4th Annual

UNDERGRADUATE RESEARCH SYMPOSIUM

Saturday, April 26th, 2025
Mossman Hall

THE UNIVERSITY OF TENNESSEE KNOXVILLE
DEPARTMENT OF CHEMISTRY

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DEPARTMENT OF CHEMISTRY

4th Annual Undergraduate Research Symposium

April 26th, 2025

12:30 PM – Kickoff Lunch (Mossman Lobby)

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

2:30 PM – Student Presentations Session I (Mossman 102)

3:30 PM – Coffee and Cookie Break

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

5:15 PM – Keynote Address: TBA (Mossman 102)

6:00 PM – Dinner and Awards Ceremony (Mossman Lobby)

7:00 PM – Closing Remarks (Mossman Lobby)

Ken and Blaire Mossman Hall

1311 Cumberland Av
Knoxville, TN 37916

Abstracts

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Surface-Enhanced Raman Spectroscopy combined with Machine Learning for Development of Point of Care Assays for Neurochemical Monitoring

Aastha Oza, Wilson Garuba, Bhavya Sharma

Neurological disorders are a leading cause of disability, impacting more than 43 percent of the world's population. Key to reducing disease progression and damage to the nervous system is early detection and treatment. Changes in the concentration of neurochemicals can serve as biomarkers for these diseases. Current detection techniques are challenged by rapid, low concentration measurements. Here, we present rapid detection of catecholamines, a class of neurotransmitters that includes epinephrine, norepinephrine, and dopamine, in artificial cerebrospinal fluid (aCSF) using surface-enhanced Raman spectroscopy (SERS) in conjunction with multivariate analysis.

Raman spectroscopy is a highly sensitive and specific vibrational spectroscopy. To measure molecules in ultralow concentrations, a nanostructured metal surface is implemented to enhance the Raman scattering. An electric field is generated at the surface through excitation of the metal electrons. This field enhances the Raman scattering signal of molecules near the nanoparticle surface.

We utilized gold nanoparticles (AuNPs) as the substrate, which allows us to detect catecholamines at low concentrations (~1μM) in aCSF. We apply multivariate analysis and machine learning to quantify and classify the neurochemicals. This combination of spectroscopy with machine learning allows for development of point-of-care diagnostic tools for neurological disorders, enabling more timely and accurate diagnoses.

Single-Molecule Conductance of Acene-Chalcogen Junctions with Gold, Silver, and Copper Electrodes

Shelby Belt, Dakota Landrie, Sharani Roy

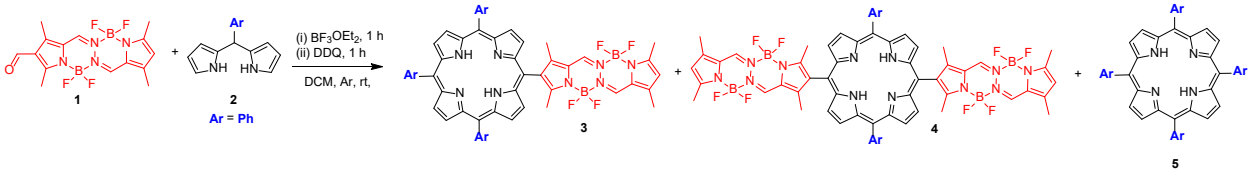
The development and application of single molecule junctions represents a significant leap forward in nanotechnology since the seminal idea by Avriam and Ratner [1]. Theory and computation offer an avenue to explore fundamental electronic properties, enabling a deeper understanding of the underlying mechanisms of quantum transport in these junctions. By constructing molecular junctions using linear acenes with systematically increasing numbers of connected rings - benzene, naphthalene, anthracene, tetracene, and pentacene - we analyzed the effects of increasing conjugation and inter-electrode distance on conductance and current. Additionally, we varied the contact atom from S, Se, to Te, and the electrodes from Au, Ag, to Cu to explore effects of the molecule-electrode interface on transport properties. Using an *ab initio* tunneling model for coherent transport, we investigated the effects of the molecule, contact, and electrode using density functional theory. We found that conductance decreases with acene length and increases with the work function of the metal electrode, i.e., the higher the work function, the greater the conductance. Moreover, conductance decreases with increasing size of the contacts, more so for longer acenes than for shorter acenes.

Aviram, A.; Ratner, M. A. Molecular Rectifiers. *Chem. Phys. Lett.* 1974, *29* (2), 277–283. DOI: 10.1016/0009-2614(74)85031-1.

Investigation of Energy Transfer in BOPHY-Porphyrin Dyads

Alden Dexter, Dijo Prasannan and Victor Nemykin

Multichromophoric assemblies with varied numbers of spacer types and lengths for energy or charge transfer have been reported by various researchers, particularly for applications in light harvesting, energy storage, sensors, and optoelectronic devices. Porphyrins, BODIPYs, and BOPHYs are fluorescent dyes widely used in such molecular energy transfer arrays. These molecules, when assembled in a molecular structure along with another chromophore, can act as an electron or energy donor/acceptor system by virtue of their photophysical properties. Here we present the energy transfer characteristics in BOPHY-porphyrin dyads. BOPHY appended porphyrins were prepared by adopting Lindsey's method. The reaction of formylated BOPHY **1** with dipyrromethene **2** in the presence of BF_3OEt_2 as catalyst afforded both A_2B_2 and A_3B type porphyrin dyads along with tetraphenyl porphyrin **5** (Scheme 1). The dyads, **3** and **4** were characterized by various spectroscopic techniques and the energy transfer properties were investigated.



Scheme 1. Synthesis of BOPHY-porphyrin dyads

Novel Molecular Rotor BODIPYs and their Supramolecular Assemblies with Zinc Porphyrinoids

Michael Gutierrez, Victoria Villarreal, Viktor Nemykin

A series of meso-isoxazole functionalized BODIPY dyes were synthesized as molecular rotors to investigate photoinduced, viscosity-dependent charge transfer dynamics. These BODIPYs undergo twisted intramolecular charge transfer (TICT), a process in which intramolecular twisting proceeds with excited-state electron transfer. In highly viscous environments, molecular rotation is reduced and TICT is suppressed, causing enhanced fluorescence. These compounds were characterized using ^{1}H-NMR and 2D COSY NMR, high-resolution mass spectrometry (HRMS), UV-Vis, and fluorescence spectroscopies. These BODIPYs will ultimately be used as electron acceptors in a supramolecular donor-acceptor assembly formed via coordination of BODIPY pyridine linker to zinc porphyrinoid donor. Electrochemical, spectroelectrochemical, and transient methods will be used to investigate redox-potentials, charge-separated state lifetimes, and the stability of the formed supramolecular assemblies.

Influence of Polar Side Chains on Solubility and Thin-Film Conductivity of Doped Conjugated Copolymers

Taylor Kearbey, Abigail Linhart, Michael Kilbey

Conjugated polymers are of interest because their optoelectronic and physical properties make them promising candidates for use in electronic devices. Although semiconducting in nature, conjugated polymers can be chemically doped to increase their conductivity, which allows them to approach metal-like electronic characteristics. Prior work aimed at increasing the efficiency of the doping process and tailoring the design of thiophene-based copolymers having alkyl side chains has been done, but these approaches can be challenged by insolubility upon doping. In this research, conjugated polymers with oligoethylene glycol side chains are synthesized to examine how increasing the polarity of the side chains affects factors such as solubility and thin-film conductivity. A synthetic route involving ether substitution was developed using 3,4-dimethoxythiophene and 2-ethoxyethanol. The resulting monomer, 3,4-bis(2-ethoxyethoxy)thiophene, was then copolymerized with 2,5-dibromothiophene to produce a conjugated, thiophene-based copolymer with polar side chains. The Hansen Solubility Parameters (HSPs) and thin film conductivity were measured to examine how solubility and conductivity differ from analogous copolymers with alkyl side chains. Initial results have shown that the HSPs have a higher polarity component than the copolymers containing alkyl side chains, as expected. In the future, this research will explore copolymer conductivity at different dopant concentrations, as well as other optoelectronic characteristics using measurements such as UV-Vis and FTIR. Ultimately, this research provides fundamental insight into how polar interactions from the side chains affect the solubility, conductivity, and optoelectronic properties of conjugated polymers.

Synthesis of N-Heterocyclic Carbene Ligands for Disparate Applications on Gold Surfaces

Anna Mahar, Kyle Schulmeister, David Jenkins

Gold surfaces and nanoparticles are highly modifiable materials that have found applications ranging from biosensing to catalysis. The functionality of gold is largely a result of the molecules adsorbed onto its surface, the self-assembled monolayers (SAMs). Since their introduction as surface modifiers, N-heterocyclic carbenes (NHCs) have revolutionized the surface chemistry field due to their ability to form stable and modifiable SAMs. Our research aims to design NHCs for two disparate purposes: amide coupling on surfaces and control over monolayer orientation.

The ability to bind biologically relevant aptamers to a metal surface can enable these materials to be used in applications such as biosensing. By modifying the backbone of an NHC, one can install carboxylic acids to enable amide coupling on the resulting monolayer. Other groups have used NHCs with a short carbon chain carboxylic acid for this purpose, however the proximity of the carboxylic acid to the surface limits the size of usable aptamers. In this study, a carboxylic acid-functionalized NHC with a long carbon chain was synthesized to improve flexibility and allow for binding of larger aptamers and other proteins.

NHCs in monolayers have been shown to adopt an upright or flat laying conformation relative to the surface. In addition, either one or two NHCs can bind to a single gold adatom, complicating surface spectroscopy. To solve this problem, we synthesized a novel bidentate macrocyclic NHC designed to form a monolayer where two NHCs are bonded to a single adatom in a flat laying conformation.

Investigation of Assemblies Between Zinc Porphyrins or Phthalocyanines and Axially Coordinated 2-Pyridone-BODIPYs

Jeffrey Manley, Victoria Villarreal, Tanner Blesener, Victor Nemykin

The interaction between electron-deficient [b]-fused 2-pyridone-BODIPYs modified with terminal pyridine or imidazole electron-withdrawing groups coordinated with zinc porphyrins and phthalocyanines is investigated to understand the behavior of their charge-separated states. The predicted binding of the nitrogen atom of the pyridine group on the electron acceptor BODIPY to the central zinc atom of the electron donor porphyrinoid by axial coordination with a 1:1 ratio is confirmed by ^{1}H NMR and mass spectrometry. Spectroelectrochemistry and electrochemistry were used to investigate the redox behavior of BODIPY electron acceptors and zinc porphyrinoid electron donors. Binding affinity and supramolecular assembly stability were analyzed using NMR, UV-Vis, and fluorescence spectroscopies.

Metabolic Labeling of Phosphatidylethanolamine (PE) Lipids using Synthetic Clickable Probe Analogs of Ethanolamine

Lynn Nguyen, Rob Maraski, Jinchao Lou, and Michael Best

Phospholipids are not only the major component of the membrane but also implicated in detecting human diseases such as cancer. PE lipid, a part of phospholipids, plays essential roles in the biological processes contributing to cellular signaling and membrane dynamics. To have a more advanced understanding of PE lipid's functions and distribution, we developed the labeling technique using a clickable probe. We first designed our azide probes and fed them to the cell, which created the attachment to our lipid in the yeast cell. We then ensure the desired product via click chemistry reaction before testing. Our study combines fluorescence microscopy data, thin-layer chromatography (TLC) technique, and mass spectrometry analysis to have multiple insights into the probe's performance and ability. We successfully observed the tagged products in live cells during fluorescence microscopy. Although in the TLC result PE did not show up very bright, it still shows that our method successfully labeled PE lipids in live cells and can be used to track their distribution and behavior. The future application of this labeling technique holds a significant role in cell research and innovation. In vivo studies, this technique will provide a deeper insight into lipids in complex biological systems.

Synthesis of Ether Ligand for Axial Coordination in Tethered Rhodium Complexes

Taylor Totorp, Ernest Bennin, Ampofo Darko

Prior investigations have demonstrated the stability of chiral thioether ligands tethered to rhodium complexes. These complexes showcase 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 a strong coordination, potentially hindering intermediate formation and thus impacting reaction efficiency. Ether ligands as proposed should exhibit a weaker coordination, potentially helping to increase intermediate formation and efficiency.

Western Diet and Chronic Alcohol Consumption Have a Systemic Impact on the Stool and Plasma Metabolome in a Non-human Primate Model.

Sydney Smith, Courtney Christopher, Shawn Campagna

The gut microbiome holds a significant amount of power in influencing metabolic pathways, immune function, and chronic disease development in the human body. Its behavior and composition are largely impacted by what nutrients the organism consumes on a regular basis. This metabolomics study investigates how the standard western diet (WD) and chronic binge alcohol (CBA) consumption alter the stool and plasma metabolome using a non-human primate (NHP) model. The method of analysis was high resolution liquid chromatography-mass spectrometry (LC-MS) on NHP extracted stool and plasma metabolites that were analyzed on a 7-month WD with or without CBA and compared to baseline samples. The results showed that both WD and CBA significantly altered metabolite abundances, impacting critical reaction pathways involved in purine metabolism, neurotransmitter synthesis, and antioxidant production. The addition of CBA habits and increased WD duration intensified these effects, leading to a larger imbalance in gut microbial composition and contributing to metabolic dysregulation. Furthermore, alcohol consumption alone affected metabolites in the stool metabolome involved in immune response and neurochemical regulation. These findings emphasized the complex relationship between diet, alcohol, and gut microbiota, revealing potential ways that these factors contribute to the onset of chronic diseases like obesity, diabetes, gastrointestinal and neurological disorders, and weakening of the body's immune defense. Despite these newer insights, the complexity of the gut microbiome is still much unexplored and ongoing research is still under way to fully understand the long-term health implications of dietary and alcohol-related shifts in gut metabolism.

Synthesis of fewer ring systems with the potential to carry out anti-inflammatory actions with reduced side effects.

Alexandria Wood, Opeyami Tade, Shawn Campagna

Glucocorticoids have proven to be a highly effective treatment in treating inflammation caused by a number of diseases. Glucocorticoids bind to the glucocorticoid receptor and trigger the anti-inflammatory action through the inhibition of transcription; however, a transactivation response is also initiated. This response is what causes glucocorticoids' undesired side effects with the most notable being steroid-induced diabetes mellitus. This research sets out to synthesize a new set of fewer ring systems and investigate their potential as being more effective glucocorticoids that could retain glucocorticoids' anti-inflammatory properties but reduce the transactivation response thus lowering the side effects. The molecule that was synthesized was then characterized using mass spectrometry, IR spectroscopy, and NMR spectroscopy. All of the potential fewer ring systems' interactions with the glucocorticoid receptor were investigated using molecular docking studies. The molecular docking studies showed that the fewer ring systems interacted with the glucocorticoid receptor in the deacyl cortivazol (DAC) binding pocket with different amino acids than the native DAC ligand. The different single ring molecules showed different binding affinities to the receptor as well.

Peeling Back the Layers of Poly(vinyl) Chloride and Polyethylene Compatibilization

Sarah Barber, Bailey Eberle, Mark Dadmun

Poly(vinyl) chloride (PVC) is the third most abundant plastic, yet it remains one of the most difficult plastics to recycle and reprocess. Fuel pyrolysis of PVC may release toxic hydrochloric gases, while mechanical recycling creates material with poor structural properties due to phase separation. This study explores the potential of compatibilizers created from waste PVC to enhance the mechanical recycling of amorphous PVC blended with semicrystalline polyolefin elastomers (POE). We evaluate the adhesion strength of the PVC/POE interface when compatibilized with hydrodechlorinated poly(vinyl) chloride (d-PVC) copolymers and compare this behavior to PVC/POE interfaces compatibilized with structurally similar and industrially available chlorinated polyethylenes (c-PE). Despite the immiscibility of PVC and POE, the compatibilizers demonstrate a significant improvement in the interfacial strength of the PVC/POE interface. Notably, the d-PVC copolymers outperform industry analogs. It appears that the more blocky polymer chain structure facilitates homogeneity across the polymer-polymer interface and allows for greater chain stitching, highlighting the importance of the copolymer's molecular design. Our findings show the compatibilization of amorphous/semicrystalline polymers with PVC-PE like compatibilizers derived from the waste stream as a promising and viable recycling strategy towards a truly circular plastic economy.

The Evolution of PET Throughout Heterogeneous Glycolysis and the Repolymerization of Oligomers

Kendra M. Day, Mark Dadmun, Viktor Nemykin

Polyethylene Terephthalate (PET) is the most common plastic and is often mechanically recycled, making it prime material for chemical recycling. Our research seeks to elucidate the evolution of chain structure during PET depolymerization to demonstrate the impact of particle size and thus particle surface area on reaction intermediates throughout depolymerization and repolymerization. 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 envisions ethylene glycol (EG) diffusing into the polymer flake to first react with amorphous polymer, and our results 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. Furthermore, we seek to understand chain evolution in order to access and control the structure of oligomer intermediates, which we repolymerize through annealing to achieve similar molecular weights and tensile strengths to virgin PET. Ultimately, our results illustrate that intermediates can be repolymerized and used to produce value-added materials through less energy-intensive methods than depolymerization to monomer.

The Influence of Mixed Chain Lipids on Membrane Phase Behavior and Nanodomain Formation

Maryam Ahmed, Emily Chaisson, Deeksha Mehta, Averi Cooper, Fred Heberle

The lipid composition of eukaryotic plasma membranes is strikingly diverse. A particularly intriguing class of lipids is the ordered hybrid lipids (OHL), which possess fully saturated hydrocarbon chains of unequal length. Here, we investigated how the backbone position of OHL chains influences the behavior of domain-forming mixtures. We examined ternary mixtures of cholesterol, DOPC, and either 14:0-18:0 PC or 18:0-14:0 PC as the high-melting lipid. Using confocal fluorescence microscopy, we find that transposing the sn-1 and sn-2 chains of OHL results in a dramatically different phase behavior. Specifically, liquid-ordered (Lo) + liquid-disordered (Ld) phase coexistence was observed over a wide range of compositions and temperatures in the 14:0-18:0PC/DOPC/Chol system, but not in the 18:0-14:0PC/DOPC/Chol system. Future work will investigate the nanoscopic phase behavior of selected compositions using FRET and cryo-EM.

Electromechanical and Kinetic Theoretical Study of Single-Molecule Cycloaddition Reactions via Single-Molecule Junctions

Sydney Cummins, Dakota Landrie, Dr. Sharani Roy

A single-molecule junction is a powerful apparatus to understand and manipulate charge transport, chemical reactivity, and light-matter interactions at the nanoscale. In this work, we performed a computational study of a Diels-Alder cycloaddition reaction between penta-1,4-diene-1,5-dithiol and ethylene at a molecular junction using density functional theory. The diene is anchored to two gold electrodes via the terminal thiol groups and reacts with a free ethylene molecule to form the (4-thiocyclohex-2-en-1-yl)methanethiol product, which remains bridged between the electrodes. By computing the pathway and kinetics of the reaction within and without the junction, our aim was to elucidate the effects of molecule-electrode interactions on the cycloaddition process. We also computed the conductance of the junction at low bias voltage along the pathway using an ab initio tunneling model. Interestingly, we find that the effects of this chemical reaction drastically decrease the conductance of the junction by several orders of magnitude, allowing for possible experimental probes into the transition state via conductance and current measurements. Furthermore, we explored mechanochemistry at the single-molecule level by studying the effects of electrode pushing and pulling on the kinetics of the reaction.

Synthesis and characterization of fluorescent metal-organic nanotubes (MONTs) and pore-expanded ligands

Joseph Cunningham, Phattananawee Nalaoh, David Jenkins

Metal-organic nanotubes (MONTs) are a unique case of one-dimensional MOFs with their own properties and applications. MONTs exhibit anisotropy, like carbon nanotubes, and are effective in size-dependent gas adsorption and molecular sensors for various guest compounds. These features indicate that by combining multiple desirable properties, MONTs are beginning to constitute an important new class of tunable materials.

The previous studies of an aryl-di-1,2,4-triazole ligand (**L1**) found MONT formations with copper and silver salts. However, the pore size of MONTs is less than 1.0 nm, which limits the variety of molecules for adsorption applications. Hence, expanding the pore size could fine tune the adsorption properties. In addition, we synthesized fluorescent MONTs from the fluorescent ligand, which could create opportunities to broaden the applications of MONTs.

Herein, we showcase two approaches for MONT syntheses. First, we employed a fluoranthene-core di-triazole ligand (**L2**) as a blue emitter for MONT synthesis. The ligand **L2** provides only two-dimensional MOFs with Group 11 metals due to the restrictions from π-π interactions. However, a small doping of the fluoranthene ligand with conventional aryl-di-1,2,4-triazole ligands produced MONTs with fluorescent properties. Second, we designed and synthesized three new organic ligands for pore-expanded MONTs, including a terphenyl-core (**L3**), 2,6-diphenylnaphthalene-core (**L4**), and 2,7-diphenylnaphthalene-core (**L5**) di-1,2,4-triazole ligands. Each ligand was synthesized *via* Suzuki coupling, bromination, triazole substitution, and deprotection of cyanoethyl groups. We characterize all expanded ligands, **L3**, **L4**, and **L5** for MONT syntheses by NMR spectroscopy and mass spectrometry. We also confirm the preliminary result of MONT formation by using SCXRD and PXRD.

Axial Coordination's Effect on the Localization of Oxidation in PctBuCo, an Electrochemical Study

Bailey Ervin Dvorak, Breanna Muldowney, Haleigh Grace, Brendon McNicholas, Viktor Nemykin

An investigation of the localization of oxidation in tetra tert-butyl substituted cobalt (II) phthalocyanine ($Pc^{tBu}Co$) was conducted. It has been previously determined that there are two possible oxidation paths the PctBuCo complex can undergo[1]. The first being the oxidation of the metal center from Co^{II} to Co^{III}, the other being the formation of the phthalocyanine cation radical $[Pc^{tBu}CoII]^{+}$. We hypothesize that the dependance on which oxidation occurs is determined by the strength of axial coordination. Using coordinating electrolytes such as tetrabutylammonium perchlorate (TBAP), tetrabutylammonium hexafluorophosphate ($TBAPF_6$), and non-coordinating electrolytes such as tetrabutylammonium tetrakis(pentafluorophenyl)borate salt ($TBAB(C_6F_5)_4$)[2] we conducted a series of electrochemical and spectroelectrochemical investigations to elucidate how axial coordination affects oxidation. Cyclic voltammetry, in conjunction with spectroelectrochemistry was used to identify key peaks indicating the localization of oxidation through these processes.

Ref 1. Lever, DMF and TBAP with PcCo (https://doi.org/10.1021/ic00251a017)

Ref. 2 Gieger, borate salts (magik electrolyte) (https://doi.org/10.1002/(SICI)1521-3773(20000103)39:1%3C248::AID-ANIE248%3E3.0.CO;2-3)

Detergent-Free Isolation of Photosystem I from *Thermosynechococcus elongatus* using αMA Copolymers

Taylor Lundquist, Godwin Ochola, Fidaa Ali, Brian Long, Barry Bruce

Photosynthesis is a vital source of energy for life on Earth, where photosynthetic organisms, such as cyanobacteria, convert solar energy into compounds such as ATP and NADPH. The initial energy conversion reactions take place in thylakoid membranes and are facilitated by two membrane-bound protein complexes, Photosystem I (PSI) and Photosystem II (PSII). PSI, in particular, is a large, multi-subunit complex that exists in various oligomeric forms depending on the organism. Because of this, studying PSI in its native oligomeric form is critical to understanding its structure and function. However, traditional detergent-based isolation methods often disrupt this native state. In contrast, styrene maleic acid (SMA) type copolymers were found to be effective, detergent-free alternatives for protein solubilization. Unfortunately, these SMA copolymers contain moieties that interfere with some analytical techniques, and they often exhibit limited stability at low pH and in the presence of divalent cations.

This study investigates an alternative class of copolymers, known as α-olefin maleic acid copolymers (αMAs), for the isolation of trimeric PSI from the thylakoid membranes of *Thermosynechococcus elongatus* (*T.e.*). The solubilization efficiency of αMAs has been shown to increase with increasing hydrophobic side chain length, but this trend is limited in that even longer hydrophobic chains (e.g., C16–C18) yield polymers that are no longer water soluble.

To test the efficacy of these copolymers with very long alkyl side chains, we must counterbalance their hydrophobicity through the introduction of additional hydrophilic moieties. This is accomplished via esterification and amidification of αMA copolymers with ethereal side chains (which are hydrophilic moieties) that enhance the hydrophobic–hydrophilic balance of these copolymers. Thylakoid membranes isolated from *T.e.* cultures will be solubilized using this new series of αMAs, followed by ultracentrifugation through a 10–50% (w/v) sucrose gradient for PSI isolation. It is expected that esterified C16 and C18 αMAs will exhibit improved solubilization efficiency relative to their shorter alkyl chain-based analogues. We also hypothesized that these copolymers will maintain adequate pH and divalent cation stability.

Pyridine Functionalization of aza-BODIPY for Use in Light-harvesting Applications

Emily Major, Viktor Nemykin

In this study, we investigated a series of BODIPY and aza-BODIPYs and their functionalization with pyridine. Nucleophilic substitution was used to attach the alkenes present to one of the aryl rings. Aldol condensation was then used to generate chalcone, which was then nitromethylated using Michael addition. The synthesis was then concluded through the chelation of dipyrroazemethane using BF_2. Click chemistry was used to attach the pyridine rings, in particular, 4-methyl-azido pyridine. The samples were successfully synthesized and then further characterized through NMR spectral analysis, HR-MS, spectroelectrochemistry, UV-Vis spectroscopy, and fluorescence spectroscopy. The goal was to examine the light-harvesting effects of aza-BODIPYs through varying photophysical processes. Binding constants (K_a) and fluorescence quenching constants (K_{sv}) were calculated through titrations with $TPP^{F20}Zn$ ($TPP^{F20}Zn$ = zinc 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin). This was chosen as an analyte because it is highly electron deficient. The aim is to eventually be able to produce viable organic solar cells using new supramolecular donor-acceptor assemblies that can withstand the industrial demands for solar-powered energy.

Investigating the Functional and Structural Differences of Insulin Isoforms in Mouse and *Xenopus laevis* islets: Implications for Diabetes Research

Caleb Ramer, Sarah Hirschbeck, Thanh Do

Gene duplication leading to isoforms with divergent functions is a well-documented evolutionary phenomenon, with insulin serving as a key example. While humans have a single insulin gene, some vertebrates—including *Mus musculus* (house mouse), *Xenopus laevis* (African clawed frog), and *Amphiprion ocellaris* (clownfish)—retain two insulin gene copies. This study investigates the functional significance of dual insulin genes in *M. musculus* and *X. laevis*, two established models for metabolic and developmental biology. Given the prominence of mice in diabetes research, understanding the expression and function of Ins1 and Ins2 is especially relevant. Using Liquid Chromatography–Ion Mobility Spectrometry–Mass Spectrometry (LC-IMS-MS), we characterized the insulin isoforms Ins1 and Ins2 in mouse pancreatic islets and InsL and InsS in whole pancreas samples from *X. laevis*. We successfully detected all four insulin isoforms, as well as two isoforms of glucagon and three variants of Glucagon-Like Peptide-1 (GLP-1A, GLP-1B, and GLP-1C). Additionally, LC-IMS-MS resolved distinct conformational variants of these hormones, suggesting possible structural and functional divergence. These findings offer new insights into the complexity of insulin regulation across species and emphasize the need for isoform-specific analysis in the study of metabolic diseases.

Metabolite-Responsive Lipid Switches for Controlled Release of Liposome Cargo

Caleb Russell, Michael Best

Lipid nanoparticles have proven a viable technique for the improved pharmacokinetics of drug transport, though the selective targeting of diseased sites using this technique remains unrealized. One promising mode of the advancement of smart nanoparticles is in developing a membrane-compatible synthetic lipid switch. These switches are designed to incorporate themselves within the nanoparticle's bilayer and disrupt its stability only in the presence of target metabolites known to be upregulated in diseased cells. We have designed several such switches, under the idea that different functional group heads with lipid tail structures can be used to create a wide variety of switches with specialized metabolite interactivity and a similar capacity to integrate with native lipids into liposomal structures. Our recent work has focused on developing a switch that employs phosphonium heads to preferentially interact with guanosine triphosphate (GTP) and tripolyphosphate (TPi). Fluorescent dye leakage assays for monitoring carge release have confirmed the selectivity of these switches for target metabolites over similar metabolites, while dynamic light scattering and transmission electron microscopy studies have been used to confirm the physical disruption of nanoparticles in response to target metabolites.