

DEPARTMENT OF CHEMISTRY



**27<sup>th</sup>**

**A P R I L**

**U n d e r g r a d u a t e  
R e s e a r c h**

**SYMPOSIUM**

in **MOSSMAN HALL**

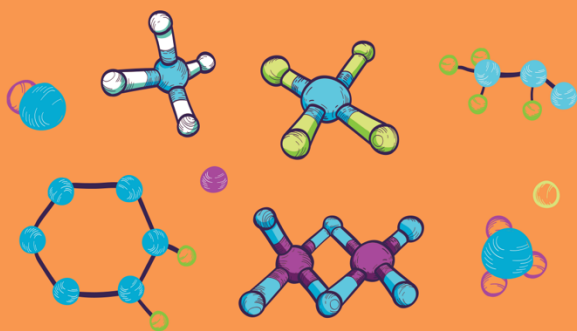
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**KEYNOTE SPEAKER**

**Dr. Benjamin Sundell** (ZwitterCo)

**Registration Deadline: April 10<sup>th</sup>**

**Abstract Deadline: April 19<sup>th</sup>**



<https://chem.utk.edu/undergraduate-students/undergraduate-research/>



Undergraduate Research Symposium  
Saturday April 27<sup>th</sup>, 2024



DEPARTMENT OF CHEMISTRY

**12:30 PM** – Kickoff Lunch (Mossman Lobby)

**1:30 PM** – Poster Session I (Mossman Lobby)

**2:30 PM** – Student Presentations (Mossman 102)

**3:30 PM** – Coffee and Cookie Break

**4:00 PM** – Poster Session II (Mossman Lobby)

**5:00 PM** – Move to Geier Hall

**5:30 PM** – Keynote Address: Dr. Benjamin Sundell (Geier Hall G033/034)

**6:00 PM** – Dinner and Awards Ceremony (Geier Hall G033/034)

**7:30 PM** – Closing Remarks (Geier Hall G033/034)

<https://chem.utk.edu/undergraduate-research-symposium/>



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CLINCH AVENUE

18TH STREET  
Cumberland Ave  
EB @ Melrose Pl

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LAUREL AVENUE

## List of Abstracts

Name		Session	Title	Page
Ahmad	Sophie	Poster 1	Synthesis of Chlorinated Polyethylenes for the Compatibilization of Mixed Polymer Waste	6
Ahmed	Maryam	Poster 2	Investigating the Phase Behavior of Biomimetic Model Membranes Containing Mixed-Chain Lipids	7
Andrews	Dylan	Poster 2	Properties of Quantum Materials	8
Barber	Sarah	Poster 1	Factors Contributing to Polymer Swelling Rates and Impact on Depolymerization of Consumer Waste	9
Byrd	Megan	Poster 1	Development of Biocompatible Nanosensors for Detection and Diagnosis of Mild TBIs	10
Cobb	Grayson	Poster 2	The Length of SMA Copolymers Influence the Extraction of Photosystem I from Thylakoids	11
Day	Kendra	Oral 1	Understanding the Impact of Particle Size on the Heterogeneous Depolymerization of Poly(ethylene terephthalate) via Glycolysis	12
Depe	Ashley	Poster 1	Exploring Copolymerization in MONTs	13
Dvorak	Bailey	Poster 2	Photochemical Magnetic Switch of Group 13 azadipyromethene (B, Al, Ga and In)	14
Gutierrez	Michael	Poster 1	An Investigation into Aza-BODIPY's precursors in Suzuki Coupling for Extended $\pi$ -systems	15
Hedges	Makayla	Oral 1	Investigating the Metabolic Fate of Isopentenyl and Dimethylallyl Pyrophosphate using <i>In-vivo</i> Isotopic Labeling	16
Lane	Nicolas	Poster 2	Probing Glycerolipid Metabolism in Yeast Cells Using a Caged Clickable Glycerol-3-Phosphate Probe	17
Larson	Madeline	Poster 1	Organic Residue Analysis: Performing FAME and GANE Analyses on Archaeological Ceramics	18
Llewellyn	Katelyn	Poster 2	Understanding the Interaction Between Iron (II) Phthalocyanine and Hydrazines	19
Millsaps	Ryan	Poster 1	Third Row Transition Metal Catalyzed Activation of CO <sub>2</sub>	20
Parikh	Rahil	Poster 2	Synthesis and Evaluation of Segmented Block Copolymer Gas Separation Membranes	21
Pate-Geames	Elokkin	Poster 1	Investigations into the Electronics of First Row Transition Metal-Oxos and the Metal-Oxo Wall	22
Russell	Caleb	Poster 2	Succinate Selective Lipid Switch for Controlled Release of Liposome Cargo	23
Sams	Ava	Poster 1	Elucidating the Structure of Mouse Glucagon	24
Steeley	Jacob	Oral 1	Capturing the Dynamic Behavior of Ring Polymers with Persistent Homology	25
Totorp	Taylor	Poster 2	Synthesis of Ether Ligands for Axial Coordination in Tethered Rhodium Complexes	26
Wilcox	Landri	Poster 2	Factors Contributing to Polymer Swelling Rates and Impact on Depolymerization of Consumer Waste	9

## **Synthesis of Chlorinated Polyethylenes for the Compatibilization of Mixed Polymer Waste**

Sophie Ahmad, Christy Witcher, Bailey Eberle, and Brian Long

The absence of proper end-of-life protocols for plastic waste has led to adverse environmental impacts with global impact. This issue arises, in part, due to a lack of established chemical and mechanical recycling processes. However, recent advancements in both chemical and mechanical recycling offer promising solutions by either transforming mixed polymer waste streams into new materials through thermal or catalytic processes or by aiding in the mechanical reprocessing of mixed plastic waste streams, respectively. For example, mechanical recycling can be enhanced through the incorporation of bespoke compatibilizers that enhance the thermomechanical properties of new products made from mixed plastic waste. These compatibilizers facilitate interactions between different polymer phases within a mixed waste blend by increasing the entropy of mixing and improving miscibility. In this research, compatibilizers containing components similar to polyvinyl chloride (PVC) and polyolefin elastomer (POE) are synthesized to passively compatibilize these common waste polymers. Therein, we synthesized compatibilizers varying in their molecular weight and chlorine content, and tested their ability to enhance the interfacial adhesion of PVC and POE. For example, series of copolymers with varied comonomer incorporation ratios and molecular weights ranging from 50-150 kg/mol were synthesized. Our results strongly suggest that the dominant mechanism for the compatibilization of PVC and POE to be co-crystallization with POE phase. These results indicate that the composition and sequence distribution of these copolymers play crucial roles in effectively compatibilizing macrophase-separated plastic waste.

## **Investigating the Phase Behavior of Biomimetic Model Membranes Containing Mixed-Chain Lipids**

Maryam Ahmed, Deeksha Mehta, Emily Chaisson, and Frederick A. Heberle

The mammalian plasma membrane is one of the most active and complex cellular membranes. In addition to its role as a barrier and structural support for the cell, the plasma membrane regulates the entry and exit of substances needed or produced by the cell and participates in cell-to-cell communication. The remarkable structural diversity of lipids in the plasma membrane contributes to its functional versatility, making it a fascinating structure for biophysical studies. Model membranes mimicking the outer leaflet composition of the plasma membrane show coexisting liquid phases when imaged with confocal fluorescence microscopy. This is primarily due to unfavorable interactions between saturated and unsaturated lipid chains, with cholesterol ensuring the overall fluidity of the membrane. The outer and inner leaflets of the plasma membrane are also asymmetric in their lipid composition, an aspect of biomembrane architecture that has yet to be fully explored. Using simplified model membranes of 1,2-dioleoyl-sn-glycero-3-phosphocholine (DOPC), 1-myristoyl-2-stearoyl-sn-glycero-3-phosphocholine (14:0-18:0PC) and cholesterol, we can investigate the biophysical properties of the outer leaflet of the PM. Chain asymmetric lipids in particular are thought to contribute to structural coupling of the two leaflets. Using confocal fluorescence microscopy, we will determine compositional phase diagrams for these lipid mixtures to establish phase coexistence regions and their boundaries.

## **Properties of Quantum Materials**

Dylan Andrews , Yanhong Gu, Luther Langston, Hans Bechtel, Stephanie Corder, and Janice L. Musfeldt

Quantum materials are an emerging interest in next-generation electronics, photovoltaics, and even quantum computing due to their unique thermal and magnetic properties. Materials like Mn<sub>12</sub>-Acetate (Mn<sub>12</sub>-Ac), 2D-TMDs, and Cr<sub>1/3</sub>TaS are some that are known and being studied for potential applications for in memory device, biomedical, and lidar applications. A thermal investigation of Mn<sub>12</sub>-Ac reveals features characteristic of ligand changes, while 2D-TMDs show interesting skyrmionics patterns, and Cr<sub>1/3</sub>TaS exhibit specific phonon Raman active modes. Future studies for these applications are still underway within the Musfeldt group, with promising results awaiting.



## **Factors Contributing to Polymer Swelling Rates and Impact on Depolymerization of Consumer Waste**

Sarah J. Barber, Landri E. Wilcox, Shelby R. Watson, and Mark D. Dadmun

Annually, over 300 million tons of plastic are produced, with over 70% of that plastic being disposed into landfills. Current alternatives to plastic disposal entail incineration, mechanical, and chemical recycling. Among these, chemical recycling is the most promising method in creating a truly circular plastic economy as it can regenerate polymers without degradation. Heterogeneous depolymerization is an effective chemical recycling method where the polymer initially swells with solvent, enabling chain scission to occur in the polymer flake. As the reaction proceeds, polymer chains begin to dissolve out of the flake which allows further depolymerization of dissolved polymer chains in the solvent. This dissolution continues until all polymer chains are dissolved in the solvent, ending in a homogeneous depolymerization reaction. This study aims to understand how polymer crystallinity and solvent-polymer compatibility impact the swelling of the polymer flake, as it is a crucial initial step of heterogeneous depolymerization. In these experiments, the rate of swelling of polyethylene terephthalate (PET) and polycarbonate (PC) with ethylene glycol (EG) and bisphenol A (BPA) was monitored by the change in mass of the flakes with exposure to the solvent. These results demonstrate that, for both solvents, PC swells faster and with more solvent due to its amorphous structure relative to that of semicrystalline PET. More importantly, BPA swells both polymers to a greater extent than EG, which aligns with the Hildebrand solubility parameters of the polymers and solvents. Previous studies within the Dadmun group, examining catalyzed depolymerization of polyesters and polycarbonates with the same solvents, indicated that the polymers depolymerize in BPA faster than in EG. This is consistent with the swelling data, demonstrating correlations between solvent-polymer compatibility, swelling, and the depolymerization process.

## **Development of Biocompatible Nanosensors for Detection and Diagnosis of Mild TBIs**

Megan Byrd and Bhavya Sharma

Traumatic brain injuries (TBI) result in a significant amount of disabilities and deaths across the world. Currently, TBI is diagnosed qualitatively, primarily based on symptoms, instead of through quantitative data, which can lead to misdiagnosis and further complications. Diagnostic techniques that are sensitive, selective, rapid, label-free, have multiplexing capabilities, and require little to no sample processing would allow for correct and timely diagnosis, enabling improved treatment options for individuals affected by TBIs. One ultrasensitive sensor platform that can provide these capabilities is utilizing surface-enhanced Raman spectroscopy (SERS)- based sensors, fabricated from plasmonic metal nanoparticles. An oscillating electric field can be generated on the surface of noble metal nanoparticles when excited by a laser, which is referred to as the localized surface plasmon resonance (LSPR). This resonance and oscillation then amplify the Raman scattered light from molecules attached to the surface of the nanoparticles, referred to as SERS. Through the development of SERS-based sensor platforms, we can attain a highly sensitive and rapid diagnostic assay that will allow for the simultaneous detection of multiple TBI biomarkers. We will present recent results on the development of SERS-based sensors for the detection and diagnosis of TBIs.

# The Length of SMA Copolymers Influence the Extraction of Photosystem I from Thylakoids

Grayson B. Cobb<sup>1</sup>, Godwin Ochola<sup>2</sup>, Cameron E. Workman<sup>3</sup>, Brian K. Long<sup>2</sup>, and Barry D. Bruce<sup>1,4</sup>

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Styrene-maleic acid copolymers (SMAs) effectively extract membrane proteins by forming nano-discs that preserve the native lipid environment of the membrane protein. Previous research has shown that SMA copolymers with extended side chains yield an increased solubilization efficiency (S.E.) of membrane-bound proteins. The mechanism through which SMA copolymers extract membrane proteins remains largely unknown. In this study, we analyzed a series of SMA copolymers with varying molecular weights and dispersity ( $\mathcal{D}$ ) on the protein extraction efficiency of trimeric Photosystem I (PSI) in the thylakoid membranes of cyanobacterium *Thermosynechococcus elongatus* (Te). The dispersity of these copolymers was altered by mixing the three different molecular weights of SMA copolymers (MN= 2.6, 8.6, & 20.0 kDa) at varying ratios to create a polymer blend, which was investigated either by 1) combining the polymers before solubilization, or 2) by a stepwise addition during solubilization. The highest yield of solubilized PSI was achieved by adding the medium molecular weight SMA copolymer alone. Interestingly, the sequence of copolymer addition appears to play a critical role in how PSI is extracted, suggesting divergent roles of copolymers with different lengths. SMA copolymer mixtures made through a step-wise addition yielded higher S.E. than mixtures synthesized before solubilization. Further research may determine how the mechanism of membrane protein extraction is affected by the sequential addition of SMA copolymers at varying molecular weights.

## **Understanding the Impact of Particle Size on the Heterogeneous Depolymerization of Poly(ethylene terephthalate) via Glycolysis**

Kendra Day and Mark D. Dadmun

Polyethylene Terephthalate (PET) is the most common plastic and is often mechanically recycled, making it prime material for chemical recycling. The heterogeneous depolymerization of PET via glycolysis has been studied by our group to elucidate the structure of reaction intermediates and their repolymerization. The reaction is often characterized as occurring at the surface of the PET flakes, where the surface area of a particle should impact reaction rate. Our research seeks to expand our understanding of the evolution of chain structure during PET depolymerization to demonstrate the impact of particle size and thus particle surface area on the evolution of PET chain structure during glycolysis. These experiments follow the decrease in molecular weight ( $M_n$ ), decrease in dispersity, and increase in percent crystallinity of depolymerized PET flakes of varying lengths (4 mm, 18 mm, or 44 mm). Our interpretation of chain evolution during glycolysis envisions ethylene glycol (EG) diffusing into the polymer flake to first react with amorphous polymer. Changing the particle length varies the surface area of the flake, altering the rate of EG diffusion into the PET particle and potentially the evolution of chain structure. However, the progression of chain  $M_n$  does not change with particle size. We interpret this data to indicate that the diffusion of EG into the smallest dimension of the polymer flake, its thickness (0.3 mm), governs the heterogeneous reaction, rather than it being controlled by the overall particle size or particle surface area. Understanding the process of PET depolymerization and the impact of flake dimensions on chain evolution offers insight to access and control the structure of oligomer intermediates. Our results illustrate that such intermediates can be repolymerized and used to produce value-added materials through less energy-intensive methods than depolymerization to monomer.

## Exploring Copolymerization in MONTs

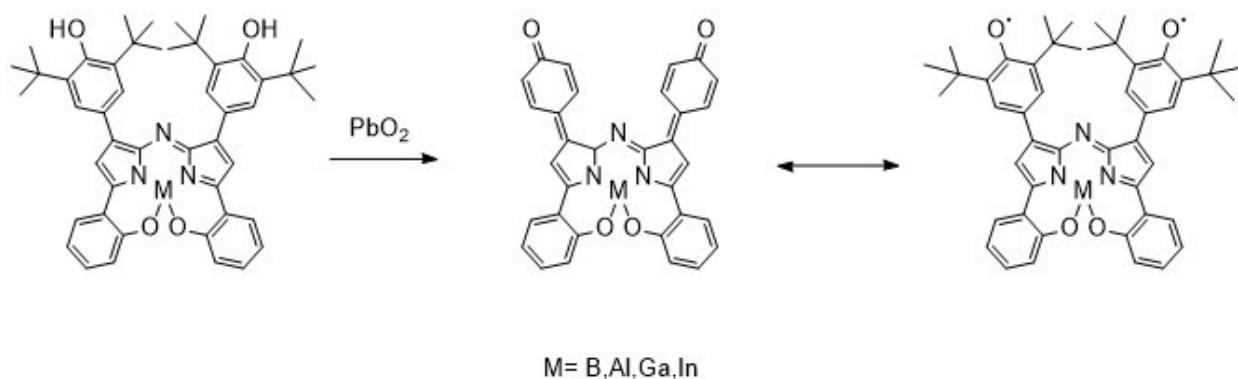
Ashley Depe, Jacob A. Barrett, and David M. Jenkins

Metal-organic nanotubes, or MONTs, are 1-dimensional crystalline structures formed by mixing a solution of a suitable ligand and metal ion, such as copper (II) bromide, in solvothermal conditions. This results in an anisotropic material formed of many small units, akin to traditional polyolefins, formed from the linkage of organic ligands with metals, as in the parent family of metal-organic frameworks, or MOFs. MOFs and MONTs share many potential applications, including catalysis, drug delivery, gas separation, and molecular sensing. Ligand multivariance, or combining different ligands to create a distinct material, has been well-studied in MOFs. In both MOFs and polyolefins, mixing of different ligands or monomers has been shown to result in a material with properties that surpass that of the pure MOF or polyolefin. Until recently, ligand multivariance has not been explored in MONTs. Our group seeks to understand the formation of these anisotropic materials to identify and employ nonlinear properties of multivariant MONTs. The synthesis and characterization of mixed-ligand MONTs is described herein.

## Photochemical Magnetic Switch of Group 13 aza-dipyrromethene (B, Al, Ga and In)

Bailey E. Dvorak, Morris Oyelowo, and Viktor Nemykin

A series of Group 13 aza-dipyrromethene (DIPY) complexes (B, Al, Ga and In), which have possible applications for data storage and quantum computing, were prepared by oxidizing their respective diphenol derivatives (Figure 1). The diradicaloid nature of these compounds was investigated using a wide range of spectroscopic methods, including NMR, mass spectrometry, EPR, UV-Vis, fluorescence, IR spectroscopy, transient absorption spectroscopy as well as variable-temperature X-ray crystallography. DFT and TDDFT calculations, variable-temperature NMR and EPR data suggest a singlet ground state for the aza-dipyrromethene (DIPY) complexes (B, Al, Ga and In) based diradicaloids. Electrochemical and spectroelectrochemical data indicate several processes in these systems. Transient absorption spectroscopy shows a dramatic decrease in the excited state lifetime of the diradicaloids compared to that of the phenols. DFT and TDDFT calculations were used to explain the unusual spectroscopy observed in the target compounds.



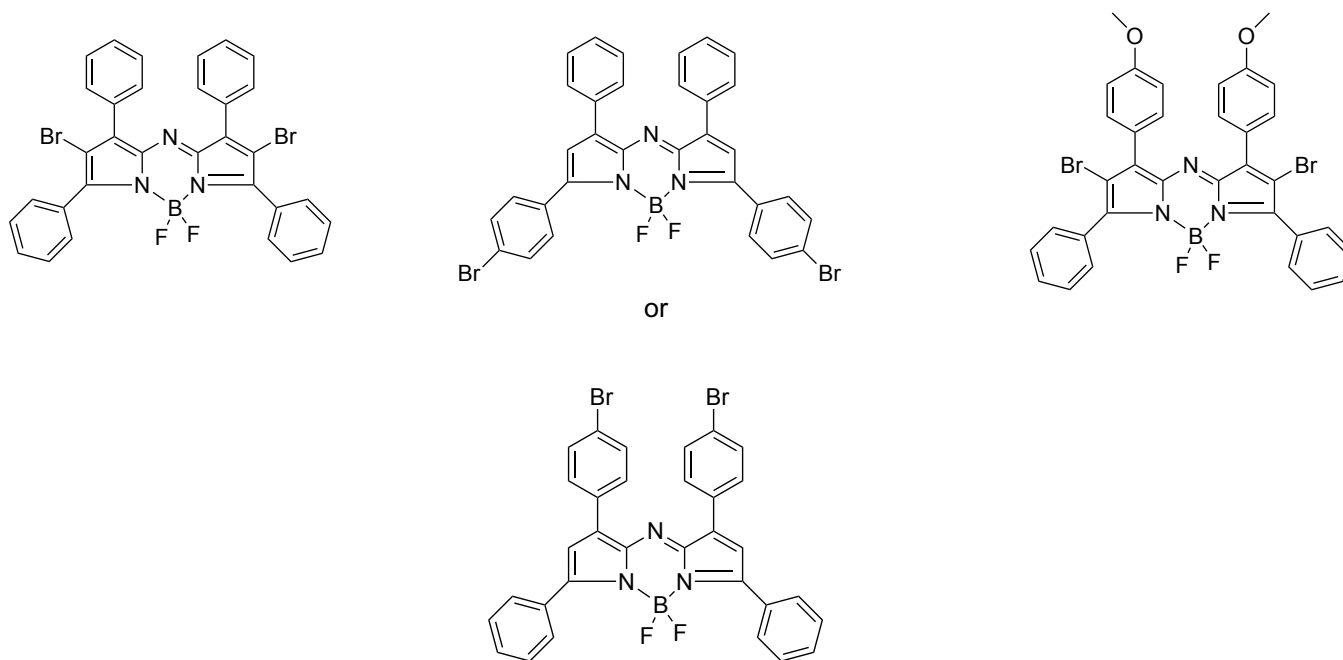
# An Investigation into Aza-BODIPY's precursors in Suzuki Coupling for Extended $\pi$ -systems

Michael Gutierrez and Viktor Nemykin

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To improve the light harvesting ability in photovoltaic cells, we plan to substitute fullerene acceptors. There are a variety of chromophore chosen from the class of the aza-BODIPY. Thus, synthesis of large array of aza-BODIPY will be discussed. One such method to use Suzuki coupling to extend of aza-BODIPYs. In this study, we synthesize the required precursors Suzuki coupling. The target molecules have been characterized by UV-VIS and NMR as well as theoretical calculations. Their redox and electronic properties will be evaluated by electrochemical and chemical methods.



*Figure 1: 2,6-dibromotetraphenyl aza-BODIPY(left); 1,7 or 3,5-p-bromo aza-BODIPY(center); 1,7-phenylmethoxy-2,6-dibromo aza-BODIPY(right)*

## **Investigating the Metabolic Fate of Isopentenyl and Dimethylallyl Pyrophosphate using *In-vivo* Isotopic Labeling**

Makayla Hedges, Zackary N. Hulsey, Dillon P. McBee, and Joshua A. Baccile

In all organisms, the structurally related five-carbon metabolites isopentenyl pyrophosphate (IPP) and dimethylallyl pyrophosphate (DMAPP) are the central precursors to all isoprenoids. Despite this, the independent chemistry of these two vital precursors remains poorly understood. The ability to chemically differentiate the metabolic fate of IPP and DMAPP in cells requires isotopically distinguishing the two structurally related precursors. This required the development of a cell permeant analog that allows for release of IPP and DMAPP within the cell. After the successful development of such a method within mammalian cells, we sought to expand the utility of the method by demonstrating exogenous delivery of IPP and DMAPP into the Gram- positive bacterium, *Bacillus subtilis*. In this talk, I will describe our recent progress in this area as it relates to the developed self immolative ester (SIE)-caging approach and the synthesis of  $^{13}\text{C}$  labeled IPP and DMAPP analogs with a known and distinct heavy isotope pattern. We have completed the synthesis of 3- $^{13}\text{C}$  prenyl through a 5-step route beginning with ethyl bromoacetate and [ $^{13}\text{C}_3$ ] acetone, as well as, its cell-permeant analog using a cleavable esterase chain for *in-vivo* application. The synthesis of 4- $^{13}\text{C}$  isoprenol has also been completed as an 8- step route starting from [1,2,3,4- $^{13}\text{C}_4$ ] ethyl acetoacetate, which is currently being converted into the cell-permeant analog. Preliminary results have been obtained showing the successful incorporation of the DMAPP-isotopologue through the  $^{13}\text{C}$  RNA labeling in *B. subtilis*. We look towards further metabolic incorporation experiments in *B. subtilis* to identify novel isoprenoids biosynthesized and distinguish their metabolic origins between IPP and DMAPP.



## **Probing Glycerolipid Metabolism in Yeast Cells Using a Caged Clickable Glycerol-3-Phosphate Probe**

Nicolas Lane, Jinchao Lou, Christelle F. Ancajas, Yue Zhou, Todd B. Reynolds, and Michael D. Best

Lipids play a critical role in controlling key biological pathways that are dysregulated in some diseases. As a result, it is important to track the production of lipids in cells. In this study, we introduce a novel lipid probe for comprehensive metabolic labeling of lipids in *S. cerevisiae* cells. Previous lipid probes encountered challenges in labeling glycerophospholipids due to the inability of probes to enter cells and infiltrate lipid biosynthetic pathways. Our new design addresses this issue by introducing a caged phosphate head group for minimal cellular alteration upon delivery. Following intracellular transport, the SATE caging group undergoes esterase-induced hydrolysis, and a fluorescence label is integrated via SPAAC click chemistry. Validation of probe infiltration and metabolic labeling of glycolipids was performed via LCMS, TLC, and fluorescence microscopy.

## **Organic Residue Analysis: Performing FAME and GANE Analyses on Archaeological Ceramics**

Madeline Larson, Vernon Stafford III, and David M. Jenkins

Organic residue analysis (ORA) of archaeological artifacts has emerged as a valuable tool for archaeologists in reconstructing past human activity. Ceramic pottery vessels, some of the most frequently encountered artifacts, are ideal targets for ORA. Unglazed pottery is composed of a porous matrix that allows for the absorption of organic compounds through prolonged heating or use. These absorbed chemicals can be extracted and identified even after long periods of time. Our group is pursuing two avenues of research in this area. The first project employs fatty acid methyl ester (FAME) analysis to extract and identify fatty acids in ancient ceramics to determine the food sources they may have originated from. The primary fatty acid biomarkers are palmitic acid, oleic acid, and stearic acid. These fatty acids are frequently encountered in living organisms, which allows for easier detection. Additionally, conclusions about food sources can be drawn by examining the ratios of these fatty acids, particularly palmitic acid and stearic acid. The second project aims to develop a method for wine identification by converting common organic acids found in wine to neopentyl esters, which we have dubbed grape acid neopentyl esters (GANEs), a similar process to lipid identification in FAME analysis. This method is able to identify classical grape biomarkers such as tartaric acid, malic acid, succinic acid, and also introduces ethyl hydrogen succinate, which provides unambiguous evidence for fermentation. The similarities between FAME and GANE analysis enable both sets of biomarkers to be detected by gas chromatography- mass spectrometry (GC-MS), a highly robust analytical technique. Identifying lipid and wine compounds in ceramics can help uncover significant anthropological insights on dietary practices, trade and exchange, regionality, and sociopolitical shifts of past societies.

## **Understanding the Interaction Between Iron (II) Phthalocyanine and Hydrazines**

Katelyn Llewellyn and Viktor Nemykin

Generally, most metal phthalocyanines are used as catalysts for a plethora of redox reactions, including the oxidation of methane, phenols, alcohols, and olefins. Iron (II) phthalocyanine, however, is a specific complex depicting the interaction of benzene rings, nitrogen groups, and iron (II). In a previous study, it was found that iron (II) phthalocyanine (FePc) has an interesting reaction with hydrazines, being the cleavage of a nitrogen-nitrogen bond for the formation of an amine group. To further examine this phenomenon, we have screened various hydrazines to understand better why this occurs. Furthermore, the synthesis of the FePc complex with hydrazine groups in an oxidative environment produces a color change reaction and crystalline structures by which the makeup and cleaving can be observed. Through the use of UV-Vis and NMR spectroscopy, these changes can be visualized and studied. Similarly, the progression of these reactions is a vital component to further understanding this relationship and determining the cause of the cleaving. In plotting and visualization of the data, one can begin to understand the interaction between these substances. These findings are directly related to the redox reactions occurring in simple batteries, as well as more complex rechargeable batteries and fuel systems. With the results of this interaction, other relationships can be examined and used to produce more sustainable, affordable, and effective solutions for energy and power production.

## **Third Row Transition Metal Catalyzed Activation of CO<sub>2</sub>**

Ryan Millsaps, Thomas Jones, and Konstantinos D. Vogiatzis

In response to global concerns over the environmental impacts of the greenhouse gas carbon dioxide, this project aims to explore the activation of the molecule to both reduce and functionalize it. Current studies have expanded on this system by utilizing density functional theory to explore reaction energies and pathways for the first row transition metals excluding Sc. This preliminary method aims to further explore plausible mechanistic pathways in efficiently functionalizing the gas. The initial study utilized the complete active space self-consistent field (CASSCF) through second order perturbation theory (CASPT2) to explore CO<sub>2</sub> activation with atomic iron and will be repeated in the future with other promising transition metal species.

# **Synthesis and Evaluation of Segmented Block Copolymer Gas Separation Membranes**

Rahil H. Parikh, Maggie Powell, and Brian K. Long

To satiate the growing demand for electrical energy, we have witnessed increasing levels of fossil fuel combustion. Unfortunately, this results in the release of carbon dioxide into Earth's atmosphere. To reduce these emissions, scientists are investigating several technologies, such as using polymeric gas separation membranes. This membrane-based technique is passive and requires little energy compared to other conventional gas separation methods. While many different types of polymers have been evaluated, Polymers of intrinsic microporosity (PIMs) exhibit outstanding permeability and selectivity, crucial properties for evaluating the effectiveness of gas separation polymer membranes. However, PIMs also have inherent drawbacks in that they show rapid physical aging and often have poor mechanical properties. To address these issues, we have synthesized a series of segmented block copolymers consisting of glassy, PIM-like units, and rubbery units that often exhibit minimal aging and enhanced mechanical properties. Herein, we show a successful route to synthesize these segmented block copolymers containing PIM-1 segments and ring-opening metathesis polymerized (ROMP) hexyl norbornene segments. These membranes show a qualitative increase in their elasticity compared to PIM-1 membranes, and we anticipate these results will lead to a better understanding of how polymer architecture impacts mechanical properties, physical aging, and gas transport properties.

## **Investigations into the Electronics of First Row Transition Metal-Oxos and the Metal-Oxo Wall**

Elokkin K. Pate-Geames, Thomas Jones, David M. Jenkins, and Konstantinos D. Vogiatzis

Metal-oxo complexes are important intermediates in a variety of oxygen-atom transfer reactions (e.g. oxidation, epoxidation). Previous work involved elucidating the epoxidation reaction mechanism catalyzed by winged tetracarbene complexes, in collaboration with the Jenkins Group (University of Tennessee – Knoxville). Density functional theory (DFT) calculations were performed on iron and chromium complexes, which helped to determine the stability and spin states of the reaction intermediates of the proposed mechanism. Of particular focus was the metal-oxo intermediate species, where the electronic structure of these reaction intermediates was explored. We have begun to focus on metal-oxo complexes of the first row of transition metals (vanadium – copper) and their electronics in regard to the metal-oxo wall. By investigating the electronics of these tetra- and pentahydrate metal-oxo complexes, greater insight can be given into the characteristics of each metal-oxo species.

## **Succinate Selective Lipid Switch for Controlled Release of Liposome Cargo**

Caleb G. Russell, Brooke Smith, and Michael D. Best

The potential of lipid nanoparticles as drug delivery vessels has proven viable, but difficulties in selective delivery still pose a major issue. A lipid nanoparticle system has been synthesized which would be viable for selective release, utilizing the presence of a target molecule upregulated in a diseased biological system. Succinate is one appealing target molecule for which a correspondingly reactive switch could be designed, as it plays a role in the generation of tumors, inflammation, and the production of reactive oxygen species. The synthesis of such a switch would destabilize the lipid nanoparticle in the presence of succinate, allowing for the creation of smart nanoparticles capable of selectively releasing cargo in diseased cells, thereby allowing the use of stronger medications and with fewer side effects. A cyclic guanidinium headed switch has been proven to successfully facilitate release of cargo in the presence of succinate. Hydrophobic Nile red release studies have proven succinate selectivity over fourteen other similar metabolites due to the unique interactions of succinate and guanidine. Further research is being conducted to build a variety of lipid switches selective for other target molecules which are upregulated in diseased cells, including metabolites GTP and Tpi.

## **Elucidating the Structure of Mouse Glucagon**

Ava Sams and Thanh Do

Type 2 diabetes (T2D) is a metabolic disorder characterized by insulin resistance and impaired insulin secretion. Glucagon, a peptide hormone produced in the pancreas as well, acts antagonistically to insulin by increasing blood glucose levels. Understanding the molecular structure of glucagon is crucial for a better understanding of its role in T2D. Recent studies by our group have revealed two distinct conformations of mouse glucagon, with one of the conformations potentially being attributed to peptide oxidation. Our liquid chromatography – ion mobility spectrometry – mass spectrometry (LC-IMS-MS) analysis has identified two oxidation peaks corresponding to stereoisomers of oxidized methionine (S and R). However, the structural implications of these oxidized forms remain unclear. In this study, we employ Replica Exchange Molecular Dynamics (REMD) simulations of both stereoisomers to investigate the different structural features of glucagon. REMD simulations produce an atomistic prediction of a peptide’s folded conformation, which is used to calculate theoretical collisional cross sections and compare with LC-IMS-MS data. By elucidating the structural ensemble of glucagon, our study aims to provide insights into its functional roles in glucose homeostasis and its potential as a therapeutic target in T2D management.



# Capturing the Dynamic Behavior of Ring Polymers with Persistent Homology

Jacob Steeley<sup>1</sup>, Grier Jones<sup>1</sup>, Siteng Zhang<sup>2</sup>, Ting Ge<sup>2</sup>, and Konstantinos D. Vogiatzis<sup>1</sup>

<sup>1</sup>*Department of Chemistry, University of Tennessee, Knoxville*

<sup>2</sup>*Department of Chemistry and Biochemistry, University of South Carolina*

Understanding the conformational behavior of polymers is tantamount to predicting the properties of the materials they produce, and linear polymers have many elegant mathematical models that can predict their behavior. However, these models fail to capture the behavior of topologically non-trivial polymers, such as non-concatenated ring polymers. In pursuit of the elucidation of the conformational behavior of ring polymers, persistent homology has been leveraged to provide conformational information in a polymer melt. We have recently developed a series of new tools based on persistent homology for understanding the shape of ring polymers in three-dimensional space. Furthermore, these tools can be applied in a dynamic environment to describe the changes of a ring polymer as deformation occurs. To this end, we utilize two-dimensional diagrams that hold the topological information (persistence diagrams), which provide an avenue to describe polymer changes over time when subjected to external forces such as increasing shear speed. This method demonstrates a correlation between the deformation of a polymer and the evolution of topological features stored on the persistence diagrams.

## **Synthesis of Ether Ligands for Axial Coordination in Tethered Rhodium Complexes**

Taylor Totorp, Ernest Bennin, and Ampofo Darko

Prior investigations have demonstrated the stability of chiral thioether ligands tethered to rhodium complexes, showcasing promising enantioselectivity in cyclopropanation reactions. Despite these advancements, the achieved yields were notably low. To address this limitation, we propose replacing the thioether ligands with chiral ether ligands. This hypothesis originates from the notion that thioether ligands may exhibit strong coordination, potentially hindering intermediate formation and thus impacting reaction efficiency.

