The 2024

Undergraduate Research Symposium

Sponsored by the Western New York Section
of the American Chemical Society

Saturday April 13, 2024

University at Buffalo, SUNY
Welcome Message from the Organizing Committee

Welcome to the 2024 Western New York American Chemical Society Undergraduate Research Symposium hosted by the Department of Chemistry at the University at Buffalo, SUNY. This symposium will highlight the exciting research executed by the undergraduate students and their mentors from Western New York and the surrounding areas, including Southern Ontario.

Undergraduate research is often cited as the critical activity that inspired the professional careers of academic and industrial chemists, health professionals, and government scientists. Since its inception in Western New York in 2008, this American Chemical Society Undergraduate Research Symposium has brought together undergraduate researchers and their mentors from area colleges and universities to share their rich and diverse undergraduate research experience.

We thank our Keynote speaker, UC Berkeley Prof. D. Kwabena Bediako for his participation in this event. I am also very thankful to the members of the Organizing Committee of this symposium and to the WNY ACS Section and the University at Buffalo for their sponsorship of this event.

Sincerely,

Sherry Chemler, Ph.D.
Chair, 2024 Symposium Committee

2024 Symposium Organizing Committee

Chair:
Dr. Sherry Chemler
Department of Chemistry, University at Buffalo, SUNY

Dr. Luis de Jesús Báez
Dr. Janet Morrow
Dr. Troy Wood
Members of the University at Buffalo Undergraduate Chemistry Club
Department of Chemistry, University at Buffalo, SUNY

Dr. Timothy M. Gregg
Department of Chemistry and Biochemistry, Canisius University
The 2024 Western New York ACS Undergraduate Research Symposium

Many thanks to our generous sponsors!!

University at Buffalo, SUNY
Department of Chemistry
Schedule of Events
April 13, 2024
All events will be held in the Natural Sciences Complex, on the UB North Campus

8:00 am – 8:45 am  Registration (Tables/Hallway adjacent to NSC 225)
8:45 am – 9:00 am  Introductory Remarks: (NSC 225)
                  Prof. Luis de Jesús Báez
9:00 am – 10:00 am Keynote Speaker:
                  Prof. D. Kwabena Bediako
                  Department of Chemistry, University of California, Berkeley
                  “Chemistry and Physics in Flatland”
10:00 am – 12:00 pm Student Oral Presentations, Moderators
                  Owen Szeglowski and Bryan Renzoni
12:00 pm – 1:00 pm  Lunch (NSC 228)
1:00 pm -2:15 pm  Student Poster Session: (2nd Floor corridor NSC, beyond snackbar)
                  Prof. Troy Wood
2:15 pm – 3:15 pm  Symposium Awards and Closing remarks: (NSC 225)
                  Prof. Janet Morrow, judge organizer
                  Prof. Sherry Chemler
Born in Ghana, West Africa, Kwabena Bediako moved to the US in 2004 for his undergraduate studies in Chemistry at Calvin College, MI, graduating with honors in 2008. After a year working at UOP Honeywell in IL where he researched new catalysts for the petrochemical and gas processing industries, he traveled from the Midwest to the East Coast to begin his graduate studies in Inorganic Chemistry with Prof. Daniel Nocera at MIT (and later Harvard University). His graduate research focused on structural and mechanistic studies of water splitting electrocatalysis at cobalt and nickel compounds. After receiving his Ph.D. in 2015 from Harvard University, Kwabena began postdoctoral work in Prof. Philip Kim's group in the Department of Physics at Harvard, where he studied ion intercalation and quantum transport in 2D van der Waals heterostructures. In July 2018, Prof. Bediako joined the faculty of the UC Berkeley Department of Chemistry.
Oral Presentations
9:00 AM - 12:00 PM NSC room 225

9:00 am    Prof. D. Kwabena Bediako  University of California Berkeley
            Keynote Address
            Chemistry and Physics in Flatland

10:00 am  Student talks  (Owen Szeglowski and Bryan Renzoni, moderators)

1.  10:05 am  Nusrat Islam  Binghamton University, SUNY, Binghamton, NY
            Complement Recruiting Bifunctional Molecules as a New Antimicrobial
            Modality Enabled by DNA-Encoded Library Screening

2.  10:25 am  Grace E Lenihan  McMaster University, Hamilton, ON
            Mechanical and Functional Characterization of Adenoviral-Vectored Oral Thin
            Film Vaccines

3.  10:45 am  Isiah M. McMurray  Nazareth University, Rochester, NY
            Characterization of Weakly Bound Complexes Between Water and N-Methyl-2-
            Pyrrolidone

4.  11:05 am  Sawyer A. Oppenheer  SUNY Fredonia, Fredonia NY
            Spectroscopic Determination of the Composition of Binary Liquids using
            Merocyanine Dyes

5.  11:25 am  Nicholas J. Reilly  University at Buffalo, SUNY, Buffalo, NY
            Photocatalytic H₂ Evolution at CdSe Quantum Dot-Ferrocene Hybrids
Complement Recruiting Bifunctional Molecules as a New Antimicrobial Modality Enabled by DNA-Encoded Library Screening

Nusrat Islam\textsuperscript{1}, Zachary Severance\textsuperscript{1,*}, and Amit Choudhary\textsuperscript{2}

\textsuperscript{1}Department of Chemistry, Binghamton University, SUNY, Binghamton, NY
\textsuperscript{2}Chemical Biology and Therapeutics Science, Broad Institute of MIT and Harvard, Cambridge, MA

Bifunctional molecules are an emerging therapeutic modality that are providing fundamentally new therapeutic strategies by inducing synthetic proximity between an effector and target of interest (e.g., PROTAC-mediated degradation). However, the development of new classes of bifunctional molecules is limited by lack of non-inhibitory ligands against effectors and targets of interest to facilitate recruitment. We have developed a new class of bifunctional molecule that allows for direct recruitment of complement components to pathogens to empower the immune system to eliminate difficult-to-treat pathogens. The complement system is a vital component of the immune system that consists of a complex group of extracellular proteins that work together to defend against pathogens. Complement proteins are present in high abundance in the blood that may be leveraged via bifunctional recruitment. Pseudomonas aeruginosa (PsA) is a challenging bacterium to treat due to its ability to cause various infections and antibiotic resistance. Herein, we employed our DNA-encoded library (DEL) screening platform in combination with our custom in-house DEL analysis app to discover ligands against complement and PsA surface proteins for bifunctional development. After DEL screening and Structure-Activity Relationship (SAR) analysis, top hits were nominated for binding validation via Surface Plasmon Resonance (SPR) and Bio-Layer Interferometry (BLI). The hits were then conjugated through a linker via click chemistry to form bifunctional molecules that displayed complement-dependent cytotoxicity against bacteria. Collectively, these studies describe the discovery of the first non-inhibitory complement protein binders as well as their application in the development of a new class of antimicrobial bifunctional modality.
Student Talk (2)

**Mechanical and Functional Characterization of Adenoviral-Vectored Oral Thin Film Vaccines**

*Grace E Lenihan, Annika Yardy, and Alex Adronov*

Department of Chemistry and Chemical Biology, McMaster University, Hamilton, ON

Oral thin films (OTFs), or rapidly dissolving polymer films, provide an improved oral drug delivery system. This is due to the longer shelf-life of OTFs, their ability to bypass metabolism in the liver and their simpler transport and distribution requirements, in comparison to intermuscular injections, due to their small size and stability at room temperature. Viral-vectored OTF vaccines produced via solvent casting (SC) are administered easily to the highly permeable oral mucosa. We have validated OTFs as a suitable viral vector delivery vehicle, using adenovirus expressing green fluorescent protein (Ad5GFP OTF). The films need to have a good infectious titer recovery (ITR) of adenovirus, as well as have desirable mechanical properties, to allow them to be suitable for application. After initial film formulations were explored, and Ultimate Tensile strength data showed the film formulations to be robust upon changing the variables PMAL (Poly Maleic Anhydride-Alt-1-Octadecene substituted with 3-Dimethylamino Propylamine), trehalose, and glycerol w/w%, interactions between PMAL (zwitterionic surfactant) and Tween80 (a cheaper surfactant and FDA approved) were investigated. These experiments were conducted to explore the relationship between the surfactants with regards to $T_g$ (glass transition temperature) and ITR. The $T_g$ for 0.01 W/w% each of Tween80 and PMAL was only approximately 1°C higher at 98°C than that for 1 W/w% each Tween80 and PMAL. For ITR, high Tween80 and PMAL (1 W/w% each) hindered the stabilisation of the OTF and ITR decreased by 34%.

The aim of this research is to find the optimum OTF formulation for drug delivery.

*Table 1. Glass transition temperature ($T_g$) Values for the varying w/w% of PMAL and Tween80.*

<table>
<thead>
<tr>
<th>W/w% of Tween80 and PMAL in each film</th>
<th>$T_g$ °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1%</td>
<td>96.69</td>
</tr>
<tr>
<td>0.50%</td>
<td>93.05</td>
</tr>
<tr>
<td>0.01%</td>
<td>97.94</td>
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Characterization of Weakly Bound Complexes Between Water and N-Methyl-2-Pyrrolidone

Isiah M. McMurray and Josh J. Newby*

Department of Chemistry, Nazareth University, Rochester, NY

Weakly-bound complexes are molecules that are bound to other molecules by only intermolecular forces. Studying these interactions helps the scientific community better understand how larger systems (e.g. proteins and enzymes) are structured and how they function. Previous research in this area focused on homocyclic ring molecules' interactions with water. Recently, there has been more research involving heterocyclic molecules. The current study looks into the interactions between N-methyl-2-pyrrolidone (NMP) and water. NMP is a common chemical used in paint thinners and removal products. It is chemically interesting as it contains multiple electronegative atoms, π-electrons, and a bulky substituent group that can all impact the binding of a water molecule. Previous studies focused on the NMP : water interactions in bulk systems. One study did posit a favored orientation, but did not confirm it. In the current study, computational analysis and matrix isolation FTIR were used to characterize the interactions of NMP and water on the molecular scale. Our computational findings suggest that there are four orientations in which the weakly bound NMP : water complex can form. The most energetically favorable structure was observed to form a hydrogen bond from the water molecule to the ketone of NMP. Spectroscopic analysis also supports this interaction as the most favored state.
Spectroscopic Determination of the Composition of Binary Liquids using Merocyanine Dyes

Sawyer A. Oppenneer, Jonas G. Simora, Isabelle R. Price, and Allan Jay P. Cardenas*

Department of Chemistry, SUNY Fredonia, Fredonia NY

Solvatochromic merocyanine dyes provide promising opportunities in spectroscopic quantitative analysis of binary liquid solutions. Three polar solvents with merocyanine dye dissolved within them were analyzed and showed changes in the composition of a binary mixture resulting in a significant change in the dielectric constant of the solution. Thus shifting the maximum wavelength of absorption in accordance with the polarity of the solvent. Using three model binary solutions, water-ethanol, water-isopropanol, and ethanol-isopropanol, a linear relationship between the maximum wavelength of absorption and concentration of the solvent of interest. This linear relationship can be used as a calibration plot in the determination of an unknown concentration. Two derivatives of Brooker's merocyanine dye, one with a hydrophobic alkyl chain and one with a tertiary butyl group, were synthesized to extend the application of this novel method to non-polar solvent systems such as benzene-toluene. This new spectroscopic method is both simple and visually appealing which makes it a great pedagogical tool for general chemistry laboratory classes.
Semiconductor nanocrystals, or “quantum dots (QDs),” are photoreactive particles that exhibit size-tunable physical and electronic properties due to quantum confinement. In particular, the tunable band gaps ($E_g$) and band-edge potentials of QDs make them exciting, flexible photocatalysts. Upon the absorption of high-energy photons ($h\nu > E_g$), valence band electrons are excited to the conduction band, leaving behind an electronic absence or “hole.” These excited electron-hole pairs store the energy of photons, which can be used to promote redox reactions such as reduction of solvated H$^+$ to H$_2$ gas. This mechanism, however, competes with electron-hole recombination, a thermodynamically favorable photoemissive event. Physically separating the electron and hole can delay the recombination event. This project aims to determine whether 6-(ferrocenyl)hexanethiol ligands ($C_6$FcSH), being strong hole acceptors, can enhance the QDs’ photocatalytic redox properties by prolonging their excited state.

QDs are first synthesized with bulky organic surface ligands, which are replaced with chloride ions and $C_6$FcSH through a series of ligand exchanges. These QDs are then spray-coated onto FTO glass slides, interfaced with an aqueous electrolyte solution, and illuminated to induce excited states, facilitating the reduction of protons to H$_2$ gas. The adsorption of hole-accepting $C_6$FcSH to CdSe has been characterized by dramatic emission-quenching effects congruent with the proposed hole-transfer mechanism. Furthermore, prolonged illumination of the QD-ferrocene system in a sealed, deaerated environment yields significant H$_2$ production at a higher yield than a control group. Current results indicate that the presence of $C_6$FcSH enhances the system’s ability to reductively generate H$_2$ gas photocatalytically.

Figure 1 - Model of a CdSe QD with a $Cd^{2+}$-Coordinated $C_6$FcSH Ligand
Student Poster Presentations List
1:00 PM - 2:15 PM

Poster 1. **Adrian Martinez**, Emily Steiner, and Luis Sanchez*

*Department of Biochemistry, Chemistry, and Physics, Niagara University, Niagara University, NY*

**Studies Toward the Synthesis of ent-Artemisinin, a Potential Anti-Malarial Compound**

Poster 2. **Michael T. Viggiani**, Bradley M. Kraft¹*, Mathew T. Heckman, and William W. Brennessel²

¹*Department of Chemistry, St. John Fisher College, Rochester, NY*  
²*Department of Chemistry, University of Rochester, Rochester, NY*

**Neutral and Cationic Dialkylsilicon Complexes of 8-Hydroxyquinoline N-oxide**

Poster 3. **Aiden J. Ward**, Ubanni J. Opashi, and Benjamin E. Partridge*

*Department of Chemistry, University of Rochester, Rochester, NY*

**Designing Hydrogen-Bonding Motifs to Break the Symmetry in Hierarchical Fibrous Materials**

Poster 4. **Cooper D. Cohen** and David C. Lacy*

*Department of Chemistry, University at Buffalo, SUNY, Buffalo, NY*

**Uncovering the Oxidizing Potential of Manganese(III) from Low-Valent Manganates: a Preliminary Study**

Poster 5. **Eline Grace van der Meer** and Benjamin E. Partridge*

*Department of Chemistry, University of Rochester, Rochester, NY*

**Hemithioindigo as a Photoswitch for Dissipative Self-Assembly**

Poster 6. **Owen D. Szeglowski**, Nayanika Kalita, Matthew R. Crawley, and Timothy R. Cook*

*Department of Chemistry, University at Buffalo, SUNY, Buffalo, NY*

**Applications of Polynuclear Porphyrin Prisms in Small Molecule Activation**

Poster 7. **Elise Spence**, Steele Burgeson, and Luis Sanchez*

*Department of Biochemistry, Chemistry, and Physics, Niagara University, Niagara University, NY*

**Development of a Biaryl Oxidative Coupling-Based Route to the Anti-Tumor Natural Products TMC-95**
Poster 8. **Faith M. Coolbeth**, Alliah S. Fluent, and Karen E. Torraca*

*Department of Chemistry, Houghton University, Houghton, NY

**Optimization of Green Oxidation Reactions of Alcohols**

Poster 9. **Gregory J. Lapp**, ² **Hannah R. Dierolf**, ² **Michael D. Clark**, ¹ **Zachery A. Schmidt**, ¹ **Kacie R. Liwosz**, ²* and **David F. Watson**¹

¹*Department of Chemistry, University at Buffalo, SUNY, Buffalo, NY
²Department of Natural Science and Mathematics, D’Youville University, Buffalo, NY

**Inorganic-Organic Coupled Systems for Solar Hydrogen Production**

Poster 10. **Henry T. Eaton**, Annemarie Lee, and John R. Swierk*

*Department of Chemistry, Binghamton University, SUNY, Binghamton, NY

**Strategies for Optimizing a Photocatalyzed [4+2] Diels-Alder Cycloaddition**

Poster 11. **Ian M. Lillie**¹, **Jianheng Ling**², and **Phillip J. Milner**²*

¹Department of Materials Science and Engineering, Cornell University, Ithaca, NY
²Department of Chemistry and Chemical Biology, Cornell University, Ithaca, NY

**Redox-Active Cumulenes: From Energy Storage to Electro(photo)catalysis**

Poster 12. **Marvin B. Wu**, Elizabeth R. Piedmont, and Benjamin E. Partridge*

*Department of Chemistry, University of Rochester, Rochester, NY

**Chirality Transfer in Supramolecular Chaperones**

Poster 13. **Isabelle R. Price**, Jonas G. Simora, Sawyer A. Oppenmeer, and Allan Jay P. Cardenas*

*Department of Chemistry, SUNY Fredonia, Fredonia NY

**Spectroscopic Determination of the Composition of Binary Liquids using Merocyanine Dyes**

Poster 14. **Jeb Braunscheidel**, John G. Federice, and Timothy M. Gregg*

*Department of Chemistry and Biochemistry, Canisius University, Buffalo, NY

**Progress Toward the Enantioselective Synthesis of Rhytismatones A and B**
Poster 15. Samantha M. Semler¹, Thomas J. Chrzanowski¹, Marina N. Eshbaugh², Jacob V. Simmons³, Luciana Aronne¹*, Gamini Mendis²,⁴ and Josephine Wee³

¹Department of Chemistry, The Pennsylvania State University- Erie, PA; ²Department of Polymer Engineering and Science, The Pennsylvania State University- Erie, PA; ³Department of Food Science, The Pennsylvania State University- State College, PA; ⁴Department of Plastics Engineering Technology, The Pennsylvania State University- Erie, PA

Determining if Pretreatment Aids in Facilitating Fungal Degradation of Plastic Films

Poster 16. Julia C. Pitolaj¹, Kaitlyn T. Keasler¹, Mary Zick¹, Emily Stacy¹, Jaehwan Kim¹, Jung-Hoon Lee², Lida Aeidartehrzan³, Tomâe Runâevski³, and Phillip J. Milner¹,*

¹Department of Chemistry & Chemical Biology, Cornell University, Ithaca, NY ²Computational Science Research Center, Korea Institute of Science and Technology, Seoul ³Department of Chemistry, Southern Methodist University, Dallas, TX

Handling Fluorinated Gases as Solid Reagents Using Metal–Organic Frameworks

Poster 17. Lee E. Schoneman¹, Adam N. Robinson¹, Rachel H. Horowitz², Carly R. Reed², and Michael L. Gleghorn¹*

¹School of Chemistry and Materials Science, Rochester Institute of Technology, Rochester, NY ²Department of Chemistry and Biochemistry, SUNY Brockport, Brockport, NY

Crystallized DNA G-Quadruplex Structure Bound to an Iridium Complex Ligand

Poster 18. LadieJocelynn Shabazz¹, Alexis D. Kelleher¹, Rati Lama², Samuel L. Galster¹, Xinjiang Wang,² and Sherry R. Chemler¹*

¹Department of Chemistry, the University at Buffalo, SUNY, Buffalo, NY ²Roswell Park Comprehensive Cancer Center, Buffalo, NY

Synthesis of Betti Quinolinols Designed for Anti-Cancer Structure-Activity Relationship Studies

Poster 19. Rebecca Reagan, Hailemariam Mitiku, Abhishek A. Kadam, and C. Rose Kennedy*

Department of Chemistry, University of Rochester, Rochester, NY

Dinuclear Iminopyridone Nickel Complexes and Their Reactivity
Poster 20. Matthew P. Ostrowski and Jamie Kim*

Department of Chemistry, Buffalo State University, SUNY, Buffalo, NY

Chemical Analysis of Ingredients in Brand-Name and Generic OTC Medications

Poster 21. Jonas G. Simora and Allan J. Cardenas*

Department of Chemistry, SUNY Fredonia, Fredonia, NY

Structural Comparison of Molecules Containing Nonconventional Hydrogen Bonds

Poster 22. Michael Vullo, Saima SayedMim, and Sourav Biswas*

Department of Chemistry, SUNY Buffalo State University, Buffalo, NY

Cu Supported on N Doped Carbon for Click Reaction: Application Beyond Electrochemistry

Poster 23. Natasha K. Gozali, Shweta Chitkara, and G. Ekin Atilla-Gokcumen*

Department of Chemistry, University at Buffalo, SUNY, Buffalo, NY

Diverging Ceramide Roles: The Decision between Apoptosis and Senescence

Poster 24. Marina E. Zapesochny, Christopher D. Hastings, William W. Brennessel, and Brandon R. Barnett*

Department of Chemistry, University of Rochester, Rochester, NY

Coordinatively Unsaturated Manganese Complexes Gated by a Rigid and Narrow Void

Poster 25. Raegan Lawton¹, Zachary E. Holmes¹, Matthew R. Crawley², and Lauren E. Rosch*¹,²

¹Department of Biochemistry, Chemistry, and Physics, Niagara University, Niagara University, NY
²Department of Chemistry, University at Buffalo, SUNY, Buffalo, NY

Single Crystal X-ray Diffraction Studies of Chalcogen-Containing Chromophores

Poster 26. Robert H. Suber, Deepak Krishnan Balaji, and Janet R. Morrow*

Department of Chemistry, University at Buffalo, SUNY, Buffalo, NY

Redox Active Macrocyclic Iron Complexes as paraSHIFT Agents
Studies Toward the Synthesis of ent-Artemisinin, a Potential Anti-Malarial Compound

Adrian Martinez, Emily Steiner, and Luis Sanchez*

Department of Biochemistry, Chemistry, and Physics, Niagara University, Niagara University, NY

Artemisinin is a natural product isolated from the plant Artemisia annua that is currently the fastest-acting treatment available against Plasmodium falciparum—the protozoan parasite that causes the deadliest form of malaria. The low bioavailability of this compound and its short half-life, however, make the cost of artemisinin therapies very high. Anti-malarial combination therapies involving artemisinin are employed to avoid the development of resistance to the drug by the parasite, as recommended by the World Health Organization.

Artemisinin’s structure contains a unique peroxide bridge that is believed to be responsible for the drug’s mechanism of action. Recent reports show that artemisinin binds covalently to a large number of proteins after being “activated” most likely by heme, which builds up in the parasite cells given its ‘blood-eating’ nature. The exceptional biological activity of this compound appears to originate in the fine-tuned chemical reactivity of its peroxide bridge, rather than the topology of the structure itself. It is expected that its enantiomer (ent- artemisinin) would be a viable alternative as an anti-malarial agent, if an affordable synthetic route were developed. The current goal of this project is to develop a reaction sequence to produce ent-artemisinin from zingiberene, a compound found in ginger oil. If successful, we believe that the low cost and high availability of ginger oil would allow for the large-scale production of ent-artemisinin.
Neutral and Cationic Dialkylsilicon Complexes of 8-Hydroxyquinoline N-oxide

Michael T. Viggiani, Bradley M. Kraft\textsuperscript{1*}, Mathew T. Heckman, and William W. Brennessel\textsuperscript{2}

1. Department of Chemistry, St. John Fisher College, Rochester, NY
2. Department of Chemistry, University of Rochester, Rochester, NY

Dialkylsilicon chelated complexes, \( \text{R}_2\text{Si(QNO)}\text{Cl} \) (QNO = 8-oxoquinoline N-oxide; \( \text{R} = \text{Me} \) (1), \( \text{Et} \) (2), \( \text{iPr} \) (3)), \( \text{Me}_2\text{Si(QNO)}\text{F} \) (4), and \( \text{Me}_2\text{Si(QNO)(OSO}_2\text{CF}_3) \) (5) were synthesized and characterized by \( ^1\text{H}, ^{13}\text{C}, ^{29}\text{Si} \), and 2D NMR spectroscopy, X-ray crystallography, and elemental analysis. In the solid state, complexes 1-4 exhibit 5-coordinate silicon in trigonal bipyramidal geometries, and 5 forms a separated ion pair with a 4-coordinate silyl cation. In CDCl\(_3\) solution, complexes 1 and 2 undergo reversible chloride ionization facilitated by decreasing temperature and increasing concentration. Evidence for a possible chelation equilibrium in 4 involving Si-ON bond dissociation is presented.
Poster 3.

Designing Hydrogen-Bonding Motifs to Break the Symmetry in Hierarchical Fibrous Materials

Aiden J. Ward, Ubanni J. Opashi, and Benjamin E. Partridge*

Department of Chemistry, University of Rochester, Rochester, NY

Rosette nanotubes (RNTs) are supramolecular fibers that perform various functions including mimicking membrane transport channels, inducing apoptosis in cells, and assembling into fibrous networks like hydrogels. RNTs form through the stacking of planar, supramolecular rosettes. Prior work has focused on rosettes assembled via hydrogen bonding between six copies of the G\(^\text{C}\) motif, a specific Janus nucleobase (molecules that present two different hydrogen-bonding motifs). However, the six-fold symmetry of these rosettes presents problems when multiple functional groups must be positioned at defined locations on the RNT, as is necessary to design structurally complex fibrous networks. Moreover, little work has been done involving the synthesis of novel Janus nucleobases beyond the G\(^\text{C}\). Here we describe the synthesis of a novel Janus nucleobase that, when introduced to its complement, should form six-membered rosettes with only three-fold symmetry. This robust synthesis allows gram-scale quantities of nucleobases to be prepared. Preliminary X-ray studies show that the Janus nucleobase is capable of hydrogen bonding to form dimers that stack atop one another in the presence of acid, hinting that the nucleobase may be able to form RNTs with its complement. These findings show that the synthesis of novel Janus nucleobases is not only viable but can be done efficiently and at large scale. Furthermore, these studies suggest that breaking the symmetry of supramolecular rosettes may indeed be possible, offering more versatility in RNT materials design. This symmetry breaking may provide opportunities to develop new force-dissipating substances and better extracellular matrix mimics.
Uncovering the Oxidizing Potential of Manganese(III) from Low-Valent Manganates: a Preliminary Study

Cooper D. Cohen and David C. Lacy*

Department of Chemistry, University at Buffalo, SUNY, Buffalo, NY

The chemical reactivity of Mn(III) halide compounds is widely more pronounced than the reactivity of their Mn(II) counterparts. This trend is corroborated by the general lack of synthetic data available for the preparation and characterization of MnX$_3$ compounds from existing manganese starting materials. From prior work in the Lacy Lab at the University at Buffalo, we have discovered a consistent methodology for synthesizing and characterizing novel Mn(III) and Mn(II) halides, such that their chemical properties are beginning to be illuminated. In this poster, we identify a new class of manganate compounds that are key to bridging the energy gap between Mn(II) and Mn(III) centers. We discuss the synthetic details of arriving at these compounds and how they will be used for future high-valent manganese chemistry. With this ongoing work, we further present a preliminary strategy for the discovery of a catalytic cycle from Mn$^{II}$Br$_2$L, capable of forming Br-Br bonds through activation by a photo-oxidant into a transient, reactive Mn$^{III}$Br$_3$L species, via a manganate salt. Analysis of these synthetic products and reactivities is conducted primarily by FTIR, UV-Vis, and SC-XRD spectroscopies, as well as by electrochemical measurements. Upon demonstration of Br-Br coupling from this work, the Lacy Lab at UB aims to expand this capability to water oxidation, which lies at a similar oxidation potential as the Mn(II)/Mn(III) couple currently being observed.
Dissipative self-assembly (DSA) underpins many natural out-of-equilibrium processes such as the formation and breakdown of microtubules in cells. Such systems require a constant input of energy to give rise to thermodynamically unstable assemblies from their constituent monomers. Upon deactivation of the monomers, energy is dissipated from the system. To date, research on DSA has primarily focused on chemically-fueled systems, whose longevity is limited by the accumulation of waste by-products. In contrast, light-fueled systems are advantageous because they do not generate chemical waste. Here we aim to develop a light-fueled DSA system by functionalizing a known self-assembling molecule, benzene-1,3,5-tricarboxamide (BTA), with a photoswitchable hemithioindigo (HTI) that converts between assembly-inert \((Z)\) and assembly-competent \((E)\) isomers upon irradiation. Successful synthesis of our desired HTI construct and preliminary UV-vis studies demonstrate fast \(Z\rightarrow E\) isomerization with 425 nm light. The \(E\)-isomer can be reverted back to the \(Z\)-isomer upon irradiation at 505 nm. Future work will focus on attaching the current HTI to a BTA core to test assembly competency using irradiation at both wavelengths and tuning the lifetime of the \(E\)-HTI to allow for spontaneous \(E\rightarrow Z\) isomerization. We anticipate that, in addition to adding to the library of DSA systems, this work could be used as a starting point for establishing nanomechanical force systems in synthetic cells.
Poster 6.

Applications of Polynuclear Porphyrin Prisms in Small Molecule Activation

Owen D. Szeglowski, Nayanika Kalita, Matthew R. Crawley, and Timothy R. Cook*

Department of Chemistry, University at Buffalo, SUNY, Buffalo, NY

Motivated by an ever-increasing demand for energy, the Cook lab has been continually exploring the use of polynuclear geometric architectures as catalysts for small molecule activation. These molecules can effectively be constructed through coordination driven self-assembly. Due to the multi-electron nature of this chemistry, polynuclear catalysts are desirable as they allow for multiple potential activation sites within one molecule. Due to this, an M₈L₆ cuboid structure is especially intriguing as it contains six facial metals and 8 metal vertices. This molecule was expected to be an efficient catalyst for small molecule activation due to this, specifically in the sections of ORR and CO₂ reduction. These molecules were synthesized and characterized using proton NMR, mass spectrometry and UV-Vis spectrometry. The potential for these molecules to perform small molecule activation has been monitored through the use of cyclic voltammetry and bulk electrolysis. The implications of this research are widespread, ranging from potential energy conversion via ORR, to the sequestering of anthropogenic CO₂ to serve as a carbon feedstock.
Poster 7.

Development of a Biaryl Oxidative Coupling-Based Route to the Anti-Tumor Natural Products TMC-95

Elise Spence, Steele Burgeson, and Luis Sanchez*

Department of Biochemistry, Chemistry, and Physics, Niagara University
Niagara University, NY

First isolated from the fermentation broth of Apiospora montagnei Sacc. TC 1093, the natural products TMC-95 A–D are of great interest because of their biological activity against the 20S proteasome. This distinctive activity makes them promising candidates as agents for the treatment of cancer. However, constructing such complex molecular structures requires many synthetic steps, which hinders their potential medical use. These active compounds feature a peptide-based structure composed of tyrosine, asparagine, a highly oxidized tryptophan, (Z)-1-propenylamine, and 3-methyl-2-oxopentanoic units. A particularly unusual bond is found in these natural products: a biaryl connection between the tryptophan and tyrosine residues and, as a result of this strange C–C linkage, axial chirality is observed around this bond. Our primary interest in this project is to develop chemical conditions to form this important biaryl linkage via oxidative coupling of suitable tripeptide-based building blocks. Such an oxidative coupling can make the synthetic production of TMC-95 significantly easier, by starting with the inexpensive and widely available natural amino acid units. With an easier synthetic route, TMC-95-based compounds could become viable anti-tumor drug candidates.
Poster 8.

**Optimization of Green Oxidation Reactions of Alcohols**

*Faith M. Coolbeth, Alliah S. Fluent, and Karen E. Torraca*  
Department of Chemistry, Houghton University, Houghton, NY

A green method for the oxidation of 1-phenylethanol to acetophenone was explored. The established conditions for the oxidation method used 2.5 mol% palladium acetate as the catalyst, 2 equivalents of sodium percarbonate as the base and oxidant, and propylene carbonate as the green solvent to yield about 89.1% of acetophenone. Variability in conversion and yield have been observed in the past along with difficulty in isolation of the final product by extraction. As a result, this research specifically focused on using catalysts and additives to improve the reaction yield and reduce variability. Different solvents were also explored to make extraction of the final product possible. Of the variables tested, use of ethyl acetate as a solvent showed the most promise.
Poster 9.

**Inorganic-Organic Coupled Systems for Solar Hydrogen Production**

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Dye-sensitized photocathodes were prepared by attaching a phosphonic acid-functionalized selenorhodamine dye (3-SeP) to CuAlO₂ thin films. The dye, 3-SeP, adsorbed with a robust stability to CuAlO₂ resulting in enhanced absorbance of visible light. Transient photovoltage measurements of these photocathode systems show a long-lived positive shift of the Fermi level, measurable as a positive open-circuit voltage within 1 Hz laser illumination. This is evidence of a mechanism in which holes are transferred from photoexcited 3-SeP to CuAlO₂. In previous linear sweep voltammetry measurements, greater reductive photocurrents were measured for 3-SeP/CuAlO₂-on-Fluorine-dopped Tin Oxide (FTO) electrodes than unfunctionalized CuAlO₂-on-FTO electrodes. This indicates excited-state hole transfer within these systems could possibly create conditions where efficient reduction of protons is possible. Through modifying conditions and electrolyte composition in chronocoulometry experiments, H₂ has been successfully measured in the headspace above the closed-photoelectrochemical cell with these cathodes in a supporting electrolyte with a reduction co-catalyst, H⁺ source, and triethanolamine (as a sacrificial electron donor). These experiments show successful reduction of H⁺ to H₂ with a Faradaic efficiency of (43 ± 27)%. These results reveal the plausibility of optimizing these organic-inorganic hybrid systems for solar fuels.
Strategies for Optimizing a Photocatalyzed [4+2] Diels-Alder Cycloaddition

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Photochemistry has the potential to make possible reactions that would otherwise be prohibitively expensive, wasteful, and unscalable. New photochemical techniques may find applications in small molecule synthesis and drug discovery. A [4+2] Diels-Alder cycloaddition between trans-anethole and isoprene serves as an excellent model reaction and can be optimized through modification of the reaction conditions. Normally this reaction is initiated when an excited ruthenium photocatalyst oxidizes trans-anethole. However, if a secondary electron acceptor (e.g., viologen) is added to the reaction mixture, it can oxidize the reduced photocatalyst and allow for chain behavior to occur. The efficiency of the chain pathway is dictated by the kinetics of the reaction, which in turn is dictated by the relative energetics of the photocatalyst and acceptor. This presentation will explore the impact of different photocatalyst and viologen combinations on the reaction kinetics and overall chain behavior.
Redox-Active Cumulenes: From Energy Storage to Electro(photo)catalysis

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Recent research has highlighted the potential of cumulenes—compounds with three or more consecutive double bonds—for applications in energy storage and electrocatalysis due to their redox-activity. However, embedding this redox-active functional group into an extended solid still poses a challenge. To better understand the potential of cumulene-based materials, three different 3-cumulene-based frameworks have been synthesized: a covalent organic framework (COF), a polymer, and a metal-organic framework (MOF). The COF was synthesized via imine condensation between a tetratopic pyrene-based amine and a tetratopic 3-cumulene-based aldehyde. The polymer was synthesized via Suzuki coupling, and the MOF was synthesized via self-assembly of a pre-formed Zirconium cluster with 3-cumulene-based organic linkers. We also prepared variants of these materials with a single double bond as a comparison. We assessed the redox-activity of these materials by cyclic voltammetry (CV), which shows that the 3-cumulene MOF uniquely displays two reversible oxidation peaks, while the COF and the polymer variants do not. Given the promising redox-activity of the 3-cumulene MOF by CV, investigations into its electro(photo)catalytic activity are being conducted, since the catalytic behavior of these materials holds potential for advancing sustainable energy technologies.
Poster 12.

Chirality Transfer in Supramolecular Chaperones

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Protein misfolding and aggregation are implicated in over 30 diseases, including Alzheimer’s disease, Parkinson’s disease, type II diabetes, and cataracts. Molecular chaperones are native proteins that prevent aggregation, promote productive folding, and refold misfolded proteins but are limited in efficiency and specificity. Previous work in our group has demonstrated that amphiphilic aryl ether dendrons assemble into spherical nanoparticles and inhibit the fibrillation of a model peptide fragment of amyloid beta protein (Aβ16–22) in water, mimicking the biological function of natural chaperones. Driven by evidence that suggests that the chirality of peptide filaments has an active role in amyloid fibrillation, we are investigating the influence of supramolecular chirality on chaperone activity and peptide recognition. Point chirality is being introduced at either the apex, core, or periphery of our molecular amphiphiles and preliminary characterization is examining whether the position of the installed stereochemistry affects overall chirality transfer on a supramolecular scale. Future work will assess the relationship between the chirality of assembly and chaperone activity. This investigation will advance mechanistic understanding of chirality transfer in aqueous media and introduce new insights into designing artificial supramolecular chaperones.
Poster 13.

Spectroscopic Determination of the Composition of Binary Liquids using Merocyanine Dyes

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The most common quantitative spectroscopy analysis for determining concentrations are Beer-Lambert plots. Although this method is quite useful, it is not applicable to liquid binary solutions. In fact, when it comes to quantifying the composition of liquid solutions, there are limited analytical methods available. In this study, the volume composition of binary liquids is spectroscopically measured using a solvatochromic merocyanine. In three different model systems (water-ethanol, water-isopropanol, and ethanol-isopropanol) a linear relationship was established between the maximum absorbed wavelength and the concentration. Similarly to Beer-Lambert's Law, the plot of the maximum absorbed wavelength and the concentration can be used as a calibration plot to accurately measure the concentration (in volume percent) of binary systems. This new spectroscopic method is simple and visually appealing, making it a great tool for general chemistry laboratory classes.

![Graph showing the optical spectrum of a merocyanine dye in water and isopropanol solutions.](image1)

![Graph showing the linear relationship between the maximum wavelength (λ_max) and concentration of isopropanol in a solution.](image2)

**Figure 1:** Optical Spectrum of Merocyanine Dye in Water and Isopropanol Solution.  
**Figure 2:** Linear Relationship Between λ_max and Percent Isopropanol in Solution.  

**Decreasing concentration of isopropanol in a solution of isopropanol and water.**
Progress Toward the Enantioselective Synthesis of Rhytismatones A and B

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Organic synthesis of natural products is the foundation for medical chemistry and can also be used in industrial applications. Rhytismatones A and B are chiral metabolites that were isolated in 2017 from an unknown fungal species, that are endophytes from the family of Rhytismataceae [1]. An endophyte is an organism that lives within a plant without causing disease. These endophytes live in the host species of P. mariana (black spruce trees). Rhytismatone B exhibited moderate antifungal activity. Neither of these biological molecules, although found in nature, have ever been synthesized in a lab. The objective of the research is to synthesize both Rhytismatone A and Rhytismatone B in their racemic form. The core 5,6-dihydropyran-2-one ring is prone to opening during acylation. To get around this problem we are pursuing a protected primary alcohol intermediate, as seen in the general scheme below.

\[
P-O\overset{\text{O}}{\text{C}}H + \overset{\text{O}}{\text{C}}O\overset{\text{O}}{\text{C}}O \rightarrow P-O\overset{\text{O}}{\text{C}}\overset{\text{O}}{\text{H}} \quad \text{Rhytismatone A}
\]
Poster 15.

**Determining if Pretreatment Aids in Facilitating Fungal Degradation of Plastic Films**

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Plastic waste pollution is an increasingly dire environmental problem, as certain types of plastic can take anywhere from 20 to 1,000 years to fully decompose. One potential method of eliminating plastics from the environment is to use fungi to biologically degrade plastic polymers. When plastics are fed to fungi as the sole carbon source, the fungi will consume the carbon that is present in the plastic. This research focuses on low-density polyethylene (LDPE), which contains hydrocarbon backbones that can be degraded using fungal strains. To increase the rate of biodegradation, the following pretreatments will be applied to the LDPE samples: nitric acid, sulfuric acid, hydrogen peroxide, heat, microwave and ultraviolet radiation to introduce more readily degradable functional groups into the polymer. The objective of this project is to find the optimal pretreatment and fungi combination that degrades LDPE most efficiently.
Handling Fluorinated Gases as Solid Reagents Using Metal–Organic Frameworks

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Fluorine is ubiquitous in pharmaceuticals. However, many fluorinating reagents are unselective and challenging to use. Vinylidene fluoride (VDF) is a simple fluorinated building block that has the potential to significantly streamline the installation of fluoroalkenes into complex molecules. Despite this interest, VDF has been overlooked in organic synthesis because it is a gas at room temperature and pressure. To address this, we demonstrate that VDF can be handled as a bench-stable solid reagent using a magnesium-based metal–organic framework (MOF). VDF–MOF reagents can be prepared on bulk scale and stored cold in air for up to a week without any gas loss. The VDF–MOF reagent is simply submerged into solvent where gas release takes place, and the MOF can later be easily removed by vacuum filtration and reused. Using VDF–MOF reagents, we optimized a Pd-catalyzed defluorinative coupling of VDF and arylboronic acids to synthesize α-fluorostyrenes. Notably, since the reaction runs at room temperature under mild conditions, we envisioned that it would tolerate substrates that might otherwise be unstable at higher temperatures. Preliminarily, moderate yields of α-fluorostyrene products have been obtained using electron-rich (hetero)arylboronic acids. Beyond VDF, our lab has found that this strategy is generalizable to the delivery of other fluorinated gases such as trifluoropropene, hexafluoropropene, and trifluoromethyl iodide. We expect that gas–MOF reagents will enable the facile handling of a wider variety of fluorinated and non-fluorinated gases (e.g., BF₃, CO, acetylene), all of which will facilitate synthetic transformations pivotal to the pharmaceutical industry and beyond.

Figure 1: Structure of VDF–MOF

Figure 2: Optimized Reaction Conditions for the Defluorinative Coupling of Arylboronic Acids and VDF
Proto-oncogenes such as c-MYC contain many tumor survival pathways that, when overexpressed, can result in carcinogenesis. One method that is currently being explored to hinder gene overexpression is the formation of different DNA arrangements in the promoter region. The G-quadruplex structure consists of numerous subunits of 4 hydrogen-bound guanines, known as G-quartets, that stack upon each other as opposed to traditional Watson-Crick base pairing. These structures tend to form naturally in guanine-rich environments, which includes the promoter regions of many proto-oncogenes. Due to the size and complexity of the quadruplex, RNA polymerase cannot advance past the structure, halting transcription. To prevent the quadruplex from dissociating, it may be possible to stabilize a quadruplex \textit{in vivo} using ligands that may be able to bind on top of or in the grooves of the quadruplex. Before creating drugs to stabilize G-quadruplexes in vivo, however, their presence must be confirmed first. Due to its increased luminescence when bound to G-quadruplexes as well as its selectivity against typical double-stranded and single-stranded DNA, a cyclometalated iridium (III) imidazole phenanthroline complex will be co-crystallized alongside an annealed oligonucleotide sequence known to form G-quadruplexes (5’-TGGGGT-3’). These crystals will then be analyzed using X-ray diffraction to determine how the iridium complex binds to the G-quadruplex. While structure determination is still in progress, understanding these interactions will provide insight into how to locate G-quadruplexes in vivo.
Synthesis of Betti Quinolinols Designed for Anti-Cancer Structure-Activity Relationship Studies

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General Scheme:

Quinolinol benzylic amines, a subset of Betti bases, have been shown to exhibit various biological characteristics ranging from enzyme inhibition to cytotoxicity. In previous research from our group, structure-activity studies for various Betti quinolinol analogs targeting leukemia cells were performed. (1) The general approach for our analog synthesis uses the Betti reaction, a multi-component reaction involving a phenol derivative, an aldehyde, and an amine derivative. We are currently investigating the anti-cancer effects of Betti quinolinols on melanoma cells. Our preliminary results indicate additional optimization is required to enhance compound stability as well as selectivity for cancer cells over non-transformed cells. We will describe current SAR of the lead compound as well as a second-generation approach. The selective synthesis of each enantiomer will enable us to assess the respective biological activities of each enantiomer, and preliminary results towards that end are presented.

Dinuclear Iminopyridone Nickel Complexes and Their Reactivity

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Multiple metal active sites are commonly found in metalloenzymes like nitrous oxide reductase; this motif has been imitated in bimetallic complexes that demonstrate reactivity beyond that observed in mononuclear systems through cooperativity between metal centers during catalysis. It is suggested that Fe-hydrogenase metalloenzymes utilize the pyridone oxygen in its secondary sphere to assist in the cleavage of hydrogen while reacting. To better understand the impact of pyridone secondary sphere effects and metal-metal cooperativity in catalysis, bimetallic Ni(I) complexes have been synthesized from iminopyridone ligands and Ni(COD)₂. These bimetallic complexes have a Ni-Ni bond and are stable in protic solvents and when exposed to boronic acids. To elicit reactivity from the complexes, oxidants, and strong Lewis and Brønsted-Lowry acids were used. This work will highlight work focusing on reactivity with oxygen, benzoic acid derivatives, and boron trifluoride diethyl etherate.
Chemical Analysis of Ingredients in Brand-Name and Generic OTC Medications

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Throughout the United States, over-the-counter (OTC) medications are used daily to treat a wide range of symptoms and illnesses. Pharmacies and various chain supermarkets sell a wide selection of these medications. When selecting a medication, one must choose between brand-name and generic medications. Though the names are different, generic and brand-name drugs work the same. According to the Food and Drug Administration (FDA), generic drugs are just as effective as their branded counterparts and offer much less cost. However, some consumers prefer brand-name products over generic ones although the prices for generic medications are much cheaper. They believe brand-name medications are more effective and contain different active ingredients. To test this question, we investigated the presence of the active ingredient and its relative abundance in several brands of painkillers and antifungal creams. These include Tylenol and Lamisil (brand-name medications) and generic name medications from Walgreen’s, CVS, and Walmart. Chemical analysis of these medications was conducted via Fourier-transform infrared spectroscopy (FTIR), gas chromatography-mass spectrometry (GC-MS), and high-performance liquid chromatography (HPLC). Our preliminary results showed that there is little to no difference in the active ingredient and other components between brand-name and generic medications used in this work. In this presentation, details of our sample preparation and results of chemical analysis are presented.
Structural Comparison of Molecules Containing Nonconventional Hydrogen Bonds

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Hydrogen bonds are very important intermolecular forces of interaction in nature, as it can dictate protein folding, reaction mechanisms and crystal structures. Though previously thought to be limited between hydrogen and electronegative atoms such as fluorine, nitrogen and oxygen, in the past few decades, several more examples of other hydrogen bond acceptors have been discovered. For this reason, it sparked particular interest in different atoms that can participate in nonconventional hydrogen bonding. In this study, we structurally explored several different nonconventional hydrogen acceptors that provide insight into the strength of these interactions.

Crystal Structure of [HBIAN(Bromopropane)]

Crystal Structure of [BIANHCl]^+
Poster 22.

Cu Supported on N Doped Carbon for Click Reaction: Application Beyond Electrochemistry

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Copper supported on nitrogen-doped carbon (Cu-N/C) catalysts have shown potential in oxygen reduction reactions due to their effectiveness and stability. This study aims to expand their application beyond electrochemistry by investigating their ability to facilitate click reactions, which are important in organic synthesis and drug discovery. Through experimentation, various nitrogen-doped copper materials were synthesized and evaluated for their catalytic activity and selectivity in click reactions. By adjusting reaction conditions and catalyst structures, the research identified key factors influencing reaction efficiency and selectivity. The overarching goal of this study is to widen the scope of Cu/N-C catalysts, offering efficient and environmentally friendly options across diverse catalytic processes. This research contributes to the advancement of sustainable and effective catalytic technologies with potential applications in various industries. By understanding the performance of Cu/N-C catalysts in click reactions, insights can be gained into their broader catalytic capabilities, paving the way for their utilization in a wide range of chemical transformations. Overall, this research provides valuable insights into the design and optimization of Cu/N-C catalysts for future applications beyond electrochemistry, contributing to the development of greener and efficient catalytic processes.
Poster 23.

Diverging Ceramide Roles: The Decision between Apoptosis and Senescence

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Lipids are organic molecules that are vital to many cellular processes. Different structure-based lipid classes are responsible for energy storage, signaling, and structural support. The idea that “structure determines function” is well established but recent discoveries have challenged this fundamental idea. Ceramides, highly bioactive signaling lipids, have structural and signaling roles. Apoptosis and senescence are two different processes caused by ceramide accumulation and challenge this fundamental idea. As such an important question arises: How do ceramides accumulate and signal these diverse functions? My goals are to elucidate the biosynthetic pathway that causes ceramide accumulation in apoptosis and identify differences between ceramide regulation in senescence. I hypothesize that different functions of ceramides are caused by their specific cellular localization and where they are synthesized. Therefore, different lipid biosynthetic enzymes cause their accumulation in apoptosis and senescence. I integrated lipidomics and differential gene expression analysis to identify the changes in both lipids and enzymes in apoptotic cells. Specifically, I utilized a targeted approach for lipid analysis in MRC5 cells, a non-cancerous fibroblast cell line from fetal lung tissue, in two conditions, doxorubicin-induced apoptotic and non-apoptotic cells. Furthermore, I performed digital drop polymerase reactions and analyzed the changes in gene expression of each enzyme involved in ceramide production in apoptosis. I observed an accumulation of ceramides and sphingomyelins which indicated increased de novo biosynthesis and decreased sphingomyelin hydrolysis that might cause the lipid changes detected in apoptosis.
Coordinatively Unsaturated Manganese Complexes Gated by a Rigid and Narrow Void

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Manganese and iron terminal oxo compounds have ample precedent in C-H functionalization in both enzymatic and synthetic systems. Isolating, characterizing, and studying terminal oxo compounds that are highly reactive toward activating strong C–H bonds can be a challenge due to their low kinetic stabilities. We have developed a ligand that localizes a rigid void around a metal coordination site, which we have used to isolate a high-spin iron(IV) oxo that possesses excellent kinetic persistence. We have now focused our efforts on accessing the corresponding terminal manganese oxo complex. Structures collected through XRD support an increased reactivity in the manganese complex. Through a complex array of spectroscopic techniques (IR, UV-Vis, EPR), further insight will be provided on the electronic structure and reactivity of the terminal manganese oxo complex.
Chalcogenopyrylium dyes are a class of cationic chromophores that consist of one or more chalcogen-containing six-membered heterocycle with varying aromatic and aliphatic substituents. This platform offers a variety of sites for diverse functionalization that enable multiple tuning pathways. Their tunability makes them useful in a wide range of applications including solar energy conversion, biomedical imaging, photocatalysis, and sensor protection. In a recent publication, we shed light on unexpected solution dynamics of these molecules by variable temperature NMR and ultrafast laser spectroscopy. In our current studies, we aim to further understand and fill outstanding gaps in knowledge of the electronic structure and the nature of bonding in these dyes. Herein, we explore structural properties using X-ray diffraction experiments and theoretical studies. We have explored a variety of pyranone, polymethine, and pyrylium chromophores. We discuss single crystal growth techniques to furnish the best possible samples and report dye structures. Ultimately, we aim to use the information gathered here to guide further high-resolution X-ray charge density studies.
Redox Active Macrocyclic Iron Complexes as paraSHIFT Agents

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Magnetic resonance spectroscopy (MRS) is an alternative to MRI that measures the concentration of endogenous or exogenous compounds in vivo. Complexes with paramagnetic metal ions—paraSHIFT agents—respond to biological conditions (e.g. pH, temperature). The proton resonances of paraSHIFT agents are shifted far from tissue proton resonances, leading to their application as MRS probes. Physiological conditions such as lesions and inflammation can be detected by redox active Fe(II)/Fe(III) paraSHIFT agents. At these sites, reactive oxygen species produced by enzymes such as peroxidases may oxidize the paraSHIFT agents, producing a change in the paramagnetically shifted proton resonances. Macrocyclic ligands based on 1,4,7-triazacyclononane alkylated with heterocyclic pendants that contain a large number of magnetically equivalent protons can be used as paraSHIFT agents. These hexadentate ligands lead to the kinetic inertness of the Fe(II)/Fe(III) complexes due to the macrocyclic effect. This poster will focus on the design, synthesis, and characterization of the ligand and its complexation with Fe(II)/Fe(III). $^1$H NMR spectroscopy will provide proton resonances of the paramagnetic iron complexes and will be used to argue their potential for MRS applications.
NOTES: