvania State University, University Park, Pennsylvania, United States*

3D printing is an umbrella term that encompasses several specific methods to build parts layer-by-layer. These vary based on materials used, surface morphology, resolution range, manufacturing speed, cost, and many others. Stereolithography (SLA) systems have made it possible to fabricate large and complex 3D objects with high surface resolution and isotropic performance properties. My group and I envision new cellulose- and lignin-containing composites that have the potential to be sustainable while simultaneously having exceptional performance properties since they mimic the hierarchical structure of plant cell walls. My talk will summarize my group's efforts to 3D print composite materials that contain biomass-derived lignin and cellulose nanomaterials. I will discuss our efforts to produce lignin-containing photopolymerizable matrix materials, which include using technical lignins such as organosolv and Kraft lignin. We have developed synthesis strategies to add photopolymerizable moieties

directly to lignin, and we characterize their chemical and mechanical properties using NMR spectroscopy and mechanical testing. Moreover, I will summarize our efforts to control nanointerfacial interactions between nanocellulose and photopolymers using amphiphilic surfactants and other synthesis strategies. I will discuss our current results and speculate on future directions to develop 3D printable plant-based nanocomposites that mimic cell wall architecture.

239. Silicon-based hybrid photo-responsive network polymers toward reusable environmental sponges

***Joseph C. Furgal**, furgalj@bgsu.edu, Cory B. Sims, Mehdi Erfani Jazi. Chemistry, Bowling Green State University, Bowling Green, Ohio, United States*

Recent work in the Furgal Laboratory at BGSU is focused on the development of photoactive silicon-based materials with high porosity, phototriggered formation of siloxane bonds, and the recycling of preformed polymeric systems such as silicones. We have developed a set of photoswitchable Q-silsesquioxane based hybrid 3D polymeric smart sponges with azobenzene actuation units. Reversible UV triggered actuation of up to 18.3% has been achieved, with excellent recovery using visible light to the native state. These smart materials also offer reversible modulus switching from 160 kPa in the swollen state to 500 kPa in the UV activated state. Various substances were tested for uptake and release capabilities with polarity and size having the greatest impact on performance. The materials have been functionalized with various groups to embed solvent/substance selectivity in uptake/releases and alterations in actuation response processes. The photo-triggered behaviors give these materials high potential for use as reusable environmental remediators (i.e. PFAS) and in soft robotics applications.

240. Computational investigation of charge transfer in ferrocene-based polymer materials

***Heidi P. Hendrickson**[1], hendrihe@lafayette.edu, Theresa Chua[1], LizaJ. Welch[1], Congyu Qian[1], Jeremy Feldblyum[2]. (1) Chemistry, Lafayette College, Easton, Pennsylvania, United States(2) Chemistry, University at Albany, Albany, New York, United States*

In this work, we study interfaces in ferrocene-based (Fc) polymers for use in bulk heterojunction (BHJ) solar cells, with the aim to improve control over BHJ device morphologies. We use density functional theory (DFT) and time-dependent (TD)DFT calculations to investigate the potential to tune the charge transfer rates between these materials and non-fullerene acceptors. Results in this study provide molecular-level insights into the charge transfer and transport properties of Fc-based polymer materials and their potential for use in BHJ devices.

241. Self-healing polymers for life cycle management

***Abdon Pena-Francesch**, abdon@umich.edu. Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan, United States*

Polymers have become ubiquitous in our modern society, dominating many industries in the packaging, textile, and healthcare sectors. However, most polymer consumer products exhibit durability problems that shorten their lifetime, resulting in their premature discarding and in the accumulation of mismanaged solid waste (from landfills to microplastics in oceans). Particularly, elastomers are vulnerable to mechanical damages (puncture, cracks, scratches, etc.) that compromise their structural integrity, deteriorate their properties, and ultimately

terminate the product function before its expected end-of-life. Our group is designing dynamic polymer networks based on reversible crosslinking and supramolecular chemistry to provide new materials-based solutions to the life-cycle management of polymers and prolong their operational lifetime. We have developed polyurethane-based elastomers with dynamic covalent disulfide bonds that recover their properties after extreme mechanical damage. Tuning their structure and healing properties open new strategies for manufacturing and assembly of soft elastomers with enhanced durability and operational lifetime. We demonstrate their application in soft wearable sensors for personal UV dose monitoring.

242. Electrochemical upcycling of poly(vinyl chloride)

***Rahul K. Jha**, rkjha@umich.edu, AnneJ. McNeil. Chemistry, University of Michigan, Ann Arbor, Michigan, United States*

Despite being the third highest production-volume polymer, poly(vinyl chloride) (PVC) has the low recycling rate. Leakage of carcinogenic plasticizer and generation of hydrochloric acid possess safety hazard that limit mechanical recycling of PVC plastics. Among various chemical recycling methods, electrochemical approaches include direct use of electrons, which is inexpensive, non-toxic and has a small ecological footprint. Previously, the McNeil group reported a redox-mediated approach to recover chlorine atoms of PVC under electroreductive conditions and then directly repurposed as feedstock in a tandem electrooxidative chlorination reaction. However, the unstable redox mediator led to use higher PVC loading (8 equivalents) as compared to the arene substrates (1 equivalent) to improve the reaction efficiency. The reaction worked without a redox mediator with lower yield of chlorinated arenes as compared to the mediated reaction, however, the mechanism of an *unmediated* reaction is not clear. We have been exploring the unmediated reaction to gain mechanistic insights and improve the reaction efficiency. Herein, the dechlorinated polymer is studied by IR spectroscopy, elemental analysis, and thermogravimetric analysis. The efforts to repurpose dechlorinated PVC to value-added commodity polymers are ongoing.

243. MALDI-MS based screening for PFAS uptake by bacteria

***Irfath Jasmin Reza**, rezaij@msu.edu, Aidan J. Reynolds, Helen J. O'Shaughnessy, Tian Qiu. Department of Chemistry, Michigan State University, East Lansing, Michigan, United States*

Per- and poly-fluoroalkyl substances, widely known as PFAS, are one of the major environmental challenges of recent times due to their non-degradable nature, exposure to biological organisms, and adverse health effects. There have been studies showing the effects of PFAS on eukaryotic cell membrane properties and membrane permeability as potential PFAS toxicity mechanisms. However, the effects of PFAS exposure on microbial communities, their membrane integrity, viability, and different biological functions are not well understood yet. In this study, we aim to develop a high-throughput matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) screening method for detecting the PFAS uptake by a model bacterium, *Escherichia coli*, using different sampling techniques. Initial studies have shown good detection of several PFAS species through MALDI-MS coupled with trapped-ion mobility spectrometry (TIMS) with PFAS standards. We are currently exploring the toxicity of several PFAS of interest on bacteria and evaluating the effect of biological matrices and different sampling techniques on the PFAS detection and quantification.

244. Elucidation of fungal cell walls structure and remodeling by antifungal drugs using solid-state NMR

Isha Gautam[1]*, Isha.gautam7@gmail.com, Liyanage D.Fernando*[1]*, Malitha Widanage*[1]*, Andrew Lipton*[3]*, Nancy M. Washton*[2]*, Frederic Vigier*[2]*, Jean P. Latgae*[4]*, Tuo Wang*[1]*. (1) Chemistry, Michigan State University, East Lansing, Michigan, United States(2) National High Magnetic Field Laboratory, Tallahassee, Florida, United States(3) Pacific Northwest National Laboratory, Richland, Washington, United States(4) Département de Mycologie, Unité des Aspergillus, Paris, France*

Invasive fungal infection has high occurrence and mortality among immunocompromised patients. Most currently available antifungal agents have limited efficacy, relatively high toxicity, and emerging resistance. The carbohydrate-rich cell wall is a promising target for antifungal drugs, but we need in-depth knowledge of the biomolecules of the cell walls, structure, assembly, and dynamics. To overcome this barrier, we have explored solid-state NMR (ssNMR), a nondestructive and atomic-resolution technique, for characterizing the polysaccharides and proteins in intact and living fungal cells. The method allowed us to understand the structural remodeling of fungal cell walls in response to mutations, antifungal drugs, and different morphological stages of the life cycle.

We first combined ssNMR, functional genomics, and biochemical analysis to identify the functionality and diversity of cell wall carbohydrates in *Aspergillus fumigatus* and four mutants depleted of major structural polysaccharides. We revealed a rigid inner core of the cell wall formed by tightly associated chitin and α-1,3-glucan, which are embedded in the soft matrix of β-glucans and capped by a mobile outer shell rich in galactosaminogalactan and galactomannan. Second, we characterized the structural responses of *A. fumigatus* cell walls to the treatment of the caspofungin drug. The drug-treated cell walls are highly hydrophobic and stiff to resist external stress. The fungi also increased chitin content and produced new forms of α-glucans to compensate for the loss of β-glucan due to drug inhibition. Third, we found that the crystalline structure of chitin bears intrinsic heterogeneity, which is resistant to caspofungin treatment. We documented the unique structural fingerprints of chitin across six fungal species, including *A. fumigatus*, *Aspergillus sydowii, Aspergillus nidulans*, *Rhizopus delemar*, *Candida albicans,* and *Candida auris.* Finally, we characterized the cell wall organization in different morphotypes that varied along with the life cycle and growth conditions, revealing a highly conserved carbohydrate core in both conidia and mycelia. These bioanalytical techniques yield essential information about carbohydrate components and structures of the cell walls and their packing interfaces at atomic levels that can serve as potential targets for discovering novel antifungal compounds with broad spectrums and improved efficacy.

245. Green approach for extracting per- and poly- fluoroalkyl substances from water

David Bwambok*, dkbwambok@gmail.com, Nicole Dominguez. Ball State University, Muncie, Indiana, United States*

Per- and polyfluoroalkyl substances (PFAS) are chemicals that persist in the environment and have resulted in water contamination. These persistent PFAS pollutants include perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS). These chemicals have high chemical and thermal stability, as well as lipophilic and hydrophilic properties. Due to these chemical properties, PFAS are used in polymers, surfactants, film-foams in fire extinguishers, textiles, and coatings. The widespread use and resistance of PFAS to degradability enable these chemicals to accumulate in the environment and have been detected in ground water, surface water, ocean waters and even marine organisms. Their toxicological impact is a big concern and they have been implicated as a cause for

reproductive toxicity that is a threat to aquatic life and humans. This study presents a green approach for extracting PFAS from water. This method is based on extraction of PFAS chemicals into paramagnetic ionic liquids medium and removal from water using an external magnet. This approach alleviates the use of toxic organic solvents used for liquid-liquid extraction. The possibility of recycling paramagnetic ionic liquids for multiple extractions is an additional advantage of this method. The toxicological evaluation of PFAS pollutants and paramagnetic ionic liquids medium was carried out.

246. Development of a yeast-based assay for bioavailable nutrients

***Heather Shepherd**, hmiller9@nd.edu, Matt Trentman, Jennifer Tank, Jennifer Praner, Anissa Cervantes, Priya Chaudhary, Jonah Gezelter, Allyson Marrs, Kathryn Myers, Jonathan Wlsh, Yueh-F . University of Notre Dame, Notre Dame, Indiana, United States*

Preventing eutrophication of inland freshwater ecosystems requires quantifying the excess nutrient (i.e., phosphorus (P) and nitrogen (N)) content of the streams and rivers that feed them. Identification of these at-risk waterways will help prevent harmful algae blooms that make drinking water unsafe. Here we present a novel method for measuring the more relevant bioavailable P (BAP). Where typical methods for measuring P assess soluble reactive P (SRP) or total P (TP) and require expensive analytical techniques that produce hazardous waste, this assay utilizes the growth of familiar baker's yeast, avoids production of hazardous waste, and reduces cost relative to measurements of SRP and TP. The yeast BAP (yBAP) assay takes advantage of the observation that yeast density at saturating growth increases linearly with provided P. We show that this relationship can be used to measure P in freshwater in concentration ranges relevant to eutrophication. In addition, we measured yBAP in water containing known amount of fertilizer and in samples from agricultural waterways. We observed that the majority of yBAP values were between those obtained from standard SRP and TP measurements, demonstrating that the assay is compatible with real-world settings. To expand the utility of such an assay, we are applying the same principles to measure the excess nutrient nitrogen, a large component of eutrophication of saltwater systems, using the yeast strain *Blastobotrys adeninivorans,* which is capable of metabolizing more complex forms of N. In either system the cost-effective and nonhazardous nature of yeast-based assays suggests that they could have utility in a range of settings, offering added insight to identify water systems at risk of eutrophication.

247. Detection and quantification of poly- and perfluoroalkyl substances using MALDI-TOF with trapped ion mobility–a novel approach to *in-situ* analysis of perfluoroalkyl substances

***Aidan J. Reynolds**, aidanreynolds1122@gmail.com, Tian Qiu. Chemistry, Michigan State University, East Lansing, Michigan, United States*

Poly- and perfluoroalkyl substances (PFAS) are a class of organic compounds that have attracted global attention for their persistence in the environment and exposure to biological organisms, and have been labeled "forever chemicals" as a result. There is an urgent need for quantification and characterization of PFAS due to their adverse health effects. The fate of these chemicals in organisms is not well understood and requires the development of a method for *in-situ* analysis. The localization of PFAS species combined with toxicological studies can help elucidate the mechanisms of toxicity for these compounds. Herein we present the preliminary results for an imaging mass spectrometry (IMS) method by matrix-assisted laser desorption/ionization (MALDI), utilizing trapped ion mobility (TIMS) and time of flight (TOF) for multi-dimensional mass spectrometry analysis of PFAS. We selected several PFAS

candidates from both perfluorocarboxylic acid (PFCA) and perfluorosulfonic acid (PFSA) families for method development using negative ion mode analysis. Method development and validation has been centered around the optimization of instrumental parameters and matrix composition to detect several PFAS–primarily long- and short-chain PFCA and PFSA compounds. We aim to expand the number of PFAS candidates in our list to include non-perfluoroalkyl acids and non-linear PFAS species. Ultimately, this research will lead to the creation of PFAS calibration curves utilizing different normalization techniques to provide the most accurate quantification across heterogenous biological samples.

248. Optimizing detection of underivatized neurochemicals using MALDI-TIMS-TOF for mass spectrometry imaging applications

***Ryutaro E. Jacobson**, jacob433@msu.edu, Tian Qiu. Chemistry, Michigan State University, East Lansing, Michigan, United States*

Understanding the distribution of neurochemicals in biological systems is important for identifying pathways related to signaling and disease pathophysiology in the central and peripheral nervous systems. In particular, the biosynthesis and metabolism of neurochemicals are being revealed as part of the chemical language for inter-kingdom crosstalk between the microbiome and gut-brain axis. Mass spectrometry imaging (MSI) using matrix-assisted laser desorption/ionization (MALDI) is a powerful tool to provide spatially resolved images of analytes *in situ*. Many current methods for neurotransmitter detection involve derivatizing agents which must be tailored to specific analyte types, reducing sensitivity and coverage of analytes in detection. We aim to develop a MALDI-MS method for detection and quantification of underivatized neurochemicals using a MALDI ionization source coupled to a trapped ion mobility-time of flight (TIMS-TOF) mass spectrometer. We are currently optimizing instrumental parameters related to the MALDI laser and TIMS tunnel while testing various MALDI chemical matrices for the optimal detection of neurochemicals. Optimized conditions will then be used to generate calibration curves and different data normalization methods will be tested in preparation for quantitative *in situ* MSI on biological samples related to the gut-brain axis.

249. Metal-catalyzed reactions as undergraduate research topics

***Jocelyn P. Lanorio**, jocelyn.lanorio@ic.edu. Chemistry, Illinois College, Jacksonville, Illinois, United States*

The use of a variety of metal complexes containing ruthenium, nickel, and copper complexes are important in homogeneous catalysis. Our group has focused on reactions that are appropriate for the resources, equipment, and level of undergraduate students. These reactions include cross-coupling reaction, bioconjugation (click chemistry), and hydration reactions. These types of reactions are important as they provide products that are either building blocks of pharmaceutical drugs or products that are biologically important. This talk will discuss the different research projects performed by undergraduate Chemistry/Biochemistry/Biology students at Illinois College, a Predominantly Undergraduate Institution.

Water-soluble ruthenium complexes were investigated as hydration catalysts of nitriles. Preliminary investigation identified some ruthenium-phosphine hydration catalysts that exhibited catalytic activities with only water as reagent.

Copper-catalyzed azide-alkyne cycloadditions (CuAAC) produce 1,4-disubstituted 1,2,3-triazoles, molecules that have many applications in pharmaceuticals. We tested various copper complexes for ease of use as homogeneous catalysts at various conditions. The 1,4-

disubstituted triazole products were obtained in moderate to excellent yields. We found that there is little that changes the outcome of the reaction upon variations in solvent and temperature conditions.

A series of nickel complexes were successfully synthesized and characterized. Most of the prepared nickel complexes showed efficiency as catalysts in the chosen Suzuki-Miyaura cross-coupling reaction.

Characterization of products and progress of reactions were done using chromatographic and spectroscopic techniques such as TLC, IR, GCMS and NMR spectroscopy.

250. Effects of intramolecular interactions on electrocatalytic CO2 reduction

***Jukai Zou**, zhoujk@umich.edu, Weixuan Ne, Charles C. McCrory. University of Michigan, Ann Arbor, Michigan, United States*

Heterogenizing molecular catalysts within multidimensional architectures is a promising strategy of developing new catalytic materials for the electrochemical CO_2 reduction reaction (CO_2RR). The goal is to develop multidimensional catalyst architectures that maintain the selectivity of discrete, molecular catalysts, but also possess high activity and stability of multi-site heterogeneous materials. However, developing such systems requires us to first understand how the interactions between molecular building units influence catalytic activity and selectivity in multimetallic assemblies. To this end, we have synthesized a series of homo- and heterobimetallic Co complexes with pyridyldiimine (PDI)-based ligands to investigate the interactions between the discrete building units. Through cyclic voltammetry and electrocatalytic studies, we have identified three interactions between molecular units: charge delocalization across the extended bimetallic structure, electronic coupling between the catalyst active sites, and intramolecular electrostatic effects. The catalytic activity of the homobimetallic bi-[Co(PDI)] complex is more than an order of magnitude higher than that of the monometallic parent complex, [Co(PDI)], due to the effects of these interactions. Through systematic modifications of the monometallic and bimetallic systems, we evaluated the individual effects of each interaction and concluded that the intramolecular electrostatic effects are likely the largest influence on the increased activity in the bimetallic systems. In particular, an extended bimetallic complex with weaker electronic coupling (bi-ex-[Co(PDI)]) has slight difference in catalytic activity compared to bi-[Co(PDI)]; whereas another bimetallic complex with mainly electrostatics (bi-[ZnCo(PDI)]) exhibits around two times higher activity than that of bi-[Co(PDI)]. DFT calculations of CO_2 binding modes are also consistent with the observed electrochemical results. Our work highlights a promising catalyst design strategy for heterogeneous, multidimensional architectures in which catalytic capacity is enhanced by incorporating intramolecular electrostatics into the backbone of multidimensional structures.

251. Electropolymerized molecular electrocatalyst films for selective nitrate reduction to ammonia

***Maiko Akari**, mjlunn@umich.edu, Jeremy Kallick, Charles C. McCrory. University of Michigan, Ann Arbor, Michigan, United States*

Nitrate pollution from industrial and agricultural runoff can have drastic negative effects on water bodies and human drinking water. Using electrocatalytic nitrate reduction, we can convert nitrate waste into ammonia that can be used as fertilizer and chemical feedstocks. Our lab has developed electropolymerized molecular films with early transition metal catalysts that catalyze the 8-electron reduction of nitrate to ammonia with high selectivity (>90% Faradaic efficiency) at rates comparable to state-of-the-art solid-state electrocatalysts. In this

presentation, we will discuss the development of this catalyst system and effects of mass transport and pH, and efforts toward uncovering the mechanism of electrochemical nitrate reduction by early transition metals. These studies allow us to illustrate how the local chemical environment influences the activity and selectivity for the multi-electron transformation of nitrate. Studying the effects of local chemical environment on activity and selectivity for nitrate reduction can better interpretation of the mechanism and design of molecular electrocatalysts.

252. Design nanoalloy catalysts for converting lignin into value-added chemicals guided by inverse molecular design theory

***Dequan Xao**, dxiao@newhaven.edu. Department of Chemistry and Chemical Engineering, University of New Haven, West Haven, Connecticut, United States*

Inverse molecular design approaches based on quantum chemistry have emerged as an intelligent computational approach for materials discovery. In this presentation, I will apply the inverse molecular design theory for the experimental design of sustainable nanoalloy catalyst for converting lignin to value-added chemicals such as polymer building blocks. The approach of inverse molecular design theory aims at searching for optimum points on the hypersurfaces defining the property-structure relationships in catalysis, and then mapping out the catalytic structures at the optimum points, leading to enhanced efficiency and success rate for catalyst discovery. The designed catalyst was verified by catalyst synthesis and characterization and reaction analysis, showing significantly enhanced catalytic activity than the reference catalyst. Our results indicate that the inverse molecular design approach can provide promising catalyst design solutions on producing sustainable fine chemicals from natural or man-made waste polymers.

253. Catalytic applications of diphosphine complexes immobilized in metal-organic frameworks

***Jordon Hlliard**, hilliard.100@osu.edu, Casey R. Wade. Chemistry and Biochemistry, The Ohio State University, Columbus, Ohio, United States*

The structural and chemical tunability of metal-organic frameworks (MOFs) makes them promising platforms for single-site heterogeneous catalysis. Our group has previously investigated MOF assembly from metallolinkers based on catalytically-active transition metal diphosphine pincer complexes. The immobilized pincer complexes benefit from site isolation and exhibit marked improvements in catalytic activity and stability compared to homogeneous analogues. This presentation will discuss our recent use of postsynthetic X-type ligand exchange strategies to append transition-metal catalysts in MFU-4*l*-OH ($[Zn_5(OH)_4(btdd)_3]$, $btdd^{2-}$ = bis(1,2,3-triazolo)dibenzodioxin). We recently reported the encapsulation of a palladium diphosphine pincer complex (H_3-P^NN^NP-PdI) in MFU-4*l*-OH, ($Zn_5(OH)_{4-nx}(btdd)_3(H_{3-n}P^NN^NP\text{-PdI})_x$, x = 0.06–0.5, n = 2.75), via a Brønsted acid-base reaction with the carboxylic acid functional groups of the complex and the Zn–OH nodes of the framework. This approach allows for precise control of catalyst loading in the framework which minimizes diffusion-limited behavior. Following oxidative ligand exchange to replace I^- with weakly-coordinating BF_4^-, we observe initial catalytic rates comparable to the homogeneous P^NN^NP-Pd analogue. This presentation will also feature our recent work in incorporating bis(diphenylphosphino) ligands with amino acid backbones (Gly, Ala, Val, and Phe) in MFU-4*l*-OH. Subsequent postsynthetic metalation with Rh, Co, and Fe precursors have generated platforms that are currently being evaluated for enantioselective catalytic transformations.

254. Development of high-throughput workflows in MOF-catalyzed organic transformations

***James R. Bour**, hf0697@wayne.edu. Chemistry, Wayne State University, Detroit, Michigan, United States*

This presentation describes the development and preliminary application of high-throughput workflows for the evaluation of metal-organic framework (MOF) catalysts in organic transformations. Owing to their extensive structural diversity and tunability, MOFs have attracted significant attention for potential applications in catalysis where catalyst microenvironment dictates reaction selectivity. However, identification and optimization of effective MOF catalysts in such applications remains challenging. Scale limitations in many MOF syntheses and their poor solution-phase processability complicate catalyst optimization through conventional high-throughput activity screens. Here we present a strategy for the rapid and small scale (<500µg) dosing of MOF catalysts into reactor wells. This method is precise and accurate for dosing catalysts on scales down to 100ug/reaction without significantly compromising MOF crystallinity or porosity. The application of this approach to the identification of a MOF-based CH oxidation catalyst is presented.

255. Rational design of redox mediators for enzymatic bioelectrocatalysis from the ground up

*Lincoln Memeri, **David Hckey**, dhickeychem@gmail.com. Chemical Engineering and Materials Science, Michigan State University, East Lansing, Michigan, United States*

Successful application of emerging bioelectrocatalysis technologies depends upon an efficient electrochemical interaction between redox enzymes as biocatalysts and conductive electrode surfaces. One common approach to establishing such enzyme-electrode interfaces employs small molecular redox mediators to act as electron shuttles between an enzyme active site and electrode surface. Furthermore, redox mediators can be incorporated into polymer hydrogels that are used as an immobilization matrix for redox enzymes. These interfaces have been shown to protect enzymes and improve their bioelectrocatalytic efficiency. The key limitation in assembling enzyme-electrode interfaces for bioelectrodes is the lack of proper redox mediator design procedures. The current design method is solely based on a guess-and-check approach for maximizing the homogenous electron transfer rates. Consequently, a better understanding of enzyme-mediator interactions will lead to more rapid, efficient, and effective methods for the design of novel enzymatic redox mediators.

We will describe our current efforts in identifying structure-function relationships in redox mediators that control bioelectrocatalytic activity in a model redox enzyme, glucose oxidase (GOx). Based on a library of quinone-based redox mediators, we have developed a quantitative structure-activity relationship (QSAR) model that highlights the importance of mediator redox potential and molecular area as key parameters predicting the activity of quinone/GOx-based electroenzymatic system. Additionally, rapid scan stopped-flow spectrophotometry was used to provide fundamental insights into nature of the reaction between quinone and the flavin adenine dinucleotide (FAD) cofactor of GOx. Finally, we will describe our most recent efforts to utilize molecular dynamics simulations to identify mass transport bottlenecks for redox mediators diffusing into the active site of GOx, and we will present possible mediator design strategies to overcome these barriers.

256. Optogenetic and chemogenetic sensors and tools for studying brain signaling

***Wenjing Wng**, wangwenjing0410@gmail.com. University of Michigan, Ann Arbor, Michigan, United States*

G-protein coupled receptors (GPCRs), including opioid receptors and dopamine receptors, play critical roles in neuromodulation. It remains a major challenge to record or manipulate GPCR signaling events both with high spatial resolution and across a large brain volume. My research group is interested in designing integration sensors that can integrate the neuromodulator signal into a permanent mark in the cells for further investigation, such as high spatial resolution imaging analysis across the brain. We have designed an opioid sensor called SPOTIT that can integrate the opioid signal and generate a green fluorescence mark. We are currently extending the SPOTIT design to detect other neuromodulators for imaging analysis across the brain. Additionally, we are engineering chemical-dependent protein switches to enable the design of genetically-encoded chemical-activated opioid peptides. They will allow cell type-selective manipulation of opioid receptors to study their causal-effect on pain modulation and addition.

257. Using small molecule anti-cancer drugs to probe mechanisms of cancer cell death

*Jeffrey Books, Florina Gjcaj, Myles Harris, Destiny Poffett, **Mara R. Livezey**, livezemr@udmercy.edu. Chemistry and Biochemistry, University of Detroit Mercy College of Engineering and Science, Detroit, Michigan, United States*

While most small molecule anti-cancer drugs trigger apoptotic cell death, many cancers are resistant, or develop resistance to this kind of cell death. Therefore, identifying and understanding small molecules that trigger alternative death pathways, such as autophagy and necrosis, is of interest. We study a small molecule, BHPI, that triggers strong and sustained activation of the anticipatory unfolded protein response, ATP depletion, and eventual necrotic cell death. There is some evidence showing BHPI also inhibits autophagy at long time points. It is currently unclear if inhibition of autophagy contributes to BHPI's ability to induce necrotic cell death in cancer cells. This study aims to elucidate crosstalk between the anticipatory unfolded protein response, necrosis, and autophagy.

358. Chemical tools to study cell biology: Kinase-catalyzed labeling

***Mary Kay Plum**, pflum@wayne.edu. Wayne State University, Detroit, Michigan, United States*

Kinases are key enzymes in cell signaling with clear roles in biological events and disease states. In fact, kinases are arguably the most important drug target of our generation. However, studies on kinases and cell signaling are limited by the paucity of tools available to fully characterized kinase activity. Kinases mediate their influence on cell signaling by catalyzing phosphorylation of substrate proteins using adenosine 5'-triphosphate (ATP) as a cosubstrate. Our laboratory recently uncovered that kinases promiscuously tolerate as cosubstrates modified ATP analogs that contain a functional tag at the terminal phosphoryl. Exploiting this new property of kinases, we developed kinase-catalyzed labeling reactions to detect substrates in cell lysates. Kinase-catalyzed biotinylation using an ATP-biotin probe was employed to monitor and visualize phosphoproteins in cells. In addition, kinase-catalyzed photocrosslinking using an ATP-arylazide probe facilitated kinase-substrate identification. In this talk, I will describe these new technologies to study kinase activities in cells, along with our recent efforts to utilize ATP analogs for kinase-substrate identification and phosphoproteomics applications. By developing kinase-catalyzed labeling, we are pioneering new chemical tools to probe kinase activity and map the cell signaling governed by kinases in both normal and diseased states.

259. Structure of the human nuclear pore complex

***Shyamal Msalaganti**, mosalaga@umich.edu. University of Michigan, Ann Arbor, Michigan, United States*

Structural biology has relied on the overexpression and purification of proteins and protein complexes of interest. However, many cellular complexes are not amenable or lose functional relevance upon purification. The combination of cryo-focused ion beam milling, a revolutionary new sample preparation method, together with cryo-electron tomography, allows us to explore unperturbed cellular landscapes and determine the structure of protein complexes directly in the cellular environment (in situ). Here by combining artificial intelligence based structure prediction with in situ structure biology, we provide a high-resolution near-complete architectural model of human nuclear pore complex scaffold.

260. Cholesterol homeostasis and TCDD-induced, AHR-mediated liver injury

***John J. LaPes**, lapres@cns.msu.edu. Biochemistry and Molecular Biology, Michigan State University, East Lansing, Michigan, United States*

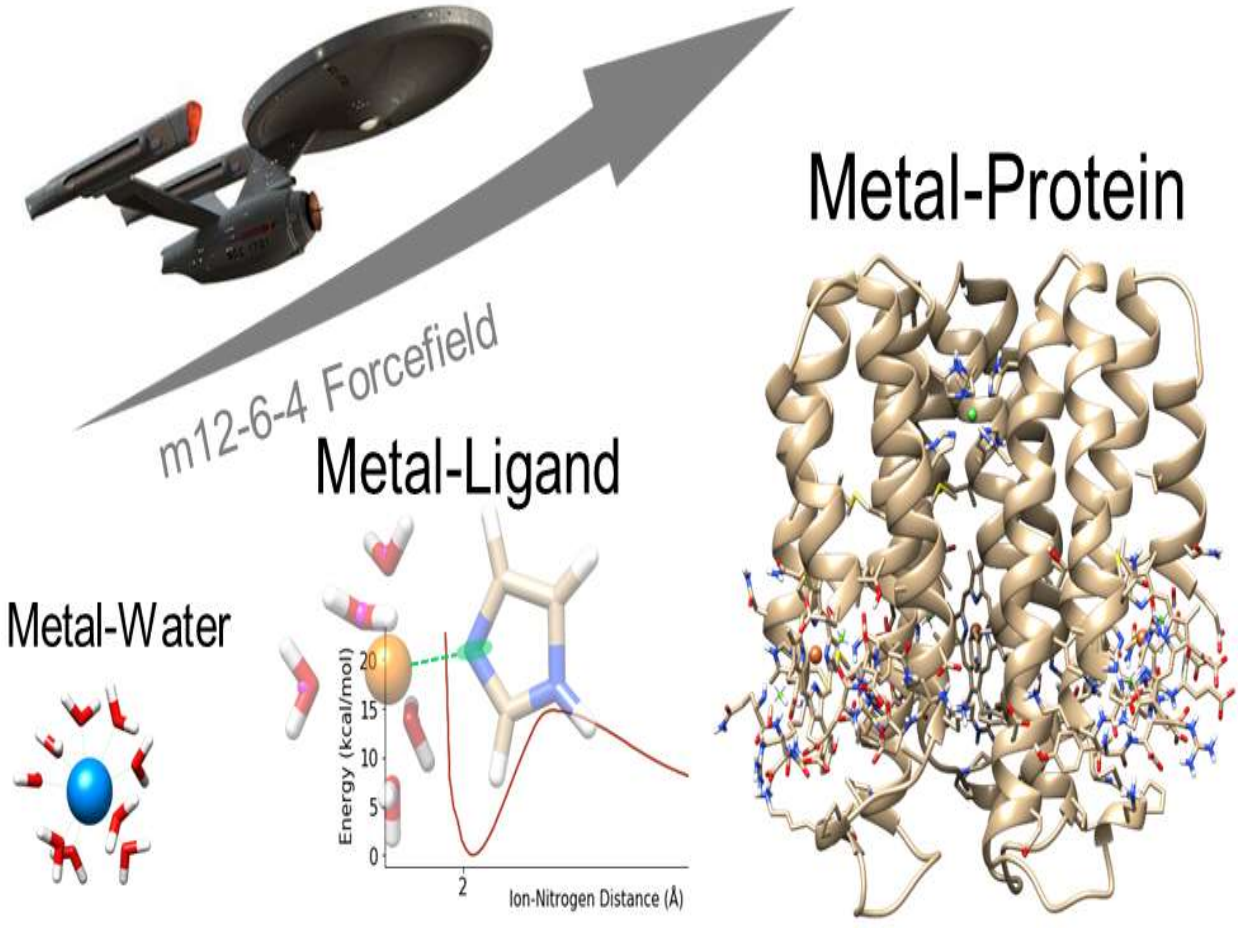
Non-alcoholic fatty liver disease (NAFLD) is a growing worldwide epidemic. NAFLD pathogenesis is associated with a group of conditions that is linked to heart disease, diabetes, stroke and cholesterol dysregulation, known as to metabolic syndrome (MetS). Interestingly, mice exposed to planar aromatic hydrocarbons, such as 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) have disrupted cholesterol homeostasis and can phenotypically mimic many aspects of NAFLD and MetS. Most, if not all, of the TCDD-induced liver damage occurs due to activation of the aryl hydrocarbon receptor (AHR). The AHR is a ligand-activated transcription factor and member of the Per-ARNT-SIM (PAS) superfamily of environmental sensors. Importantly, the AHR has also been linked to cholesterol dysregulation and increased risk of MetS in humans. Our laboratory has used genome-wide association studies, both human and rodents, to demonstrate a link between the AHR, cholesterol homeostasis, and NAFLD progression. These results have shown that AHR-mediated regulation of 3-Hydroxy-3-Methylglutaryl-CoA Reductase (HMGCR), the rate-limiting step of cholesterol synthesis, plays an important role in TCDD-induced liver injury. In addition, the results demonstrate that simvastatin, a competitive HMGCR inhibitor, can alter TCDD-induced toxicity, and in some treatment paradigms, make it worse. Using single nuclei RNA sequencing we have shown that simvastatin co-exposure alters the cellularity of the liver and the data suggest that a change in inflammation and metabolic signaling explain these differences compared to TCDD alone. Overall, the research demonstrates that TCDD-induced, AHR-mediated liver damage involves cholesterol homeostasis and suggest that people taking statins are at an increased risk of liver damage cause by certain environmental pollutants.

261. Accurate predictions on metal diffusion and metal-water-ligand-protein interactions

***Zhen L**[1], lizhen6@msu.edu, KennethM. Merz[1,2]. (1) Chemistry, Michigan State University, East Lansing, Michigan, United States(2) Biochemistry and Molecular Biology, Michigan State University, East Lansing, Michigan, United States*

Accurately predicting the behavior of a metal ion in a protein system has always been the holy grail of the computational chemistry community. To achieve this ultimate goal, three consecutive projects have been conducted recently to provide pivotal information and close the gap between metal-water system and metal-protein system. First, using an automatic workflow, diffusion coefficients of 15 ions in four water models were predicted. This work systematically tested all combinations of parameter sets and water models, due to the strong

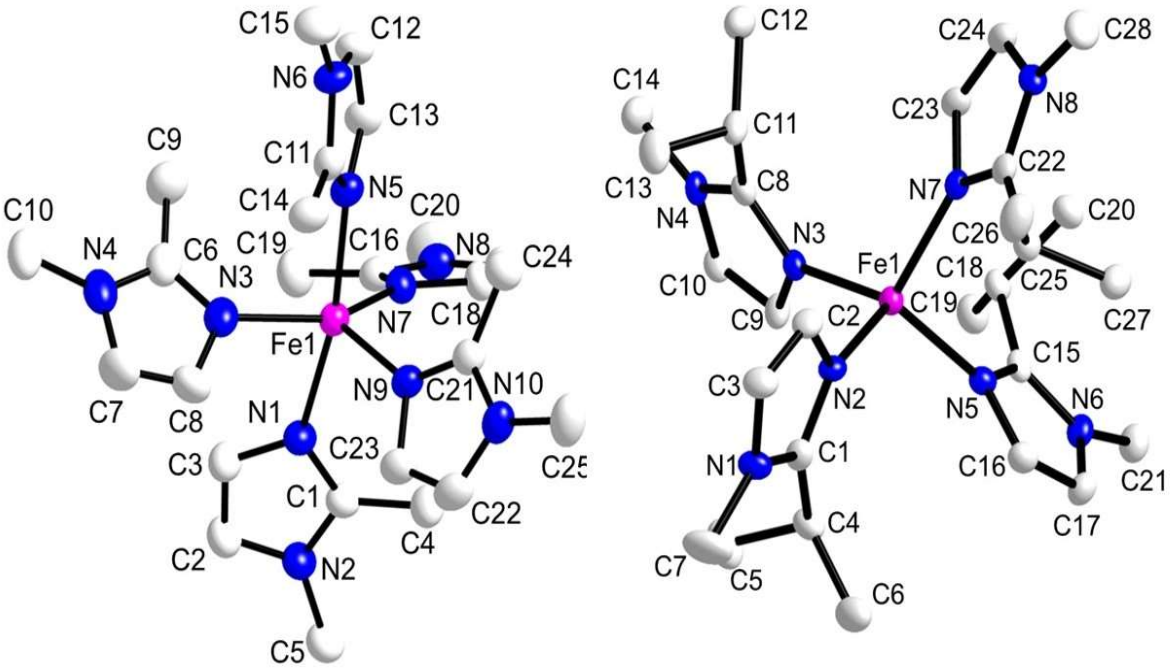
randomness of diffusion coefficients. The results indicated that either 12-6 or 12-6-4 models should be used conditionally depends on the specific ion and water model. Second, using the potential of mean force (PMF) method, the polarizabilities of the metal-chelating atoms from acetate and imidazole molecules were parametrized for 11 ions in three water models. The reason to change the polarizabilities is that both 12-6 and 12-6-4 nonbonded models cannot reproduce the binding free energy, since it is unable to consider the low-high spin effect (although 12-6-4 has already considered the induced dipole).The results successfully reproduced metal-ligand binding free energy based on the 12-6-4 nonbonded model (hence named as m12-6-4 model). Third, the m12-6-4 parameters were applied onto two protein systems. The first application is an artificial protein TriCyt3 (PDB ID: 6WZC). This protein is selected to test the robustness of parameters on a protein that is totally unknown by homology models. While the second application is a membrane protein hZIP8 (PDB ID: 5TSA with homology modification). This protein is selected to test the transferability of parameters in a complex environment that yields water, lipid, and protein. All three projects further established the flexibility and reliability of 12-6-4 nonbonded model, which can correctly describe interactions between metal, solvent, ligand, and protein by simply tuning the polarizability of ion-chelating atoms. Moreover, the transferability of this model was tested, showing the capability of describing metal-water-ligand-protein interactions in various environments.



262. Synthetic models for alkene dioxygenase

FermanA. Chavez*, chavez@oakland.edu. Chemistry, Oakland University, Rochester, Michigan, United States*

Carotenoids, a family of molecules that are categorized by their alternating carbon-carbon double bonds, are responsible for a variety of important processes in all forms of life. In plants, Carotenoid Cleavage Dioxygenases (CCDs) are iron-containing enzymes capable of converting carotenoids to carotenoid derivatives (apocarotenoids), which are necessary for biological functions in all forms of life. CCDs cleave the carbon-carbon double bond, which convert carotenoids into biologically-active molecules. Here we report the first example of a sterically-controlled imidazole-ligated iron site based on non-chelating imidazole ligands. Adding 6 equiv of 1,2-dimethylimidazole (1,2-Me_2Im) to $Fe(OTf)_2 \times 2CH_3CN$ affords the first example of a 5-cordinate non-chelating imidazole-iron distorted square pyramidal complex ($[Fe(1,2\text{-}Me_2Im)_5](OTf)_2$, **1**). When an ^{i}Pr group is substituted for the methyl group at the 2-position on the imidazole (1-Me-2-^{i}PrIm), the 14 electron complex ($[Fe(1\text{-}Me\text{-}4\text{-}^i PrIm)_4](OTf)_2$, **2**) is obtained. This complex exhibits slightly distorted tetrahedral geometry with four N-donors and serves as a 4-His iron structural model complex for carotonoid cleavage dioxygenase (CCD). The electronic structure of **1** and **2** were characterized by Mössbauer spectroscopy. Reactions of **1** and **2** with model olefin substrates in the presence of oxygen result in olefin cleavage yielding ketone and aldehyde products although **2** yields more products than **1**. Support for a proposed reaction mechanism for **2** is offered from DFT calculations.



263. QM/MM spin-restricted ensemble-referenced Kohn–Sham nonadiabatic molecular dynamics via an OpenMolcas-GAMESS-US/Tinker interface

Danil Kaliakin[1], *dskalyakin@gmail.com, Miquel Huix-Rotllant*[2], *Nicolas Ferre*[2], *Michael Filatov*[3], *Alejandro Blanco-González*[1], *Xuchun Yang*[1], *Massimo Olivucci*[1,4]. *(1) Department of Chemistry, Bowling Green State University, Bowling Green, Ohio, United States(2) Institut de Chimie Radicalaire, Aix-Marseille Universite, Marseille, Provence-Alpes-Côte d'Azu, France(3) Department of Chemistry, Kyungpook National University College of Natural Sciences, Daegu, Korea (the Republic of)(4) Department of Biotechnology, Chemistry and Pharmacy, Universita degli Studi di Siena, Siena, Toscana, Italy*

The simulation of the photodynamics of photochemical and photobiological processes unavoidably requires an atomistic treatment of the molecular environment. This commonly enabled by the quantum mechanics/molecular mechanics (QM/MM) non-adiabatic molecular dynamics (NAMD) simulations. The characterization of photo and thermal reactivities of even medium-size organic molecules becomes computationally expensive when multi-reference methods are employed in picosecond timescale simulations of the reactive dynamics. The spin-restricted ensemble-referenced Kohn–Sham (REKS) method and its state-interaction state-averaged (SSR) extension employ ensemble-density functional theory (eDFT) to introduce non-dynamic electron correlation into the description of the ground and excited electronic states of molecules and to obtain the excitation energies in a way reminiscent of multi-state multi-configurational methods of wave function-based theories. The SSR method offers a substantially more economical treatment of the electronic structure making the systematic simulations of photochemical and photobiological processes occurring on picosecond time scale more feasible. Our research group established a protocol allowing generation of QM/MM models of photoresponsive systems, where this protocol utilizes the NAMD functionality of OpenMolcas. To integrate the SSR method within our QM/MM protocol we recently constructed and applied a novel interface created to link OpenMolcas and the GAMESS-US/Tinker software packages. In this interface the GAMESS-US/Tinker produces the SSR energies and analytical gradients, while the OpenMolcas provides the NAMD driver. As an example of the flexibility of this new interface we present a recent application of the OpenMolcas–GAMESS-US/Tinker interface to the SSR NAMD simulation of photoisomerization dynamics of (E)-3′-(2-methyl-2,3-di-hydro-1H-benzo[b]cyclo-penta[d]thiophen-1-ylidene)pyrrolidin-2-one molecular motor. The new interface played a crucial role in demonstration of the fact that the NAMD QM/MM simulations in solution yield results consistent with the experimentally observed transient absorption spectroscopy data, which allowed for detailed understanding of the functionality of novel molecular motor.

264. Quantum chemistry explains why cells activate carboxylic acid by converting it to thioester

***Mohamed E. Ayoub**, ayoubm@uwm.edu. University of Wisconsin-Milwaukee, West Bend, Wisconsin, United States*

This study intends to answer the following question: What allows a thioester to survive in the aqueous environment of the cell without being hydrolyzed, while waiting to be used as a reactant in a nucleophilic addition-elimination reaction. We adopted B3LYP/6-311++G** variant of hybrid density functional theory (DFT) along with Natural Bond Orbital / Natural Resonance Theory to examine electronic origin causing the reactivity of thioester. Our work shows that the electron delocalization into antibonding of carbonyl oxygen ($n_e \rightarrow \pi^*_{CO}$) is weaker (reduced) for thioester than esters which increases the carbonyl group's susceptibility to nucleophilic addition. In addition, we provide stabilization energies due to delocalization (ΔE), associated charge transfer (n_{CT}) and overlap integral (S_{ij}) along with overlap plots for both thioesters and oxygen ester to support the conclusion.

265. Integrating metal coordination bonding into materials for enhanced stability and photoresponse

***Alexis D. Ostrowski**, alexiso@bgsu.edu. Departments of Chemistry, Bowling Green State University, Bowling Green, Ohio, United States*

Our group is focused taking advantage of the new metal coordination interactions that occur when metal complexes are integrated into biopolymers . For example, we show that the

introduction of the V(V) metal coordination bonding interactions in polysaccharide-based bioplastics creates materials with enhanced stiffness and elasticity, as well as water stability. The materials without V(V) degrade in water, but the V(V) materials show remarkable stability. This is attributed to the changes in assembly of the polymer network after the metal coordination bonds are formed. These V(V) polysaccharide bioplastic films are also photoresponsive, where reduction to V(IV) is seen along with changes in mechanical properties and assembly in the films. We are currently investigating other biopolymers with coordination to transition metal ions such as Fe to show how the mechanical properties of biopolymer networks can be tuned and controlled with the metal ion coordination.

266. Completing the cycle: Photodegradation as a tool for upcycling polymers

***Jayaraman Sivaguru**, sivagj@bgsu.edu. Departments of Chemistry, Bowling Green State University, Bowling Green, Ohio, United States*

Most polymeric materials derived from fossil fuels are not sustainable or degradable, and persist in the environment causing irreversible damage to h mans and the eco-system. Increase in the demand for the production of polymeric materials with superior properties and projected decrease in the availability of fossil fuels adds urgency to consider viable alternatives such as renewable biomass for making sustainable materials. Keeping this in mind, the presentation will highlight our approach of developing biomass derived polymers/oligomers that can be degraded on demand and recycled.1-4 The ability to manipulate the wavelength using different light absorbing unit from biomass with programmed degradability will be highlighted.

267. Towards enediyne substituted polycaprolactones in an attempt to generate Calicheamicin-like anticancer activity

***Abhi Bhadran**, abhiptr8@gmail.com. Chemistry and Biochemistry, The University of Texas at Dallas, Richardson, Texas, United States*

Enediynes are the warhead in Calicheamicin, one of the most potent small molecular anticancer drugs. However, enediynes are not selective and can be toxic to normal healthy cells. To address this issue, we have developed a new approach that involves functionalizing enediynes to micellar nanoformulations that can selectively target cancer cells. Specifically, we synthesized enediyne-substituted polycaprolactones that can self-assemble to form polymeric micelles. These micelles have a hydrophobic block comprised of maleimide-derived enediynes (MDE) functionalized PCL, and a hydrophilic block consisting of thermoresponsive tri(ethylene) glycol (ME3). When these micelles are exposed to elevated temperatures, they collapse, exposing the reactive MDE group, which inhibits tumor cell growth.

The inherent fluorescence of the MDE system was studied and was used to compare their efficiency with doxorubicin (DOX) and DOX-loaded micelles. The MDE functionalized nanoformulations induced DNA cleavage and exhibited cytotoxicity towards MDA-MB-231 breast cancer cells by producing diradicals through Myers-Saito Cyclization. Electrophoretic mobility shift assay was performed to examine the DNA binding affinity of the nanoformulations, which revealed their ability to bind to the DNA backbone. By creating MDE functionalized nanoformulations, we developed the first class of enediyne-based biodegradable anticancer agent that specifically targets cancer cells.

268. Probing ion diffusion in plant secondary cell wall models at different relative humidity using molecular simulations and X-ray fluorescence

Daipayan Sarkar[1], *sarkarda@msu.edu, Lintao Bu*[4], *Joseph E. Jakes*[2], *Jacob Zieba*[3], *Isaiah Kaufman*[3], *Michael F. Crowley*[4], *Peter Ciesielski*[4], *Josh V. Vermaas*[1,3]*. (1) DOE Plant Research Laboratory, Michigan State University, East Lansing, Michigan, United States(2) Forest Biopolymers Science and Engineering, USDA Forest Service, Forest Products Laboratory, Madison, Wisconsin, United States(3) Michigan State University Department of Biochemistry and Molecular Biology, East Lansing, Michigan, United States(4) Renewable Resources and Enabling Sciences Center, National Renewable Energy Laboratory, Golden, Colorado, United States*

Secondary plant cell walls are composed from carbohydrate and lignin polymers, and collectively represent a significant renewable resource. Leveraging these resources depends in part on a mechanistic understanding for diffusive processes within plant cell walls. For instance, the effectiveness of both common wood protection treatments and biomass pretreatments for biorefineries typically depend on ionic diffusion within the cell wall. Xray fluorescence microscopy experiments have determined that ionic diffusion rates are dependent on cell wall hydration as well as the ionic species through non-linear relationships. In this work, we use classical molecular dynamics simulations to map the diffusion behavior of different plant cell wall components (cellulose, hemicellulose, lignin), ions (Na^+, K^+, Cu^{2+}, Cl^-) and water within a model for an intact plant cell wall, depending on the hydration index (3 – 30%). From these simulations, we analyze the contacts between different plant cell wall components with each other and their interaction with the ions. The positively charged cations are found to diffuse freely in the secondary cell wall, and preferentially interact with hemicellulose components. Carboxylate groups on our hemicellulose model are negatively charged, forming strong and stable electrostatic interactions with the cation, hindering cation diffusion. Diffusion measurements within our simulations show that diffusivity grows nonlinearly with increasing moisture content within the cell wall. These observations shed light onto the molecular mechanisms for diffusive processes within secondary plant cell walls at atomic resolution. Armed with this mechanism, it is possible to design and engineer pathways to alter the mechano-chemical properties of lignocellulosic biomass, catering to applications in sustainable and biomedical engineering.

269. Catalytic transformations between forms of silicon

Kalani D. Edirisinghe*, Ediride@bgsu.edu, Joseph C. Furgal. Chemistry, Bowling Green State University, Bowling Green, Ohio, United States*

Siloxane-based polymers are well known as less reactive and low toxic material because of their chemical, mechanical, and thermal stability. Based on the high energy cost in making these materials, recycling these materials is of great interest. However, most of the present recycling techniques are complex and involve high energy. In our previous work, we introduced an efficient room-temperature technique using low catalytic amounts of fluoride in high swell organic solvents. The depolymerization results in cyclic siloxane units mainly D_4, D_5, and D_6 as the end products. However, D_4 is of higher interest in reusability, based on the possibility to reform silicones. Now we are focusing on different solvent systems, to ensure the depolymerization to form higher amounts of D_4. The catalytic transformation between forms of silicon is verified mainly by ^{29}Si nuclear magnetic resonance and GCMS. Initial results showed different forms of cyclic siloxane units in different organic solvents. This process has the potential as a reusable depolymerization method in mild conditions.