2021 GLRM 1

Intrusive advising and research mentorship for academic improvement in underrepresented minority student groups in STEM

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Within a community college series of cohorts, underrepresented minority students in chemistry and other STEM fields were supported through a number of means including intrusive advising through a part-time success coach, peer and faculty mentoring, and a summer research program available through alliance institutions. Data indicating success and failure of these means in disaggregated data show across the board improvement of academic success indicators such as retention, course completion, and transfer/graduation for students involved in activities as compared with the general student population. Implications of this success and ideas for integration into general community college infrastructure will be discussed.

2021 GLRM 2

Culturally responsive teaching and learning in undergraduate chemistry

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Illinois is facing a shortage of qualified STEM teachers, especially those who are culturally diverse and underrepresented in the field of STEM education. Aurora University's NSF Noyce Building Capacity grant addresses methods to increase STEM secondary education teachers at a Hispanic Serving Institution. One of the activities include developing new faculty and program development opportunities to promote STEM education as a career option. A workshop titled Culturally Responsive Teaching and Learning was provided to the university faculty. The chemistry faculty implemented several ideas into the courses. The success and challenges of some of the strategies will be presented.

2021 GLRM 3

Institutional environment and departmental values: a case study at Kenyon College

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We offer a case study on how our institutional environment has shaped our departmental efforts in diversity, equity, and inclusion in general, and in responding to anti-Black racism specifically. As with many institutions, Kenyon College has seen years of equity and inclusion efforts with their own triumphs and failures. In the past five years, DEI efforts at Kenyon benefited from the creation of new administrative structures (Office of Diversity, Equity, and Inclusion and Civil Rights Office) and initiatives funded by extramural programs (NSF S-STEM, Clare Boothe Luce, and HHMI Inclusive Excellence). These interventions fostered changes in institutional climate, values, and ability to take action. We reflect on how these changes enabled, hindered, or otherwise shaped different aspects of our departmental response to the murder of George Floyd in June of 2020. This response began with an extensive discussion to draft and revise a letter to students and ourselves, about our professional value to acknowledge complicity in systemic racism and commit to fight it with humility. It branched into individual efforts to transform our research and teaching practice. Finally, we reflect on our difficulty in fostering structured conversations with students and faculty on anti-Black racism within the field, and seek insight and advice from participants. We hope to spark an active discussion with other chemists committed to similar efforts.

2021 GLRM 4

Working toward wellness, equity, and liberation in the NSF Center for Sustainable Nanotechnology

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The scientific mission of the NSF Center for Sustainable Nanotechnology (CSN) is focused on using fundamental chemistry to enable emerging nanotechnologies. The CSN is also a community of scientists, and we have prioritized creating a welcoming and inclusive climate since the Center formed. However, events of the past year demonstrated that our diversity, equity, and inclusion (DEI) efforts were not doing nearly enough to dismantle anti-Black racism and other systemic barriers that disproportionately harm people from historically marginalized and oppressed groups. On June 10, 2020, the CSN collectively participated in #ShutDownSTEM to brainstorm strategies for supporting social justice and antiracism as a Center. The action plan that emerged was the first step towards developing a DEI strategy centered around

understanding and dismantling anti-Black racism and White Supremacy culture in the CSN and the broader STEM community.

One of the highest priorities on our action plan was to engage with a subject matter expert as a collaborator. In spring 2021 a new phase of our work began as we welcomed Dr. Della Mosley to the CSN as our new Wellness, Equity, and Liberation Consultant. Dr. Mosley is a Professor of Counseling Psychology at the University of Florida who brings Black feminist, social justice, and activist-informed approaches that are grounded in Radical Healing and Radical Hope theories that she helped pioneer, making this work quite different from many activities designed to promote diversity, equity, and inclusion in chemistry. In her new role, Dr. Mosley will provide a critical review of the center's existing strengths and growth opportunities, and this extensive evaluation will be used to guide the co-construction of an intervention plan for further enhancing wellness, equity, and liberation throughout the CSN. She will also conduct workshops based on the Academics for Black Survival and Wellness (#Academics4BlackLives) initiative that she co-founded in the Summer of 2020. These workshops will simultaneously provide empirically grounded and culturally relevant training to people with privilege and healing to people experiencing oppression.

This presentation will provide a brief overview of the CSN's early DEI work, highlight progress towards implementing our action plan from Summer 2020, and introduce Dr. Mosley's vision for wellness, equity, and liberation, which we hope will empower others to pursue this type of work in their own organizations.

2021 GLRM 5

Effect of selective atom substitution in guanine on the electronic relaxation mechanism

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The natural RNA and DNA nucleobases absorb harmful ultraviolet radiation but the ability to dissipate this excess electronic energy efficiently to the ground state makes them highly photostable. Investigating how minor structural modifications affect their photochemical properties is important for understanding the molecular origins of life and for the advancement in biological and chemical applications. For example, 7-deazaguanosine (7dza) has been used for decades to probe the charge transfer dynamics in DNA, due to its lowered oxidation potential relative to guanosine. However, its electronic relaxation mechanism has not been previously investigated.

Using steady-state and time-resolved spectroscopic techniques, combined with quantum-chemical calculations, we have investigated the electronic relaxation mechanism of guanosine 5'-monophosphate (GMP) and 7dza in in aqueous solution and in a mixture of methanol and water following excitation at 267 nm. The following mechanism has been proposed for both molecules: $L_b \rightarrow L_a \rightarrow {}^1\pi\sigma^*(ICT) \rightarrow S_0$, where

the $^1\pi\sigma^*$(ICT) stands for an intramolecular charge transfer excited singlet state with significant ps* character. In 7dza, however, the relaxation dynamics is slightly slowed compared to GMP, which adjudicate to stabilization of the two lowest-energy singlet states and to the alteration of the topology of the excited state potential energy surfaces.

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2021 GLRM 6

Enhancement of the Two-photon Absorption Cross Section in a Series of Nitrodibenzofuran Based Photocages

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Photocages are a class of molecule that inhibit the reactivity of molecules chemically bound to them and release active molecules upon irradiation with light. Using photocages, drugs can be delivered with very high spatial and temporal resolution, minimizing side effects and increasing drug efficacy. Key to this application is a photocage with a large absorption cross section and high dissociation quantum yield. Two-photon absorption (2PA) is often used to initiate the dissociation of photocages. Due to this process using two red or near IR photons instead of one blue or UV photon it can penetrate tissue more readily, has a lower chance of damaging tissue, and has the ability to three dimensionally control the area of dissociation. In this presentation I will focus on the potential to increase the absorption cross section of the nitrodibenzofuran (NDBF) photocage by the addition of electron donating groups and extending the conjugation of the system. A broadband 2PA technique is used to measure cross sections over a range of wavelengths simultaneously. Experimental cross sections and absorption maxima are compared to the results from standard computational methods. It is observed that increasing the conjugation of the NDBF system greatly enhances its 2PA cross section. The addition of electron donating groups increases the cross section to a lesser extent and causes a redshift in the 2PA spectrum. The difference between the calculated and experimental 2PA maxima was determined to be 0.20 eV. The cross sections between the two differ by an order of magnitude. It is observed that the modifications made to the NDBF framework result in more efficient photocages due to their larger 2PA cross sections.

2021 GLRM 7

Determining the Two-Photon Absorption Coefficient of GaAs and MoS_2 Using Time-Resolved Terahertz Spectroscopy

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Semiconductors remain important optoelectronic materials for real-world technologies ranging from light bulbs and displays to solar cells and lasers. Despite decades of research into the optical properties of semiconductors, important nonlinear optical properties such as the two-photon absorption coefficient remain difficult to measure directly. We present estimates of the two-photon absorption coefficient of two pervasive semiconductors, GaAs and MoS_2, using time-resolved terahertz (THz) spectroscopy. By tuning the power of pump pulses resonant with one- and two-photon absorption processes, we demonstrate we can produce the same attenuation of an incident THz probe pulse. We propose the attenuation of the THz pulse observed stems from intraband absorption by free charge carriers in the conduction band of each material. We assess the photoconductivity of each photoexcited material for pump-probe time delays at which we know the pump pulse has transmitted through each sample completely. We use this assessment to show one can make the same density of charge carriers via single and multiple photon absorption and determine if these different absorption processes populate carriers in different regions of each respective material's conduction band structure. By using a spectroscopic technique directly sensitive to the number of charge carriers produced by two-photon absorption, researchers can design optoelectronic devices to leverage multi-photon processes to improve energy efficiency in lighting and energy storage technologies.

2021 GLRM 8

Determination of the IR Refractive Indices Through Modeled Sum Frequency Generation

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Pulsed high intensity lasers propagating through a layered optically-nonlinear material stack can engender higher order wave-mixing events. Generation of an outbound sum frequency beam can occur at the noncentrosymmetric material boundaries. The presence of a vibrational mode within the frequency range of the incident IR beam leads to resonant enhancement of the signal. Quantitative knowledge of the nonlinear responses is only possible through a modeling routine. In a transfer matrix based routine the geometry of the system along with the refractive indices of each material layer are essential. Outsourced determination of the refractive indices in the IR range can be both time-intensive and costly if an analysis method is not readily available to the user. To overcome this restraint we have developed a vibrational sum frequency generation spectroscopy fitting routine capable of approximating the refractive indices of a vibrationally active material layer in tandem with the nonlinear responses. A number of experimental pathways are available to a user to improve confidence in the measurement; the viability and error of several are discussed. The uncharacterized

material overtop a range of resonantly-inactive substrate thicknesses sampled across a series of polarization measurements supplies the highest confidence when used to globally fit the refractive indices.

2021 GLRM 9

Energetically Remote Modulation of Spin-Polarized States in Metalloporphyrins using Cavity Polariton Formation

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When a molecular electronic excitation exchanges energy with a resonant optical mode faster than either system's respective decay rate, the combined molecule-cavity system enters the strong light-matter coupling limit and drives formation of cavity polariton states. In addition to the fact that the energies of the polaritons states can differ from those of free space molecule by 100s of meV, cavity polariton formation causes quantum entanglement between molecular electrons and cavity photons. Porphyrins serve as excellent systems for studying cavity polaritons due to their application as a model light harvesting molecule, their large transition dipole moment, and the ability to tune their excited state dynamics through ligation of different metal cations to the porphine ring. In this study we examine how the phtophysics of two sets of porphyrin samples are impacted by formation of molecular polaritons. First, we show polariton formation causes changes in the energy splitting between the doublet and quartet states of the porphyrin triplet manifold which decreases the lifetime of the triplet state. Second, we examine the properties of cavity polariton states formed from nearly degenerate electronic transitions localized on two distinct porphyrin species. We form polaritons by constructing a Fabry-Pérot resonator consisting of three layers: distinct polymer layers doped with free base tetraphenylporpyrin and CuTPP, respectively, spatially separated a silicon dioxide layer. We use steady-state light emission spectra to assess how the entanglement between different porphyrin species mediated by cavity polariton formation facilitates interactions between the triplet manifolds of each respective molecule. This study demonstrates how the excited state populations of lower lying excited states are impacted by cavity polariton formation and highlights the role cavity polaritons may play in spin-dependent excited state photophysical processes such as singlet fission.

2021 GLRM 10

On the impact of amino and carbonyl functionalization on the photostability of canonical RNA and DNA pyrimidine nucleobases

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The nucleic acid bases that we know today are thought to have originated from simple precursors also referred to as proto-biotic RNA. These molecular ancestors of RNA and DNA may have formed from a vast number of organic compounds found on early Earth and/or delivered by meteorite infall. Understanding the evolution of chemical synthesis ranging from those precursors to today's canonical nucleobases is essential in answering questions to the chemical origins of life. Among other factors, ultraviolet radiation (UVR) from the sun should have played a key role in shaping and selecting the building blocks of life. Whether the carbonyl and/or amino group substituents played any role in regulating the photostability of the canonical pyrimidine nucleobases is currently unknown. The biological relevance of the pyrimidine chromophore and its carbonyl- and amino-substituted derivatives make these molecules excellent candidates for investigating how their interaction with UVR may have enabled the selection of the RNA and DNA pyrimidine nucleobases on early Earth. Time-resolved spectroscopic results, complemented with quantum-chemical calculations, will be presented, which lend support to the idea that functionalization at the C2 and C4 positions of the pyrimidine chromophore has a preponderant role in controlling the inherent electronic relaxation mechanisms and photostability of the DNA and RNA pyrimidine nucleobases and their derivatives.

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2021 GLRM 11

Structure and Nucleation of Water and Ice next to Charged Polymer Brushes

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Materials and coatings that prohibit ice nucleation or show a low ice adhesion strength are of interest to protect structures such as aircraft, solar panels, wind turbines, and power lines from severe icing events. Specifically, polymer brush coatings have been shown to exhibit low ice adhesion strength by holding "non-freezable water" at their interface below 0 °C which acts as a lubrication layer when shearing the ice off of the surface. Additionally, it has been shown that changing the counterion of a charged polymer brush significantly affects its ice nucleation temperature. Here, we examine the molecular structure of water and ice next to charged polymer brush surfaces with sum frequency generation spectroscopy (SFG). An SFG signal only results from a break in centrosymmetry, meaning it is surface and interface selective on the order of a few molecular layers. Thus, the vibrational peak locations and intensities is used to gain understanding of the molecular structure of both the polymer brush and the water molecules at their interface. Collecting SFG spectra at various temperatures provides a precise measurement of the heterogeneous nucleation temperature on the polymer brush surfaces. Comparison of the heterogeneous nucleation temperature and molecular structure of ice at the polymer brush interface as a function of temperature

between differently charged brushes provides insights on the mechanisms behind anti-icing and low ice adhesion surfaces.

2021 GLRM 12

NOVEL TRIPLET ORGANIC DONOR-ACCEPTOR DYADS FOR LIGHT HARVESTING APPLICATIONS

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Donor–acceptor chromophoric systems (**D**–**A**) are important scaffolds for several light–harvesting/initiated processes and devices including light emitting diodes, photo–catalytic/redox systems and photovoltaics cells. In a **D**–**A** system, to maximize the energy/charge transfer processes or excited state interactions, it is ideal to link the donor and acceptor chromophores using a molecular template or spacer. To this end, we devised several dyads using purely organic triplet energy donor and readily available polyaromatic chromophores (e.g. perylenes and anthracenes). Furthermore, using advanced spectroscopic methods, we characterized our **D**–**A** dyads. Importantly, the dyads of our interest can also harvest, transform and modulate visible light. My presentation will detail the synthesis and photophysical characterization of novel triplet **D**–**A** dyads. I will also highlight our ongoing efforts in utilizing these dyads to achieve triplet-triplet annihilation based photon upconversion.

2021 GLRM 13

Spectroscopic study of the stabilized single-site Ru-based water oxidation catalysts by incorporation in UiO-67 MOF

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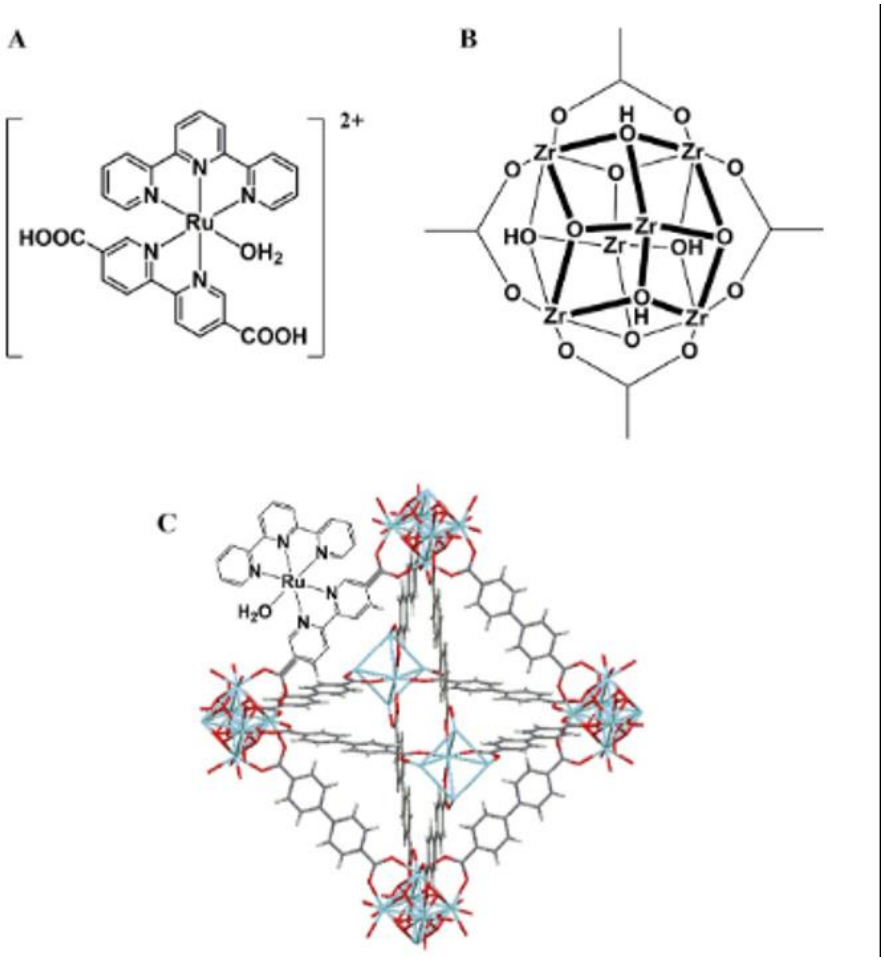
Artificial photosynthesis could promise abundant energy, but implementation is currently limited by a lack of control over the multi-electron catalysis of water oxidation and the availability of active and stable water oxidation catalysts. $[Ru(tpy)(5,5'\text{-dcbpy})(H_2O)]^{2+}$ **(1)** and *cis*-$[Ru(bpy)(5,5'\text{-dcbpy})(H_2O)_2]^{2+}$ **(2)** (tpy=2,2′;6′,2″-terpyridine; bpy=2,2′-bipyridine; 5,5′-dcbpy=2,2′-bipyridine-5,5′-dicarboxylic acid) water oxidation catalysts were investigated. Both **(1)** and **(2)** contain 5,5'-dcbpy ligand, making it possible to incorporate them into UiO-67 metal-organic frameworks (MOF), **Figure 1**.
For **(1)**, we showed in-MOF catalytic activity by comparing the amount of oxygen that evolved for the particle of different sizes. We concluded the redox-hopping charge transport is sufficient to promote chemistry throughout the MOF particles. This in-MOF reactivity and immobilization of the catalyst shut off the degradation pathways that are common in homogeneous solution and hence makes the catalyst more robust.

Resonance Raman spectroscopy incorporates **(1)** into MOF prevents dimerization. Raman measurement confirms the Ru oxo bond formation in MOF. These measurements were possible because the resonance Raman only enhances the signal form **(1)**, not the bulk part of MOF.
For **(2)**, it's oxidation in solutions, at pH=1, by Ce^{IV} results in activity ~40 times faster than parent *cis*-$[Ru(bpy)_2(H_2O)_2]^{2+}$ compound. The rate of O_2 evolution by **(2)** is first order on catalyst indicating reactivity via water nucleophilic attack pathway. Ru^V intermediate was detected in the reaction mixtures by XAS and Raman. The Ru^V=O was found to be ~1.72 Å by EXAFS and having ~810 cm^{-1} frequency in Resonance Raman (-40 cm^{-1} $^{16}O/^{18}O$ isotope shift). DFT calculations of redox potentials, vibrations and DG of the reactions are in good agreement with the experiment.



The structure of A) $[Ru(tpy)(dcbpy)(OH_2)]^{2+}$, B) $Zr_6O_4(OH)_4(COO)_{12}$ cluster, and C) Ru-UiO-67 MOF

2021 GLRM 14

Resonance Raman characterization of the cyano adducts of human heme oxygenase

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The human body contains an abundance of heme enzymes that have diverse functions, including catalysis, oxygen transport and redox reactions. Since free heme is cytotoxic, it is essential for the body to metabolize the free heme that comes from degradation of these proteins. Human heme oxygenase (hHO-1) is an enzyme that catabolizes heme through a multi-step reaction into biliverdin, with the release of CO and ferrous iron. Heme degradation is stereospecific to the α - meso carbon, facilitated by a hydrogen bond network cluster that comprises the aspartate 140 residue and two water molecules. To probe this hydrogen bond network, we investigated the cyanide adducts of hHO-1. Cyanide is highly anionic and sensitive to subtle changes in active site polarity and steric hindrance, therefore, it is an efficient probe for active site perturbations. In this work, we used resonance Raman spectroscopy to probe the CN- adducts of wild-type (WT) hHO-1 and its D140 mutants. We showed that the Fe-C-N fragment adopts a tilted configuration with a tilting angle larger than that of typical histidine ligated heme proteins.

2021 GLRM 15

Molecular Vibrational Insights into Ice Nucleation: Interfacial Electric Fields and Fatty Alcohol and Acid Hydration

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Atmospheric ice nucleation (IN) has a great impact on clouds' radiative properties and global precipitation patterns in regions where temperatures are lower. Prior studies have shown that sea spray aerosol (SSA) composition contributes to cloud and ice formation in our atmosphere. Despite their evident environmental importance, existing global climate models do not properly account for the effects of SSA ice nucleation. It is well known that alcohol monolayers favor IN than its fatty acid counterparts. Yet, recent evidence suggests that when the crystalline phase is present in long-chain fatty monolayers, they can nucleate ice at warmer temperatures than -36 °C. Thus, further studies on fatty acid and alcohol monolayers are crucial to understanding the chemical and physical mechanisms of ice nucleation. In this work, long-chain alcohol and long-chain acid monolayers at the air/water interface are studied via surface pressure - surface potential isotherms as well as infrared reflection-absorption spectroscopy (IRRAS) at 21 °C and 0 °C to investigate interfacial electric fields, hydrations effects, and the vibrational spectral signals of the ice-nucleating process. A large enhancement in surface potential (+100 mV) of the long-chain fatty alcohol monolayer is observed, suggesting an increase in ordering relative to the surface normal. In the OH stretching region of the IRRAS spectra, two main bands are observed at ~3250 and ~3600 cm^{-1}.

Surprisingly, analysis of the -OH stretching features in the IRRAS spectra showed remarkably similar 1st hydration shell signatures for the alcohol -OH moiety and carboxylic acid head group, contrary to their significant chemical differences. To identify the underlying vibrational structure of these bands along with their temperature dependence, the following cluster systems are studied: propanol + 6H_2O and propionic acid + 10H_2O to simulate the infrared (IR) spectra which are computed from *ab initio* molecular dynamics (AIMD) calculations and the fundamental vibrational structure of IR features is analyzed at room and freezing temperatures.

2021 GLRM 16

Probing Macroscopic Properties of Ferroelectric Materials Using the Microscopic Description of Vibrational Anharmonicity

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The spontaneous switching of electric polarization in ferroelectric material has provided diverse entries into applications such as electronics, electromechanical and optical devices. However, there are gaps in understanding how microscopic electrostatic interactions of hydrogen-bonded ferroelectric materials such as 2-methylbenzoimidazole (MBI) control the macroscopic properties used in the above applications. According to the literature, the molecular vibrations can act as a probe for microscopic electrostatics. We performed temperature-dependent polarized Raman spectroscopic measurements for the MBI powder to determine if molecular vibrations can assess microscopic electrostatics of a molecular ferroelectric crystal. We observed that few Raman peaks have been shifted to higher frequencies when reducing the temperature from 298 K to 78 K. Furthermore, an uneven distribution of peak shifts was observed around 198 K-168 K. The density functional theory (DFT) calculations were used to understand the fundamental physical phenomena behind these vibrational shifts with respect to temperature. Temperature-dependent X-ray diffraction experiment revealed that the observed uneven peak distribution was not due to a phase transition in MBI. DFT calculations and the developed theoretical anharmonic model in our lab was used to examine whether vibrational anharmonicity could describe these peak shifts. Specifically, we measure the relationship between temperature-dependent changes in the electronic densities and anharmonic vibrational properties using the quartic term expansion of the interatomic potential energy of MBI. We compared the anharmonic model with experimental peak frequencies using the curve fitting method. Best fitting parameters were observed while changing the experimental frequency towards harmonic frequency. DFT calculated data has overestimated the peak positions due to harmonic approximation. In conclusion, we note the peak shifts observed are most likely due to thermally driven changes to the average occupation of other lower frequency intermolecular vibrations interacting with the higher frequency Raman-active vibrations of MBI. This study thus provides a fundamental insight into the microscopic properties of MBI, central to their importance in next-generation electronic applications.

2021 GLRM 17

The Detection of Biomarkers Using SERS

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This paper explores the use of surface enhanced Raman spectroscopy (SERS) as a detection method applied to the immunological sandwich assay to detect biomarkers and ways to further enhance the method. The detection of biomarkers is fundamental to the treatment and control of diseases. Early detection (often before clinical observation) is required for the control of many diseases. Tuberculosis being an example where a person can have dormant bacteria that needs to be treated to eliminate propagation from occurring at a later time. SERS provides a very sensitive, semi-quantitative way to detect biomarkers when there are available antibodies to the biomarkers. This approach also is a candidate for field testing in areas with limited technology due to the rapid development of portable Raman systems and lateral flow sampling technology. We have developed a biomarker/antibody model system that can be safely handled in all labs to work on sampling methodology improvements. We have also begun to apply this approach to looking at the HER2 breast cancer biomarker which is significant to which treatment method should be used for effective results.

2021 GLRM 18

Hydroxyapatite: Structure Modification with Bisphosphonates to Increase Substrate Affinities

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Dyes, metal ions, and other toxic byproducts from numerous industries have polluted bodies of water for a long time and have desolated homeostatic ecological conditions. Dyes are often used in paper, plastic, and textile production. Dyes such as methylene blue, phenol red, and Janus Green B are known to cause many health and ecological problems and are the focus of our studies since it is vital to have a method of purifying textile wastewater.

Hydroxyapatite (HAP), $Ca_5(PO_4)_3(OH)$, is an environmentally safe and inexpensive salt that can function as an adsorbent to purify water of ecosystem-threatening pollutants. Our objective was to convert HAP into a new biocompatible material with a very high affinity for substrates such as dyes. Modifying the HAP by adding 1 Ethylidene-1,1-Diphosphonic Acid (HEDPA) can increase the affinity for dyes, one of the major pollutants of bodies of water, and may improve its selectivity. This study reports results with HEDPA modification.

To test modified HAPs' (mHAPs') affinities for different concentrations of dyes, we have been developing an isotherm contact procedure, where we have HAP or mHAP come into contact with various concentrations of dye solution, and a control set alongside them to determine the extent of adsorption. Performing many of these contact experiments on different dyes with varying concentrations will also show the difference in adsorption patterns between dyes.

The improved isotherm contact procedure tested with dye and HAP modified with HEDPA will determine the strength difference in their adsorption of dyes in aqueous solutions. The modified crystals are studied in terms of FTIR, XRD, and NMR. The isotherms for HAP and modified HAP were analyzed with the Langmuir and Hill Equations. The significance of the difference between the S-shaped isotherm for HAP and the standard isotherm behavior for modified HAP will be discussed.

2021 GLRM 19

Exploring the Structural and Optical Properties of Vacancy Ordered Quadruple Perovskites

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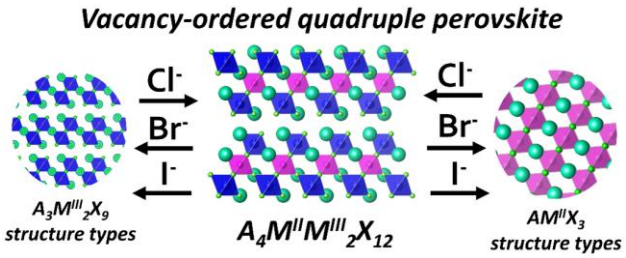
The structural, optical, and magnetic properties of the vacancy-ordered quadruple perovskites $Cs_4CdBi_2Cl_{12}$ and $Cs_4MnBi_2Cl_{12}$ and their solid solution have been investigated. Both compounds are found to crystallize with *R*-3*m* space group symmetry that arises from ordering of Bi^{3+}, Mn^{2+}/Cd^{2+}, and cation vacancies into layers that run perpendicular to the <111> direction of the cubic perovskite structure. We further explored the structural and optical properties by substituting Br^- and I^- into $Cs_4M^{II}M^{III}_2Cl_{12}$ (M^{II} = Cd^{2+}, Mn^{2+} and M^{III} = Bi^{3+}, Sb^{3+}). The larger halide ions (Br^- or I^-) preferentially occupy the anion sites adjacent to the cation-vacancy layer. In those compositions where M^{II} is Cd^{2+}, incorporation of bromide ions leads to substantial M^{II}/vacancy antisite disorder, which is accompanied by a more even distribution of bromide substitution over the two chemically distinct anion sites. The $Cs_4CdM^{III}_2Cl_{12}$ compounds can incorporate over twice the amount of bromide as analogous Mn^{2+} containing compounds, with a maximum of 29(2)% bromide substitution found for $Cs_4CdSb_2Cl_{12}$. Iodide incorporation is more limited, with a maximum of ~6% halide substitution for $Cs_4CdBi_2Cl_{12}$. The incorporation of the heavier, less electronegative Br^- and I^- ions results in a red shift of the onset of optical absorption in a Vegard's Law type fashion. The effect is largest for $Cs_4CdBi_2Cl_{12-z}X_z$, where the absorption onset shifts from 3.20(1) eV to 2.99(1) eV as the composition changes from $Cs_4CdBi_2Cl_{12}$ to $Cs_4CdBi_2Cl_{8.9}Br_{3.1}$.



2021 GLRM 20

Topochemical deintercalation of Li from layered LiNiB: towards 2D MBene

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MXenes ($M_{n+1}X_n$) are analogous to graphene where M=early transition metal, X=C or N. Recent advances in the synthesis of these 2D layered materials by deintercalation of MAX phases ($M_{n+1}AX_n$, A=element of groups 13-14) and their applications in various fields (supercapacitors, sensors etc.) have incited huge interest in exploring their B analogs, MBenes. Even though bulk preparation of MBenes is still challenging, they are theoretically predicted to have a plethora of applications in electrocatalysis, magnetic devices etc. We studied two layered polymorphs in the Li-Ni-B system: *RT*-LiNiB and *HT*-LiNiB (RT-room temperature, HT-high temperature). Unique layered topology with alternating Li and [NiB] layers, along with a substantial amount of Li (33 at.%) stored in between [NiB] layers, made these compounds promising candidates for topochemical deintercalation of Li layers to access isolated sheets of 2D MBenes. Topochemical deintercalation involves elimination of loosely-bonded "guest" entities from the "host" frameworks thereby structural motif of the parent phase is preserved. Since the structural changes are minimal, mild reaction conditions are adequate. Owing to this, we have utilized soft chemical methods for the topochemical deintercalation of Li layers from the LiNiB polymorphs where, different deintercalation rates are observed depending on the chemical environment its exposed to (air, ethanol etc.). Scanning transmission electron microscopy (STEM) and solid-state ^{7}Li and ^{11}B NMR spectroscopy revealed the deintercalation process to be incomplete. Instead, stabilization of novel metastable borides ($Li_{\sim 0.5}NiB$) is observed. Utilizing a state-of-the-art synergistic combo of divergent techniques (STEM-Pair Distribution Function-Density Functional Theory), complex crystal structures of *RT*-$Li_{0.6}NiB$ and *HT*-$Li_{0.4}NiB$ are determined. Their crystal structures are best described as a random intergrowth of the ordered single [NiB], double $[NiB]_2$, or triple $[NiB]_3$ layers alternating with single Li layers. STEM data also revealed the deintercalation process to proceed layer by layer through a "zip-lock" mechanism: where once a Li layer is deintercalated, the "zip-lock" is closed and adjacent [NiB] layers condense. A change in magnetic behavior, due to the enhanced magnetic coupling of Ni spins through the formation of $[NiB]_2$ and $[NiB]_3$

fragments, from temperature-independent paramagnets (parent LiNiB) to the spin-glassiness is observed upon partial Li-deintercalation.

2021 GLRM 21

Enabling Low Temperature K^+ Single Cation Ionic Liquids Through an Unusual Low Melting Asymmetric Sulfonamide Salt

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A K^+ single cation ionic liquid (K-SCIL) contains only K^+ cations. When used as an electrolyte in potassium batteries, it not only possesses the properties of conventional ionic liquids such as nonflammability, negligible vapor pressure and good electrochemical stability, but also increases the K^+ transference number, which reduce concentration polarization of the electrolyte and improve the battery power performance. In this study, we report K-SCILs based on the low melting (Tm ~50°C) potassium salt of (3-methoxypropyl)((trifluoromethyl)sulfonyl) amide ($MPSA^-$). The low melting point of KMPSA is attributed to a relatively high degree of disorder, an unusual uncoordinated ether moiety, and a very short K-K distance of only 3.4348(7) Å amongst other factors. Combined with potassium bis(fluorosulfonyl)imide (KFSI) the mixture of the two salts exists as a liquid as low as -13°C, generating for the first time a room temperature K-SCIL. This K-SCIL shows remarkable stability with K metal, plating and stripping over 300 cycles at an average CE of >95%. Evidence for a lack of K^+ concentration gradient as well as a near unity K transference number were also found in this K-SCIL. This report hopes to serve as inspiration for the discovery of even lower melting K salts to enable low temperature K-SCIL electrolytes to take advantage of the numerous benefits of SCILs in practical cells.

2021 GLRM 22

Nitrogen Deficient Graphitic Carbon Nitride as a Host Cathode Material for Metal-Sulfur Batteries

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Lithium-sulfur batteries have attracted interest as a viable alternative to replacing Li-ion batteries due to their high theoretical specific capacity (1675 $mAhg^{-1}$), which can meet the energy demands of mobile communication devices and electric vehicles. However,

poor cyclability and capacity fading, primarily due to polysulfide shuttling, have hindered the commercialization of Li-S batteries. This study focuses on using mesoporous nitrogen-deficient graphitic carbon nitride as a host for the sulfur cathode. The cathode material will be characterized by powder X-ray diffraction (XRD), BET pore size and surface area analysis, scanning electron microscopy (SEM), transmission electron microscopy (TEM), and elemental analysis. Enhanced electrochemical stability resulting from the porous morphology is anticipated based on the literature precedents of nitrogen-deficient graphitic carbon nitride, which will impart electrical conductivity, high surface area, strong sulfur adsorption, and large pore volumes to sequester large concentrations of elemental sulfur. Furthermore, the porous composite structure should offset the volume expansion and lithium dendrite formation during the charging and discharging cycles while entraining the polysulfides intermediates, thus avoiding parasitic reactions that deplete the sulfur cathode and corrode the lithium anode.

2021 GLRM 23

Deep eutectic solvent assisted synthesis of functional materials

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Deep eutectic solvents (DESs) are analogs of ionic liquids which are made up of a hydrogen bond donor and hydrogen bond acceptors. DES components combine to give a eutectic mixture whose melting point is lower than that of the individual components, typically below room temperature. This allows elevated temperatures to be avoided in material synthesis. DESs are biodegradable, non-toxic, and affordable. They effectively dissolve transition metal oxides that are insoluble in aqueous solvents, and as a result, they are a good replacement for corrosive acids in the solution synthesis of materials. $AgBiS_2$ and Cu_3BiS_3 are semiconductors that are being investigated for the photovoltaic properties as well as their thermoelectric properties. The properties of these functional sulfides can be tuned depending on their synthesis routes, as this can affect their morphology, particle size, tolerance to doping, etc. $AgBiS_2$ and Cu_3BiS_3 have been synthesized via solid-state synthesis as well as solution synthesis involving a capping ligand.
Here, we investigate the synthesis of $AgBiS_2$ and Cu_3BiS_3 via a microwave-assisted DES synthesis This route is a fast and facile synthesis that excludes the need for a capping ligand. We utilized choline chloride and thiourea as the DES of choice in these syntheses, where thiourea is both the hydrogen bond donor and the sulfur source. The optimal synthesis conditions, thermal stabilities, and morphologies of both compounds were investigated. The *in-situ* high-temperature synchrotron powder X-ray diffraction data which shows a polymorphic change in Cu_3BiS_3 with changing temperature as well as its thermoelectric properties will be presented.

2021 GLRM 24

New expedited synthetic pathway to a multitude of novel Oxazolidinone antibacterial agents

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A new pathway to synthesize a multitude of novel oxazolidinone antibacterial agents was designed. The route incorporates a starting material with a bromine substituent that ends up on a benzene ring furthest from the oxazolidinone ring. The bromine was replaced with a pyridine group and in the future can be replaced with various groups so as to make further derivatives. Both the bromine substituted and the pyridine substituted oxazolidinone compound will now be tested for antibacterial activity and bioavailability through our CO-ADD partner in Australia. The successful route to the bromine containing oxazolidinone can now be further used to create a variety of new oxazolidinone derivatives by substituting the bromine with various functional groups using Suzuki or Sonogashira reactions.

2021 GLRM 25

Synthesis and Structural Study of Potential Antimalarial Drug: 1-(5-(3,4-dichlorophenyl)furan-2-yl)-*N*-(piperidin-4-ylmethyl)methanamine

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In vitro studies of 1-(5-(4-bromo-2-chlorophenyl)furan-2-yl)-*N*-(piperidin-4-ylmethyl)methanamine have shown potency against *P. falciparum* with IC_{50}<1000nM. The compound has favorable properties for drug development due to the molecular structure, with the scaffold consist of a hydrophobic head, a linker, and a basic amine chain. A synthesis strategy based on Meerwein's arylation and reductive amination was proposed. Lipophilicity and pH of the analogs were expected to change upon using different substituents for the aromatic ring at the hydrophobic head, or different amines for the basic chain. Chemicalize by ChemAxon was used to predict both partition coefficient (logP) and pH of potential analogs. Here, the synthesis of 1-(5-(3,4-dichlorophenyl)furan-2-yl)-*N*-(piperidin-4-ylmethyl)methanamine was focused on, and the results will be presented.

2021 GLRM 26

Non-Precious Metal-Based MOFs As Catalysts For Decarboxylative Coupling Reactions

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

2021 GLRM 27

$FeCl_3$-Mediated Formal Paternò-Büchi Reaction

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The Paternò-Büchi reaction is a common and efficient method for synthesizing oxetanes. This method employs a high-energy UV-light source to activate the carbonyl towards [2+2] cycloaddition with an alkene. Due to its radical mechanism, the Paternò-Büchi reaction often yields mixtures of regio- diastereomers. The use of a high energy light source may limit the Paternò-Büchi reaction's application and safety. Alternatively, $FeCl_3$ is a low cost, abundant catalyst frequently employed in organic synthesis. The development of a $FeCl_3$-mediated formal Paternò-Büchi reaction is presented. This method allows for the formation of oxetanes in up to quantitative yields without the use of high energy UV light with high regio- and diastereoselectivity. We propose that this reaction occurs through a concerted asynchronous formation of the oxetane, consistent with the mechanism of carbonyl-olefin metathesis.

2021 GLRM 28

Silyl-chlorides as additives for enhancing ring-closing $FeCl_3$ catalyzed carbonyl olefin metathesis

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Ring-closing $FeCl_3$ catalyzed carbonyl-olefin metathesis (COM) is a powerful method for the construction of cycloalkenes. As the reaction proceeds, a byproduct carbonyl accumulates, forming an octahedral complex $[(R_2CO)_4FeCl_2]Cl$. We have shown kinetically that when a COM reaction reaches conditions conducive to aggregate formation, the rate of the reaction decreases. If aggregate formation can be inhibited, reaction efficiency will be enhanced. We present a method for the inhibition of aggregate formation via the addition of ligands. Spectroscopic and kinetic evidence will be presented to demonstrate the effectiveness of this simple procedural modification.

2021 GLRM 29

Thiophene Fused Contorted Aromatics via a Palladium catalyzed Cyclopentannulation and Scholl Cyclodehydrogenation strategy

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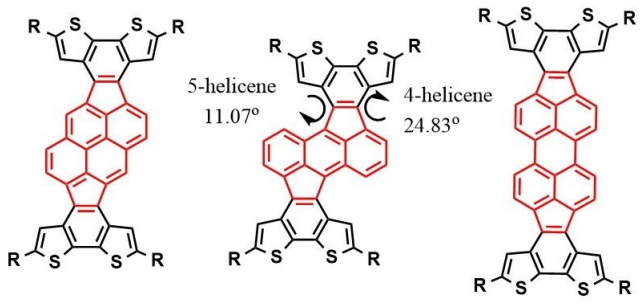
We have shown the synthesis of new class of contorted cyclopentafused polyaromatic hydrocarbons CP-PAHs. These contorted CP-PAHs were prepared utilizing the modified version of our previously developed palladium catalyzed cyclopentannulation strategy. This work shows the broadening of the scope of cyclpentannulation chemistry to 1,2-bis(5-hexylthiophen-3-yl)ethyne with aryl dibromo derivatives of anthracene, pyrene and perylene to yield 4,4',4'',4'''-(cyclopenta[hi]aceanthrylene-1,2,6,7-tetrayl)tetrakis(2-hexylthiophene) **1A**, 4,4',4'',4'''-(dicyclopenta[cd,*jk*]pyrene-1,2,6,7-tetrayl)tetrakis(2-hexylthiophene) **2A** and 1,2,7,8-tetrakis(5-hexylthiophen-3-yl)-1,2,7,8-tetrahydrodicyclopenta[cd,lm]perylene **3A**. Scholl cyclodehydrogenation of the cyclopentafused thiophene units with suitably substituted hydrocarbons chains provided access to p-extended polyaromatic systems including 2,5,11,14-tetrahexylrubiceno[5,4-b:6,7-b':12,11-b'':13,14-b''']tetrathiophene **1**, 2,5,11,14-tetrahexyldithieno-[4,5:6,7]indeno[1,2,3-*cd*]dithieno[4,5:6,7]indeno-[1,2,3-*jk*]pyrenes **2**, and 2,9,12,19-tetrahexyldithieno[4,5:6,7]indaceno[1,2,3-cd]dithieno[4,5:6,7]indaceno[1,2,3-*lm*]perylene **3**. The fully conjugated contorted small molecules 1-3 provide low optical band gaps, decent mobilities and broad absorption. The HOMO and LUMO energies of these Cp-PAHs were found to be in the range of -5.48 to -5.05 eV and -3.48 to -3.14 eV, respectively. Besides showing broad band absorption features, compound 1 was found to operate as a p-type semiconductor when tested in organic field effect transistor.



2021 GLRM 30

Investigating ligand design characteristics in copper complexation compounds relevant to Alzheimer's Disease

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Alzheimer's disease (AD) is one of the leading causes of death in the United States and is characterized by memory loss due to neurodegeneration from oxidative stress and over-expression of the Amyloid β peptide (Aβ-42) within the brain. This neurodegeneration is the result of Reactive Oxygen Species (ROS) formed via Fenton Decomposition and Haber-Weiss Reactions when Aβ-42 interacts with copper ions. Metal chelation therapy has proven to be a promising area of research to combat ROS-induced neurodegeneration by disrupting the redox cycling of copper that occurs upon binding to the active site of Aβ-42. The work presented herein discusses the syntheses of a series of sulfur containing ligands that could potentially inhibit redox cycling of the copper-amyloid complex. Two of these ligands, 2,2'-thiodipyridine (D2PS) and 1,10-phenanthroline-2-thiopyridine (TPP), have previously shown potential as effective Alzheimer's disease treatments. Previous cyclic voltammetry studies suggest these ligands are effective copper chelators that limit reduction of Cu^{II} to Cu^{I} thereby decreasing the production of ROS. The novel sulfur containing quinoline ligands, 1-(2'-thiopyridyl)isoquinoline (1TPIQ) and 2-(2'-thiopyridyl)quinoline (2TPQ), were also synthesized for this study based on important ligand design characteristics commonly implemented in copper chelators from the literature. Furthermore, UV/Vis titrations were conducted to determine the protonation equilibria of these ligands in solution at different pH.

2021 GLRM 31

Growth of Lab Safety Teams at the University of Minnesota

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The University of Minnesota has rapidly produced one of the most prominent, student-led safety organizations in the country since the Joint Safety Team (JST) began in 2012. Initially, the organization began with a handful of individuals and faculties who were aware of major differences and deficiencies between academic and industrial safety culture. The JST has expanded to include teams associated with training and developing research safety habits to incoming student scientists. Here, I will discuss the growth and progression of the JST including many of the fallbacks and difficulties such that arising organizations can avoid them. Further, I will discuss the importance of lab safety teams (LSTs) and their role on the effectiveness of the JST. Specifically, under the Minnesota model, each research group has designated officers who lead their specialized research team under the guidance of the principle investigator. These leaders work within broader teams of the JST to develop procedures, habits and a community which values safety in conjunction with science rather than as a hurdle. Overall, the safety culture at the University has been built on a platform of community and dedication which has produced a premier environment for students and postdoctoral researchers and I intend to share the development that I observed during my time in the organization.

2021 GLRM 32

Learning experience reports improve academic research safety

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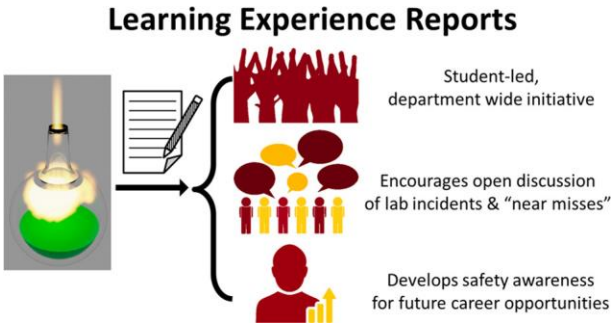
While lab accidents that involved personal injuries or significant property damage are required to be reported by law, many minor lab incidents or near misses are less frequently reported, especially in an academic research environment. However, public awareness of these stories and incidents create valuable learning opportunities and can prevent similar mishaps from happening in the future. Inspired by a near miss reporting system from the Dow Chemical Company, the University of Minnesota Joint Safety Team, a student-led safety initiative between the departments of Chemistry and Chemical Engineering and Materials Science, developed the Learning Experience Reports (LERs) system as a platform to self-report and share safety stories occurring within the two departments. LERs are short, anonymous, voluntary submissions by researchers who were either directly involved with or witnessed a safety-related incident, near miss, or observation of unsafe practices. In this report, we compiled and analyzed 85 LERs submitted by researchers from Departments of Chemistry and Chemical Engineering & Materials Science at the University of Minnesota during 2014–2019. Most notable from our results was that the top three most frequently occurring hazards were spill, fire, and equipment failures. LERs encourage open discussions of lab incidents and near misses through honest, compelling stories among academic

researchers and educate researchers to follow better lab practices. For university administrators, LERs complement existing hazard assessment and incident reporting methods and allow a better understanding of the current research safety landscape among the student body. For researchers, the LER system allows them to develop safety awareness at an early stage and benefit their future careers. Hence, we strongly recommend academic research institutions to adopt a similar LER system to improve the safety culture in academia. Here, we outline the logistics required to implement an effective LER distribution system as well as provide the cumulative data in order to ease the setup of a system for others.



2021 GLRM 33

Recent Advancements in Northwestern University's Research Safety Student Initiative

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In late 2017, Northwestern University (NU) graduate students formed a student-led safety task force known as the Research Safety Student Initiative. Similar to other Lab Safety Teams (LSTs) that have formed in recent years, our mission is to advocate for academic research safety from a student perspective by providing education, resources, and training to the Northwestern community and beyond. RSSI has organized events that have become tradition for the Northwestern STEM community, such as our annual Safety Awareness Week (SAW). This event has historically involved a keynote address followed by daily in-person booths highlighting a daily safety topic to the STEM research community. Our typical programming for SAW was adapted to a virtual format in light of COVID-19 restrictions. We developed a comprehensive series of events including virtual scavenger hunts, workshops, and trivia to engage the NU community. Through the daily scavenger hunts, we introduced the NU community to RSSI and

research safety resources in addition to general lab safety information, while the workshops more specifically focused on fire safety and peroxide-forming chemicals. We also identified two key areas - glove compatibility and electrical safety - where the research community requested more information, and we will develop further training modules and other initiatives to fill these needs.

2021 GLRM 34

Supporting Student-Led Safety Initiatives | What does it take to help others lead?

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Student-centric safety initiatives in higher education continue to grow across the country. Fundamental to this process is providing the right balance of institutional support, independence, and autonomy to allow students to lead without compromising the autonomy they needed to be successful and sustainable.

In this presentation, Northwestern will share how the Research Safety Student Initiative (RSSI) has grown since its inception nearly five years ago and how Research Safety provided a base of operations and budget support without interfering in how RSSI operates or sets its agenda. The discussion will cover a wide range of topics will -- from the practical to the philosophical. The presentation is intended for anyone interested in supporting student programs—faculty, staff, students and administrators, alike.

2021 GLRM 35

Evaluating the success of a workshop focused on student researcher-led academic laboratory safety

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The aim of the ACS CHAS “Empowering Academic Researchers to Strengthen Safety Culture” workshop is to provide resources and strategic direction for individuals who are interested in starting or improving graduate and postdoctoral researcher-driven safety programs at their own institutions. To determine whether or not the workshop was succeeding, two surveys were designed and distributed among attendees at three different time points the workshop was conducted. One survey was distributed right after the attendees completed the workshop, and the second survey was distributed 3 months after the attendees completed the workshop. The surveys were designed to probe attendee knowledge acquisition of key topics throughout the workshop, personal attitudes towards components of laboratory safety, and actions planned and taken around laboratory safety in the months after completing the workshop. The results of these surveys will be discussed.

2021 GLRM 36

Toward gender equity in the sciences: IUPAC and the ISC gender gap project

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The proportions of women in chemistry and the natural sciences has been historically low, and there are persistent gaps between women and men in terms of opportunity, pay, and life experiences. The International Science Council funded a three-year project in 2017-2019 entitled, “A Global Approach to the Gender Gap in Mathematical, Computing and Natural Sciences: How to Measure It, How to Reduce It?” to gather data to measure these gaps and to develop recommendations for improvement in gender equity. A global survey gathered information from more than 24,000 respondents about their educational backgrounds, experiences in their academic training and employment, home environment, and opportunities for growth in their professions. A study of publication patterns examined the proportions of women authors of articles in scientific journals, including trends over time. A Web-based searchable compilation of good practice highlights initiatives from around the world that aim to reduce the gender gap. In their report, the gender gap project team make a series of recommendations for increasing the participation of women in science, including recommendations aimed at teachers and parents, scientific unions, and local and national organizations. In the International Union of Pure and Applied Chemistry, IUPAC, work continues on measuring the gender gap and revealing trends toward gender equity in the chemical sciences. Finally, a new Standing Committee for Gender Equality in the Sciences has been formed by several international scientific unions with the aim of continuing work toward gender equity.

2021 GLRM 37

Identifying Opportunities to Improve Gender Diversity Among Chemistry Faculty

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Despite significant success in addressing gender disparities in chemistry at the undergraduate and graduate level, gender disparities among chemistry faculty members persist. This gender gap is particularly acute among tenured, full professors, which has led policy makers to conclude that a "leaky pipeline" exists for female chemistry faculty members. Opportunities to address this leaky pipeline abound, and include both formal policy change and informal culture change. As a female associate professor who has worked in two institutions across two continents, I have both experienced issues that can contribute to the "leaky pipeline" and worked directly on efforts to address those leaks. A general perspective, focused on opportunities for increasing gender diversity through comprehensive change, will be presented herein.

2021 GLRM 38

Improving recruitment and retention of women in science

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The Chemistry Chapter of Women in Science and Engineering (WISE) at the University of Minnesota has existed in some form since the early 1990s. WISE is composed of faculty, staff, postdoctoral researchers and graduate students within the departments of Chemistry and Chemical Engineering. Throughout the years, the focus has been on improving the recruitment and retention of women in the chemical sciences. This is accomplished through a variety of programming initiatives geared towards networking, professional development and outreach. WISE currently focuses on an annual hands-on outreach event for junior high girls (“Cool Chemistry”) and monthly seminars with invited female professionals. Through Cool Chemistry, WISE is able to introduce young girls to fundamental chemistry concepts using science demonstrations with the ultimate goal of sparking their interest in a career in STEM. Our monthly seminars feature speakers from a variety of careers to provide members of WISE with an opportunity to network and learn more about different careers in chemistry and related sciences.

WISE has served as a model for other student organizations, particularly as an established chemistry graduate student organization that provided leadership opportunities for the department’s graduate community. Prior to the formation of these other student groups, WISE was leading nearly all of the “service events” (besides seminars) for the department (e.g., written and oral help sessions, career workshops). This presentation will provide an introduction to WISE in addition to various programming efforts to improve the recruitment and retention of women in science.

2021 GLRM 39

Radium, the Women's Element: A Historical Analysis of Radium and its Disproportional Effect on Women During the Radium Craze

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Radium turned the world of chemistry upside down. Not only was the discovery made by Marie Curie in partnership with her husband, earning her a Nobel Prize, the element also became entwined in mainstream culture. It was a household name due to its advertisement as a "wonder drug", but also a fascination with the glow that the element naturally had. Radium was everywhere, from makeup to medicine to musicals. While research was catching on to the dangers of radium, it would take many years to get it off the main ingredients list. Until then, radium was a staple in the lives of women everywhere, especially in the early 1900s as they were hired to paint watch-faces with a glowing radium paint that would eventually lead to numerous health side-effects. So, throughout radium's time in the public eye, women also came front and center. For better or for worse, radium pulled women into the world's spotlight. This presentation intends to show the correlation between the prominent radium consumerism and the disproportionate effect that these products had on women during the Radium Craze through a feminist lens. Topics include exploring the response to Marie Curie discovering the element and how she developed radium's uses in medicine, how the Radium Craze affected the make-up industry, and how the Radium Girls were able to reform industry policies regarding health and safety, through biographies and other prominent literature on the subject.

2021 GLRM 40

Female, Russian, Jewish, successful. Irma Goldberg (1871-1939+) and her eponymous reaction.

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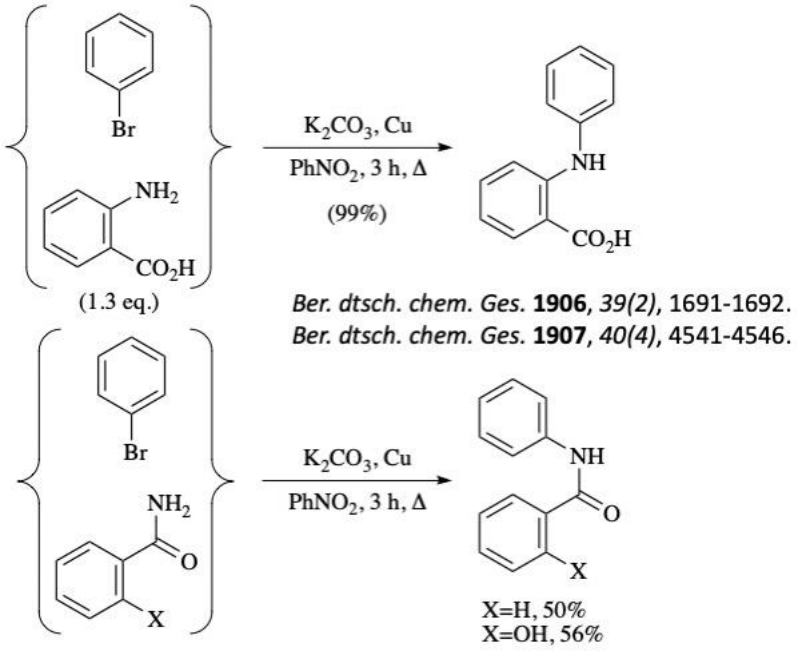
Irma Goldberg is the only woman organic chemist to have an eponymous reaction under her name alone: the Goldberg reaction, which is an amination of halobenzenes with anilines and benzamides in the presenve of a copper catalyst and potassium carbonate as a base. In an era when women were seldom accorded the accolades for their discoveries (look at Lise Meitner and Oto Hahn: he left her off the paper describing her discovery, and he got the Nobel Prize for her work), this makes Goldberg unique. Goldberg was born in Moscow in 1871. Twenty years later, the Jews were expelled from Moscow, so she and her family moved to Geneva soon thereafter to allow Irma to study chemistry. In 1895, she met Fritz Ullmann, unde whom she took her Ph.D. in 1897. She remained as Ullmann's Assistant until 1910, following him to the Technisches Hochschule in Berlin in 1905. She and Ullman married in 1910; they returned to Geneva in 1923 when Ullmann took up a Professorship there. Details of her death are unknown,

but she did appear in the list of signatories to a memorial celebrating her husband in 1939.



The Goldberg reaction

2021 GLRM 41

Dual Inhibition of Protein Tyrosine Phosphatase-1β and Lipoxygenase by Terpenoids

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Protein tyrosine phosphatase-1B (PTP1β) is responsible for the negative regulation of insulin signaling and a therapeutic target for diabetes, cancer, and inflammation. Tremendous growth has been made in finding PTP1B inhibitors that come from natural sources and exploring PTP1B regulatory mechanisms. Lipoxygenase is also indicated in trigerring inflammation and allergic reactions. The goal of our research is to see if the terpenoids, Thymoquinone and D-Carvone inhibit protein tyrosine phosphatase-1B (PTP1β) and lipoxygenase (LOX). Thymoquinone is a monoterpenoid and has been used as a drug for many ailments since ancient history such as asthma, hypertension, diabetes, inflammation, cough, bronchitis, headache, eczema, fever, vertigo, and influenza. Carvone is a terpenoid that has D and L enantiomers which have very different reactivity. For this research, we are using the D enantiomer which has been used for digestive drugs in humans and animals but has also been used in some

essential oils for its pungent caraway smell. Our present results indicate that Thymoquinone and D-Carvone at 100 micromolar concentration inhibit Lipoxygenase by 50.8% and 34.3% respectively and inhibit PTP1β by 62.6% and 20.3%.

2021 GLRM 42

Mediation of the uncoupled eNOS pathway following oxidative stress using tetrahydrobiopterin and nitric oxide donor drugs

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The eNOS pathway, found in the endothelium of blood vessels, is a key regulator of nitric oxide levels in the circulatory system. The pathway is controlled through several positive and negative feedback loops. The cofactor tetrahydrobiopterin (BH4) is a major control point in this pathway and under conditions of stress can be reduced to dihydrobiopterin (BH2). When the reduced form is predominant, the pathway produces reactive oxygen species (ROS) rather than nitric oxide, causing stress and damage to the vessels. In this study, different treatments were studied to determine which was most effective in restoring BH4 levels in the eNOS pathway of bovine aortic endothelial cells (BAECs). Nitric oxide supplementation was the main focus of this study and was tested as a stand-alone treatment and as a combined treatment along with a BH4 donor drug, sapropterin dihydrochloride. Following the two treatments, only the BAECs given the nitric oxide donor drug showed levels of BH4 higher than the untreated control cells. The cells treated with 25 mM nitric oxide donor drug and 2.5 mM BH4 donor drug showed levels of BH4 that were most similar to the untreated control cells with a concentration of approximately 27 mM BH4.

2021 GLRM 43

Identification of Novel Uric Acid Gluconucleosides in *Caenorhabditis elegans*

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Few nucleoside-derived natural products have been identified from animals, despite the ubiquity of nucleosides in living organisms. Here, we use a combination of synthesis and the emerging electron microscopy technique microcrystal electron diffraction (MicroED) to determine the structures of several N^3-(β-glucopyranosyl)uric acid derivatives in *Caenorhabditis elegans*. These noncanonical gluconucleosides further integrate an ascaroside moiety, through which production of a phosphorylated derivative

is influenced by evolutionarily conserved insulin signaling and requires a carboxylesterase for its biosynthesis.

2021 GLRM 44

Identification of glutathionylated cysteines regulating cell migration

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Cell migration plays an important role in many physiological processes such as wound repair and metastasis. Reactive oxygen species (ROS) or hydrogen peroxide (H_2O_2) are known to play an important role as a second messenger in redox signaling during migration. A major mechanism of ROS regulating redox signaling is oxidative protein modifications. Protein S-glutathionylation, one of the oxidative modifications, is known to regulate some proteins involved in migration, such as actin, LMW-PTP, and MAPKP-1. Despite these proteins, it is expected that H_2O_2 can react with many other proteins to regulate migration, and we are exploring the identity and reactivity of specific cysteines which undergo glutathionylation and regulate cell migration. For the identification of glutathionylated cysteines, we apply the clickable glutathione approach developed by our lab together with mass analysis.

During migration, ROS production is controlled spatially, temporally, and in concentration. To achieve these conditions, we have successfully adapted the D-amino acid oxidase (DAAO)/D-Ala system. DAAO consumes D-Ala and produces H_2O_2 and this allows us to control the production of H_2O_2 by changing D-Ala concentration. This system also gives the advantage of targeting it to different organelles. Using this system, we have observed that H_2O_2 production and migration increase in a D-Ala-dependent manner in the MCF-7 cell line. Moreover, glutathionylation was also induced at these conditions. The proteins undergoing glutathionylation under migration conditions will be identified using the clickable glutathione method linked to mass analysis in the future study. Alternatively, with the use of bioinformatics tools, we have narrowed down 37 glutathionylated proteins whose cysteine glutathionylation may regulate migration. We have investigated nine proteins out of 37 so far by wound healing assays and identified that glutathionylation of specific cysteines of three proteins (PP2Cα, NISCH, ARHGEF7) are regulating migration under glucose starvation. Subsequently, we have evaluated glutathionylation and functional changes of PP2Cα upon its glutathionylation and hope to move on to the other two proteins as well. Putting together, our findings will help to understand redox-mediated mechanisms of cell migration.

2021 GLRM 45

LXR and INSIG Act as Differentiators in the Regulation of the Gene Expression of G6PDH and FAS Under Insulin Resistant Conditions

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Diabetes, a chronic metabolic disease that affects nearly 10% of the world's population can lead to very serious complications such as renal failure, liver cirrhosis, and heart attacks. The most common type is Type 2 diabetes and is diagnosed when a person has elevated amounts of blood glucose due to insulin resistance. This resistance to insulin leads to problems with glucose transport into tissues for subsequent metabolism. Over the years it has been shown that insulin regulates the expression of several key enzymes in both carbohydrate and fatty acid metabolic pathways via the phosphatidyl inositol 3-kinase (PI3K) pathway. Previously, using glucosamine, a precursor of the hexosamine biosynthetic pathway, we had established a model of insulin resistance in primary rat hepatocytes in culture. Using this primary cell culture model, we showed that under insulin resistant conditions, the expression of glucose 6 phosphate dehydrogenase (G6PDH), a key enzyme in carbohydrate metabolism and fatty acid synthase (FAS), a key enzyme in fat metabolism were differently regulated but the mechanism of this differentiation was unclear. Under this model of insulin resistance, we now show that this differential regulation is due to two proteins downstream of PI3K, the liver X receptor (LXR) and insulin induced gene (INSIG).

2021 GLRM 46

Use of lysis buffer additives to improve the solubility of recombinant influenza Polymerase Acidic Protein

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With only four current antivirals effective against influenza, the development of anti-influenza therapeutics is an imperative. Polymerase Acidic (PA) Protein is an attractive target for the creation of anti-influenza therapeutics; however, we have observed limited solubility of recombinant PA protein domains overexpressed in bacterial systems . The focus of my undergraduate research project has been to test the ability of lysis buffer additives, including salts, amino acids and sugars, to solubilize recombinant PA. I will present the results of this additive screen on PA solubility at various lysate concentrations. We hope these lysis buffer modifications will enable large scale expression and purification of PA protein to enable structure-based drug design.

2021 GLRM 47

Our Chemical Safety Journey

***Kenneth P. Fivizzani**, kfivizzani@wowway.com. Division of Chemical Health and Safety, Naperville, Illinois, United States*

The science and applications of chemical safety have evolved during the forty-two years of CHAS's existence. New regulations and a new federal agency have increased understanding of some major issues and expanded the boundaries of compliance. The Globally Harmonized System of classification and labelling of chemicals (GHS) is becoming a major source of hazard information for all types of chemicals. Documentation of accumulated chemical safety knowledge has increased dramatically as has access to this knowledge. There are several useful publications available to students and those starting their professions in chemistry. *ACS Chemical Health and Safety* is a peer-reviewed scientific journal. The chemical safety journey has had some significant setbacks that hopefully have made chemists more cognizant of hazards and more determined to keep workplaces safe. Attitudes are more positive and supportive of proactive safety policies and procedures. The journey is not yet over, but perhaps we can see the ultimate destination.

2021 GLRM 48

Growing the laboratory safety program and improving the safety culture at Metropolitan State University

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Laboratory safety has many interrelated components-some governmental (federal, state and local) and others considered prudent practices. There is flexibility in the way these requirements and recommendations are met. When developing a laboratory safety program, it can be challenging to incorporate new systems around existing practices and cultures. Come hear about some laboratory safety elements that have been implemented at Metropolitan State University's small Natural Science department, including a hands-on scavenger hunt for new faculty orientation, collaborative lab clean-ups and convenient access to hazard stickers for improved labeling.

2021 GLRM 49

Safety Leadership: Critical Skills for Improving Safety Performance

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Traditional ruled-based safety programs have been effective at reducing injures, but in many instances gains in safety have plateaued and easily preventable injuries still occur. According to OSHA "it has been observed…and confirmed by independent research that developing strong safety cultures have the single greatest impact on incident reduction of any process", but strong safety cultures are difficult to develop and maintain. Some organizations—while they may be interested in taking steps to reduce

injuries—are not willing or able to commit to a years-long, and sometimes costly, effort to transform their safety culture.

A key step in the path to a positive safety culture is the development of effective safety leadership. In fact, effective safety leadership can significantly improve safety performance without undertaking a complete safety culture transformation. For the individual, enhancing safety leadership skills has the added benefit of enhancing leadership skills in general. Excellent leadership skills are critical to the success of a supervisor or manager of people. Excellent *safety* leadership skills can help supervisors and managers become even more effective leaders of people and projects while achieving safety goals and minimizing costs associated with poor safety performance.

This session will introduce the concept of safety culture and several tools for effective safety leadership. The overall goal is to foster leadership skills that help create and support a positive safety culture, even where an organization has not committed to a safety culture transformation. Observations from more than five years of safety leadership training and consulting in a variety of settings will be presented.

2021 GLRM 50

Student-Led Climate Assessment Promotes a Healthier Graduate School Environment

Madeleine Beasley*, mbeasley@smith.edu, Margaret Lumley, Tesia Janicki, Rebeca Fernandez, Andrew Buller. Chemistry, University of Wisconsin-Madison, Madison, Wisconsin, United States*

This talk will describe a graduate student-led effort to develop a climate survey to assess, advocate for, and improve the well-being and mental health of graduate students and postdocs in the Department of Chemistry at the University of Wisconsin−Madison. Graduate students have an increased incidence of depression relative to the general population, and given the transient nature of the student population, understanding and addressing mental health concerns can be challenging. The goal of this work is to illustrate how students, with the support of departmental faculty, staff, and existing on-campus mental health resources, can take the lead to investigate and assess issues related to the challenging graduate school environment. We describe the student-led development and implementation of and the subsequent follow-up to a department-wide survey aimed at destigmatizing the subject of mental health and fostering a more supportive community. Our efforts serve as a framework to assist other interested and motivated graduate students who, with the support of local faculty, wish to develop and initiate a similar process in their own departments. We demonstrate that student-led actions can effectively tackle department-level problems and encourage other interested students to initiate a similar effort.

2021 GLRM 51

Barriers in chemistry, part I: African-American chemists

***David E. Lewis**, lewisd@uwec.edu. Chemistry Department, UW-Eau Claire, Eau Claire, Wisconsin, United States*

Chemistry is full of discussions of barriers: the barrier to rotation is a fundamental question in conformaional analysis, and activation barriers are an intrinsic characteristic of organic reactions. Differences in the heights of the activation barriers in competing reactions give us such things as kinetic *vs.* thermodynamic control of reactions and kinetic isotope effects.
For the African-American chemist, the barriers to learning imposed by the course material itself have historically been augmented by problems arising from the overt racism of the era. Percy Julian, for example, had his teaching assistantship for support during his Ph.D. revoked by Harvard University because the administration feared the reaction from their audience if a black man were to be placed in a position of authority over white students. Most African American educators spent the bulk of their teaching careers at Historically Black Colleges and Universities, where the infrastructure to support their work—many (most) of their students were from black high schools where the curriculum was not strong—was woefully inadequate, and neglected by the government.
This talk will focus on the barriers faced by African-American chemists up to the end of the first half of the twentieth century.

2021 GLRM 52

Barriers in chemistry, part II: Gender and religion as hurdles to advancement

***David E. Lewis**, lewisd@uwec.edu. Chemistry and Biochemistry, University of Wisconsin-Eau Claire, Eau Claire, Wisconsin, United States*

In Part I of this presentation, the barriers to advancement imposed on African-American chemists due to race was discussed. In this part, we will focus on the other two major barriers to advancement in chemistry until the last quarter of the twentieth century or so: gender and religion.
Under the guise of women being the "weaker sex," they were often excluded completely from universities, or were segregated into "Women's Colleges and Universities." The conventional wisdom of the time was that women were not equipped physically or intellectually to study the physical sciences in general, and chemistry in particular. Women's advocates were few and far between—one proponent of women being allowed to study in the universities alongside male students was Vladimir Vasil'evich Markovnikov (he of the eponymous Rule), but he was part of a very small minority. Just how fallacious the idea of women being unsuited to science was, found compelling proof on October 7, 2020, with the announcement of the Nobel Prize for Chemistry—by two women, Emanuelle Charpentier and Jennifer Doudna.
The other barrier to advancement in Chemistry was religion. Most people have heard the story of Galileo's muttered remark, "*sed movet!*" when forced to repudiate his findings of heliocentrism in the solar system. In a world dominated by Christianity in Europe, the most persecuted religious minority was the Jews. The persecution came to its logical end in the Nazi Holocaust. In Russia, Jews had been subjected to pogroms for centuries: Irma Goldberg, the only woman to have a single-name eponymous reaction, was forced to leave Moscow in 1891 due to an Imperial Decree evicting all Jews from the city. As with race, the barriers due to religion have taken a long time to break down. In fact, we still see anti-semitism—against both Jews and Arabs—today. Despite their second-class status, many women and Jews have made lasting contributions to chemistry. In this talk, the question of gender and religion on the careers of chemists will be addressed.

2021 GLRM 53

Highlighting the voices of chemists from underrepresented groups in sophomore organic chemistry

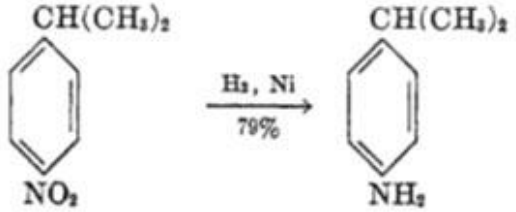
John B. Friesen*, jbfriesen@dom.edu. Rosary College of Arts and Sciences, Physical Sciences Department, Dominican University, River Forest, Illinois, United States*

In response to the challenge of engaging The HistoryMakers project, a collection of video interviews with prominent African Americans, with first semester Sophomore Organic Chemistry instruction a module was created that highlighted the life and work of Samuel Massie. Students participated in reading Samuel Massie’s personal history as well as selected original literature. The synthetic chemistry described by this author was applied to the analysis of bonds broken and bonds formed during the course of a chemical reaction. With this information, the thermodynamics of the reaction were estimated. Mechanistic features of Samuel Massie’s reactions were illustrated with classic arrow pushing mechanisms. Students not only engaged the chemistry, but they also learned about the challenges faced by Samuel Massie as an African American Chemist and related them to the challenges they have faced and will face as they

pursue their academic goals. This methodology was extended to create another module that highlighted the work of a prominent Mexican Chemist, Luis Ernesto Miramontes. Students gained insights into the achievements of chemists from underrepresented groups and the cultural context of chemical advancements. In addition, they read original literature and discovered that advanced synthetic schemes may be broken down into manageable analyses.

Consider the following reaction from "Synthesis of N-methyl-3-isopropyl-4-dimethylaminophenylcarbamate and Some Related Compounds," *The Journal of Organic Chemistry*, 19, 1067-1079 (1954). H. Gilman, S. Avakian, R. A. Benkeser, H. S. Broadbent, R. M. Clark, George Karmas, F. J. Marshall, S. M. **Massie**, D. A. Shirley, and L. A. Woods.

a) Redraw the molecules in Lewis structures.
b) Balance the equation.
c) Indicate bonds broken and bonds formed.



XII XIII

2021 GLRM 54

Diversifying Clean Water: an Examination of Drinking Water Quality and Social Disparities in Michigan

***Tyra Blair**, tyra.blair96@gmail.com, Ryan Beni, Sujata Guha. Chemistry, Tennessee State University, Nashville, Tennessee, United States*

Water is one of the most essential resources required to sustain life; however, it could be detrimental to the health of those without access to water that is properly treated. The Safe Drinking Water Act of 1974 set regulations to protect citizens from naturally occurring and man-made contaminants, but some are still without clean and safe water and is speculated to be because of their race. This research examines the disproportionality of available clean water provided by government sources in Michigan and its correlation with race and household income. In the study, it has been found that one of the leading causes of water contamination is industrial activity, with the automobile industry being responsible for approximately 300 million tons of lead contamination in water, and that manufacturing company's locations mostly centered in minority and low-income areas. Lower income cities, such as Hamtramck and Benton Harbor, have an average of 14.8 drinking water standard violations totaled with the highest being 99 total violations, while higher income cities, like Novi and Bloomfield hills, have an average of 4 total violations. Cities, like Flint and Detroit, that have a

higher minority population are 10 times more likely to have a water standard violation, and the minority population is proportionally related to the possibility of industrial manufacturing being located in the area. These communities also face a higher risk of birth defects, developmental issues in children, and organ failure in adults due to continuous exposure to water contaminants. Race as a direct causation could not be proven, but there are links to direct correlation through historical redlining and housing trends.

2021 GLRM 55

Chem Club Diversity in Diverse Outreach Demos

Lawrence H. Kolopajlo*, lkolopajl@emich.edu, Micaela Shempf, Chloe Catallo. Chemistry, Eastern Michigan University, Sylvania, Ohio, United States*

Chem Club students have undertaken diverse outreach projects in rocketry and 3D-printing. In this poster are shown those outreach projects administered by diverse students. One diverse student balanced division I athletics with academics. Other students promote diversity in urban areas.

2021 GLRM 56

Julia (Yuliya Vsevolodovna) Lermontova (1847-1919)

Megan L. Gawlitta*, gawlitml4137@uwec.edu, David E. Lewis. Chemistry and Biochemistry, University of Wisconsin-Eau Claire, Eau Claire, Wisconsin, United States*

Despite having been born into the aristocratic Lermontov family, having an especially brilliant mind when it came to scientific inquiry, and the support of many of the most nfluential chemists in Russia, Lermontova was unable to earn a doctoral degree in chemistry simply because she was a woman. Consequently, she decided to travel to Germany to continue her education abroad. But, as a single woman, she was only able to do so with a chaperone. A family friend Sofia Kovalevskaya (the mathematician) contracted a marriage of convenience to allow her to act as chaperone so that the two women could study abroad. Though the opportunities in Germany were much more promising, obtaining admission to a post-graduate program was still difficult for a woman. Between 1869 and 1871, she audited lectures by Bunsen, Helmholtz, and Kopp, and from 1871-1874 she worked as an Assistant in the Berlin laboratory of A. W. von Hofmann. After defending her dissertation on an analysis of methylene compounds at Göttingen in 1874, Julia Lermontova became the first woman in Germany (and worldwide) to officially become a Ph.D. in chemistry.
On her return to Russia from Germany, she was feted as a returning heroine, and she courted by Mikhail Aleksandrovich Butlerov as an Assistant in his St. Petersburg laboratory. In the late 1870s, she accepted his invitation, working with him from 1876-1879. However, she first chose to work with Vladimir Markovnikov at the University of

Moscow. She spent two stints in Markovnikov's laboratory: 1875 - 1876 and 1880-1882. In 1883 she left chemistry and retired to her estate.

Julia (Yuliya Vsevolodovna) Lermontova (1847-1919)

2021 GLRM 57

High Field Dielectric Properties of Clay filler - Silicone polymer matrix composites.

Dipankar Ghosh[1]*, dghosh2@gmail.com, Maryam Sarkarat*[2]*, Michael Lanagan*[2]*, Andrew C. Lottes*[1]*, Kent Budd*[1]*, Ramakrishnan Rajagopalan*[2]*. (1) Corporate Research Laboratory, 3M Company, Saint Paul, Minnesota, United States (2) The Pennsylvania State University, University Park, Pennsylvania, United States*

Liquid silicone polymer matrix composites were developed using two different types of clays as filler materials: organically modified montmorillonite (ommt) and calcined and surface treated kaolin (commercially known as Translink 37, T37) for power applications. It was observed that addition of the clay fillers in the silicone polymer matrix resulted in well dispersed fillers when kaolin clay (T37) was added, in contrast to micron size agglomeration with ommt clay. The surface chemistry of the fillers played a significant role in the kinetics of curing and as a result had significant effect on the overall dielectric properties of the composites. The negative surface charge on the modified kaolin had detrimental effect on the catalytic activity of the platinum complex in the liquid silicone matrix and this led to incomplete crosslinking in the composite and caused higher dielectric loss and DC conductivity.

On the other hand, ommt clay was more difficult to disperse in the silicone polymer matrix. However, the DC conductivity of the composite was relatively lower than the neat silicone polymer at high temperature, thus indicating the presence of interfacial traps between the agglomerated macroparticles and the polymer matrix which limited the migration of the charge carriers over long distances. OMMT clay filler - Silicone

composites were also able to withstand higher electric fields as compared to kaolin clay (T 37) silicone matrix composites.

2021 GLRM 58

Multifunctional Silica Sorbent Materials: For trace collection of nitrate and phosphate anions

***Kara M. Nell**, knell@morris.umn.edu, Emily Robinson, Matthew DeSmith, Breanna Dragseth, Abi Bartlett. Chemistry, University of Minnesota Morris, Morris, Minnesota, United States*

Nitrates and phosphates exist naturally but are present in elevated concentrations in many areas primarily due to agriculture; these elevated concentrations are concerning for human and environmental health. A variety of methods are being investigated and utilized for removing nitrate and phosphate from water systems, we have focused on functionalized silica-based sorbent materials. We have designed, synthesized, and characterized a set of silica-based functionalized materials for removal of these unwanted compounds from natural waters. These materials are multifunctional, having been functionalized with both amine groups as well as electron deficient aromatics. We chose amine groups because they are known to non-selectively bind anions from natural waters. Electron deficient arene rings were selected due to their ability to form anion-π interactions with the target anion; anion-π binding has shown preference to nitrate in some examples. A series of ligands containing electron deficient arene rings have been incorporated onto the silica surface using Cab-o-sil® as the silica base. Performance testing is ongoing, but initial results are promising.

2021 GLRM 59

Investigating the Energy and Electron Transfer Dynamics of Triplet-Triplet Annihilation Upconversion in Sensitizer and Acceptor Dyes Attached to the Metal Oxide Nanocrystal

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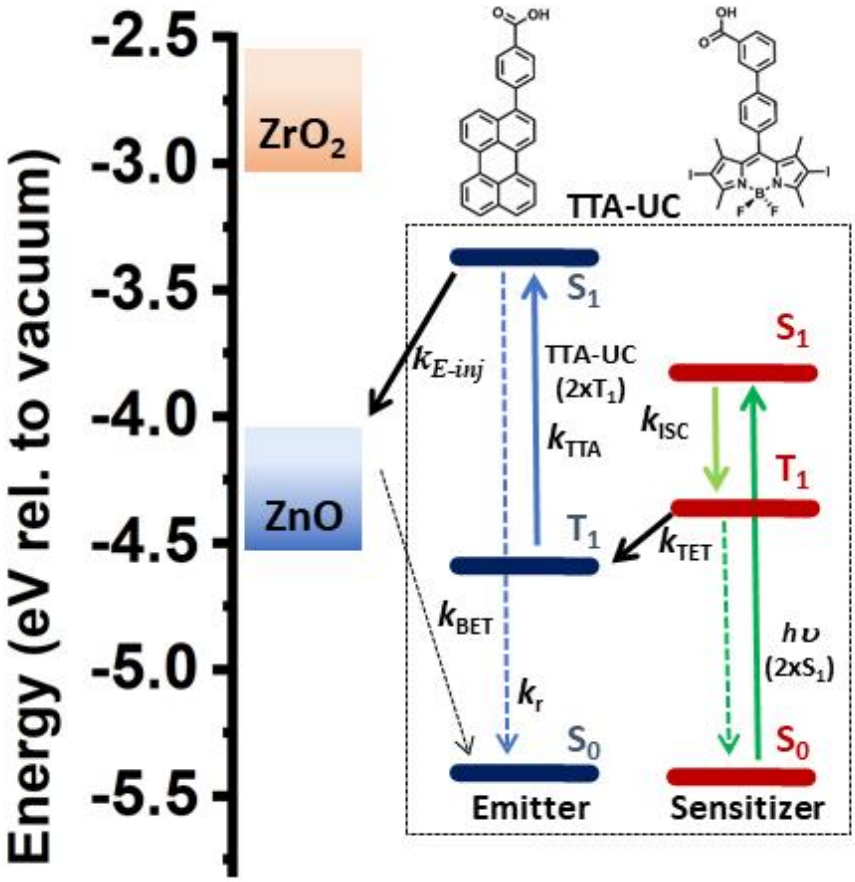
Molecular photon upconversion based on triplet annihilation upconversion (TTA-UC) involves combining low energy photons to generate higher energy excited states is emerging as a potential technique to increase the maximum theoretical solar cell efficiency. Here we demonstrate the energy and electron transfer dynamics in pre-organized co-assemblies of sensitizers and emitters attached to zirconium oxide (ZrO_2, ~6 nm) and zinc oxide (ZnO, ~4 nm) nanocrystals (NCs). The synthesized NCs are fully dispersed in the organic solvent e.g. dichloromethane that allows systematic control over the dye:NC stoichiometric ratio. Carboxylic acid functionalized boron dipyrromethene (BODIPY) sensitizer and perylene emitter have been synthesized and

fully characterized. In steady state experiments selective excitation of the BODIPY sensitizer (λ_{ex}: 532 nm) in dichloromethane solutions, which also contain the perylene emitter, produces anti-Stokes emission at 470 nm resulting from TTA-UC. Photon upconversion was also observed when the BODIPY and perylene dyes were coadsorbed on ZrO_2 NC. No emission was observed, however, when both dyes were coadsorbed on ZnO NCs. Ultrafast transient absorption measurements established that following TTA-UC the singlet excited state of the perylene is quenched by electron transfer to the ZnO conduction band.



2021 GLRM 60

Understanding the charge transfer mechanism in protic ionic liquids

Christopher Arntsen, *carntsen@ysu.edu. Department of Chemical and Biological Sciences, Youngstown State University, Youngstown, Ohio, United States*

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

2021 GLRM 61

The atomistic simulation of absorbed water on the thermomechanical properties of crosslinked epoxy networks using ReaxFF

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The atomistic scale simulation of cross-linking process within polymeric systems is conventionally carried out by connecting reactive sites of monomer. This does not capture the reaction pathway from reactants to final products through transition states. The ReaxFF reactive force field framework that applied in molecular dynamics simulations is used to provide the reactants with a sufficient amount of energy equivalent to or slightly larger than their lowest reaction barrier energy, to overcome the barrier for cross-linking. The reactive molecular dynamics method allows the simulation of the realistic crosslinked polymeric network at a computationally accessible time scale. This framework is implemented to crosslink the diglycidyl ether bisphenol A (BisA) with aliphatic amine (JEFAFMINE D-230) and aromatic amine (DETDA) to achieve a reasonably high crosslink percentage (70%). It is well known that water diffusion through cross-linked epoxy polymers seriously affects the durability of epoxy coatings and accelerates the corrosion of the substrate. In this study, the effect of water absorption on thermo-mechanical properties of epoxy networks was investigated. The interplay between free volume effects and hydrogen bonding interactions is analyzed for the deterioration and recovery of elastic modulus of the epoxy networks. It is observed that water molecules tend to locate within the proximity of polar groups of epoxy networks and have a propensity to aggregate at higher water content. The diffusion coefficient of water in a croslinked epoxy network increases with water content. The ReaxFF framework is also utilized to investigate the hygrothermal degradation of the crosslinked epoxy network. The JEFAFMINE D-230 cured epoxy network is more susceptible to hydrolytic degradation than DETDA cured epoxy network. This lower hydrolytic degradation of DETDA cured epoxy polymers is accounted for the inaccessibility of water molecules to interact with ether linkages in the DETDA cured epoxy network. The results from performed simulations can help to understand the cross-linked polymers' properties, as well as characteristics of water absorption in

epoxy networks, to guide designing new cross-linked epoxy polymers with desired properties to broaden the applications of epoxy materials, including humid environments.

2021 GLRM 62

Molybdenum carbide catalysts for biomass upgrading – from bulk to nanoscale

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Ex situ catalytic fast pyrolysis (CFP) of biomass is an emerging route for the production of renewable liquid hydrocarbon fuels that are infrastructure compatible and cost competitive. By immediately upgrading the pyrolysis vapors prior to condensation, this process aims to simultaneously stabilize the bio-oil product, while enhancing its fuel properties with hydrogenation, deoxygenation, and C-C coupling reactions. The realization of these goals will require new catalysts that possess bifunctional properties - that is, a balance of acidic and metallic sites - such that they can activate H_2 under low pressure, high temperature conditions, and favor cleavage of C-O bonds over C-C bonds. Early transition-metal carbides are one class of materials that possess these bifunctional properties, and in particular, beta-Mo2C has received attention from our laboratory and others as an effective hydrodeoxygenation (HDO) catalyst for a variety of biomass oxygenate intermediates. In this presentation, our research into the bulk-Mo_2C surface chemistry, identity of the active sites, and deoxygenation pathways will be presented. Further, our recent results that build upon this knowledge to design and synthesize nanocrystalline alpha-MoC_{1-x} materials with tuned acidic-site/metallic-site ratios will be discussed, along with changes to the surface chemistry and the resulting catalytic performance, including CO_2 hydrogenation as a probe reaction for these nano-scale catalysts.

2021 GLRM 63

Lactone Bridged Oligophenyenes and Derivatives as Optical Materials with pH Switching Capabilities

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The electronic and spectroscopic properties of compounds containing aryl aryl bonds are highly dependent on aryl aryl torsional angles. Coplanar configurations of the arene subunits leads to more efficient pi orbital overlap resulting in higher conductance of electrons as well as more efficient absorption and emission of light. Unsubstitituted oligophenylenes are nonplanar compounds but chemical bridging units incorporated between the arene subunits can lead to planarity and rigidity. Our group has been actively exploring the lactone unit as a novel bridging group. We will describe the synthesis a variety of lacone bridged oligophenylenes and their derivates as well as how

the lactone bridging group affects optical properties of these molecules. Additionally, the lactone unit is capable of pH induced cleavage and re-formation resulting in reversible aryl aryl bond geometry switching. This directly leads to molecules with the ability to modulate optical properties in response to the pH of the environment.

2021 GLRM 64

Reimagining Formative Assessment of Organic Chemistry Mechanisms

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Routinely, organic chemists communicate via mechanisms, which can be described as visual diagrams with curved arrows showing the movement of electrons during a reaction. Naturally, mechanisms are central in the teaching and assessing of the subject material. Problematically though, many students struggle to understand this symbolic notation causing a barrier for learning the underlying principles of chemical reactions. In terms of assessment, evaluation of student hand drawn mechanisms is time intensive which limits the ability of instructors to provide individualize formative feedback prior to summative assessments. Current online homework systems for submitting mechanisms are often not user friendly which detracts from focus on understanding how to move electrons to understanding how to enter in the answer. Since 2016, Alchemie has been researching and designing interactives to improve students' learning of mechanisms through experiential game-based learning. In 2018, Alchemie launched the Mechanisms App and is now researching and developing a 3D mechanisms tool. This talk will review the literature-based rational for design, findings of research studies comparing paper-pencil to digital tools, assessment capabilities of the interactives, and present preliminary findings for the new 3D system.

2021 GLRM 65

Stimuli-responsive polymer dispersants and viscosifiers

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Stimuli-responsive polymers are polymers that dramatically change properties, such as viscosity or interfacial activity, in response to a small change in an external trigger including pH and temperature. Poly((2-dimethylamino)ethyl methacrylate) or PDMAEMA is a dually-responsive polymer that switches solubility, viscosity, and interfacial activity as a function of pH and temperature. Controlling polymer structure, including block architecture, allows for tuning of the stimuli-responsive properties for target applications. PDMAEMA-containing copolymers were synthesized using Activator Regenerated Electron Transfer Atom Transfer Radical Polymerization (ARGET ATRP) to minimize the amount of copper catalyst needed and to increase the oxygen tolerance of the

polymerization. Diblock and triblock PDMAEMA-containing copolymers with low dispersity and controlled degree of polymerization were achieved using ARGET ATRP. Solubility and self-assembly as a function of temperature, pH, polymer concentration, and polymer composition were determined using UV-Vis spectroscopy and dynamic light scattering. In addition, viscosity, viscoelasticity, and interfacial tension were determined for the PDMAEMA-containing copolymers. PDMAEMA-containing copolymers are being tested in polymer dispersant and viscosifier applications.

2021 GLRM 66

Can you cure cancer with curry powder? Connecting bench chemistry to real-world problems for student researchers

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If you ask an undergraduate student if they want to do organic chemistry research, they may not be interested, or think it is too hard. But if you ask them if they want to work to find a cure for cancer, you will likely pique their interest. You get to say, “sure, running this column is tedious, but you are synthesizing a new chemical entity nobody else has ever made, and that compound could cure cancer!” The Zingales lab recruits undergraduate students to accomplish organic chemistry research with two collaborative projects focused on design and synthesis of new small-molecule organic compounds that could be used to treat cancer or Alzheimer’s Disease. This talk presents recent results from these projects as well as strategies for facilitating this kind of research in a primarily undergraduate university setting.

2021 GLRM 67

Comparison of mechanical and photodynamic behavior of crystalline Schiff bases

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Mechanically responsive crystals respond mechanically to external stimuli, such as light, heat, and mechanical pressure. These crystals gained much interest in recent years as they can act as energy transformers in various applications. Salicylideneaniline is a well-studied photochromic system that can change the crystal color upon irradiation, through intramolecular proton transfer in the excited state to form the corresponding keto-tautomers. We compared the mechanical properties of two o-((o-tolylimino)methyl)phenol derivatives A and B. Long needle-like crystals of derivative A were bendable elastically and regained its original shape once the mechanical stress was released. On the other hand, long block like crystals of B were brittle and broke into pieces upon applying mechanical stress. Herein, we compare their mechanical and

photodynamic behavior. We used transient spectroscopy, force field calculation, X-ray structure analysis and SEM to explain their dynamic behavior.

2021 GLRM 68

Reactivity of Vinyl Hydroperoxides and new Rearrangement Pathways in Isoprene Ozonolysis

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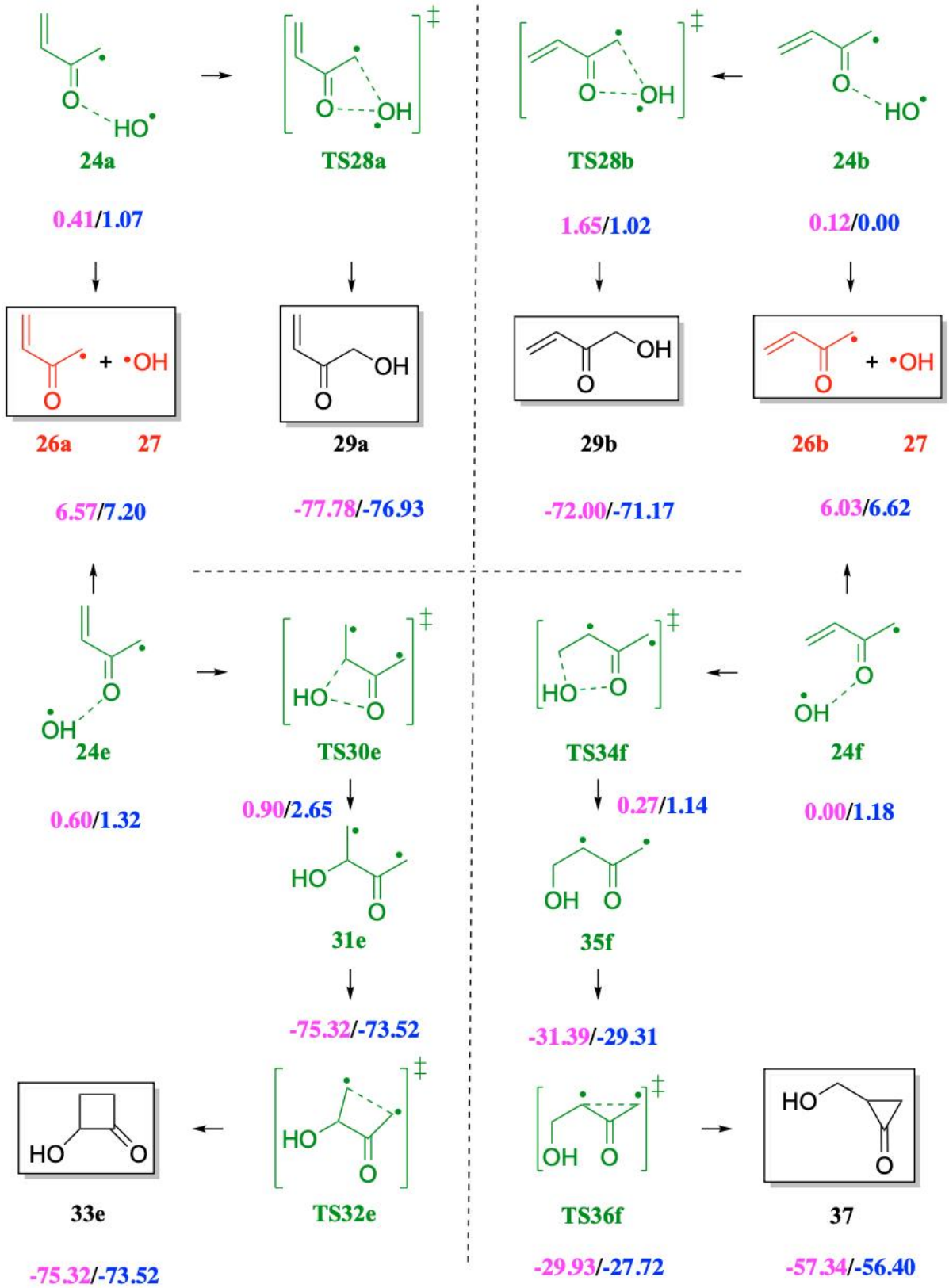
Isoprene ozonolysis is the reactive process between ozone and isoprene – the most abundant alkene in the troposphere. This process generates many different products, a significant portion of which are known to be hazardous to human health and harmful to the environment. Though the ozonolysis of alkenes has been well studied, the specific mechanisms of isoprene ozonolysis have not been completely reported in the chemical literature.
Given the need to understand the reactions that generate the aforementioned dangerous products, our primary research goal was to construct mechanisms and identify intermediates in the process of isoprene ozonolysis. It is necessary to use computational methods to study these reactions due to the very high energy of the transition structures; their instability causes them to decompose extremely quickly, preventing researchers from being able to effectively measure them experimentally. Isoprene ozonolysis involves the initial formation of a primary ozonide whose cycloreversion leads to Criegee intermediates. The syn conformer of a Criegee intermediate preferentially undergo an intramolecular 1,4-hydrogen shift to form an unsaturated vinyl hydroperoxide, which can either fall apart to give a hydroxyl radical or undergo a 1,3-shift to the hydroxyl group to form hydroxy acetaldehyde. Given the possibility of the radical pair rearrangement instead of falling apart, our research goal is to consider the rearrangement pathways for vinoxy and hydroxyl radicals that result from isoprene ozonolysis as well as comparing reactivity of vinyl hydroperoxides.



Relative Energies (kcal mol^{-1}) from (U)M06L/6-31+G(d,p) 0 = lowest energy conformer (24f) and (U)M06L /def2TZVP 0 = lowest energy conformer (24b)

2021 GLRM 69

Photodissociation of the N_2-NO complex between 225.8 and 224.0 nm

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The velocity map ion images of NO photofragments resulting from the dissociation of the N_2–NO complex excited between ~225.8 and 224.0 nm were recorded. This wavelength range spans the photodissociation threshold, where one photon dissociates the complex through the N_2 (X)–NO (A) ← N_2 (X)–NO (X) transition and a second photon non-resonantly ionizes the NO (A) photofragment. Althought the lowest energy photons do not have sufficient energy to photodissociate the Ã state of the complex, dissociation is observed with increasing photon energy. We experimentally determined the appearance energy for the NO (A) photoproduct to be 44284.7 ± 2.8 cm^{-1}. This appearance energy and the NO A ← X origin band transition were used to determine a ground state dissociation energy of 85.8 ± 2.8 cm^{-1}. As the photon energy increased, any excess energy was partitioned into rotational modes of the diatomic products as well as photofragment translational energy. Good agreement was found between the average fraction of rotational energy and the predictions of a simple pseudo three atom impulsive model.

2021 GLRM 70

Navigating the Aromaticity, Stability, and Photophysics of Novel Quinoidal Acenes through Annulative lateral pi extension and Quinoidization

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Polyaromatic acene chromophores have excellent light-harvesting properties and have been applied in various areas due to their tunable optoelectronic bandgap and photophysical properties. Recently, there are proposals to tune the ground and excited states aromaticity of acene chromophores leading to impacting their photophysical properties. In our current effort on using aromaticity to tune the photophysical properties of acenes, we designed and synthesized π-extended quinoidal acene thioamides, which exhibit non-classical or Baird type aromaticity in the ground state. The latest results from our group suggested that a higher degree of π-extension in quinoidal acene chromophores have great impact on the ground state features namely aromaticity and photophysics with the former being compromised due to a higher resonance energy of stabilization from classical aromatic units.

My presentation will showcase the synthesis and photophysical characterization of the novel π-extended quinoidal acene chromophores.

2021 GLRM 71

Synthesis and Photophysical Characterization of *bis*-iodo-dipyrrolonaphthyridine-dione: a Novel Photodynamic Therapy Agent

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Photodynamic therapy (PDT) is a biomedical protocol which involves the use of visible light-harvesting photosensitizers to generate reactive oxygen species (ROS). In the last few decades, PDT has greatly revolutionized the treatment of various malignancies from severe acne to certain types of localized cancerous tumors. Importantly, the role of the light-harvesting photosensitizer is crucial to achieve excellent efficacies of the PDT. Upon visible light irradiation, the sensitizer undergoes a photophysical process, which leads to energy transfer to molecular oxygen. From the energy transfer process ROS (such as singlet oxygen) are generated and subsequently react with biological tissues/cancer cells leading to apoptosis. Using *bis*-iodo-dipyrrolonaphthyridine-dione (I_2-DPND), which was synthesized and fully characterized in our group, we successfully generated singlet oxygen *in vitro* from green-to-red light irradiation of I_2-DPND (used as the sensitizer). Trapping experiments using 9,10-diphenyl-anthracene was also achieved. But, our studies revealed a modest (6-8%) quantum yield of singlet oxygen generation using I_2-DPND. This low value of singlet oxygen was attributed to a likely photobleaching of I_2-DPND when irradiated for a longer period of time.
My presentation will highlight the synthesis and photophysical characterization of I_2-DPND. I will also detail the singlet oxygen generation investigation and our ongoing effort in the derivatization of I_2-DPND to enhance its photostability.

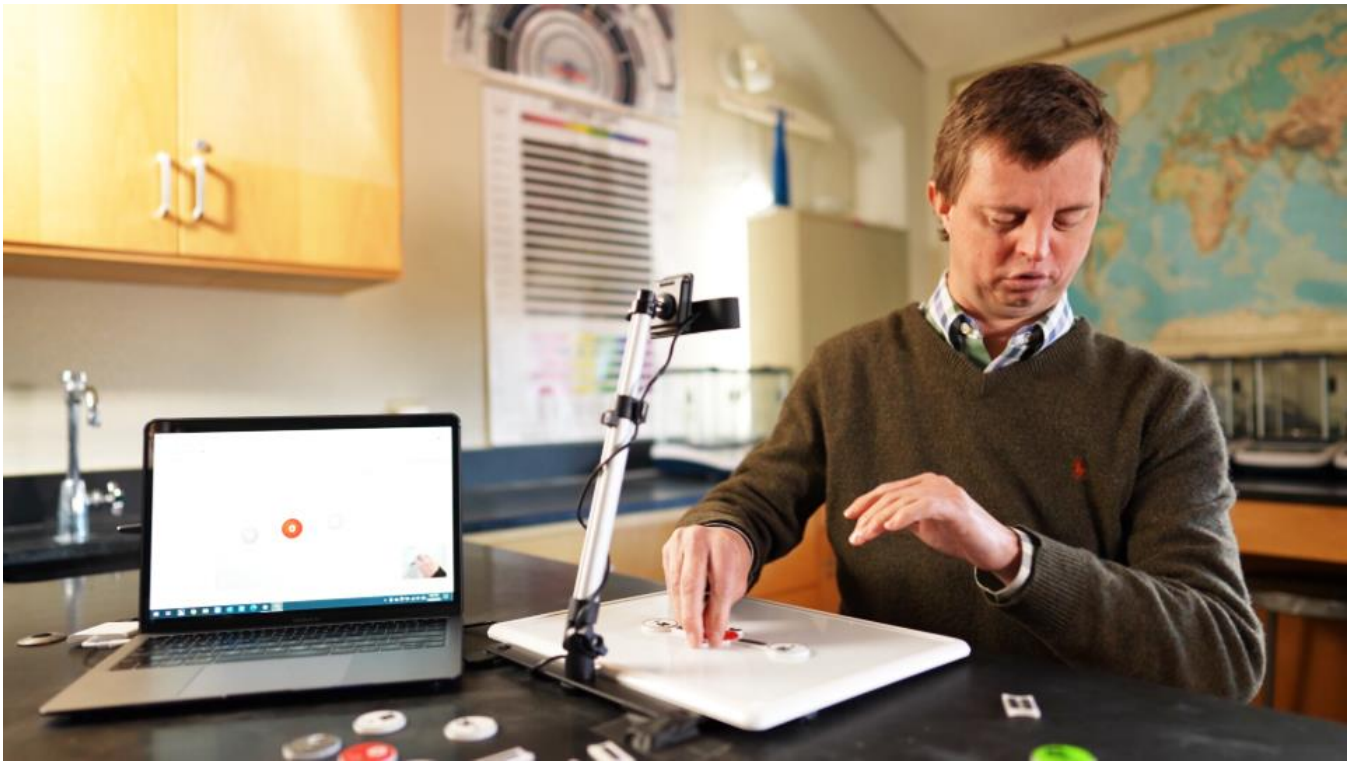
2021 GLRM 72

Kasi: An inclusive learning system for chemistry using multi-sensory augmented reality and computer vision

Julia Winter*, julia@alchem.ie. Alchemie Solutions, Inc, Troy, Michigan, United States*

In this talk a new software platform for inclusive learning of chemistry is presented. The system, brand named Kasi, creates a sound-based Augmented Reality (AR) interface to provide formative assessment to users as they interact with physical manipulatives to explore Lewis Structures. The goal of the project is to create an inclusive multi-sensory method for all students, and particularly those with visual challenges, to explore science concepts. This new AR learning system uses Computer Vision (CV) algorithms to read the position of 3D-printed tactile pieces placed on a magnetic whiteboard and matches a completely digital interactive learning system. Kasi is a web-based software

application designed to be used on devices students and schools already own. The AR / CV software interface provides audio feedback and scaffolded hints to students as they use the physical manipulatives. A key innovation is using data collected from both the AR and digital-only interfaces to improve the learning experience for all students. Key findings will be presented from the research studies with both sighted and blind or visually impaired high school students. The next steps in the research and development of this learning system will also be shared.



Dr. Hoby Wedler using the Kasi learning system

2021 GLRM 73

Disability is not disqualification: Nikolai Matveevich Kizhner and the Wolff-Kishner reduction.

David E. Lewis, *lewisd@uwec.edu. Chemistry and Biochemistry, University of Wisconsin-Eau Claire, Eau Claire, Wisconsin, United States*

Chemists with disabilities have made important contributions to chemistry, and some without their disabilities being obvious to those around them. Both Alfred Nobel and Wallace Hume Carothers suffered frm debilitating depression; Nobel laureate, Sir John Cornforth became deaf while at University; and the subject of this paper, Nikolai Matveevich Kizhner, became a double amputee before 1910. Nevertheless all these (and many others) made important contributions to chemistry before accommodations

for persons with disabilities was even thought of.
The subject of this talk, Nikolai Matveevich Kizhner (1867-1935) was born in Moscow, was educated there, and died there. To the knowledge of the author, he may be the only Russian chemist to have been exiled *from* Siberia! As a student of Markovnikov, he not only absorbed his mentor's approach to chemistry, but also his political progressivism.
In 1900, Kizhner became (with Mendeleev's help) the inaugural professor of organic chemstry at the new Tomsk Technological Institute, in Tomsk, Siberia. He lost his left leg above the ankle in 1904 due to "gangrene of the extremities." In 1905, the political unrest in the western part of Russia had moved east, and there were student strikes in Tomsk. Kizhner refused to discipline students who had missed his classes, and even went to the extent of addressing the students (despite having just one leg). This earned him enemies in high places, so while he was in St. Petersburg, they struck; he was given just 48 hours to leave Tomsk. Just over a year later, he was reinstated, but his enemies still worked on ousting him from his position. Eventually, he left Tomsk for Moscow, where he became an important part of the Soviet dye industry.
After losing his left foot, Kizhner continued teaching in the auditorium, but he gave up his research laboratory because the pain of his disease made standing for long times difficult. When he lost his right foot also, making him wheelchair-bound, he could no longer enter the auditorium to teach, but he returned to the research lab. There, in the two years 1911-1912, he published over 12 papers that described the reduction of aldehydes and ketones with hydrazine and base. And this he did despite there being no accommodations for disabilities—accessibility did not count!
Kizhner's life and contributions will be addressed in this talk.

2021 GLRM 74

Utilizing Design-Based Implementation Research as an Iterative Approach to Developing a Culturally Responsive Unit

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The Arctic is warming at a rate of nearly twice the global average, resulting in declining sea ice and melting permafrost. These changes are affecting the traditional knowledge practices of Iñupiat residents in Utqiagvik, Alaska, a community situated at the northernmost point of the United States. Because Utqiagvik has a large presence of scientists conducting research on the changing Arctic, local and Native Alaskan students have worldviews that contain ideas from both traditional knowledge and western science. By developing a culturally responsive science unit that engages undergraduate students in research questions focused on climate change, students may have more meaningful science learning experiences in the classroom. Utilizing Design-Based Implementation Research methodology, we collaborated with community

members, scientists, instructors, and education researchers to develop a culturally affirming snow chemistry unit at Ilisagvik College, a tribal college in Utqiagvik. The snow chemistry unit has been implemented in both undergraduate chemistry and climate science courses at Ilisagvik College. Through the analysis of student and instructor interviews and student artifacts, we have adapted the unit over three semesters to provide a detailed account on how culture, context, and place influence the development of a unit throughout multiple design cycles. In each iteration of the project, Alaskan Arctic students have been able to access traditional, local, and western science knowledge sources to conduct polar science research in the classroom and investigate the processes behind Arctic snow chemistry in an authentic research context.

2021 GLRM 75

The Chemistry of Indigenuos Peoples

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The contribution of non-European cultures to science and technology, primarily to chemistry, has gained very little attentions until now. Especially, the high technological intelligence and inventiveness of South American native populations shall be put into a different light by our contribution. The purpose of this study was to show that mainly in the area of chemical practices; the indigenous competence was considerable and has led to inventions profitable nowadays to millions of people in the western world and especially to the pharmacy corporations. We would like to illustrate this assumption by giving some examples of chemical practices of transformation of substances, mainly those unknown in the old world. The indigenous capacity to gain and to transform substances shall be shown here by the manufacture of poisons, such as curare or the extraction of toxic substances of plants, like during the fabrication of manioc flower. We shall mention as well other processes of multi-stage transformations and the discovery and the use of highly effective natural substances by Amazonian native populations, such as for example, rubber, ichthyotoxic substances or psychoactive drugs.

2021 GLRM 76

COVID-19: Nutrients, diet and immunity

***Julie M. Jones**, jmjones@stkate.edu. Nutrition and Exercise Science, St. Catherine University, Minneapolis, Minnesota, United States*

The COVID-19 pandemic underscores the need for a strong immune system and allows an opportunity to showcase diet as on important pathway to reduce risk of contracting the virus. It is well known that 'best offense is a good defense," and diets such as USDA MyPlate, NIH's DASH diet, or the Mediterranean Diet contain all the food groups in their recommended proportions. Such plans not only provide a template for building a diet that includes key nutrients needed for overall health, but they also bolster immunity. This talk will briefly review the diverse roles of various lymphocytes and conditions required for differentiation and functioning of both the innate and acquired immune system. This will be followed with update on current literature on the immune-supporting functions of fat- and water-soluble vitamins; minerals such as iron, zinc, magnesium, and selenium; nutraceuticals from fruits, vegetables, fish, whole grains, nuts, seeds and legumes; and nutrients added through enrichment and fortification. The impact of polyunsaturated fatty acids, prebiotics and dietary fibers such as -glucan and their metabolites such as short-chain fatty acids in strengthening the immune system will be discussed. The inadequacy in intakes for many dietary constituents not only explains one of the reasons for the high rate of COVID in the U.S., but also illuminates the disparities for those at higher risk due to underlying conditions, socioeconomic status, race and age.

2021 GLRM 77

Rewiring Redox Signal Transduction Pathways in M. Tuberculosis

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Infectious diseases like Tuberculosis (TB) have been a major global health burden due to their prolonged treatment timelines and resistance to the existing antimicrobial drugs. We need new therapeutic strategies that target non-replicating physiological persistence of pathogens inside human host system. Our group is currently pursuing metalloenzyme-dependent redox signaling pathways that enable microbes to survive and overcome redox stress experienced in their microenvironment. Modulation of these pathways would disrupt microbe's defense mechanism, rendering them more susceptible to current antimicrobial treatments. At this ACS meeting, I will present our research towards rewiring DosS-DosR redox signaling pathway in *M. tuberculosis* (*Mtb*). The bacteria uses this pathway to sense the presence of NO redox reagent and transforms into a non-replicating persistent form. By using rational and computational protein design strategies, we have demonstrated complete 'rewiring' of the heme iron based NO sensing/signaling pathway in the DosS sensor to an O_2 sensing/signaling pathway. Specifically, we have modulated heme's tertiary coordination sphere and incorporated a hydrogen bond (H-bond) triad in the heme's distal pocket through successive mutations. Thermodynamic, kinetic, and computational studies of the 'rewired' heme proteins shed light on the relative contribution of various factors (ligand

geometry, sterics, electronics, and H-bond positioning) that result in >700-fold switch in O_2:NO sensing selectivity. The 'rewired' sensing-selectivity is further amplified downstream along the transduction pathway with >250,000-fold switch in O_2:NO kinase signaling-selectivity. Our results establish the importance of tertiary coordination sphere in determining redox specificity of microbial signal transduction systems. At the same time, we demonstrate that rational rewiring of redox signal transduction can have implications towards controlling redox biology as well as non-replicating physiological persistence of various infectious microbes including TB.

2021 GLRM 78

Steady-state kinetic analysis and binding studies of flavin reductase AbeF: A smaller component of flavin-dependent halogenase system

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AbeF is a short-chain flavin reductase belonging to the *Abe* gene cluster identified from environmental DNA library of soil bacteria, encoding the biosynthesis of the antitumor bisindole alkaloid BE-54017. AbeF uses NADH to reduce FAD to $FADH_2$, a substrate used by Tryptophan-5-Halogenase AbeH to regioselectively halogenate the tryptophan in the two-component halogenase system. The investigation of the kinetics and mechanism of the flavin reductase component leads to pave the path for potential applications of flavin-dependent halogenase systems in the aryl halide synthesis as the synergic green catalysts.
After being overexpressed in *E. coli* and purified as a homodimer, the reductase activity of AbeF was confirmed by monitoring the oxidation of NADH to NAD^+ at 340 nm using absorbance spectrometry. The substrate substitution experiments suggested that AbeF prefers FAD over FMN or Riboflavin and requires NADH over NADPH. The steady state kinetic analysis revealed that AbeF follows sequential kinetic mechanism involving an AbeF-FAD-NADH ternary complex.
Moreover, the inhibition studies done with lumichrome (a structural mimic of FAD) as a dead-end inhibitor and NAD^+ as a product inhibitor suggested that AbeF follows the random sequential mechanism. Lumichrome acts as a competitive inhibitor of AbeF for FAD and a mixed inhibitor for NADH. NAD^+ acts as a competitive inhibitor of AbeF for both FAD and NADH at the lower concentrations of the fixed substrate, but this inhibition is completely overcome by higher concentrations of fixed substrate. The predicted mechanisms were cross-validated with binding studies of AbeF done by monitoring the fluorescence quenching of AbeF at 330 nm upon addition of ligands. FAD and NADH could bind to AbeF in the absence of second substrate and $FADH_2$ exhibited lower affinity as compared to FAD. Additionally, binding parameters of NADH for AbeF saturated with lumichrome did not change and vice versa, supplementing our mechanistic findings.

2021 GLRM 79

Development of an artificial heme-based enzyme

***Kathryn E. Splan**, splank@macalester.edu. Macalester College, Saint Paul, Minnesota, United States*

Artificial enzymes, which combine the selectivity afforded by a protein-based scaffold with the versatility of an abiological catalyst, constitute a powerful strategy to produce catalysts for new reactions and alternative catalysts to existing reactions. The lactococcal multidrug resistance regulator (LmrR) transcription factor protein from *Lactococcus lactis* has proved to be an exceptionally versatile scaffold with which to develop new artificial enzymes. Variants have been developed that enhance the regio- and enantioselectivity of multiple copper catalyzed reactions, organo-catalyzed reactions, and recently, hemin catalyzed cyclopropanation. In this presentation, we report on efforts to expand the reactivity of this new hemin-enzyme to peroxidase activity via site-directed mutagenesis and directed evolution. Significant enhancements in activity are observed after one round of evolution, which further support the utility of the LmrR scaffold in artificial enzyme design.

2021 GLRM 80

Discovering natural and synthetic ligands for the PfGCN5 bromodomain

***Scott Bur**, sbur@gustavus.edu. Gustavus Adolphas College, Saint Peter, Minnesota, United States*

Understanding the epigenetic regulation of gene expression could have significant impact on human health. In order to understand the role that the bromodomain of the Plasmodium falciparum GCN5 homolog (PfGCN5) plays in regulating gene expression of the malarial-causing parasite, chemical probes are being developed to disrupt the binding of the bromodomain with its preferred epigenetic mark. Virtual screening of fragment molecules from the ZINK database was combined with structure-activity relationship (SAR) studies guided by Protein-Observed ^{19}F (PrOF) NMR to identify a series of tetrahydroquinolines as potential chemical probes. Work continues to enhance binding to the PfGCN5 bromodomain and the selectivity compared with other bromodomains.

2021 GLRM 81

Regulation of Mitochondrial DNA Transcription by Protein Post-translational Modifications

***Kristin Dittenhafer-Reed**, dittenhaferreed@hope.edu. Chemistry and Biochemistry, Hope College, Holland, Michigan, United States*

Mammalian cells contain genetic information in two compartments, the nucleus and the mitochondria. Mitochondrial DNA (mtDNA) encodes thirteen protein subunits required

for oxidative phosphorylation. The remaining mitochondrial proteome, including additional oxidative phosphorylation subunits, and the proteins necessary for mtDNA replication, expression, and stability, is encoded by the nuclear genome. Therefore, to respond to metabolic changes, mitochondrial gene expression must be coordinated with nuclear gene expression. To gain insight into the coordination between the nucleus and mitochondria, there is a need to investigate the regulation of mtDNA transcription. Reversible protein post-translational modification of the mtDNA transcriptional machinery may be one way to control mtDNA transcription. Using *in vitro* biochemical and cell biology approaches, we are studying the effects of lysine acetylation and serine/threonine phosphorylation on the mtDNA binding ability and transcriptional activity of mitochondrial transcription factor B2 (TFB2M) and the mitochondrial polymerase (POLRMT). TFB2M melts mtDNA at the promoter to allow POLRMT access to the DNA template to initiate transcription. Three phosphorylation sites have been previously identified on TFB2M and many modifications have been documented on POLRMT by mass spectrometry. Mutant proteins mimicking the modified and unmodified states were generated, purified, and screened for their ability to bind mtDNA and initiate transcription *in vitro*. Our results indicate phosphorylation of TFB2M at threonine 184 and threonine 313 impairs promoter binding and prevents transcription. These findings provide a potential regulatory mechanism of mtDNA transcription and help clarify the importance of protein post-translational modifications in regulating aspects of mitochondrial function.

2021 GLRM 82

Live cell measurements of membrane protein interactions that regulate cell signaling and disease

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Cells have a complex mixture of membrane proteins to process environmental cues and drive biological function. The formation of membrane protein dimers and small oligomers regulate function at the protein, cell, and organism levels. Resolving membrane protein interactions in a live cell environment is challenging because of the chemical diversity and spatial heterogeneity of the PM. My presentation will describe a fluorescence technique called pulsed interleaved excitation fluorescence cross-correlation spectroscopy (PIE-FCCS) that is ideally suited to quantify membrane protein organization in live cells. PIE-FCCS is a two-color fluorescence fluctuation method that can simultaneously measure the concentration, mobility, proximity, and oligomerization state of membrane proteins in situ. Our recent efforts have been to resolve the interaction network of receptor tyrosine kinases (RTKs). This large family of membrane proteins regulates diverse processes like cell growth, morphology, and proliferation. Several combinations of heteromeric interactions between RTKs has been reported in recent years. However, there is no systematic understanding of the network-level effect of these interactions. Our approach is to start with subfamilies of RTK’s and quantify each pairwise interaction in situ. This approach has revealed a surprising level of

crosstalk between RTK's and lays the groundwork for a systems level understanding of their function.

2021 GLRM 83

Writing the Rules for Targeting Dynamic Transcriptional Coactivators with Small Molecules

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Transcriptional coactivators and their partner transcription factors have been labeled as intrinsically disordered, fuzzy, and undruggable. We propose that the identification of conserved mechanisms of engagement between coactivators and their cognate activators should provide general principles for small-molecule modulator discovery. Towards that end, biophysical characterization of the structurally divergent coactivator Med25 reveals that it forms short-lived and dynamic complexes with three different transcriptional activators and that conformational shifts are mediated by a flexible substructure of two dynamical helices and flanking loops. Analogous substructures are found across eukaryotic coactivators. Further, targeting one of the flexible structures with a small molecule modulates Med25-activator complexes. Thus, the two conclusions of the work are actionable for the discovery of small-molecule modulators of this functionally important protein class.

2021 GLRM 84

CASPT2 molecular geometries and electronic structure of dichromium complexes

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Optimization of molecular geometries for systems with multiconfigurational electronic structures can be performed using analytical gradients with the complete active space SCF method (CASPT2). This method has been applied to several dichromium complexes where single determinant methods cannot describe the partial occupation of antibonding orbitals correctly. As such, methods such as density functional theory do not yield geometries and vibrational frequencies in agreement with experiment. We will show that CASPT2 can be used successfully for these complexes.

2021 GLRM 85

Heavy Ligand Atom Induced Large Magnetic Anisotropy in Mn(II) Complexes

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In search of Single Molecule Magnets (SMM) metal ions are considered pivotal towards achieving large magnetic anisotropy barriers. A metal ion with strong spin-orbit coupling constant and low coordination number, which results in the retention of unquenched metal-orbital angular momentum, produces large magnetic anisotropy. In this context, the influence of ligands with heavy elements, showing large spin-orbit coupling, on magnetic anisotropy barriers was investigated using a series of Mn(II)-based complexes, in which the metal ion did not have any orbital contribution. The mixing of metal and ligand orbitals was achieved by explicitly correlating the metal and ligand valence electrons with Complete Active Space Self-Consistent Field (CASSCF) calculations. The CASSCF wave functions were further used for evaluating spin-orbit coupling and zero-field splitting parameters for these complexes. For Mn(II) complexes with heavy ligand atoms, such as Br and I, several interesting inter-state mixing occur via the spin–orbit operator, which results in large magnetic anisotropy in these Mn(II) complexes.

2021 GLRM 86

Electronic Structure of Actinide Oxide Nanoclusters

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Low valent actinide ions in the aqueous solution aggregate through the complex network of reactions such as hydrolysis, olation, and oxidation reactions. The study of An(IV) nanoclusters has potential applications in nuclear waste reprocessing, storage, and disposal. The Pu_{38} nanocluster contains a $[Pu_{38}O_{56}]^{40+}$ core stabilized by inorganic capping ligands. Interestingly, Pu_{38} species exhibits the rapid change of the aqueous spectral signature through acidification and dilution upon altering the ratio of water and chloride in the cluster surface while leaving $[Pu_{38}O_{56}]^{40+}$ inner core structurally unaltered. This phenomenon confirms a dependency of the cluster's physiochemical properties on its surface speciation. Here, we present a density functional theory study of the electronic structure of $[Pu_{38}O_{56}Cl_{42}(H_2O)_{20}]^{2-}$ and $[Pu_{38}O_{56}Cl_{54}(H_2O)_8]_{14-}$ to explain the $[Pu_{38}O_{56}]_{40+}$ stability and physiochemical properties with different surface speciations.

2021 GLRM 87

Qualitative diagnostic index for pseudo Jan-Teller Distortion Based on Natural Bond Orbital Theory: Case Study for Silicene

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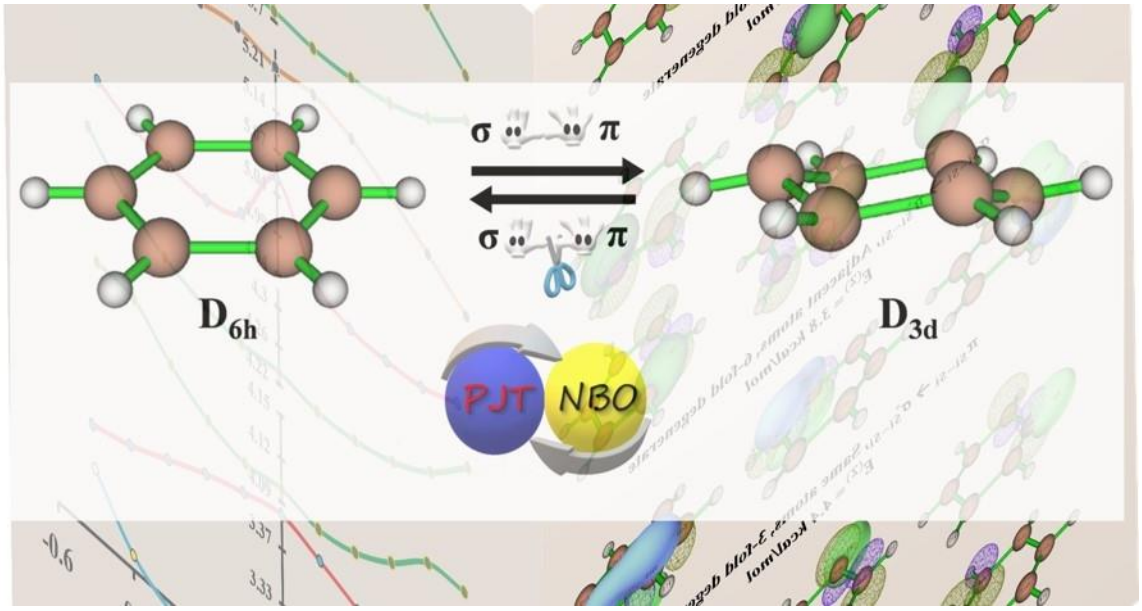
Instability of ground state (GS) of non-degenerate high symmetric molecules are often described through Pseudo Jahn-Teller mixing of the electronic states through vibronic coupling. Most common approach to tackle Pseudo Jahn-Teller (PJT) problem is to consider one or more symmetry allowed excited states that can couple with the ground-state to impose vibrational instability in the system along particular normal modes. However, this approach faces two major difficulties namely (a) predicting the adiabatic potential energy surfaces (APES) for the excited states which are often hard to define in case the excited states having charge-transfer (CT) or multi-excitonic (ME) character and (b) finding out the number of symmetric excited states need to be coupled with the GS to get solve the PJT problem. A parallel alternative method described here for the well- known case of symmetry breaking molecule hexasilabenzene (Si_6H_6) that undergo PJT- distortion from planar (D_{6h}) to the buckled (D_{3d}) structure requires detecting the second-order donor-acceptor, hyperconjugative interactions ($E^2_{i\rightarrow j}$) that stabilize the distorted structure. It is observed that orbitals involved in the vibronic coupling between the S0-Sn states and those for the donor (filled)-acceptor (empty) interactions are indistinguishable. Moreover, removal of any of particular $E^2_{i\rightarrow j}$ interaction develops vibrational instability in the buckled structure and on the other hand, deleting it for the planar high symmetric structure removes its instability. The one-to-one connection between the natural bond orbital (NBO) theory and PJT theory assists in an intuitive recognition of the relevant excited states from a manifold of computed ones that control symmetry breaking via vibronic coupling.



2021 GLRM 88

Electrochemical Characterization of Redox-active Deep Eutectic Solvents for Energy Storage

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Deep eutectic solvents (DESs) provide most of the distinct properties of ionic liquids but are inexpensive and easier to prepare.[1] DESs are green electrolytes that could potentially address the solubility issues related to the traditional electrolytes for redox flow batteries (RFBs) and enhance their energy density by dissolving a significant amount of redox-active species.[2] Redox-active organic molecules represent a promising class of active materials for organic RFBs, exhibiting several benefits over inorganic redox-active molecules such as synthetic tunability and high solubility of redox carriers, as well as earth abundance of the constituent elements.[3] Designing redox-active DESs with reversible redox behavior, appropriate solubility, and stability is still a challenge hindering their practical applications for RFBs. Understanding the electrochemical behavior, as well as diffusion and transport properties of the redox-active molecules in DESs will bring insight into their applications for energy storage devices. In this study, the electrochemical characterizations of various viologen derivatives in choline chloride (ChCl) and ethylene glycol (EG) (1:4 molar ratio) mixture were performed by cyclic voltammetry in a three-electrodes configuration cell. Viologen salts are among the most suitable redox-active carriers for RFBs, showing two successive electron-transfer processes. Diffusion coefficients and solvated radii of viologen derivatives were evaluated by cyclic voltammetry. The mobility of ions in mixtures containing different salt concentrations was also estimated through conductivity measurements. This study provides perspectives on designing redox-active DESs for energy storage systems.

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2021 GLRM 89

Investigating homogeneous nucleation of propane and *n*-butane in supersonic nozzle expansions

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Supersonic separators have been proposed as an environmentally friendly way to remove heavier alkanes from natural gas. Understanding the non-equilibrium vapor-liquid phase transitions of *n*-alkanes is therefore essential to the development of these devices. Homogeneous nucleation rates have been measured in supersonic laval nozzles for *n*-alkanes down to *n*-pentane, and, thus, *n*-butane and propane are the next logical candidates from both the experimental and theoretical points of view. A second goal of our research is to determine the critical cluster sizes from isothermal nucleation rate measurements. Working with these short chain alkanes should then let us compare our nucleation results to those determined via direct mass spectrometric sampling in post-nozzle flows carried out at ETH Zürich. In particular, we can follow the nucleation process as it changes from one controlled by a free energy barrier to the barrier-free, collisional limit. All experiments use argon as the carrier gas. Pressure Trace Measurements (PTMs) provide estimates of the temperature, pressure, mass fraction of condensate, flow velocity, and area ratio of flow. The conditions corresponding to the onset of condensation and the characteristic times required by the phase transition are presented and discussed for *n*-butane and propane. Classical Nucleation Theory (CNT) fails to describe the particle formation process under our conditions because of its incorrect description of the smallest clusters. The determination of experimental nucleation rates requires the combination of PTMs results and number densities measured by Small Angle X-ray Scattering (SAXS) experiments. Correlation functions between number densities and initial partial pressure of *n*-pentane and *n*-hexane were used to estimate the number densities of propane and *n*-butane. Further SAXS experiments will be conducted once the Advanced Photon Source is again available for outside researchers.

2021 GLRM 90

Investigation of the Liquid Crystalline Properties of Sunset Yellow Water Solutions with the addition of Gold Nanoparticles

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While liquid crystals (LCs) are commonly associated with displays, such as LCD televisions, LCs or substances that have liquid crystalline properties can be formed from everyday materials, including food. An example is Sunset Yellow (SSY), a water-soluble, disk-like molecule that at sufficient concentrations in water forms stacks that may align, forming a lyotropic chromonic LC (LCLC). This study investigates those LCLC properties upon the addition of gold nanoparticles (AuNPs) through the use of polarized optical microscopy, x-ray scattering techniques, and other techniques. Concentration changes of both SSY and AuNP cause variation in phase transition temperature of SSY-H_2O solutions, and we expect the addition of AuNPs will affect the order and alignment of SSY LCLC. The interactions of SSY and the AuNPs, for example, how the SSY molecules stack and arrange themselves, will be presented.

2021 GLRM 91

Pseudocontact Shifts Measurements in a Natively Diamagnetic Protein using Proton Detected Solid-State NMR Spectroscopy facilitated by Co^{2+} Binding Tag

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Magic angle spinning (MAS) solid-state nuclear magnetic resonance (SSNMR) spectroscopy is a widely used technique for exploring the structure and dynamics of biomolecules. The conventional methods in MAS NMR rely on the measurement of the distance-dependent dipole-dipole couplings between the ^{1}H, ^{13}C and ^{15}N nuclei for structure calculations. However, such studies are limited by inadequate number of long-distance (>5 Å) restraints. The paucity of long-range distance information can be overcome by the insertion of non-native paramagnetic centers that can be covalently attached to proteins. Inclusion of paramagnetic metal center results electron–nucleus distance dependent pseudocontact shifts (PCSs) and paramagnetic relaxation enhancements (PREs). In solution-state NMR, PCSs restraints have been used for the structural determination of biomolecules. However, in solid-state NMR, such studies are restricted because of the limited availability of the non–native tags that can incorporate paramagnetic metal center in a protein. Here we show PCSs measurements in natively diamagnetic protein facilitated by a thiol-reactive, compact cyclen-based, high affinity Co^{2+}binding tag, 2,2'-(4,10-bis(2-(pyridin-2-yldisulfanyl)ethyl)-1,4,7,10-tetraazacyclododecane-1,7-diyl)diacetic acid (TETACD), which can be rigidly attached to protein via two disulfide bridges. The resonance assignment experiments performed on microcrystalline U-^{2}H, ^{13}C, ^{15}N-labeled K38C-Q32C-TETACD + Co^{2+}/Zn^{2+} and D40C-E42C-TETACD + Co^{2+}/Zn^{2+} mutants of B1 immunoglobulin-binding domain of protein G using ultrafast (60 kHz) MAS proton detected chemical shift assignment pulse sequences. About 200 PCS restraints observed for nuclei up to ~20 Å from the metal center. The anisotropic tensor (χ tensor) was calculated using NUMBAT software and the calculated PCSs values were found in good agreement with the experimental PCS measurements.

2021 GLRM 92

Spreading and oscillation of single droplet impacting on a solid substrate

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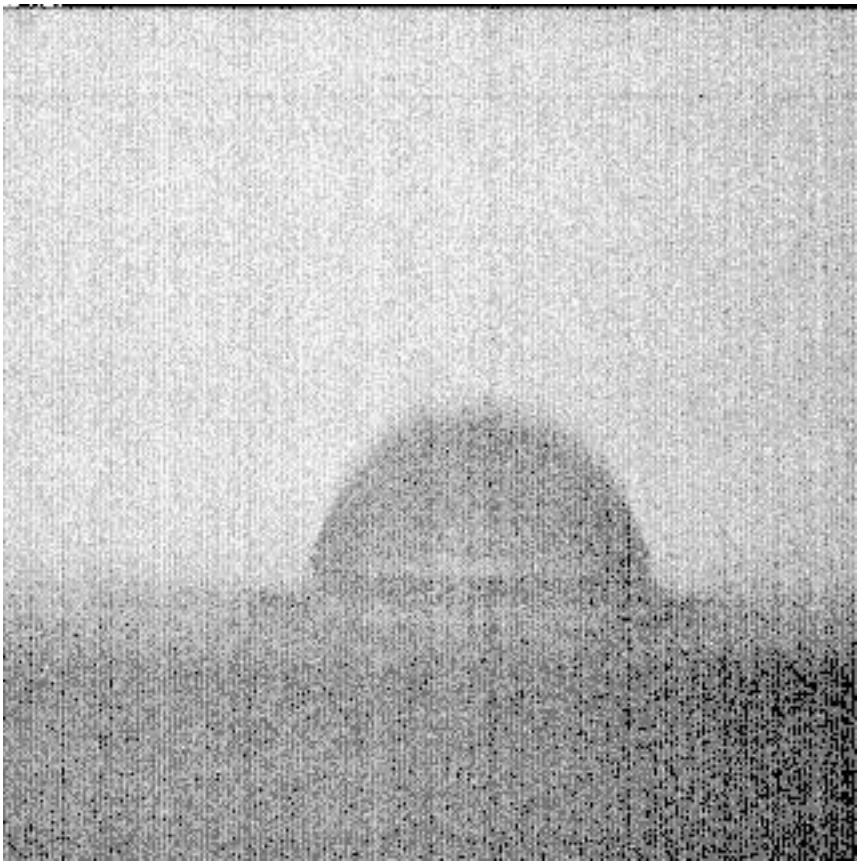
In this study the liquid droplet impacting on a solid surface is observed and the dynamics of droplet spreading and oscillation on a substrate is studied. We are particularly interested in the change of the dimensions of the droplet (height and width) with time. Droplets of various liquid types with different impacting velocity are tested. Wetting property of the substrate surface is also varied from hydrophilic to hydrophobic.

Droplet dynamics during the impingement and the following oscillating period are captured directly using high speed camera, and the characteristic parameters of interaction, such as droplet diameter, spreading factor, shape flatness, and dynamic contact angle, are captured from the obtained images.
Oscillating characteristics of the droplet dimensions are fitted with a second order damped harmonic oscillator model. However, the visualization results show that the first cycle including the impacting moment and the following cycles have significant differences in the oscillation amplitude as well as the peak-to-peak intervals. Therefore, the harmonic oscillation model based on single damped coefficient and constant oscillation frequency does not predict well the experimental results. Thus, we would like to propose the two-stage model. The first stage is to model the first cycle including the impacting, and the second stage separately models the oscillation dynamics in the second cycles and after. The model uses the dimensionless numbers and the wettability of the substrate as input.



2021 GLRM 93

Freezing of aqueous-alcohol nanodroplets in a supersonic nozzle: Effects of chain length and structure

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Ice nucleation from supercooled water droplets is frequently encountered in nature and industry. The prevalence of organic vapors in the atmosphere encourages investigation of ice nucleation in the presence of such contaminants. Here we investigate freezing of aqueous-alcohol nanodroplets for pentanol and hexanol and their isomers. The structure of water droplets containing a low mole percent of short-chain alcohol has been reported to be core-shell, with the hydrophobic alkyl tails of alcohol molecules pointing outward from the droplet and the hydrophilic heads forming hydrogen bonds with water. The effects of theses alcohols on freezing is expected to be affected by their different desire to partition between droplet surface and bulk phase. The aqueous-alcohol nanodroplets are produced in a supersonic nozzle by homogeneous condensation and further cooled to freeze them. By measuring the position-resolved pressure in the nozzle and integrating the compressible flow equations, the temperature, density, velocity of the gas mixture and mass fraction of the condensate are obtained. The aerosol freezing process is characterized by IR spectroscopy by monitoring the O-H stretch region and further quantified by Self Modeling Curve Resolution (SMCR) analysis. This analysis technique decomposes the aerosol absorption spectra into three linear independent components: a high temperature liquid reference, a low temperature liquid and an ice component. The ice components blue shift and broaden as more alcohol is added to the system, indicating a less ordered structure in the H-bonding network that can be achieved. For aerosols that clearly freeze, the freezing kinetics is derived from the ice fraction. The results show that the tetrahedral structure of ice is most perturbed by 3-pentanol and 3-hexanol due to their lower surface concentration than the corresponding linear isomers. For alcohols adopting the same conformation, solubility in water is a secondary factor in determining the effects of alcohols on freezing.

2021 GLRM 94

Sustainability in Industrial Applications

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As a manufacturing business with a global footprint and diverse product portfolio, advancing sustainability for a company like 3M poses unique challenges and opportunities. The company’s pathways to reduced carbon emissions, waste, water and energy use requires complex and collaborative problem-solving, but as evidenced by its commitments and annual progress, 3M consistently moves the needle. Beyond improving their own operational footprint, manufacturing companies like 3M have the opportunity to drive even greater positive impact through their customers and the products they create. This keynote will share approaches to developing a sustainability strategy, and best practices for building and advancing more sustainable operations and customer solutions.

2021 GLRM 95

Sustainably sourced and synthesized biomass microbeads to replace plastics in consumer products

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Plastic microbeads are ubiquitous in personal care and cosmetic products (PCCPs), used as exfoliants or rheological modifiers to improve viscosity, bulking, and film formation. While >95% of microbeads are captured during wastewater treatment, trillions of microbeads enter US aquatic habitats daily, detrimentally impacting marine life. Despite legislation, most plastic microbeads in personal care and rinse-off products are not regulated. Thus to develop a biocompatible and biodegradable alternative to plastic microbeads, we developed biomass-based microbeads with dual adsorption capabilities. As the target PCCP microbead size is substantially larger (300-800 μm) than produced in typical biomass syntheses, an emulsion process was required. With an eye toward sustainable industrial scale-up, biomass (cellulose, Kraft lignin) was dissolved in a non-toxic, recyclable ionic liquid (IL). To ensure safe degradation products, microbeads were created via precipitation in anti-solvents including water and ethanol to eliminate the need for covalent crosslinking. Cellulose microbeads within the target range were achieved by adjusting processing parameters like nozzle size and height. Subsequently varying the anti-solvent and biomass concentration produced beads of varying density and stiffness, demonstrating that microbead stability and mechanical properties can be easily tuned. Finally, Kraft lignin was incorporated into solutions to further tailor bead size and stiffness, and to assess the robustness of the method to variable feedstocks. Stable cellulose-lignin microbeads were produced in several anti-solvents. In aqueous anti-solvents, lignin leached from the bead to variable extents, producing lower density, porous microbeads that may potentially enhance adsorption and PCCP suspension stability. Subsequent rheology on detergents demonstrated that adding sustainable microbeads, even in small quantities (1% wt), substantially altered PCCP flow behavior. As the non-volatile IL can be recovered and reused and microbeads are stable without covalent crosslinking, this facile and highly tunable synthesis can be easily translated to industry to create sustainable alternatives to plastic microbeads in PCCPs.

2021 GLRM 96

Chemical Strategies for Perfect Sustainable Polymers

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The emerging challenge of polymer/plastic waste necessitates a new approach to designing, using, and handling waste materials including flexible end-of-life polymer

strategies. As part of the NSF Center for Sustainable Polymers, two overarching strategies are presented to meet the requirements of a perfect polymer including: biodegradability, cost parity with existing materials, low energy production requirements, comparable or better performance to existing materials, and the built-in capability to completely recycle the waste polymer back to the original monomer. Recovery of the monomer (e.g., ethylene from polyethylene) ensures that the waste material is recycled and regenerated to a new recycled polymer that has identical performance characteristics, even after hundreds or thousands of cycles through use and recycle. Specific examples of strategies for perfect polymers are outlined including existing systems around polyolefins, polyurethanes, PET, and elastomers in addition to entirely new polymers with advanced performance that also meet all of the sustainability requirements.

2021 GLRM 97

Post Consumer Recycled Polymer Quality Challenges

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Post-consumer recycled materials remain underutilized in the circular economy industrially due to issues of “poor quality” compared to virgin materials. Key challenges include the need for separation of desired materials from complex formulations or multilayer structures, and the presence of contaminants causing poor organoleptics, aesthetics or mechanical performance. These issues exist for both mechanically and chemically recycled polymers. The contaminants can also be highly diverse mixtures including decomposition products, requiring advanced methods of analysis. An exploration of these challenges and potential options to enable quality improvement will be presented, using polyethylene and polyurethane waste as examples.

2021 GLRM 98

Improving the mechanical properties of aliphatic polyester thermoplastic elastomers through star architectures

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A series of sustainable aliphatic polyester thermoplastic elastomers (APTPEs), consisting of multi-arm star polymers with arms of poly(L-lactide)-*block*-poly(γ-methylcaprolactone), were investigated and compared to analogous linear poly(L-lactide)-*block*-poly(γ-methylcaprolactone)-*block*-poly(L-lactide) triblock polymers. Linear analogues with comparable arm molar mass and comparable overall molar mass were synthesized to distinguish the impact of architecture from molar mass effects. The star block polymers significantly outperformed their linear analogues with respect to ultimate tensile strength and toughness, exhibiting more pronounced strain hardening than

corresponding linear APTPEs. The stars exhibited high ultimate tensile strengths (~33 MPa) and large elongations at break (~1400 %), outperforming commercial, petroleum-derived styrenic TPEs. The star polymers also exhibited superior recovery compared to the linear APTPEs when subjected to cyclic strain cycles, suggestive of the impact of architecture towards improved polymer mechanical properties. Upon exploration of the polymer stress relaxation behavior, the star APTPEs demonstrated slower relaxation than their linear analogues, indicating the improved performance at a broader range of operating conditions provided by the star architecture. Dynamic mechanical thermal analysis indicates that the star architecture does not negatively impact processability, an important feature for potential industrial applications. Overall, this work illustrates that simple changes in the macromolecular architecture in sustainable APTPEs results in materials with greatly enhanced mechanical properties. A comprehensive understanding of the relationship between polymer architecture and mechanical properties can be capitalized on to develop property-specific and industrially relevant sustainable materials.

2021 GLRM 99

Nano-layered, Nano-structured, and Micro-structured Polymeric Films for Energy Efficiency

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Multilayer optical film technologies made with hundreds of nanolayers and micro-structured film technologies can be used to manage building energy while maintaining architectural aesthetics. For example, visibly transparent (invisible) infrared mirror films are useful for rejecting infrared energy from building windows, and walls, to reduce air conditioning cooling energy loads by 10-30%. Rather than just rejecting infrared energy, the infrared energy can be redirected to where it may be converted to electricity, or solar thermal energy, with concentrated solar optical designs made with these transparent infrared mirror films. Infrared concentrated solar designs have been modeled which simultaneously provide building daylighting and solar energy generation. Nanostructured and micro-structured films can be used for anti-reflection to capture more solar energy for solar panels and greenhouses. Both multilayer optical films and micro-structured films can be used to bring daylighting further into a building enabling reduced electrical energy consumption for lighting. 3M Company manufactures specular mirror films having greater than 99% reflectivity and this high reflectivity enables ducting of sunlight greater distances into a building without loss in light quality. 3M Company's precision micro-structured film technologies have been applied to windows to refract light further into a building while simultaneously reducing unwanted glare. Multilayer optical films are also useful for passive radiation cooling during the day. Previously, passive radiation cooling was demonstrated for cooling only at night, but more recently, broadband solar mirror films created with multilayer optical films have enabled passive radiation cooling in broad daylight. Multilayer optical film technologies have been

applied to the creation of Ultra-Violet mirror films which are useful for providing durable long lasting film protection in outdoor applications and even increasing the efficiency of UVC disinfection.

2021 GLRM 100

Designing Coffee Pods for Performance and Compostability with Ingeo Biopolymer

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Coffee pods in use today face tremendous pressures from the market to address mounting waste concerns. Current multi-component structures and the small size of a typical capsule means that recycling is not straightforward. A fully compostable capsule provides an elegant and simple system for diverting used coffee grounds to industrial compost, while also eliminating conventional plastic waste.

In the past, the performance attributes required by coffee roasters and consumers have not been available in compostable capsules. Using our material characterization and modeling capabilities, we have been able to quantify what it takes to create a high performing coffee pod in terms of barrier, heat resistance, and puncture properties. We can apply this information to our understanding of Ingeo as a biobased, compostable material to help design better pod components including rigid capsules, nonwoven filters, and multi-layer lidding that add up to a better cup of coffee for consumers.

2021 GLRM 101

Nanomaterial Transformations and Environmental Sustainability: Opportunities for Next-generation Chemists

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Nanomaterials are revolutionizing science and improving our lives by enhancing performance and lowering the cost of many new and emerging technologies and processes. While nanomaterials are often designed and synthesized to yield specific performance characteristics in a specific application, much less is known about the longer-term reactivity and chemical transformations of nanomaterials in environmental and biological environments and the impact of these transformations on living systems. The Center for Sustainable Nanotechnology is a multidisciplinary effort aimed at understanding nanomaterial chemical transformations with an eye toward using identifying new compositions and structures that can maximize the overall environmental sustainability associated with nanomaterials. Using an integrated “measure, measure, model, and control” paradigm, CSN studies are providing new insights into reactivity of complex transition metals oxides, identifying the role of the

molecular structure and morphology of surface ligands in controlling biological impact, and identifying cross-species biochemical pathways that control biological impact. Ultimately, these are leading to the ability to control nanomaterials transformations in advantageous ways, such as controlled delivery of micronutrients to plants that yield improved plant health and crop yield. In the talk I will summarize some of the new chemical insights and the practical implications of nanomaterial transformations, with an emphasis on opportunities for nano-chemists to enhance sustainability through chemical insights into nanomaterial structure and function.

2021 GLRM 102

Bifunctional Nickel and Copper Electrocatalysts for CO2 Reduction and the Oxygen Evolution Reaction

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

2021 GLRM 103

Adsorption and reaction of SO_2 and H_2S on graphene/ruthenium(0001) - an ultra-high vacuum surface science study

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Noble metal-free catalysis using (functionalized) carbon is an emerging alternative to traditional chemical synthesis. Examples are known for liquid phase and gas-phase reactions. In particular, reactivity towards adsorption and reaction of sulfur compounds has been demonstrated in the literature. However, gas-surface reactions are not well characterized. In this study, kinetics techniques (thermal desorption spectroscopy) and

spectroscopy (Auger electron spectroscopy) indeed show that SO_2 and H_2S undergo chemical transformations on graphene epitaxially grown on ruthenium. In case of SO_2, SO and O_2 desorb, sulfur remains on the surface. In addition, a molecular adsorption pathway is evident.

2021 GLRM 104

One-pot Synthesis of Ruthenium Nanocatalyst Using Reduced Graphene Oxide as Matrix for Electrochemical Synthesis of Ammonia

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Ammonia production consumes a significant energy supply and causes enormous carbon dioxide (CO_2) emission globally. To lower energy consumption and CO_2 emission, in this work, a facile, environmentally friendly, and cost-effective one-pot synthetic method for ruthenium-based nanocatalyst has been developed using reduced graphene oxide (rGO) as a matrix. The developed nanocatalyst can reduce energy usage through the electrochemical synthesis of ammonia at ambient conditions. The synthesis of the nanocatalyst was based on a single step of reduction of $RuCl_3$ into ruthenium nanoparticles (Ru-NPs) and graphene oxide (GO) into rGO using glucose as the reducing agent. The developed ruthenium-based nanocatalyst was characterized using transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), UV-Vis absorption spectroscopy, X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), and dynamic light scattering (DLS). The results demonstrated the morphology of the Ru/rGO nanocatalyst with a size of 1.93 ± 0.24 nm and the metal content of 20 wt.%. Bulk electrolysis measurements were conducted on the thin-layer electrodes at various cathodic potentials in N_2-saturated 0.1 M H_2SO_4 electrolyte. Based on the chronoamperometric measurements, the maximum Faradaic efficiency (F.E) of 5.4 % for ammonia production on the nanostructured Ru/rGO catalyst was achieved at the potential of -0.20 V versus reversible hydrogen electrode (RHE). This electrocatalyst attains a significantly high ammonia production rate of 29.2 $\mu g/h/mg_{cat.}$, which is paving the way to the scaling-up electrochemical ammonia synthesis. Compared to the reported nitrogen and phosphorus co-doped hierarchical porous carbon (NPC) electrocatalysts for the nitrogen reduction reaction (NRR) with the F.E and ammonia production rate reached 4.2% and 0.97 $\mu g/h/mg_{cat.}$. Our results clearly demonstrated the feasibility of reducing N_2 into ammonia under ambient conditions using the nanostructured Ru/rGO electrocatalyst.

2021 GLRM 105

Synthesis of highly near-infrared fluorescent graphene quantum dots (GQDs) using biomass-derived materials for *in vitro* cell imaging and metal ion detection

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Graphene quantum dots (GQDs) are a subset of nanoparticles that have peaked recent interest due to their photoluminescence properties, low toxicity and biocompatibility features for bioimaging applications. However, it is still a challenge to prepare highly near-infrared (NIR) fluorescent GQDs using a facile pathway. In this study, NIR GQDs were synthesized from a biomass-derived organic molecule *cis*-cyclobutane-3,4-di(furan-2-yl)cyclobutane-1,2-dicarboxylic acid via one-step pyrolysis. The resulting GQDs were then characterized by various analytical methods such as absorption spectroscopy, fluorescence spectroscopy, dynamic light scattering (DLS), high resolution transmission electron microscopy (HRTEM), Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). Moreover, the photostability and stability over pH were also investigated, which indicated the excellent stability of the prepared GQDs. Additionally, two peaks were found in the emission spectra of the GQDs, one of which was located at about 860 nm. Incubating the GQDs with RAW 246.7 cells resulted in the GQDs entering the cells through endocytosis and thus could be used as fluorescent bioimaging agents. Moreover, the GQDs depicted relatively enhanced fluorescence when treated with different metal ions, indicating that the GQDs could be used for metal ion detection in biological samples as well.

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Fe^{3+} - doped Graphene Quantum Dots for Ultrasensitive Detection of H_2O_2 and Glucose

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High blood sugar levels will result in diabetes and other serious diseases. Therefore, finding an effective way to determine the blood glucose concentration is of great importance. In this paper, a new graphene quantum dots (GQDs-Fe)with size smaller than 10 nm and zeta potential around 10 mV (measured by dynamic light scattering method) were successfully synthesized with Fe(III) ion and hydrophilic polyethylenimine

(PEI) under 200 for 15 h to detect H_2O_2 and glucose. Due to the redox reaction between of Fe(III) ion and H_2O_2, the concentration of H_2O_2 would be determined by the variation in fluorescence intensity. However, the existence of H_2O_2 is produced by the oxidation of glucose, therefore, the detection of glucose can be realized. The optical properties, morphology, and surface functional groups of the newly synthesized GQDs were systematically characterized by analytical spectroscopy methods. Results showed that the GQDs-Fe have adsorption peak, excitation and emission at 334nm, 340nm and 466nm, respectively. Most importantly, the quantum yield of the proposed GQDs-Fe was 70.86%, which was much higher than other GQDs (usually 10-20%). In addition, in order to obtain the optimal detection conditions, the reaction time and pH were optimized. The GQDs-Fe showed a significant decrease in fluorescence with the reaction of H_2O_2. Under the high performance of Fe(III) oxidization, the newly synthesized GQDs show high potential for its application in H_2O_2 and glucose detection.

2021 GLRM 107

ACS Division of Small Chemical Businesses (SCHB) member benefits

Joseph E. Sabol*, jsabol@chem-consult.com. Program Committee, ACS SCHB, Racine, Wisconsin, United States*

ACS Division of Small Chemical Businesses (SCHB) organizes informative and collaborative chemical business themed symposia and programs at ACS national, regional, and local section meetings. Starting in the year 2020, after the COVID lock down, SCHB has held weekly internet-based virtual "discuss business", "lunch and learn", and the social "happy hour" for business-minded chemical professional to share information on topics such as how to adapt to personnel and supply disruptions, work from home bandwidth limitations, and the social interaction and problem solving that we miss from in-person conferences. SCHB continues to partner with other ACS units on thematic, critical, and contemporary topics that are of high interest to chemical enterprise. Get the most out your ACS membership by joining SCHB, raise the visibility of your brand, and learn from business-savvy chemists and entrepreneurs. SCHB provides valuable member benefits, including the most valuable: building relationships with a network of members from whom you can draw on for inspiration.

2021 GLRM 108

Five mistakes small businesses make with their intellectual property (and how to avoid them all!)

Randy Micheletti*, randy.micheletti@gmail.com. Incubate IP, Glen Ellyn, Illinois, United States*

Growing businesses need strong intellectual property strategies to succeed in today's economy. But many trip over the same issues, often through no fault of their own. Explore 5 of the most common missteps emerging companies make with intellectual

property and--more importantly--how to avoid all of them. Presenter Randy Micheletti is a chemist-turned-IP-lawyer with over a decade of experience helping businesses of all sizes build strong IP portfolios while avoiding disputes over competitors' intellectual property assets.

Five Mistakes Startups Make with Their Innovations

(And How To Avoid Them All!)

Randy Micheletti, Esq.

2021 GLRM 109

Covid-19 nearly killed our business: The survival story of Laboratory Equipment Services through the pandemic

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Laboratory Equipment Services, LLC started operating live in the last quarter of 2019. A few month later Covid-19 was disrupting businesses and supply chains worldwide. Chemical businesses were impacted with the lockdown. Because we service laboratory instruments (pipettes, analytical balances) on site, all our scheduled jobs were cancelled or postponed indefinitely at the end of March 2020.
This is the story of our journey through the first year of the pandemic. With the help of ACS Division of Small Chemical Business (SCHB), the Illinois Small Business Development Center (SBDC), Startup Tree (City of Evanston/ Northwestern University) and others, we were able to tap into resources and information that made our survival possible. Sharing experiences with other small businesses has been vital.

2021 GLRM 110

Accessibility and inclusivity as a business case for educational technology

***Julia Winter**, julia@alchem.ie. Alchemie Solutions, Inc, Troy, Michigan, United States*

As educational content delivery systems shift to completely digital experiences, that primarily utilize the visual sense, further marginalization of blind or visually impaired (BVI) students will occur if new digital platforms consider accessibility as an add-on. This problem is magnified in STEM learning, due to the visual and spatial nature of the curricula, as BVI students are less likely to pursue careers in the sciences as barriers to visualizations increase. The company Alchemie has been building software-based interactive learning tools since 2016, and with a SaaS business model has been working with higher ed publishers to embed these learning tools in digital textbooks. Building accessible learning tools is a difficult challenge for publishers, due to the expense of meeting the needs of a very small subset of the student population. In this talk, the concept of building for inclusivity first is presented with commercialization through licensing agreements. In addition, distribution to special education departments of school districts will be a key part of the go-to-market strategy. The business value of this product is not only that it fits Special Educational market needs but is also an inclusive educational delivery system. Students with visual challenges, and their sighted peers, can use the same technology, thus increasing the scalability of the product in the commercial marketplace.

2021 GLRM 111

Commercialization strategies for sustainable chemicals and renewable energy

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The transition from the laboratory to a startup company of chemical and energy technology requires unique strategy to address the challenges of this technology sector. Building on experience in forming startup companies Sironix Renewables and enVerde LLC and creating the flagship technology for Activated Research Company, Professor Dauenhauer will discuss his approach to selecting research that leads to new commercial technology with impact on the renewable chemical and energy industry. Selection of specific laboratory research topics were identified for disruptive commercial products in surfactant and detergents, chemical analysis, and waste processing based on pre-determined commercial opportunities. Transitioning these technologies to industry has required overcoming challenges associated with chemical manufacturing, chemical complexity, and combined technical and business barriers, all of which are feasible in a lean startup approach.

2021 GLRM 112

Starting and running a distillery

***Karl Loepke**, kloepke@skepticdistillery.com. Skeptic Distillery Co., Melrose Park, Illinois, United States*

Operating a successful distillery requires knowledge of analytical, organic, and physical chemistry - and business acumen, too! Advertising, trademarks, regulatory, and personnel issues are also part of the daily business. This presentation is about the technical and other issues encountered when starting and running a distillery.

2021 GLRM 113

He didn't just quaternize amines: the career of Nikolai Aleksandrovich Menshutkin.

***David E. Lewis**, lewisd@uwec.edu. Chemistry and Biochemistry, University of Wisconsin-Eau Claire, Eau Claire, Wisconsin, United States*

Nikolai Aleksandrovich Menshutkin (1842-1907) was a Russian organic chemist who is best known today for the quaternization reaction of amines that now bears his name. He was, however, much more than that: a pioneer in the study or structure-reactivity relationships, a founding member of the Russian Chemical Society, the first Editor of the *Journal of the Russian Chemical Society*, and the author of the first Russian-language textbook of Analytical Chemistry (which went through 16 editions until 1931). The career of this multifaceted individual will be highlighted.

Nikolai Aleksandrovich Menshutkin

2021 GLRM 114

Employing Manganese-nickel Alloy Balls as a Mixing Agent and Versatile Catalyst/reagent for Mechanochemical Organic Transformations

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As the chemical community continues to recognize the importance of choosing greener solvents and reducing solvent waste whenever possible, new methodologies are added to the chemist's synthetic toolbox. One method that reduces solvent waste, high speed ball milling, is a type of mechanochemistry. Mechanochemistry has long been known to facilitate reactions between metals but has only emerged as an effective technique for organic synthesis in recent decades. Solvent is not necessary for an organic reaction to take place mechanochemically, so researchers have started to explore the idea of using insoluble (in organic solvents) metal materials like balls, pellets, foils, or even reaction jars to catalyze a reaction. This method has shown to be successful with various metals.

To name a few examples, copper reaction jars catalyze Sonogashira and azide-alkyne click reactions, and nickel pellets may be used successfully to synthesize cyclooctatetraene molecules by a [2 + 2 + 2 + 2] alkyne cycloaddition. One area that has yet to be explored, though, is the use of alloyed metals in mechanochemical organic reactions. This work seeks to show that Mn-Ni alloy balls are efficient at mixing reagents as well as imparting reactivity to a mechanochemical system. The Mn-Ni alloy material has so far been used to facilitate ketone reduction to alcohol in the presence of water. Additionally, it has been used for electrophilic coupling of aryl iodides to synthesize biaryl motifs. The work presented here will detail how these mechanochemical reactions were optimized, the scope of the reactions, and how undergraduate students are able to take ownership over their mechanochemical research projects.

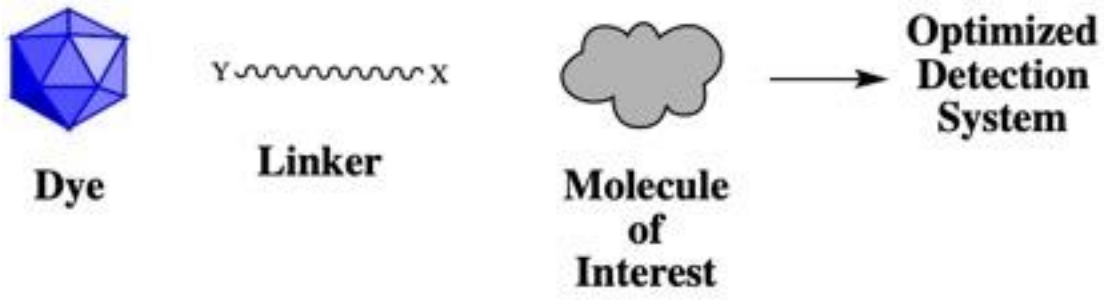
2021 GLRM 115

Developing a flexible methodology for the fluorescent tagging of biomolecules

*Emma Paulsen, Luc Fisk, Malka Samri, **Rita S. Majerle**, rmajerle01@hamline.edu. Chemistry, Hamline University, Saint Paul, Minnesota, United States*

The selective labeling of biomolecules is a multi-million dollar industry that crosses a wide range of fields. The ideal combination of materials includes a fluorescent molecule to detect a target, a linker to tether the biomolecule of interest and the dye and a bio molecule of interest while keeping the bioactivity of the molecule intact.

In this talk, we will present the results from our ongoing research in designing these systems using glucosamine and cortisol along with a series of linkers of various lengths and materials, and fluorescent dyes including NBD, dansyl chloride and FITC.



2021 GLRM 116

Derivatives of the fluorescent *N*-alkyl-4-alkylamino-1,8-naphthalimides: Synthetic and structural studies.

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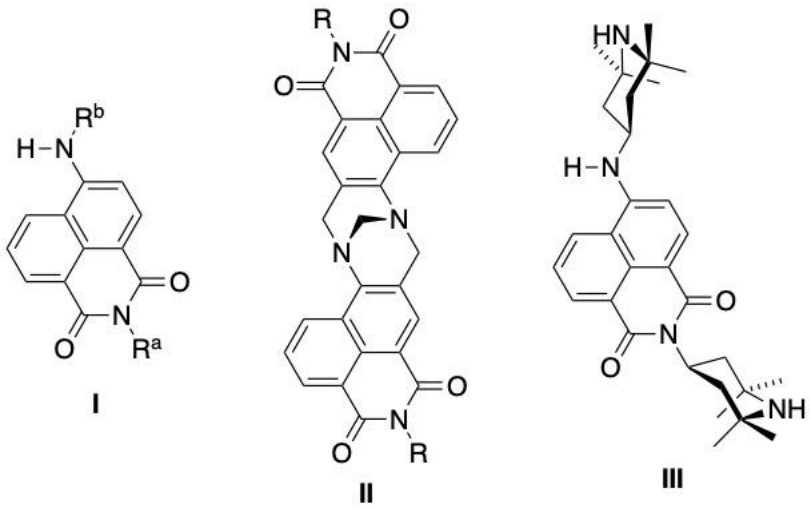
The 4-amino-1,8-naphthalimide fluorophore (**I**) has found applications in fields as diverse as crack detection in metals, to determination of acidity of lubricating oils in internal combustion engines, to photochemical inactivation of enveloped viruses, to the fluorescent detection of nucleic acids, to laser tissue welding with visible light. Nitro derivatives have found applications as antineoplastic agents.
We were the first to synthesize a Tröger's base (**II**) based on this fluorophore, and at that time we reported its photophysical and spectroscopic properties. However, the compound has proved to be singularly resistant to crystallization until very recently. The single-crystal X-ray structure determination of the first of these compounds has now given us important structural information.
The function of naphthalimide dyes in detecting DNA is based on intercalation, but we sought to develop a fluorscent molecule that might detect DNA without intercalation. We have succeeded in obtaining a non-intercalating compound (**III**) by placing bulky 2,2,6,6-tetramethyl-4-piperidinylamino groups at both ends of the molecule. The X-ray crystal structure of this molecule has proved to be especially interesting.
The syntheses and structures of these compounds will be reported.



I II III

I: the base naphthalimide fluorophore
II: a Tröger's base containing two naphthalimide fluorophores
III: a fluorescent naphthalimide containing bulky side chains that will not intercalate into DNA

2021 GLRM 117

An Agile Approach to Undergraduate Research

***Eric H. Fort**, ehfort@stthomas.edu. Department of Chemistry, University of Saint Thomas College of Arts and Sciences, Saint Paul, Minnesota, United States*

Though a pandemic has been a lesson in managing an ever-changing university and research environment, the need for an undergraduate primary investigator to rapidly adapt to change is perennial. The ability to quickly process information and adjust course are tenets of an *Agile Mindset*. Applying these principles to developing an undergraduate research program can increase productivity, funding, and satisfaction. This talk will discuss the principles of an *Agile Mindset* and how they might be used to overcome common challenges to those leading and working in undergraduate research.

2021 GLRM 118

New Frontiers in Low-Coordinate Iron Imido Chemistry

***Jeremy M. Smith**, smith962@indiana.edu. Indiana University, Bloomington, Indiana, United States*

The last decade has established the utility of low-coordinate iron imido complexes in nitrene group transfer reactions, including catalytic C-H functionalization. This lecture will demonstrate that strongly donating ligands, in the form of bulky bis(carbene)borates, expand the scope of iron imido chemistry. Most notably, rare examples of isolable iron(V) and iron(VI) bis(imido) complexes have been prepared and structurally characterized. Spectroscopic characterization, supported by electronic structure calculations, provides strong evidence for low spin (S = 1/2) d^3 and d^2 (S = 0) electron configurations. These low d-electron counts dictate the unusual “see-saw” geometries of these complexes. These high valent bis(imido) complexes are built on the platform provided by isolable three-coordinate iron imido synthons. One-electron reduction of the iron(III) imido provides a high spin (S = 2) iron(II) imido complex that retains iron-nitrogen multiple bond character. The unusual electrophilicity of this complex leads to reactivity patterns that are akin to those of early transition metals, including [2+2] cycloadditions that form the basis for the catalytic guanylation of carbodiimides under mild conditions.

2021 GLRM 119

Electrochemical Investigation on Ti-Mediated Oxidation-Induced Formal N-N Reductive Elimination

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Pyrazoles are a prominent class of heterocycles with an array of biological applications in fields such as medicine and agriculture. Recently, our group reported on the synthesis of highly substituted pyrazoles through multicomponent oxidative coupling of alkynes, nitriles, and Ti imido complexes, involving a 2-electron oxidation-induced N-N

reductive elimination. The mechanism of this N-N coupling likely follows an electrocyclic Nazarov-like pathway by oxidation of the ligand π-system. Our initial studies showed that weak oxidants such as TEMPO and $PhICl_2$ are capable of accessing 2-electron-oxidized intermediates for reductive elimination by a disproportionation of the 1-electron oxidized species. However, little is known regarding the roles of these oxidants in each elementary step throughout this process. The oxidation may follow either an inner sphere or an outer sphere mechanism and the driving force for one may not be the same for the other. Therefore, mechanistic studies will allow us to determine whether the oxidation proceeds through a stepwise inner-sphere electron transfer process or an outer-sphere radical addition process and provide insight into oxidant criteria to expand the scope of this method. Electrochemical techniques will be used to examine outer sphere oxidation reactivity and potentially demonstrate solutions to the limitations of chemical oxidants. Following initial efforts at isolating a series of these titanacycles with varying substituents, cyclic voltammetry will be used to investigate the redox properties of the titanacycle intermediates as well as evaluate the viability of using electrochemistry to induce catalytic turnover.

2021 GLRM 120

Synthesis and reactivity of a Mn(II) chelating bis(alkoxide) complex towards aziridination with iminoiodinane as the nitrene source

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Aziridines are three membered cyclic nitrogen heterocycles with applications in the synthesis of natural products, pharmaceuticals, and polymer chemistry. One of the efficient ways to synthesize this functional group is by using transition metal catalyzed group transfer reaction of a nitrene precursor to alkenes. Our recently developed $Fe[OO]^{Ph}$ complex with a chelating bis(alkoxide) ligand $H_2[OO]^{Ph}$ ([1,1':4',1''-terphenyl]-2,2''-diylbis(diphenylmethanol)) showed excellent reactivity with sterically small azides to form azoarenes. However, the reactivity of the complex with azides in presence of styrene did not yield the corresponding aziridines. On changing the nitrene precursor from azide to PhI=NTs (Ph = benzene and Ts = p-toluenesulfonyl) the catalyst formed aziridine only in 32% yield. To explore the effect of metal on reactivity, we developed the Mn analogue of the complex. The $Mn[OO]^{Ph}$ did not show any reactivity with sterically large or small azides. The reaction of the complex with PhI=NTs formed aziridine in 76% yield with styrene. Similarly, the complex showed very good reactivity with electron-rich 4-methoxy styrene and moderate reactivity with electron-deficient substituents. Reaction with aliphatic alkenes did not yield any aziridine. Formation of both *cis* and *trans* isomers of aziridine with β-substituted styrenes displays the lack of stereoselectivity in the catalyst. Spectroscopic and stereochemical experiments and

DFT calculations suggest the presence of Mn-imido radical intermediate in the mechanism.

2021 GLRM 121

Origin of Bond Elongation in a Uranium(IV) *cis*-bis(imido)

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Efficient chemical processing of spent nuclear fuels represents a major hurdle in the nuclear fuel cycle, as strong actinide-element multiple bonds prevent conversion to useful materials. These bonds can be weakened in systems that are electron- rich or sterically saturated. Herein, activation of uranium-nitrogen multiple bonds in an imido analogue of the uranyl ion is accomplished with these strategies. Treating the uranium(VI) *trans*-bis(imido), $UI_2(NDIPP)_2(THF)_3$ (DIPP=2,6-diisopropylphenyl), with *tert*-butyl(dimethylsilyl)amide (NTSA) results in reduction and rearrangement to form the uranium(IV) *cis*-bis(imido), $[U(NDIPP)_2(NTSA)_2]K_2$. This compound features long U-N bonds, pointing towards substantial activation of the N=U=N unit, as determined by X-ray crystallography, ^{1}H NMR, infrared, and electronic absorption spectroscopies. Computational analyses show that the U(IV)-imido bonds are significantly weakened multiple bonds due to polarization towards antibonding and non-bonding orbitals. These uranium imido studies highlight the importance of electron donating ligands such as -$N(SiHMe_2)^tBu$ for disruption of the inverse *trans*-influence seen in uranium element multiple bonds.

2021 GLRM 122

The release and uptake of materials by chitosan-alginate bioplastics

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Chitosan-alginate bioplastics have become the focus of a class based undergraduate research experience (CURE) at Concordia College, Moorhead, Mn. Freshman students study these, their preparation and strength alongside looking at some experiments which model pharmaceutical release using commercial food dyes. Our earliest results saw a direct effect of salt concentration on the rate of release and later experiments have revealed the system to be more complex with a range of parameters including film composition, solution type and material being released affecting the release and uptake of a range of materials including food dyes and simple analgesics such as ibuprofen, acetaminophen and salicylic acid. Preliminary results measured from spectroscopy and HPLC from a number of undergraduate projects in the Wyllie lab will be discussed.

2021 GLRM 123

Be a 4-H Scientist: Bringing sustainable polymers to informal science audiences in grades K-8

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Learn how new STEM activity guides on polymer science were developed through an innovative collaboration between the NSF Center for Sustainable Polymers, a Center for Chemical Innovation, and 4-H, the nation's largest youth organization. Educators from three states (MN, CA, NY) came together to develop activity modules using guided-inquiry that offer sustained learning experiences for young audiences. Centered on polymer science, the content includes topics such as: properties of materials, uses of plastics, problems identified with existing plastics, and reducing/reusing of materials. Activities also build upon the 8 Practices of Science and Engineering outlined in the Next Generation Science Standards (NGSS) and utilize gender-equitable best practices developed by PBS/TPT *SciGirls*. This project includes details on curriculum design and the evaluation of learning objectives through pilot tests. Completed curriculum

developed for K-8 audiences will be shared with discussion of how the collaboration between the research center and informal science experts continues for the development of materials for grades 9-12.

2021 GLRM 124

Potential effects of microplastics on Harmful Algal Bloom-causing species in the Great Lakes

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The increase in agricultural and urban runoff contribute to Harmful Algal Blooms (HABs) formation in the Great Lakes, particularly Lake Erie. HABs produce potent neurotoxins such as microcystins, which threaten water supplies and recreational use of lakes. Both forms of runoff contain nutrients and other pollutants that stimulate the growth of HAB-causing species. Microplastics are being detected at increasingly higher concentrations in the runoff, lakes, and surrounding watershed, however, the direct effect of microplastic contamination on HAB formation and toxin production is largely unknown. As microplastic pollutant concentrations increase, we hypothesize that microplastics may serve as surfaces which facilitate HAB growth and binding and longer distance transport of toxins. We are assaying the effects of different plastic characteristics (polymer type, size, concentration, and environmental exposure/ageing time) on the growth and microcystins production rates in two HAB-causing species, *Microcystis aeruginosa PCC7806* and *Dolichospermum flos-aquae CPCC 64* (formerly *Anabaena*). Through the utilization of statistical Design of Experiments and microbial growth assays, each of the variables will be analyzed for their relation and significance in the changes of toxin production and growth rate of each of the HAB-causing species. Results will inform future lake mesocosm and sampling experiments in an effort to better understand direct interactions between microbes and microplastics in the aquatic environment.

2021 GLRM 125

Novel Materials Derived from Agriculture-based Biomass

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Biomass has emerged as an important source of chemical. Lignin is an important constituent of biomass. Despite several efforts, lignin valorization is still underutilized as biomass. In this presentation, I will present the recent progress in my research group on designing materials from agricutural biomass with emphasis on lignin. Some examples

are foam, composites, thin filims, among others. Detailed characterization of these novel materials will be presented. It is expected that these materials can be used for multifunctional applications.

2021 GLRM 126

Cottonseed oil based UV-curable resins

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In this work, a study on the preparation of ultraviolet (UV) curable resin based on cottonseed oil was done. The multifunctional bio-based resin—acrylated-epoxidized cottonseed oil (AECO) was synthesized and transformed into a crosslinked network by photopolymerization technology. The synthesis process was performed by the epoxidation of cottonseed oil via the peracetic acid method, followed by the acrylation of the epoxidized oil using acrylic acid. Acrylated-epoxidized bio-based resin was used in the formulation of UV-curable coatings systems. In order to achieve high crosslink density and obtain coatings with good mechanical properties, formulations containing AECO were prepared with the addition of two different reactive diluents, such as: 1,6-hexandioldiacrylate (HDDA) and trimethylolpropane trimethacrylate (TMPTA). Coatings were cured under UV radiation using different weight ratios of reactive diluents and 2-hydroxy-2-methyl-1-phenylpropanone photoinitiator. Coating properties, such as hardness, adhesion, impact resistance, chemical resistance were tested. Furthermore, thermal and mechanical properties of these formulations were evaluated using ARES Rheometry, Thermogravimetric Analysis (TGA), Dynamic Mechanical Analysis (DMA), and Differential Scanning Calorimetry (DSC). The potential industrial use of AECO was evaluated based on comparing it to already existent commercially available product with the similar structure acrylated epoxidized soybean oil (AESO).
The study concluded that synthesized via epoxidation and acrylation processes AECO resin exhibit good potential in photopolymerization process. The incorporation of TMPTA reactive diluent produced harder and more brittle coatings than those with HDDA. Moreover, the results indicated in general the more flexible nature of coatings based on AECO and their better adhesion to metal substrates compared to coatings with commercially available AESO.

2021 GLRM 127

Investigating the Role of Turn Position Residues in Beta-Hairpin Peptide Catalysts

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Peptides and peptidomimetics are appealing catalysts because they occupy a middle ground between enzymes and organocatalysts, retaining some of the complexity of the

former and the synthetic accessibility and robustness of the latter. Although short oligomers lack the intricate three-dimensional environment of a folded protein, a commonly used strategy in peptide catalysis is to design sequences that induce a secondary structure conformation. Beta-hairpin peptides can be used to spatially orient reactive groups; however, there remains a need to more fully explore their sequence-catalytic activity relationship. We have been investigating the effects of beta-hairpin turn residues, cross-strand interactions, and reactive dyad positioning. Our work on development of techniques to study catalyst activity and our findings on the effect of turn-nucleating positions on catalytic activity for aldol and ester hydrolysis reactions will be presented.

2021 GLRM 128

Dissecting the Histone Code Involving Bromodomains and the Histone Variant, H2A.Z

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Gene specific recruitment of bromodomain-containing proteins to chromatin is affected by post-translational acetylation of lysine on histones. Whereas bromodomain interactions with acetylation patterns of native histones (H2A, H2B, H3, and H4) have been well characterized, the recognition motif for histone variants H2A.Z I and H2A.Z II by bromodomains has yet to be fully investigated. Elucidating these molecular mechanisms is crucial for understanding transcriptional regulation in cellular processes involved in both development and disease. Here, we have used protein-observed fluorine NMR (PrOF NMR) to fully characterize the affinities of H2A.Z I and II acetylation patterns for BPTF’s bromodomain, and found the diacetylated mark of lysine 7 and 13 on H2A.Z II to have the strongest interaction with K7ac preferentially engaging the binding site. We further paneled the selectivity of H2A.Z histones against a variety of bromodomains, revealing that the bromodomain of CECR2 binds with the highest affinity and specificity for acetylated H2A.Z I over isoform II. These results support a possible role for different H2A.Z transcriptional activation mechanisms through recruitment of chromatin remodeling complexes.

2021 GLRM 129

Protein Substrates Engage the Lumen of O-GlcNAc Transferase's Tetratricopeptide Repeat Domain in Different Ways

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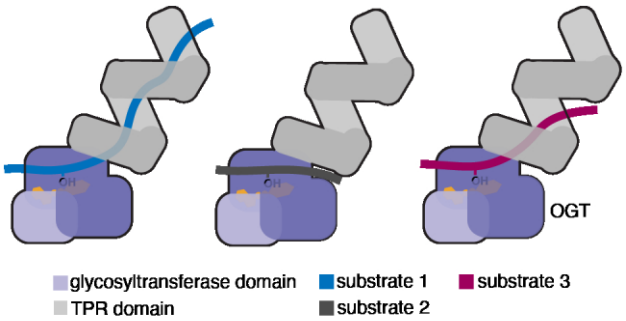
Glycosylation of nuclear and cytoplasmic proteins is an essential post-translational modification in mammals. O-GlcNAc transferase (OGT), the sole enzyme responsible for this modification, glycosylates over a thousand unique nuclear and cytoplasmic substrates. How OGT selects its substrates is a fundamental question that must be answered to understand OGT's unsual biology. OGT contains a long tetratricopeptide repeat (TPR) domain that has been implicated in substrate selection, but these is almost no information about how changes to this domain affect glycosylation of individual substrates. Here, we used cell extract glycome profiling and probed glycosylation of selected purified substrates to show that asparagine and aspartate ladders that extend the full length of OGT's TPR lumen control substrate glycosylation. We also found that substrates with glycosylation sites close to the C-terminus bypass lumenal binding. Our findings demonstrate that substrates can engage OGT in a variety of different ways for glycosylation.



2021 GLRM 130

The development of a selective CBX2 Chromodomain Ligand for preventing Neuroendocrine Differentiation of Prostate Cancer

sijie wang, surbhi sood, casey krusemark, ***Emily Dykhuizen****, edykhui@purdue.com. Medicinal Chemistry, Purdue University, West Lafayette, Indiana, United States*

Improved therapies to target the androgen receptor (AR) has improved the prognosis for thousands of men diagnosed with prostate cancer each year; however, the number of patients diagnosed with the highly aggressive, therapy-resistant form of prostate cancer called neuroendocrine prostate cancer (NEPC) continues to rise. NEPC occurs in response to anti-androgen therapies as a differentiation process that requires the

upregulation of several epigenetic regulators, including several Polycomb group (PcG) proteins. PcG proteins form numerous different complexes that are roughly divided into two categories: Polycomb repressive complex 1 (PRC1), containg a RING1 ubiquitin ligase, and Polycomb repressive complex 2 (PRC2), containing an EZH methyltransferase. In canonical polycomb-mediated gene repression, PRC2 trimethylates histone H3 lysine 27 (H3K27me3), which is recognized by the N-terminal chromodomain of CBX subunit of canonical PRC1, which compacts chromatin. EZH2 is specifically upregulated in NEPC and is required for the repression of AR-target genes. There are five PcG CBX paralogs in human; however, CBX2 is the most robustly upregulated in NEPC, indicating that it may be the "reader" of H3K27me3 required for AR-target gene repression during neuroendocrine prostate cancer. The shhallow binding pocket and high structural similarity among the CBX ChDs has been challenging for developing potent and selective CBX chromodomain inhibitors. Utilizing focused DNA encoded libraries (DELs), we discovered the first selective CBX2 chromodomain probe, SW2_152F, which binds to CBX2 ChD with a K_d of ~80 nM and displays 24 to1000-fold selectivity for CBX2 ChD over other CBX paralogs *in vitro*. SW2_152F is cell permeable and selectively inhibits CBX2 association with chromatin in cells. In prostate cancer, SW2_152F is capable of preventing CBX2-facilitated neuroendocrine differentiation in response to androgen deprivation by preventing CBX2-mediated repression of AR-target genes.

2021 GLRM 131

Quantifying the Selectivity of Protein−Protein and Small Molecule Interactions with Fluorinated Tandem Bromodomain Reader Proteins

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Multidomain bromodomain-containing proteins regulate gene expression via chromatin binding, interactions with the transcriptional machinery, and by recruiting enzymatic activity. Selective inhibition of members of the bromodomain and extra-terminal (BET) family is important to understand their role in disease and gene regulation, although due to the similar binding sites of BET bromodomains, selective inhibitor discovery has been challenging. To support the bromodomain inhibitor discovery process, here we report the first application of protein-observed fluorine (PrOF) NMR to the tandem bromodomains of BRD4 and BRDT to quantify the selectivity of their interactions with acetylated histones as well as small molecules. We further determine the selectivity profile of a new class of

ligands,
1,4-acylthiazepanes, and find them to have ≥3−10-fold selectivity for the C-terminal bromodomain of both BRD4 and BRDT. Given the speed and lower protein concentration
required over traditional protein-observed NMR methods, we envision that these fluorinated
tandem proteins may find use in fragment screening and evaluating nucleosome and transcription factor interactions. Using the structural biology strategy described, I am trying to elucidate the biological roles of BET proteins.
Considering the master transcriptional regulator, BRD4, after BD2 it has a region comprised of multiple polar residues called the N-terminal cluster of phosphorylation sites (NPS) followed by a lysine-rich stretch called basic residue-enriched interaction domain (BID). Low-resolution data has been used to propose that the NPS folds back to interact with BD2 and BD1, thus inhibiting BRD4 from binding to acetylated chromatin. When serine residues in NPS get phosphorylated (another type of protein modification), it unmasks BD2 enabling BRD4 to interact with acetylated chromatin and in turn interacts with the BID region downstream. Although studies have explored the role of phosphorylation to regulate BRD4 function, there are still big gaps regarding the interaction mode between NPS and BRD4 bromodomains. Exploring these novel interactions will help to unravel binding determinants and diverse structural features that may be targeted for therapeutic inhibition.

2021 GLRM 132

Assessing the Structures and Interactions of γD-Crystallin Deamidation Variants

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Cataracts, or the opacification of the eye lens, is the leading cause of visual impairment worldwide. Cataracts are formed by aggregation of the crystallin proteins, resulting in opacification of the eye lens, and in turn reduces the access of light to the retina. As there is essentially no protein turnover in the eye lens, crystallins have to last for the entire lifetime of the host organism. As a result, crystallins have evolved to possess great stability and solubility. Chronic exposure to chemical attacks, such as UV light or hazardous compounds, results in irreversible covalent modifications, which are hypothesized to decrease protein stability and solubility thus inducing aggregation. In this study, we focused on γD-crystallin, the most abundant γ-crystallin in the lens nucleus, and how deamidation, the conversion of Asn residues to Asp, influence the structure and function of the protein. We used solution NMR to assess structural changes in Asn to Asp deamidation variants and solved the X-ray structures of two γD-crystallin deamidation variants. To compliment our structural studies, biophysical characterization of γD-crystallin variants were done by DSC and DLS. We used DSC to evaluate thermal stability where all variants showed minimal changes in T_m. We used DLS to understand self-interactions probed by dynamic light scattering and diffusion

interaction parameters (DIP), a measure similar to the 2nd viral coefficients, were determined for all mutants to be within the uncertainty of wild-type. Our results suggest that deamidation alone is likely not a driver of cataract formation.

2021 GLRM 133

Enzymatic protein modification using prenyltransferases

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Protein-based conjugates are valuable constructs for a variety of applications in medicine and biotechnology. Enzyme catalyzed protein modification coupled with subsequent bioorthogonal reactions has enormous potential for the creation of a plethora of site-specifically modified conjugates. Protein prenyltransferases catalyze the covalent modification of proteins that possess a C-terminal tetrapeptide CaaX-box sequence; virtually any protein containing such a tag is a substrate. Here, three applications of this enzymatic labeling approach will be described. In the first, an aldehyde-containing isoprenoid analogue was transferred to a DARPin (Designed Ankyrin Repeat Protein) scaffold engineered to target cancer cells. Oxime ligation using an MMAE-based (monomethyl auristatin) reagent with that aldehyde-containing construct produced a protein that was able to selectively kill cancer cells. In a second application, a polymer initiator was enzymatically installed onto the above DARPin protein followed by polymerization with monomers containing bioorthogonal azides and alkynes to yield protein-polymer conjugates with improved pharmacological properties. Subsequent elaboration of the azides and alkynes with fluorphores and toxins enabled simultaneous visualization and targeting of these proteins to cancer cells. Finally, prenylation of fibronectin domain-based dihydrofolate reductase (DHFR) fusion proteins and subsequent assembly into chemically self-assembled nanorings allowed lymphocytes to be targeted to cancer cells for directed killing. These three examples highlight the enormous versatility of this approach.

2021 GLRM 134

University of Minnesota student ACS chapter: A virtual year of learning, collaborating, and experimenting with chemistry

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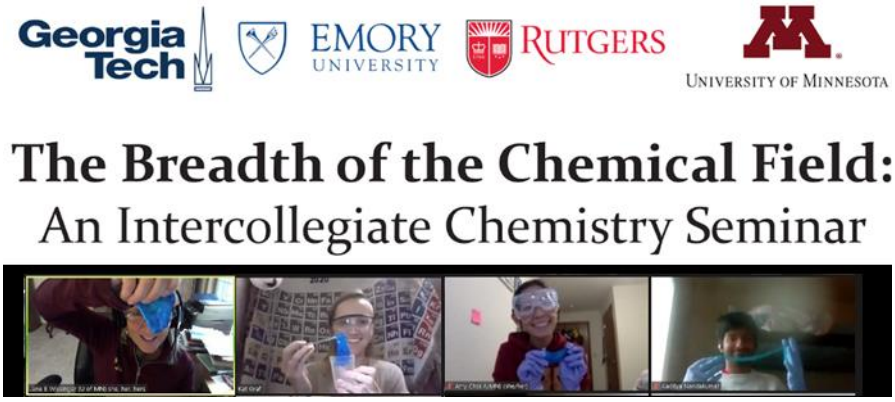
With an online academic year, our student ACS chapter faced a challenging situation – how do we remotely excite and educate chemistry undergraduates on our campus? By utilizing technology in all forms, creating new partnerships with other universities, and holding virtual chemistry experiments and meetings, we made distance learning into a powerful tool for our community. We began with our Study Group Initiative, where we

worked with first-year general chemistry courses to connect interested undergraduates using an algorithm made by a UMN student. In the fall semester, we helped 100 students form important connections that they missed with an online semester, making a difference in the education of our undergraduates and inspiring them to continue in their chemical training. At the same time, a new opportunity came from an unexpected source: a group email sent to our chapter, Emory University, Georgia Tech, and Rutgers University. Together, we planned and held a three-day virtual event entitled “The Breadth of the Chemical Field: An Intercollegiate Chemistry Seminar” in November of 2020. With over 80 students viewing from across the nation, eight professors gave lectures on biochemistry, organic chemistry, and materials chemistry. This event demonstrated the power of online conferences, showing that students and researchers across the globe can interact and learn from the comfort of their own homes. Similarly, our UMN ACS chapter also celebrated National Chemistry Week with Emory University, sending the chemicals necessary to make slime across the country and teaching students about polymer chemistry. We witnessed firsthand the efficacy of distance learning through this event, and while online learning for undergraduates is a challenge, we have found that undergraduates and faculty alike can make a significant and positive impact in the virtual education of our next generation of chemists.



2021 GLRM 135

Online chemistry labs - should they persist post-pandemic?

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Chemistry is a hands-on discipline...especially in lab. Yet. during the COVID Pandemic, many schools pivoted quickly to an online format for classes. I know these met with varying levels of success at my own institution and others.

To "complicate matters", the American Chemical Society has an official policy statement regarding hands-on labs that states "there is no equivalent substitute for hands-on

activities where materials and equipment are used safely and student experiences are guided".

The question I want to pose and, perhaps, answer, is whether we can effectively teach the principles of a laboratory science in a remote format. I do not think we can come to a broad answer but want to start a discussion and encourage continuing dialogue on this topic.

2021 GLRM 136

Development of the Organonitrogen Biodegradation Database: A Bioinformatics Approach to Study the Microbial Degradation of Cyanoguanidine and Related Compounds

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The use of nitrogen-rich fertilizers, pesticides, herbicides, and similar agriculturally-applied chemicals has increased to millions of tons as agriculture consumes more land and demands greater yield. An average of 80% of these organonitrogen compounds are lost to the environment through means such as soil leaching, where these chemicals enter into waterways and cause extensive nitrogen pollution. As these chemicals break down, they create toxic ammonia buildup, foster massive algae blooms, and cause hypoxia, the "dead zones" of coastal waters that suffocate aquatic life. Previous research has shown microbes have the ability to degrade organonitrogen compounds into harmless products that can enter the natural biogeochemical cycles: this approach is known as bioremediation and has been used in many scenarios with repeated success. The goal of this project was to investigate the microbial degradation of cyanoguanidine, a fertilizer additive widely used in agricultural operations worldwide. Extensive literature reviews, computational programming, and bioinformatics tools were employed to identify bacteria, enzymes, and biochemical pathways leading to the biodegradation of cyanoguanidine and similar organonitrogen compounds. A predictive biodegradation tool was used to identify potential intermediates and biochemical reactions. These efforts resulted in the creation of the Organonitrogen Degradation Database (ONDB), a resource that contains data on the microbial degradation of cyanoguanidine and related organonitrogen compounds. In this database, each compound page has a general overview, basic chemical information, common use, transformation products, enzymes, and bacteria capable of degradation. The ONDB, which we intend to expand with future research, serves as a reference for researchers interested in solving the issue of organonitrogen compound pollution. This database will allow researchers and the general public to learn about organonitrogen compounds and address the knowledge gaps regarding the biodegradation of these chemicals.

2021 GLRM 137

Communicating Chemical Representations in an Online Environment: The Hybridization Explorer

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Hybridization of atomic orbitals to form hybrid orbitals is a tough concept for students to grasp. Until recently, instructors have been limited to how they could illustrate this abstract model. Predominantly static 2-dimensional images have been used. More

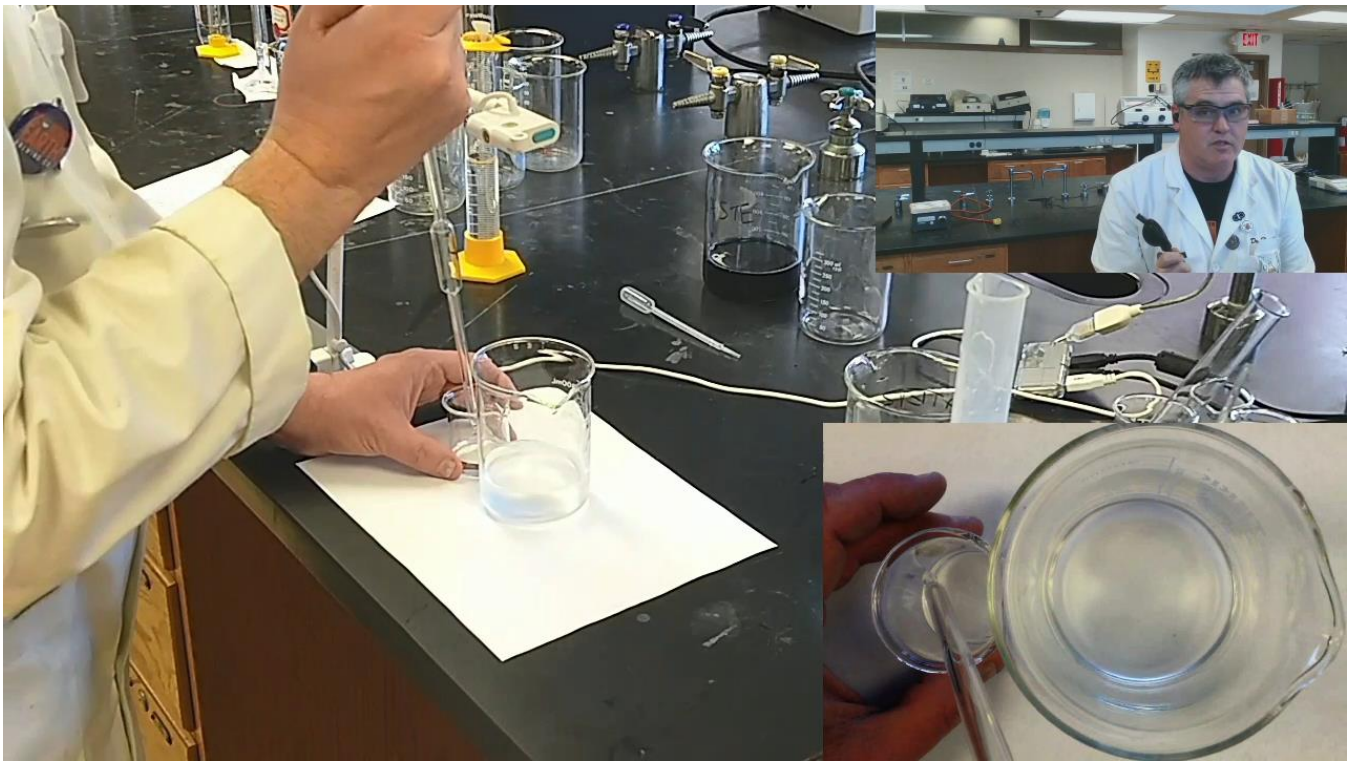
creative methods utilized balloons or toothpicks and marshmallows to help students with the 3-dimensional aspects. With the recent prevalence of distance learning and online instruction, presentation of this concept is even more difficult. Thus, Alchemie saw the opportunity to develop a hybridization explorer to help with the presentation and understanding of hybrid and atomic orbitals. This explorer has three modes: present, explore, and assess, all of which provide users the experience of viewing and manipulating orbitals, and even assists in the sharing of such diagrams in an online environment, both synchronously and asynchronously. The goal of this interactive is to lead to a more intuitive understanding of the geometrical and bonding explanations that result from hybridization theory. In this presentation, the features of the hybridization explorer will be discussed. Additionally, initial research into the impacts of the explorer on student understanding and confidence in the concept will be presented.

2021 GLRM 138

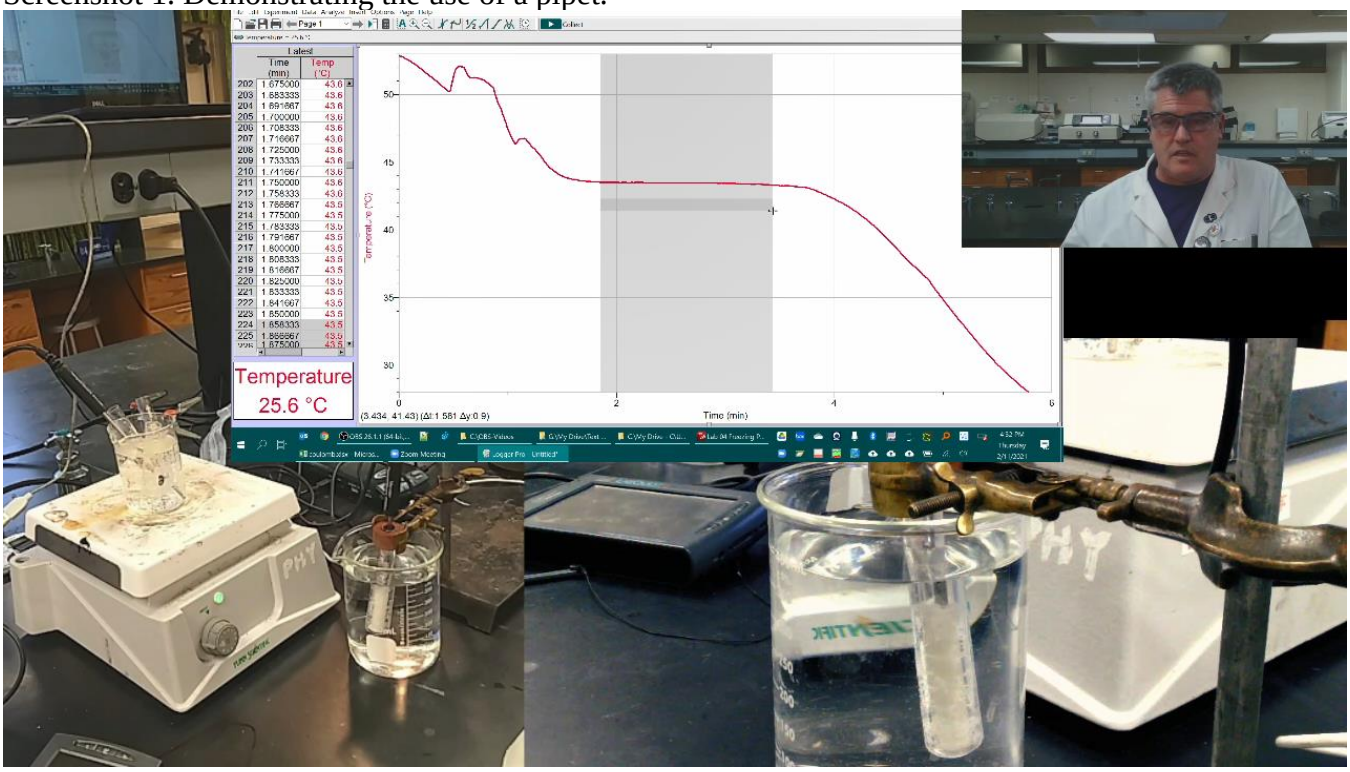
Live-streaming of Instructor Completed Labs During the Pandemic: Initial Impressions

***Vincent P. Hradil**, vincent.hradil@cuchicago.edu. Concordia University Chicago, River Forest, Illinois, United States*

Many higher education institutions have had to cancel all face-to-face instruction during the pandemic. This has necessitated several major changes in the way that classes are instructed. Though technology has helped by allowing such things as remote lectures and office hours, many science instructors have struggled to adopt meaningful and effective replacements to face-to-face laboratory exercises. Many have turned to mail-order labs for home use, computer simulations, and videotaping experiments. During the spring of 2021, I decided that I would live-stream to my second-semester General Chemistry laboratory sections while performing the lab experiments myself. My goal was to make the experience as interactive as possible to give the students an experience close to that of a normal lab section. By streaming the experiments live, I was able to interact with the students, have them make observations, and record measurements while I act as their hands and eyes.
In this presentation, I will describe the technologies and software used to present several camera angles simultaneously, thus allowing students to see everything happening from overview to detail. I will also discuss some early impressions about the difficulties and successes involved in the process. In the future, I hope to be able to compare live-streaming with other remote laboratory approaches to determine if there are benefits in regards to learning outcomes. If successful, this technique may be an excellent addition to on-line learning science courses offered post-pandemic.



Screenshot 1. Demonstrating the use of a pipet.



Screenshot 2. Demonstrating the use of live graphical data analysis.

2021 GLRM 139

Embedding Success Strategies into Online Introductory Chemistry

***Christine Pruis**, cpruis@kvcc.edu. Chemistry, Kalamazoo Valley Community College, Kalamazoo, Michigan, United States*

The abrupt switch to remote learning in March 2020 highlighted student, instructor, and institutional lack of preparedness. While faculty and staff development series were readily created and available, such was not the case for students. Unfortunately, students often were left alone to navigate the unfamiliar territory of online learning, resulting in frustration, confusion, and, for some, poor performance. To aid students in adapting to an online learning environment, a customized "course success" module aimed at overcoming technical hurdles and establishing emotional preparedness was created and assigned the first week of class. It guided students to success by ensuring adequate technology, creating LMS familiarity, and shaping time management skills. Completion was required to unlock future content within the course. In an online class of 140 students, the participation rate for this introductory success-oriented module was 99%, with one student withdrawing due to a COVID diagnosis. Additional low stakes formative follow-up assignments focusing on study and review skills were developed and assigned at strategic moments throughout the term. Some examples of follow-ups were note taking strategies, brain dump exercise, and student discussion boards focused on resources and best practices. The embedded success strategies were effective. This was clear though self-reported evidence as the number of issues related to technology struggles and poor student planning plummeted from summer to fall despite a 2 fold increase in class size. In an anonymous survey completed by 114 students, 48% reported the "course success" module as "helpful" and 42% as "very helpful." Finally, despite the class being reported in surveys as being challenging, the DFWI rate was low at 15%.

2021 GLRM 140

CONNECTING CHEMISTRY TO SOCIETY AND FOSTERING COMMUNITY APPRECIATION OF SCIENCE

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Today our biggest challenge is to help sustain Earth and its people in the face of population growth, finite resources, malnutrition, spreading disease, deadly violence, war, climate change, and the denial of basic human rights, especially the right to benefit from scientific and technological progress. Science and society have what is essentially a social contract that enables great intellectual achievements but comes with mutual expectations of benefiting the human condition and protecting our planet. Our

excellence in research and our commitment to high quality classroom teaching must be accompanied by sincere convictions to successfully connect with the public at large on all matters that relate to science and technology. We aim to educate future scientists and to achieve science literacy among all students, institutional colleagues, and employees. Science literacy enlightens and enables people to make informed choices, to be skeptical, and to reject shams, quackery, unproven conjecture, and to avoid being bamboozled into making foolish decisions where matters of science and technology are concerned. Science literacy is for everyone—scientists, artists, humanists, all professionals, the general public, youth and adults alike. I shall give specific examples of our work and also share how we have adapted our programs to on-line interactions.

2021 GLRM 141

Cysteine Determination based on the Fluorescence Resonance Energy Transfer of an Assembled Nanohybrid

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We have developed a nanohybrid using gold nanoclusters (AuNCs) and conjugated polyvinylcarbazole polymer nanoparticles (PVK PNs) that demonstrates a strong fluorescence resonance energy transfer (FRET). The hybrid had two distinct fluorescence emission peaks at 385 nm and 630 nm and displayed bright orange fluorescence under the excitation of 342 nm. Standard fluorescence measurements of the nanohybrid confirm enhanced AuNCs fluorescence quantum yield (QY) from 1 % to 3 % through FRET with the PVK PNs. Fluorescence lifetime decay measurements indicate a 59 % FRET efficiency. Furthermore, the fluorescent nanohybrid is sensitive to cysteine concentration though a quenching process at 630 nm due to the contribution of decomposition of aurophilic bonds consisting of Au (I)-thiolate ligands under high pH value and the etching ability of cysteine toward gold atom. The assembly can be used to determine cysteine over a dynamic range of 0.5 μM to 600 μM. The limit of detection for determination of cysteine is achieved to as low as 0.18 μM. Therefore, the nanohybrid has a potential for determination of other biomolecules.

2021 GLRM 142

Investigations of succinylated polyethyleneimine derivatives for enhanced transfections in serum

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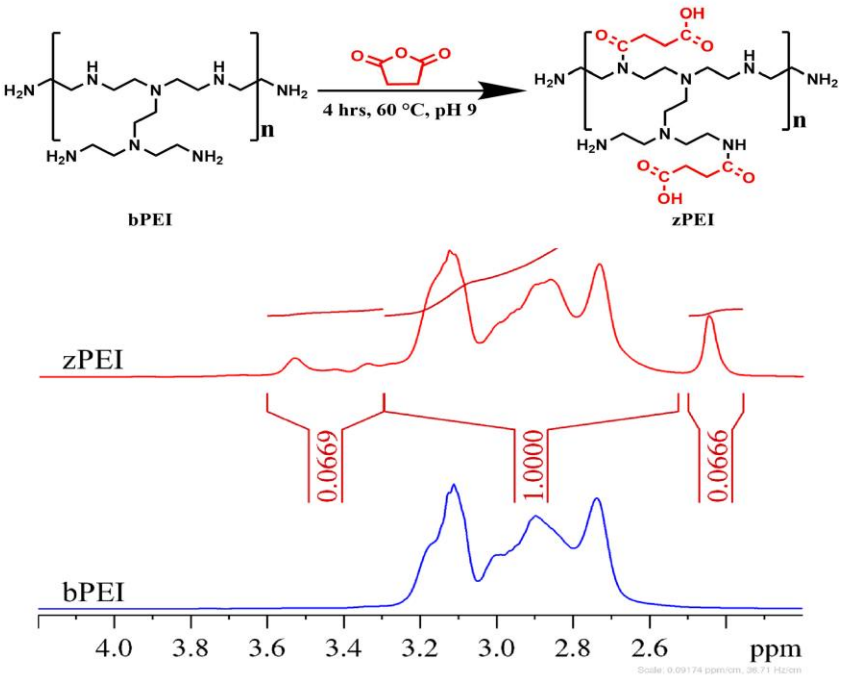
Although gene therapy has promised to treat serious inherited and acquired diseases, its clinical success has been hindered because of safety concerns or lack of efficiency and biocompatibility of various gene delivery agents. Currently, viral vectors account for roughly 70% of clinical trials due to their inherent gene delivery activity, they suffer from substantial safety concerns including immunogenicity and oncogenicity as well as concerns for commercial production. In contrast, synthetic polymeric materials are an attractive platform due to ease of production as well as reduced immune responses, but to date, have lacked the efficiency and biocompatibility to be clinically relevant. Addressing these issues, we have produced zwitterion-like derivatives of polyethylenimine (zPEIs) via succinylation of primary and secondary amines. Evaluation of polymer/DNA interactions revealed these polyampholytes decreased buffering capacity, increased serum stability, and created tunable particle stability in the resulting PEI/DNA polyplexes. In vitro gene delivery in the absence of serum was moderately improved, however, transgene expression in the presence of serum was increased 51-fold compared to unmodified bPEI/DNA. Lastly, we'll discuss more recent results focusing on low percent modified zPEIs to more fully comprehend the correlation between enhancement of transfection and CRISPR/Cas9 homology-directed repair in serum-containing media and succinylation.



Post polymerization modification with succinic anhydride and subsequent NMR characterization

FRET-based Pdot@SiQDs Nanocomposite for Enhancing Quantum Yield and Stability

Di Sun[1]*, di.sun@und.edu, Xu Wu*[1]*, Diane Darland*[2]*, Julia X. Zhao*[1]*. (1) Chemistry, University of North Dakota, Grand Forks, North Dakota, United States (2) Biology, University of North Dakota, Grand Forks, North Dakota, United States*

Luminescent semiconductor quantum dots (QDs) would have a wide range of biological applications due to their strong photostability and multiple emission wavelengths under a single excitation. However, the majority of traditional QDs are heavy metal-based (CdSe, CdTe). The toxicity of these heavy metals limits QDs' applications in biological fields. To solve this problem, silicon as a nontoxic element has been used to generate QDs (SiQDs). However, the SiQDs are very unstable and are susceptible to aggregation, which would significantly reduce the quantum yield of SiQDs. In order to improve the stability and fluorescence quantum yield of SiQDs, using highly florescent p-conjugated polymer dots (Pdots) we constructed a Pdot@SiQDs nanocomposite. In the nanocomposite, the Förster resonance energy transfer (FRET) occurred where the Pdot was used as an energy donor to excite SiQDs to emit strong fluorescence. Two polymers were used, poly(9-vinylcarbazole) (PVK) as a light-emitting polymer, and poly (styrene-co-maleic anhydride) (PSMA) was used as an amphiphilic polymer linked to the amine functional group terminated SiQDs. Through the coprecipitation method, the Pdot@SiQDs nanocomposite was generated. As a result, the SiQDs doped inside Pdots were protected from the aggregation. The stable and strong fluorescent hybrid was developed for bioimaging and biosensing.

2021 GLRM 144

Antimicrobial properties of silver nanoparticle-impregnated wheat gluten biofilms

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Wheat gluten (WG) biofilms result in a more affordable and biodegradable alternative for medical first aid bandages. WG biofilms were prepared by denaturing the WG protein with acid and heat, mixing with glycerol, and then drying to remove excess liquid. WG film properties such as density and porosity were measured. Different concentrations of silver nanoparticles (AgNPs) were synthesized and incorporated into the WG films to test their antimicrobial properties using several different pathogens. It was concluded that as the concentration of silver decreases, the diameter of the zone of inhibition also decreases, conveying that higher amounts of silver exhibit stronger antimicrobial properties. Incorporation of silver nanoparticles into WG biofilms had weaker antimicrobial properties than the silver disks alone. Some pathogens such as *Klebsiella pneumoniae* were more susceptible to the antimicrobial properties of WG with 0% AgNPs than WG with 100% AgNPs.

2021 GLRM 145

Silver Nanoparticles as Catalysts for the Reduction of 4-Nitrophenol

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This research seeks to determine the efficacy of silver (Ag) nanoparticles as catalysts for the reduction of 4-nitrophenol with sodium borohydride. Ag nanoparticles were synthesized by different reduction methods using sodium citrate and/or sodium borohydride in order to change the size and shape of the nanoparticles. The reduction reaction was monitored by UV-vis spectroscopy in order to determine which Ag nanoparticle synthesis method was optimal for the catalytic reduction reaction.

2021 GLRM 146

Systematic Study of Aminoacid Adsorption in Carbon Nanotubes

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The growing utility of carbon nanotubes as a material for future medical devices, such as a “lab on a chip”, or electrical devices makes them an increasingly researched area of science. Their unique physical and electrical properties as well as their hollow interior makes them ideal for the transportation of nanomaterial. However, at the nanoscale, macroscale fluid flow predictions begin to break down and do not accurately estimate the flow and properties. Previous research used molecular dynamics (MD) simulations to begin to better understand principles behind nanoflow. Using these similar techniques, the effects of nanoflow on amino acid and peptide adsorption in carbon nanotubes were investigated. The MD simulation, large-scale atomic/molecular massively parallel simulator (LAMMPS). Research here focused on setting up the system carbon-nanotube-solvent-amino-acid, and it will be followed it by a systematic study of the adsorption patterns of the amino acids.

2021 GLRM 147

Varied Dissolution Silica Nanoparticles for Nano-enabled Disease Suppression in Plants

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With the world's population expected to reach 10 billion by 2050, feeding humanity will require a 60% increase in food production. The prevalence of numerous plant diseases contributes to the grand challenge of attaining global food security. It is clear that there is a need to invest in creative, sustainable, and economically feasible solutions to improve agricultural crop production. Nanoparticles (NPs) are increasingly being used as alternatives to commercial agrochemicals due to their unique nanoscale properties that allow for enhanced delivery of nutrients to promote plant growth. Silica nanoparticles have shown promise in improving stress- and disease-resistance in plants, thereby improving yield and agricultural productivity. These benefits are due to the dissolution of silica nanoparticles to form silicic acid, which has been shown to fortify plant cell walls and enable plants to fight off disease. This study investigates the dissolution of silica NPs using different functionalization strategies enabled by inclusion of (3-aminopropyl)triethoxysilane (APTES). Four types of silica NPs that vary based on the presence and location of APTES were prepared and characterized using transmission electron microscopy and nitrogen physisorption (for physical characterization) and the silicomolybdic acid (SMA) assay (for dissolution characterization). This study shows that when APTES is located in the silica NP core, the NPs dissolve to generate hollow structures within 8 hours of incubation, introducing a burst of silicic acid release into the surrounding environment. However, silica NPs with APTES on the surface do not exhibit the same transformation. Thus, understanding the role of localization of APTES on NP transformation will facilitate future design of optimal NPs for agricultural applications.

2021 GLRM 148

Comparative Study of Poly-Diaminonaphthalnene Nanocomposite Based on Different Electrode Substrates

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Recently, carbon nanomaterials with high surface areas and excellent electrical conductivity have been widely used in fabrication of electrochemical sensors and biosensors. The carbon nanofibers(CNF) present excellent mechanical, thermal and electrical properties; it has been used as modified material of electrodes for electrochemical sensing. Conducting polymers, especially aromatic diamines, have been a field of intensive studies due to their unique properties, as well as possible applications in electrocatalysis, electrochromic devices, capacitors, batteries, and sensors**.**
Polymer (1,5-diaminonaphthalene)/CNF nanocomposites can be prepared by different routes, including in situ electropolymerization, solution processing.
Herein, the aim of this paper is to study in detail the behavior of nanocomposites poly(1,5-DAN)/CNFs at different substrates electrodes (carbon paste, glassy carbon, platinum…), its electropolymerization in acidic medium HCl 0,1M, characterization and

electroactivity in Fe^{2+}/Fe^{3+}, $Fe(CN)_6^{4-/3-}$. The results were achieved by means of SEM, cyclic voltammetry and electrochemical impedance spectroscopy.

2021 GLRM 149

Tuning the hydricities and acidities of metal triphosphine complexes to achieve efficient CO_2 hydrogenation

***Christopher Zall**, kitzall@gmail.com, William Fernandez, Makenzie Kuehn, Dorothea B. Hudson. Department of Chemistry, Sam Houston State University, Huntsville, Texas, United States*

Transition metal hydrides are ubiquitous intermediates in catalysis, and the character of the M–H bond can significantly impact the catalytic activity and selectivity. Quantification of this reactivity, using thermodynamic parameters such as hydricity and acidity values, can help design and tune catalysts. Thus far, quantitative relationships, such as periodic trends and steric, electronic, and geometric relationships, have been elucidated only for a small number of structural types. This data has been used most notably in the development of metal bis(diphosphine) complexes for H_2 electrocatalysis and CO_2 reduction. In this presentation, hydricity and acidity data will be presented for analogous complexes containing triphosphine and monophosphine ligands. While the electronic relationships mirror those of the bis(diphosphine) complexes, a distinct series of structural factors govern the reactivity of these mixed-ligand complexes. The data has led to the identification of active catalysts for CO_2 hydrogenation with balanced hydride and proton donor abilities.

2021 GLRM 150

Exploration of Low-Valent Uranium-Pnictogen Interactions

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A family of rare low-valent uranium(III)-pnictogen complexes supported by the bulky hydrotris(3,5-dimethylpyrazolyl)borate (Tp*) ligand was synthesized by protonation of Tp^*_2UBn (Bn = benzyl) with anilines, including 4-[2,6-di(pyridin-2-yl)pyridin-4-yl]benzenamine and p-toluidine, to make the corresponding U(III) anilidos, $Tp^*_2U(NH\text{-}C_6H_4\text{-}p\text{-}terpyridine)$ and $Tp^*_2U(NHC_6H_4\text{-}p\text{-}CH_3)$. Conversion to the uranium(IV) imido species was achieved by oxidation/deprotonation, forming $Tp^*_2U(N\text{-}C_6H_4\text{-}p\text{-}terpyridine)$ and $Tp^*_2U(N\text{-}C_6H_4\text{-}p\text{-}CH_3)$. The synthesis of additional pnictogen analogues, including the uranium phosphorus and arsenic complexes, are also explored with reagents with varying steric bulk including phenyl, mesityl, and 2,4,6-tri-tert-butylphenyl. All compounds were characterized by multinuclear NMR spectroscopy, infrared spectroscopy, electronic absorption spectroscopy, and single crystal X-ray crystallography.

2021 GLRM 151

Pincer-ligated manganese dicarbonyl complexes featuring an N-heterocyclic phosphenium/phosphido moiety

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While N-heterocyclic carbenes (NHCs) have been well-studied ligands for transition metal complexes, their group 14 analogues, which instead incorporate a phosphorus atom in the heterocycle, remain relatively unexplored in comparison. In contrast to NHCs, N-heterocyclic phosphenium cations (NHP^+s) are weak σ-donors and strong π-acceptors, leading to different reactivity, properties, and potential applications. Similar to nitrosyl ligands, NHPs are thought to interconvert between a phosphenium (NHP^+) and a phosphido (NHP^-) through a two-electron process, which may offer a new avenue to unique properties and coordination. Incorporation of an NHP unit into the center of a rigid chelating pincer ligand and coordination to a manganese center has yielded a $(PP^{Cl}P)Mn(CO)_2Br$ complex, which can further be treated with two equivalents of a reducing agent to afford a coordinatively unsaturated manganese complex $(PPP)Mn(CO)_2$. Structural characterization of this compound reveals a fluxional geometric process about the manganese center that varies in the solution and solid state. In the solution phase, $(PPP)Mn(CO)_2$ adopts a trigonal bipyramidal geometry and is analogous to pincer-ligated manganese dicarbonyl complexes used for hydrogenation and dehydrogenative coupling catalysis in the literature. Progress toward reactivity of $(PPP)Mn(CO)_2$ and the nature of the metal-phosphorus bonding in the NHP^+/NHP^- moiety will be discussed.

2021 GLRM 152

Developing a carbon-carbon bond forming method using sigma-bond metathesis

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Mechanisms for carbon-carbon bond formation at d^0 metals are limited due to a lack of free valence electrons. Sigma-bond metathesis is a non-redox mechanism that occurs at d^0 metals which involves the breaking and formation of two sigma-bonds through a highly ordered “kite-like” transition state. However, sigma-bond metathesis has not been shown to form carbon-carbon bonds due to limitations found in the transition state. This research aims to overcome these limitations by utilizing non-traditional carbon-based coupling partners. Preliminary data indicates carbon-carbon bond formation between sp^3-sp^3 and sp^3-sp^2 carbon centers.

2021 GLRM 153

Biobased Latexes from 3-Allyl-5-vinylveratrole and High Oleic Soybean Oil-based Acrylic Monomer

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Being structural analog to petroleum-based Styrene, vanillin derived 3-Allyl-5-vinylveratrole (AVV) may function as its renewable alternative in free radical polymerization, in particular in sustainable latexes. Investigation on polymerizability of (AVV) and its application as a building block (monomer) for macromolecules synthesized by free radical mechanism was addressed first. Further, to show feasibility of AVV in a role of biobased co-monomer, latex copolymers from AVV and plant oil-based acrylic monomer (POBM) were synthesized. Library of POBMs has been recently developed in our group using one-step direct transesterification of a broad variety of plant/vegetable oils. Ability of AVV to undergo chain radical propagation reactions is demonstrated by 1H NMR spectra of homopolymer and confirmed utilization of AVV's vinyl group in chain growth reaction and macromolecular backbone formation. The allylic unsaturation of AVV is retained during chain propagation and can be utilized in post-polymerization crosslinking to form polymer network. The glass transition temperature of homopolymer from AVV (Tg = 77 oC) indicates that incorporating its fragments into copolymers might considerably change the intermolecular interactions and physico-chemical properties of the resulting materials. To investigate this effect, latex copolymers from AVV and renewable acrylic monomer from high oleic soybean oil (HOSBM) were synthesized using miniemulsion process. Thermal analysis shows that incorporation of aromatic AVV fragments into copolymers with HOSBM increase glass transition temperatures resulted latexes. Retained allylic groups of AVV distributed along polymer backbone provide crosslinking sites additionally to the allylic fatty fragments of HOSBM. Observed increase in crosslink density values of polymer network which followed higher content of AVV in feed, confirms participation of AVV fragments in crosslinking reaction along with HOSBM counterpart by formation of additional crosslinking nodes. Tensile properties of crosslinked latex films indicate that their thermomechanical properties are determined by crosslink density controlled by combination of "rigid" (AVV) and "soft" (HOSBM) constituents. Obtained polymeric materials exhibited wide range of viscoelastic behavior, thus combining AVV with vinyl monomers from plant oils in chain copolymerization into a macromolecular structure is a promising platform for controlling properties of biobased latex polymer networks.

2021 GLRM 154

Lignin solubilization and fractionation in aqueous aprotic and protic solvents

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Lignin is an organic macromolecule that is found in plant cell walls and is recovered as a large-scale waste byproduct of the paper making industry. Lignin utilization often centers on its solubility and fractionation in various solvents. In this study the solubilization of Kraft alkali lignin in various organic solvents was investigated using their various ratios with water. The lignin solubility was assessed by gravimetry and confirmed by thermal carbon analysis (TCA). The molecular weight (MW) of soluble and insoluble fractions was evaluated by gel permeation chromatography GPC. Aprotic polar solvents in a 1:1 ratio with water yielded the best solubility. Thermal desorption-pyrolysis- gas chromatography- mass spectrometry was utilized to characterize both solid and liquid fractions, showing some selectivity fractionation via dissolution. Hansen sSolubility parameters and solvent properties are being investigated to predictfind lignin solubility trends.

2021 GLRM 155

Sustainability and Adhesive Performance of Plant Oil-Based Latexes

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The sustainability of the adhesives prepared from fossil-based materials has become a growing concern. Thus, replacement of petroleum-based materials by ones derived from renewable resources is pursued as a sustainable strategy for reducing their carbon footprint. Biobased latexes can be widely used as waterborne adhesives if their performance and properties are competitive to those currently available in the market. This work aims to evaluate the performance of latex adhesives with higher biobased content recently developed in our group. For this purpose, plant oil-based vinyl monomers HOSBM and CMM (derived from high oleic soybean oil and camelina oil, respectively) in combination with methyl methacrylate (MMA) and butyl acrylate (BA) were copolymerized using miniemulsion to yield latexes to be tested as adhesives. The MMA (“rigid” fragment) content was kept at 55 wt%, while BA (within remaining 45 wt% of the “soft” fragments) has been gradually replaced by either CMM or HOSBM.
The effect of partial substitution of the BA by CMM or HOSBM on adhesive properties was assessed using peel testing (ASTM D 1876-08) on the multiple substrates. The presence of plant oil-based fragments in latex copolymers improves adhesives peel

strength on most substrates. Plant oil-based latexes with the maximum content of CMM or HOSBM (up to 45wt %) and their optimal adhesive performance were determined on various carpet and paperboard substrates.
Additionally, Life Cycle Assessment (LCA) method was used as a tool to evaluate the environmental performance of the synthesized latex adhesives as well as identify the hotspots in the synthesis of these plant-derived adhesives in their early design stages. LCA of plant oil-based monomers can explain to which extent the sustainability of the biobased latex adhesives can be improved.
The authors thank the NSF Industry and University Cooperative Research Center for Bioplastic and Biocomposites for financial support.

2021 GLRM 156

Analysis of organics and noncondensable gases present in subcritical water-treated alkali lignin

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Products (organics and noncondensable gases) of subcritical water (SW) depolymerization of lignin at 300 °C were analyzed by thermal desorption/pyrolysis (temperature fractionation) through pyroprobe-gas chromatography-mass spectrometry (Py-GC-MS) and thermal carbon analysis. Oxygen content of simple SW products in the liquid fraction led to moderate gas evolution in the thermal desorption (TD) fraction and extensive gas evolution beyond 300 °C during pyrolytic analysis, leading to condensed (repolymerized) compounds. Gas evolution during analysis of untreated lignin also occurred, but was not as extensive, showing that breakdown materials were more easily volatized as well as revealing that subcritical water treatment was best at low TD temperatures. Determination of evolved gases allowed carbon mass balance of Py-GC-MS data to thermal carbon analysis data. Organic species generated were low in abundance (monomers at 6 wt% C of original C), but consisted largely of guaiacols at low analysis temperatures instead of at pyrolytic temperatures in untreated lignin. This showed promise of SW treatment yielding guaiacol monomers with post-process heating at TD temperatures as low as 110 °C. Heating at low temperatures such as this (post SW treatment) would prevent large-scale repolymerization if flow in a loop system were applied. However, size exclusion chromatography demonstrated that MW in residue solids was consistent with an amount of breakdown similar to untreated lignin- showing less repolymerization than anticipated. Overall, the study also served as a baseline study for SW treatment alone- no additives were used- and monomer yields were similar to some studies with added catalysts, etc. in a heated water solvent, showing that subcritical water may have been the primary agent of depolymerization.

2021 GLRM 157

High-Oleic Sunflower Oil-Based Vinyl Monomer in Latex Polymers Synthesis

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During the last two decades, there is a constant growing interest in bioresources for the formation of polymeric materials. It is expected that usage of renewable materials, in particular vegetable oils, allow to reduce the negative impact on the environment and human health, to obtain biocompatible materials with improved properties that people contact every day. Promising raw material for chemical synthesis is high-oleic sunflower oil, which has particular fatty acid compositions (oleic acid content up to 98%), thermo-oxidative stability, physical properties, availability and low cost.
A new vinyl high-oleic sunflower oil-based monomer (HOSFM) was synthesized through a one-step process of direct transesterification of high-oleic sunflower oil triglyceride's with N-(hydroxyethyl)acrylamide. The iodine value, density, and refractive index were determined for bio-based monomer. In this work, latex copolymers were synthesized using mini-emulsion polymerization of HOSFM with conventional monomer, such as methyl methacrylate. Based on the obtained results, it was confirmed that HOSFM behaves as a traditional vinyl monomer in free radical (co)polymerization reactions. The chemical composition of the obtained latex copolymers was confirmed using ^{1}H NMR spectroscopy. The double bonds of the HOSFM fatty acid fragments remain mainly unaffected during the (co)polymerization and make the resulting macromolecules capable of oxidative reactions and further formation of cross-linked latex films and coatings. It was demonstrated that the presence of HOSFM fragments has an effect on latex thermo-mechanical properties by providing the plasticizing and hydrophobizing effects to the latex films. The resulted bio-based latexes have promise to be alternatives of petroleum-based conventional counterparts to be used in various applications, including but not limited to paints, coatings and adhesives.

2021 GLRM 158

A Mild, 2-Step Approach to Strained Cyclooctynes

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While the strain-accelerated cycloaddition of cyclooctynes has played a critical role in the advent of biomolecule conjugation methods, the preparation of these highly reactive alkynes remains a challenging proposition. In this context, we report an efficient, two-step method for synthesizing cyclooctynes from cycloheptanones by way of 5-hydroxyalkyl-1*H*-tetrazoles. Treatment of these substrates with carbodiimide reagents leads to the formation and 1,2-rearrangement of a putative alkylidenecarbene intermediate, generating the desired products in good to excellent yield. This ring expansion strategy displays broad substrate scope and functional group tolerance and

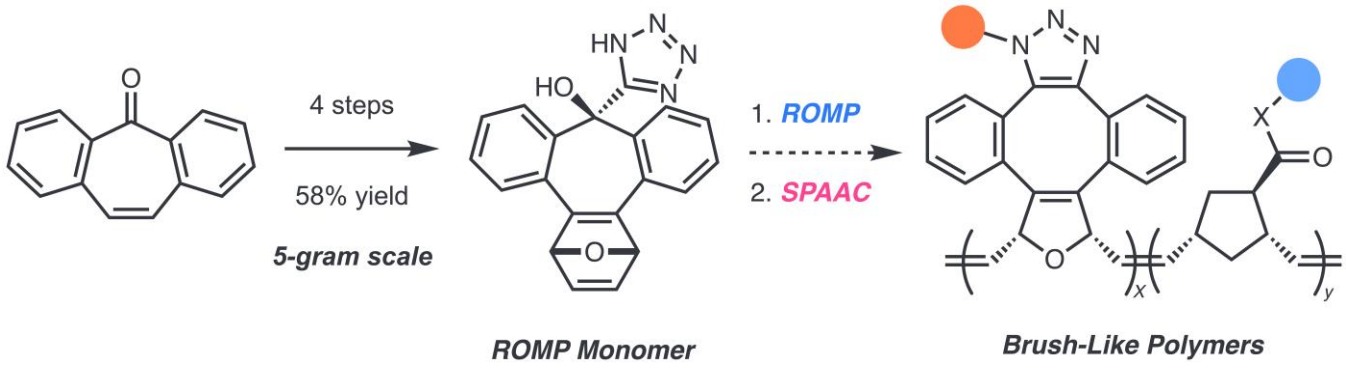
proceeds under mild, non-basic conditions. Details of this methodology and its application to the synthesis of cyclooctynes, both stable and transient, will be described.

2021 GLRM 159

Preparation of a ROMP monomer for post-polymerization click chemistry

***Mario A. Noboa**, marionoboa1@gmail.com, Duncan J. Wardrop. Department of Chemistry, University of Illinois at Chicago, Chicago, Illinois, United States*

The application of azide-alkyne 1,3-dipolar cycloadditions reactions, i.e., click chemistry, in polymer science has proven transformative because it allows for the rapid generation of well-defined polymeric structures in yields that were previously unachievable. We report on our preparation of a strained ROMP monomer which encompasses a latent, strained cyclooctyne in the guise of a 1-(1*H*-tetrazol-5-yl)cycloheptan-1-ol moiety. Details of the diastereoselective synthesis of this monomer, our evaluation of its competency in ROMP reactions, and our efforts to prepare brush-like polymers through post-cyclization click chemistry will be discussed.



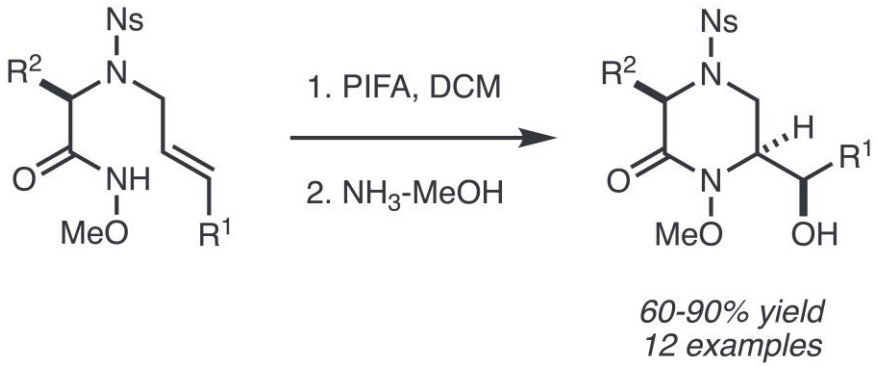
2021 GLRM 160

Diastereoselective synthesis of 6-(hydroxyalkyl)piperazinones via alkene oxamidation

***Jose Ortiz**, kimikortiz@gmail.com, Duncan J. Wardrop. Department of Chemistry, University of Illinois at Chicago, Chicago, Illinois, United States*

Nonaromatic six-membered nitrogen heterocycles feature predominantly in FDA-approved pharmaceuticals and therefore are important targets for method development. Our development of a method for the preparation of 6-(hydroxyalkyl)piperazin-2-ones involving intermolecular alkene oxamidation will be discussed. Treatment ω-unsaturated *O*-alkyl hydroxamates with the hypervalent iodine reagent PIFA mediates cyclization to

yield the products of *anti*-amidotrifluoroacetoxylation. In-situ deacetylation using methanolic ammonia then provides the desired 6-(hydroxyalkyl)piperazinones in good yield. In addition to displaying broad substrate scope, this transformation proceeds with high 1,4-stereoinduction. The origin of this stereoselectivity will be discussed.



2021 GLRM 161

Generation of Azamethide Ylides Through a Multi-Ion Bridge Mechanism

Thomas D. Montgomery*, thomasdmontgomery@gmail.com. Chemistry, Duquesne University, Pittsburgh, Pennsylvania, United States*

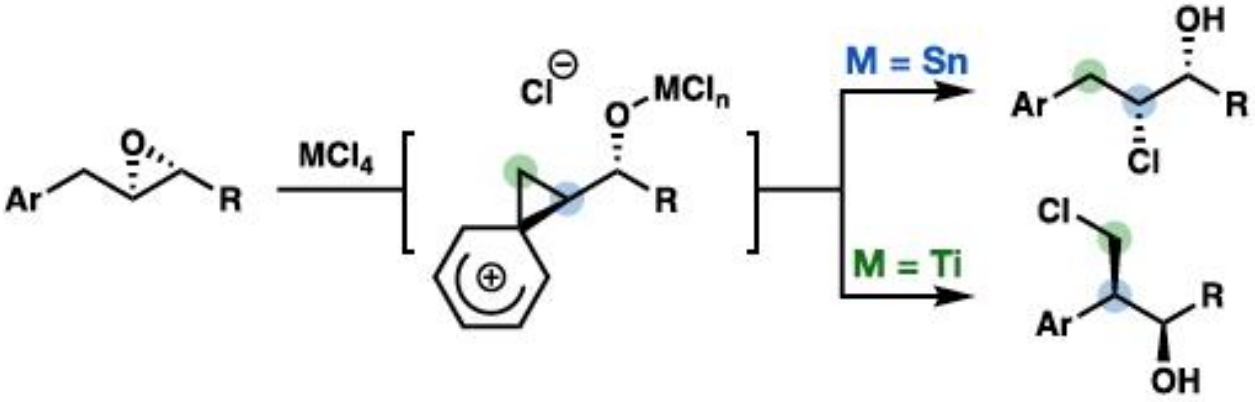
The generation of azamethide ylides from N-oxides was first reported by Roussi over forty years ago. This method offers an atom economical and efficient method for accessing highly functionalized N-heterocycles from base starting materials. However, this chemistry has not been well developed, nor widely utilized, likely due to a lack of a fundimental understanding in how the reaction mechanism occurs. We have used computational tools to probe the likely mechanism of this reaction and have discovered a new reaction pathway that has not been reported previously. This reaction pathway proceeds through a "multi-ion bridge" intermediate and involve no electrophilic intermediates, in contrast to prior understanding and other related systems. We are using this information to inform our own future studies into related mechanisms and developing this system for the synthesis of novel molecules.

2021 GLRM 162

Regiodivergent Opening of Unsymmetrical Phenonium Ions Derived from Epoxides

Nicholas Race*, nrace@umn.edu, Shiyan Xu, Hannah Holst, Shelby B. Mcguire. Chemistry, University of Minnesota, Minneapolis, Minnesota, United States*

In this talk I will discuss our recent work involving selective and regiodivergent opening of unsymmetrical phenonium ions with chloride ions. These reactions employ simple epoxide starting materials and are enabled by the dual role of SnCl4 and TiCl4 as Lewis acids and nucleophilic chloride source. The chemistry is highly selective, stereospecific, operationally simple, and proceeds in good to excellent yields. Product utility will be discussed.

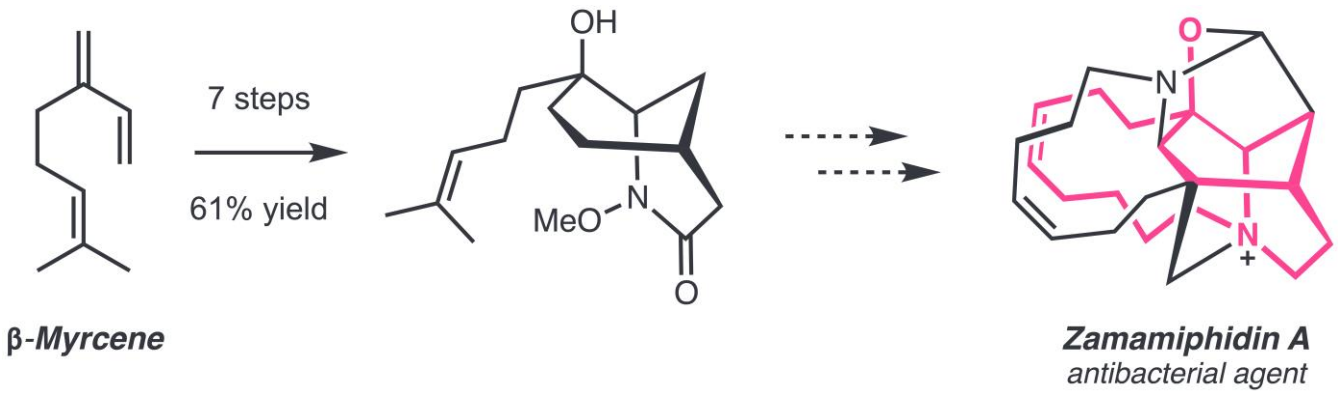


2021 GLRM 163

Progress towards a tricyclic model of the antibacterial agent zamimaphidin A

Mihir Chavda*, mchavd2@uic.edu, Duncan J. Wardrop. Department of Chemistry, University of Illinois at Chicago, Chicago, Illinois, United States*

Zamimaphidin A is an antibacterial alkaloid isolated from the Okinawan marine sponge *Amphimedon* sp. (SS-1231). Although biogenetically related to the manzamine alkaloids, this natural product is imbued with an unprecedented heptacyclic framework encompassing eight contiguous stereocenters within a pentacyclic 1-azatwistane core and two flanking 11-membered rings. The structural novelty of this molecule, coupled with our interest in applying heteroatom-stabilized nitrenium ions to organic synthesis, has led us to explore strategies to access its core structure. Central to this approach's success has been the intramolecular oxamidation of an unsaturated *O*-methyl hydroxamate, which proceeds in high yield and with complete regioselectivity to generate the 2-azabicyclo[3.3.1]nonane core at the heart of the target. Details of this work, together with our progress towards completing our model study, will be presented.



2021 GLRM 164

Approaches for Searching, Characterization and Synthesis of Naturally Occurring Molecules

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Natural Substances have been used as traditional medicaments for centuries. We have also witnessed unprecedented growth in discovery of new biologically active natural substances in modern times. However, in ever increasing number of cases the sources from which the natural product is isolated becomes scarce or nearly extinct. To ensure the stable supply of the compounds traditionally derived from natural sources, the development of new synthetic procedures becomes high priority. The use of chemistry databases is essential to develop an efficient synthesis plan for a specific compound. Reaxys has unique, researcher friendly way to provide both the exhaustive property information and synthesis plans for wide variety of naturally derived substances. We will show several examples how to search natural substance in Reaxys, extract associated properties and identify synthesis plans. We also show how to prioritize the selection of the synthesis plans based on the predefined criteria. The discussed scenarios would be very useful for both novice and expert Reaxys users and can be generalized to other databases as well.

2021 GLRM 165

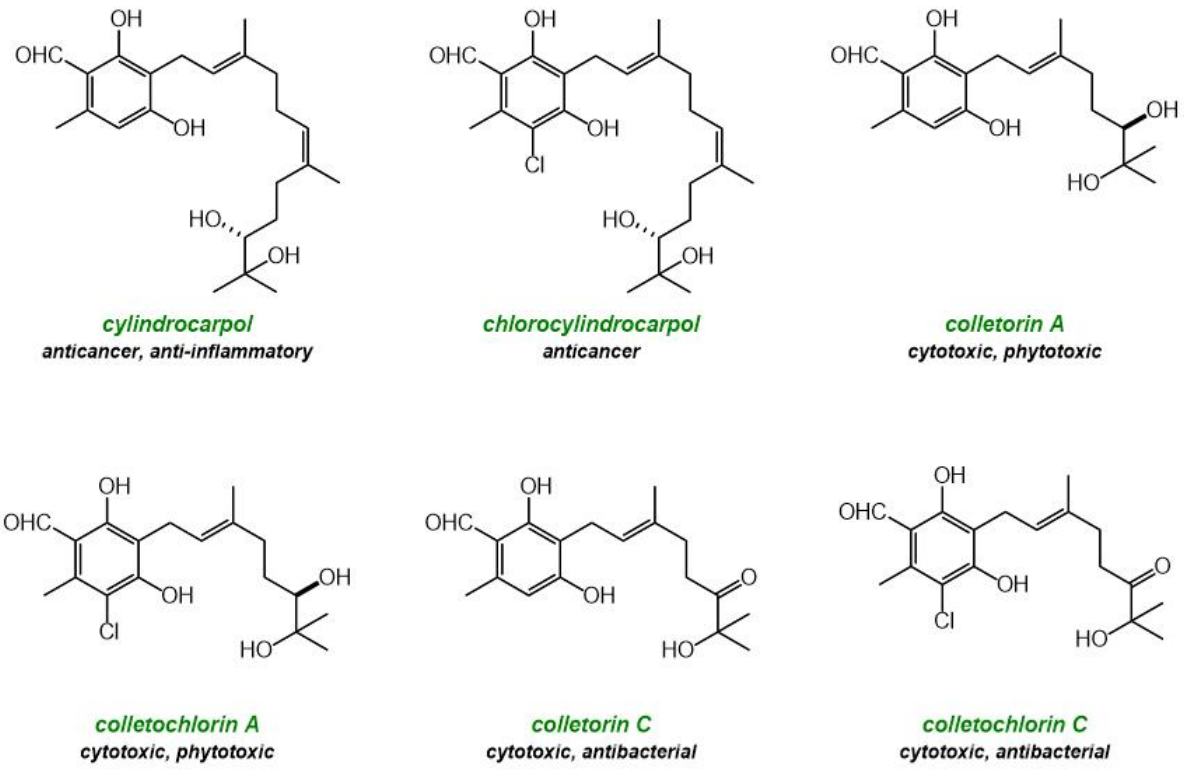
Progress towards the total synthesis of resorcylic natural products.

Daria Galaktionova*, dgalak2@uic.edu, Gennadii Grabovyi, Justin T. Mohr. Chemistry, University of Illinois at Chicago, Chicago, Illinois, United States*

Resorcylic natural products are of an interest due to their variety of fascinating biological properties. However, the dependence on aromatic systems as the starting point of currently available methodologies has thus far impeded the synthesis of a diverse array

of substituted resorcinols. In particular, the synthesis of colletorin A and C, colletochlorin A and C, cylindrocarpol, and chlorocylindrocarpol remains challenging.

Our methodology includes flexible functionalization of a non-aromatic substrate, followed by late-stage halogenative-oxidative aromatization with the controlled regioselective placement of a halogen atom in an aromatic ring in a single step. Different strategies for the late-stage oxidation are explored.



2021 GLRM 166

Developments in enantioselective γ-arylation

***Mihir Chavda**, mchavd2@uic.edu, Daria Galaktionova, Gennadii Grabovyi, Justin T. Mohr. Chemistry, University of Illinois at Chicago, Chicago, Illinois, United States*

C-C bond formation of the distal γ-position is a valuable transformation that leads to a great simplification in the total synthesis, however these types of transformations are often hard to achieve. Challenges often faced when functionalizing the gamma position come from the decrease in nucleophilicity as well as control in regioselectivity. Here, we present our development in enantioselective nickel catalyzed γ-arylation and its applicability to the total synthesis of valuable natural products.

2021 GLRM 167

Studies into the application of phenonium ion intermediates in the synthesis of 4-membered spirocycles

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Phenonium ion formation occurs through anchimeric assistance of aryl rings and has been extensively studied by physical organic chemists. One of the goals of the Race group is to develop operationally simple methods for the synthesis of chiral building blocks from simple starting materials via phenonium ion intermediates.

Our lab recently reported the regiodivergent opening of unsymmetrical phenonium ions with chloride nucleophiles under reagent control. Treatment of 2,3-disubstituted epoxides with $TiCl_4$ or $SnCl_4$ enables the formation of a phenonium ion which can itself be opened by regioselective chloride attack, depending on the Lewis acid employed. I will present my contribution on this project, focused specifically on exploring the functional group tolerance of the $TiCl_4$ reaction conditions and demonstrating the utility of the products obtained.

Following this, I will discuss my more recent work involving the application of the phenonium ion rearrangement chemistry to access spirocyclic scaffolds. These types of molecules are currently challenging to synthesize using known routes yet hold great opportunity for exploring new chemical space. I will present preliminary data highlighting the utility of this approach to access aza- and oxaspiro [3,3] heptane moieties in moderate yields.

2021 GLRM 168

Gamma Functionalization of Unsaturated Ketones via Nitroso Diels–Alder Reaction

SRUTHI MOHAN*, smohan29@uic.edu. CHEMISTRY, University of Illinois at Chicago, Chicago, Illinois, United States*

Despite significant advances in synthetic strategies aimed at functionalizing alpha and beta positions of enones or carbonyl groups, functionalizing their gamma position

remains challenging. Here we report Cu catalyzed regioselective gamma C-N bond formation of enones via Nitroso Diels–Alder reaction followed by N-O bond cleavage using phosphate dienol ether as diene and nitroso benzene as a dienophile. This methodology will lead to a wide variety of drugs and natural products incorporated with gamma amino ketone moiety.

2021 GLRM 169

Synthesis of dihydrofuran derivatives via tandem gamma C–C bond/C–O bond formation with acyclic protected-dienolates

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The synthesis of dihydrofuran derivatives has gained relevance due to their presence in natural products and its applications in medicinal chemistry. Although the synthesis of these moieties has been reported, continuing synthetic methods are still in develop. In this context, we report a new synthetic method via regioselective gamma C–C bond formation of novel acyclic protected dienolates. This approach allows a novel route to a wide range of polysubstituted products in high to excellent yields, from easily accesed starting materials modifications. Details of this methodology will be described.

2021 GLRM 170

Iron-catalyzed γ-Haloalkylation and Haloalkenylation of Enones

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Functionalization of gamma-carbons in enone substrates is a synthetically valuable, yet relatively unexplored reaction. Carbon–halogen bonds are unique bonds in chemistry that are useful for further transformations due to their strong bond polarities. Herein we report our findings for an iron-catalyzed polyhaloalkylation and haloalkenylation at the gamma-carbon of enone containing substrates.

2021 GLRM 171

Design of antibiotics to overcome resistance in mycobacteria

***Courtney C. Aldrich**, aldri015@umn.edu. Medicinal Chemistry, University of Minnesota, Minneapolis, Minnesota, United States*

Mycobacterium tuberculosis remains the leading cause of death due to infection in humans. Although antibiotics are available to treat drug sensitive M. tuberculosis infections, the increasing incidence of drug resistant strains is threating our ability to gain hold of this pandemic. In addition, infections caused by non-tuberculous

mycobacteria (NTM) are increasing globally. These infections are intrinsically resistant to most antibiotics. In this presentation, three short stories will be described of complimentary strategies to overcome drug resistance in mycobacteria including design of novel prodrugs for selective drug delivery with the mycobacterial periplasm, synthesis of rationally designed rifamycin analogs to overcome intrinsic drug resistance by NTMs, and design of antibiotics targeting biotin metabolism that prevent development of resistance.

2021 GLRM 172

Structural Modeling and Analysis of the SARS-CoV-2 Cell Entry Inhibitor Camostat Bound to the Trypsin-like Protease TMPRSS2

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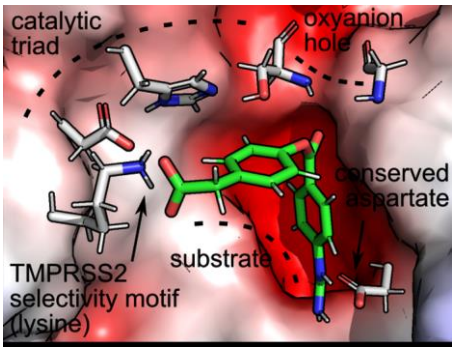
The type II transmembrane serine protease TMPRSS2 facilitates the entry of coronaviruses such as SARS-CoV-2 into host cells. Based on structural data derived from X-ray crystallographic data of related trypsin-like proteases, a homology model of TMPRSS2 is described and validated using the broad spectrum COVID-19 drug candidate camostat as a probe. Both active site recognition and catalytic function are examined using quantum mechanics/molecular mechanics molecular dynamic (QM/MM MD) simulations of camostat and its active metabolite, 4-(4-guanidinobenzoyloxy) phenylacetate (GBPA). Substrate binding is shown to be primarily stabilized through salt bridge formation between the shared guanidinyl pharmacophore and D435 in pocket A (flanking the catalytic S441). Based on the binding mode of GBPA, residues K342 and W461 have been identified as potential contacts involved in TMPRSS2 selective binding and activity. Additional data is reported that indicates the transition state structure is stabilized through H bonding interactions with the backbone N-H groups within an oxyanion hole following bottom side attack of the carbonyl by S441. This is supported by prior work on related serine proteases suggesting further strategies to exploit in the design of more potent inhibitors. Taken overall, the proposed structure along with the key contact sites and mechanistic features identified should prove highly advantageous to the design and rational development of safe and effective therapeutics that target TMPRSS2 and avoid inhibition of other trypsin-dependent processes.



2021 GLRM 173

Development of bioorthogonal chemical probes to study penicillin-binding proteins

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Penicillin-binding proteins (PBPs) are an essential component of bacterial cell growth and division processes. The PBPs function to synthesize and remodel the peptidoglycan layer of the cell wall and do so, in part, using a conserved serine residue in the active site of the transpeptidase domain. This conserved residue has been exploited since the 1940s as an antibacterial target by the β-lactam antibiotics. Despite this, the individual functions and regulation of each PBP homolog are not well understood. A key issue in addressing this is a lack of chemical tools that specifically target each homolog to promote their study. With the rapid and uncurbed rise in antibiotic resistance, it is essential that we further our understanding of the enzymes that are most critical to bacterial cell survival.

To overcome the gaps in PBP knowledge, we have employed β-lactams and β-lactones for the design of PBP-selective activity-based probes that target the active site serine. Importantly, we have identified a β-lactone scaffold that possesses a unique PBP selectivity profile in *Streptococcus pneumoniae*. These probes were designed with a chromophore directly conjugated to the β-lactone to enable selective visualization of active PBP2x and PBP2b via gel-analysis and fluorescence imaging. To expand the utility of our probes, we have generated analogs containing bioorthogonal moieties for addition of the fluorophore after PBP labeling. Beyond increased utility for both fluorescence and mass spectrometry experiments, we found that direct conjugation of differing chromophores to our original probes affected their PBP-selectivity profile — this is a key reason for the use of a biorthogonal group to enable post-protein tagging conjugation to a fluorophore or affinity group. Our next-generation probes are being used to directly visualize PBP activity and spatiotemporal localization throughout cell wall biosynthesis, as well as facilitate the identification of protein partners of the PBPs.

These studies will provide foundational knowledge that will be invaluable in the elucidation of members of the cell division complexes that have yet to be discovered and studying their respective roles and regulations. Our efforts to address gaps in the fundamental knowledge regarding PBPs and cell wall synthesis machinery will contribute to the development of new antibiotics, identification of novel antibacterial targets, and ultimately improve antimicrobial stewardship and public health.

2021 GLRM 174

Paleopharmaceuticals: Prospective drugs from Baltic amber

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Amber is formed through the fossilization of tree resin from various species of pine and pine-like trees over millions of years. The largest known deposits of amber, which originate from now extinct conifers of the family *Sciadopityaceae*, are located in the Baltic Sea region. Amber from this region, referred to as Baltic amber, has been used medicinally for centuries due to its immune-boosting, wound-healing, analgesic, anti-inflammatory, anti-infective, antifungal, and anticancer properties. Despite its well established use in folk medicine, a comprehensive study of the bioactive constituents of Baltic amber has yet to be conducted to explain its therapeutic effects. Furthermore, fossils are an underinvestigated yet promising source of novel drug scaffolds due to the transformations that occur during the fossilization process and the different metabolic products generated by extinct species. Here we report optimized conditions for extraction and identification of compounds present in Baltic amber. We also present a comparison of the compounds extracted from samples of Baltic amber and *Sciadopitys verticillata*, the closest living relative to the extinct conifers that produced the resin that became Baltic amber. Finally, we report *in vitro* antibacterial activity data for parent structures of the identified compounds of interest.

2021 GLRM 175

Design and synthesis of DapE inhibitors as potential antibiotics with a new mechanism of action

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The dapE-encoded *N*-succinyl-L,L-diaminopimelic acid desuccinylase bacterial enzyme (DapE) is an underexplored target that offers the possibility of discovering antibiotics with a new mechanism of action as DapE is essential in all Gram-negative and most Gram-positive bacteria. DapE is a di-zinc metalloenzyme that catalyzes the hydrolysis of *N*-succinyl-L,L-diaminopimelic acid (L,L-SDAP) to succinate and L,L-diaminopimelic acid (L,L-DAP) which is a key reaction in the lysine biosynthetic pathway in bacteria as well as the source of mDAP for cell wall biosynthesis. Due to the absence of lysine biosynthetic pathways including DapE in humans, inhibitors of DapE should serve as broad-spectrum antibiotics with selective toxicity toward infectious bacterial strains without mechanism-based toxicity in humans. DapE enzymes are homodimers where each subunit consists of a catalytic domain and a dimeric domain. We have reported a product-bound crystal structure of *Haemophilus influenzae* DapE enzyme (*Hi*DapE) revealing a dynamic modulation between the open and closed conformations of the receptor which also shows the importance of the dimerization domain in catalysis. We have identified several diverse chemical classes of DapE inhibitors through a high-throughput-screen including *N*-acetylindoline sulfonamides. The inhibition of the DapE enzyme is measured using our newly developed ninhydrin-based assay. Synthetic targets are prioritized by calculating ligand binding modes and binding energies utilizing molecular docking tools including SwissDock and MOE (Molecular Operating Environment). We are also synthesizing thioamide analogs of SDAP, *N*-Me-SDAP, and *N*-di-Me-SDAP as co-crystallization tools to obtain substrate-bound crystal structures of the DapE enzyme. Progress in inhibitor/substrate synthesis and potency will be presented.

2021 GLRM 176

Design, synthesis, and characterization of small molecule inhibitors of HIV-1 capsid protein (CA)

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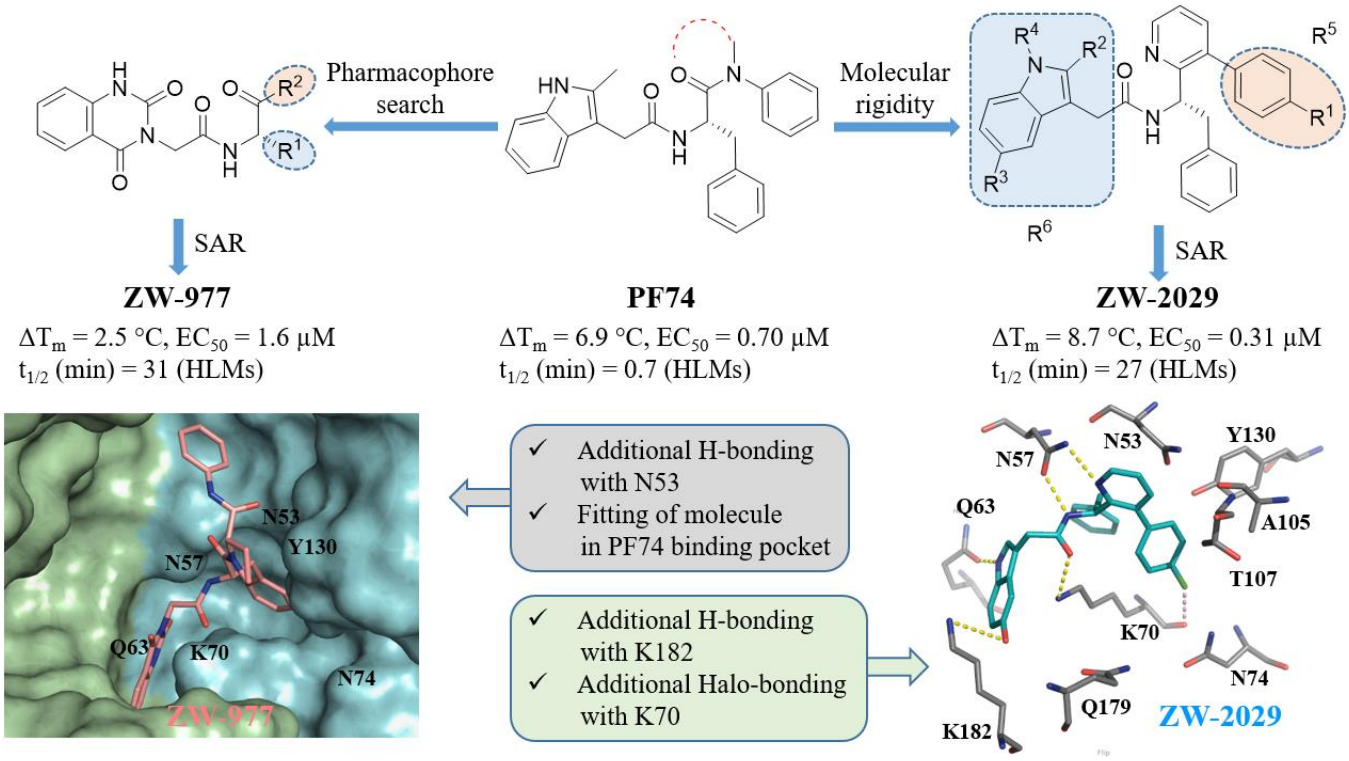
HIV-1 capsid protein (CA) functions in both early and late stages of viral replication. In early stage, CA mediates numerous post entry events leading up to productive viral integration: uncoating, cytoplasmic trafficking, reverse transcription, nuclear import, and integration site targeting. In late stage, CA directs the assembly of immature and mature HIV-1 particles. Therefore, CA is an emerging target for developing mechanistically novel antivirals against HIV-1. Although a few HIV-1 CA-targeting chemotypes have been reported, the peptidomimetic **PF-74** is particularly attractive. By binding to a well-defined pocket at the CA-CA interface which is also used by a few important host

factors, such as Nup153 and CPSF6, **PF74** confers a concentration-dependent bimodal antiviral mechanisms of action. At high concentration it disrupts the CA-CA interactions to impact core stability, whereas at low concentration it inhibits viral nuclear entry and integration site directing by competing against host factors for CA binding. However, the development of **PF74** is largely hindered by its complete lack of metabolic stability. We describe herein two distinct medicinal chemistry approaches to identify small molecules targeting the **PF74** binding site with potent antiviral activity and enhanced metabolic stability. The first approach features a shape-similarity pharmacophore search to find two hits and the subsequent optimization via analog synthesis and SAR. The second approach focuses on introducing molecular rigidity in **PF74** backbone. All newly designed analogs were characterized for their CA hexamer stabilizing/destabilizing effects, antiviral activity, cytotoxicity, and *in vitro* metabolic stability. These assays identified two compounds that showed strong stabilization of CA hexamers, improved or comparable HIV-1 inhibition in comparison to **PF74**, and drastically improved metabolic stability in liver microsomes.



Graphical Abstract

2021 GLRM 177

Binding Modes of N_2P_2 ligands with First-Row Transition Metals

Elodie Marlier[1], *marlier@stolaf.edu, Maddie Logelin*[1], *Burke Meader*[1], *Emily Nolan*[1], *Anna Olson*[1], *Monica Osnaya*[1], *Michelle Soltis*[1], *Meg Swanson*[1], *GH Wood*[1], *Daron E.*

Janzen[2]. (1) Chemistry, St. Olaf College, Northfield, Minnesota, United States (2) Department of Chemistry and Biochemistry, St. Catherine University, St. Paul, Minnesota, United States

Monoanionic mixed N_2P_2 donor beta-diketiminate (BDI) ligands with phosphine pendant arms have been synthesized and metallated with late first-row transition metals. The ligand features both hard and soft donors in an attempt to create an ideal environment for first-row transition metals of varying oxidation states. To understand the binding modes of the ligand with first-row transition metals, substituents have been introduced at different positions on the phenyl linkers. The different binding modes as well as the synthesis and characterization of cobalt, nickel and zinc complexes will be discussed.

2021 GLRM 178

Synthesis of unsymmetrical bisphosphines via secondary phosphine oxides

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Unsymmetric bisphosphines have been synthesized from secondary phosphine oxides (SPOs) as precursors. Traditional phosphine synthetic pathways typically require highly air- and water-sensitive starting materials. SPOs are advantageous as they are both air- and moisture-stable, allowing them to be used on the benchtop without sophisticated air-free techniques. Prepared SPOs were deprotonated with NaHMDS and added to excess 1-bromo-3-chloropropane. The resulting (3-chloropropyl)dialkylphosphine oxides were reacted with different deprotonated SPOs resulting in bis(phosphine) oxides (R2PO(CH2)3OPR’2, R, R’ = Me, Et, i-Pr, Ph, Cy, R ≠ R') which were then reduced to unsymmetric bisphosphines. The phosphines can be coordinated to metal ions as bidentate ligands, potentially creating “chiral-at-metal” complexes depending on metal ion geometry and stoichiometries. Future work will investigate catalytic transfer hydrogenation studies with Ru-complexes bearing these ligands.

2021 GLRM 179

Adsorption of per- and polyfluoroalkyl substances utilizing metal-organic framework materials

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Metal-organic frameworks (MOFs) are readily tailored porous materials capable of adsorbing a wide range of molecules and ions. Here we describe the use of MOFs for the adsorption of per- and polyfluoroalkyl substances (PFAS). Our focus has been on utilizing rapid MOF syntheses and reliable monitoring methods that can be easily carried out by undergraduate students. This talk will describe the results of

undergraduate student researchers, students carrying out senior capstone projects, as well as students in sophomore level laboratory courses.

2021 GLRM 180

Mechanochemistry of Coordination Complexes: Synthesis, Solid-state Photoluminescence, and X-ray Structures

***Daron E. Janzen**, dejanzen@stkate.edu, Nika Rabaey, Maya Butler, Ashley Wilke, Emily Kahlow. Department of Chemistry and Biochemistry, St. Catherine University, St. Paul, Minnesota, United States*

Mechanochemical synthetic methods have been employed in chemical reactions dating as far back as the extraction of mercury from cinnabar described by Theophrastus in the fourth century B.C.E. Not only do mechanochemical methods promote principles of green chemistry, including omission of wasteful solvent, but also can provide access to products for which no solution methods have been reported. Additional reaction condition variables with no parallel solution reaction partner allow for additional synthetic control and opportunities for efficient and selective preparations. Our work has focused on mechanochemical preparation of coordination compounds of Earth-abundant transition metals copper and manganese with solid-state photoluminescence for ease of reaction monitoring as well as applications including triboluminescence. Synthesis and characterization of neutral and complex ion salts including X-ray crystallography and solid-state photoluminescence will be presented. Unexpected mechanochemical milling results including scale-up effects and sample history effects will be described in light of the unique features of mechanochemical reactions.

2021 GLRM 181

Enhanced Nitrogen Oxyanion Reduction Through the Use of Cobalt-based Hybrid-system Electrocatalysts

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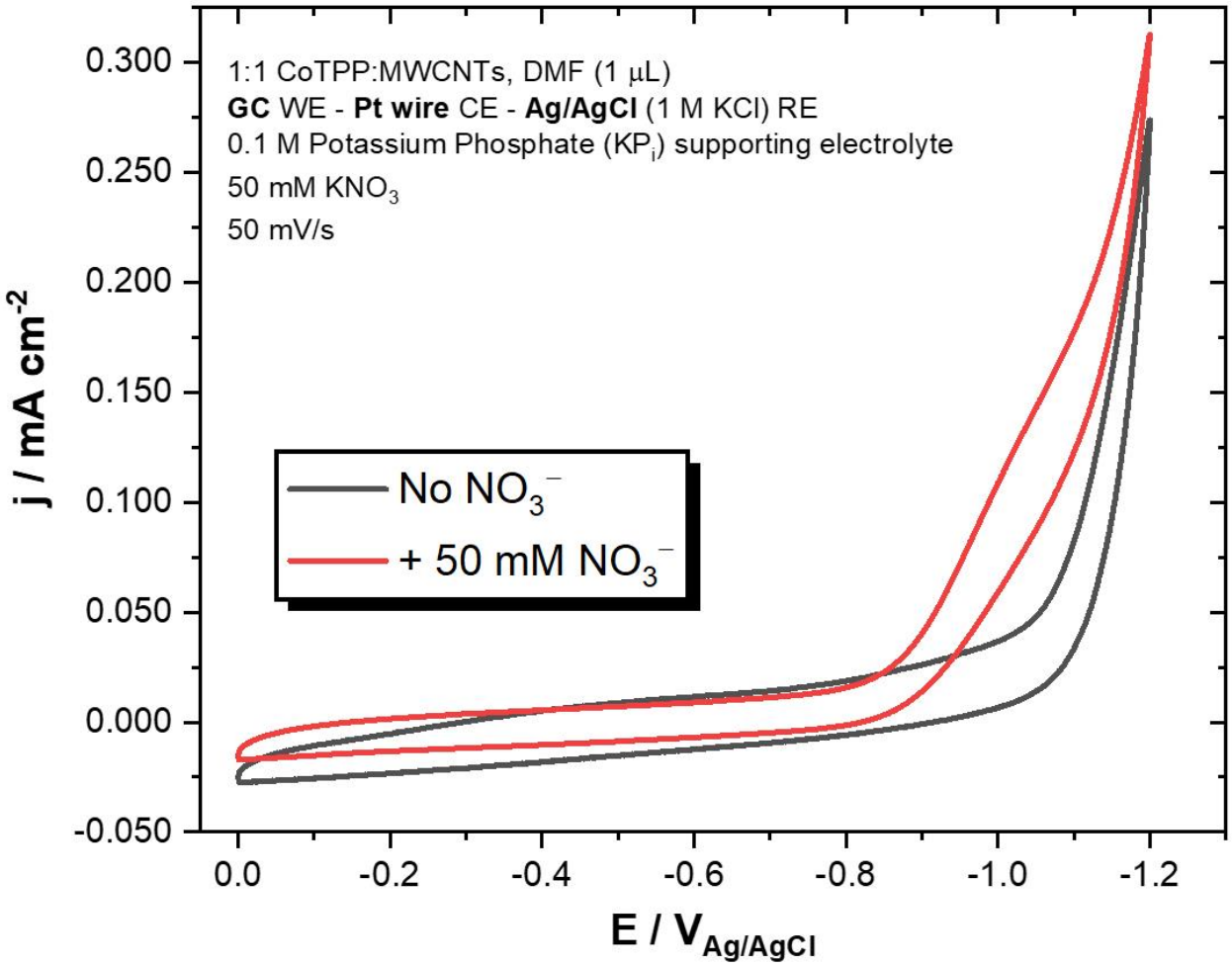
Each year, trillions of tons of Haber-Bosch fertilizers are required to maintain global feedstocks. Booming populations increase industrial demands for Haber-Bosch ammonia, which in turn fuels agriculture and construction. Though the world relies on the Haber-Bosch process for growth and sustenance, harmful nitrogen oxyanion (NO_x) waste generated as byproducts threaten the health of aquatic ecosystems. Nitrogen oxides such as NO_3^- feed cyanobacterial overgrowths, creating hypoxic and unlivable waters. Transition metal electrocatalysts can selectively reduce these water-soluble NO_x compounds in aqueous conditions, without destruction of the catalyst. Here, graphitic electrode surfaces have been modified with the molecular catalyst cobalt (II) tetraphenylporphyrin (CoTPP). The CoTPP macrocycle was immobilized through π-

stacking on multi-walled carbon nanotubes (MWCNT) to create a hybrid electrocatalytic system, which was then drop-casted onto the electrode surface. Remarkably, this hybrid system reduces nitrate in the presence of competitive buffer anions. Preliminary work with a similar graphene-CoTPP hybrid shows promise toward composite characterization and scalability. Future studies aim to optimize robust ammonia production from nitrate in buffer and probe buffer anion and counter-cation influence on Faradaic efficiency.



Electrocatayltic activity of the CoTPP-MWCNTs hybrid system in pH 7 phosphate buffer

2021 GLRM 182

Gold nanoparticles synthesis with the antioxidant flavonoid quercetin

***Annika Holm**, holm9680@bears.unco.edu, Murielle Watzky. Department of Chemistry and Biochemistry, University of Northern Colorado, Greeley, Colorado, United States*

Gold metal nanoparticles are of interest to the scientific community due to their potential applications as biosensors and/or in drug delivery. The goal of this project is to investigate the preparation of gold nanoparticles that could be biocompatible via a green synthesis method. This work looks at modifications of a literature procedure for the bottom-up synthesis of gold nanoparticles in the presence of the readily available flavonoid quercetin, which acts as both a reducing and stabilizing agent. Efforts were focused towards optimizing synthetic reproducibility and nanoparticle stability. UV-visible spectroscopy was used to follow the reaction kinetics by monitoring changes in surface plasmon resonance for the gold nanoparticles. Other methods such as scanning electron microscopy with energy-dispersive X-ray were utilized to characterize the nanoparticles.

2021 GLRM 183

Investigating electron transfer properties between copper complexes for potential Alzheimer's therapeutics

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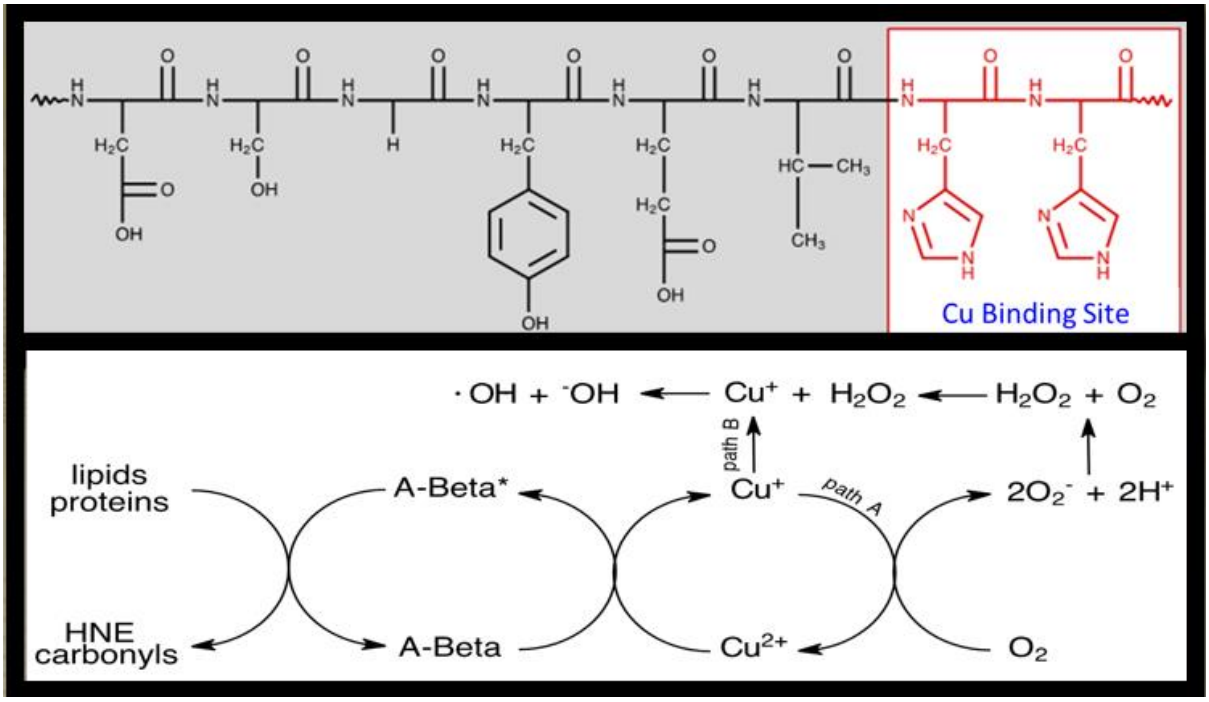
Alzheimer's Disease (AD) is currently the sixth leading cause of death in the United States, and the number of patients affected by AD is only expected to increase as average life expectancy continues to grow. Although there has been a great deal of research focused on understanding the neurochemistry and neuropathology of Alzheimer's Disease, the underlying biochemical mechanism of neurodegeneration remains elusive and misunderstood. In an effort to better understand this mechanism, the role of copper binding to amyloid peptide in AD has been investigated by studying electron transfer properties, reactivities, and peptide aggregation in solution. The relative efficiencies of electron transfers in different copper complexes were investigated using cyclic voltammetry and the relative reactivities were studied by monitoring changes in the production of reactive oxygen species (ROS) over time using different conditions. Overall, the data shows that altering electron transfer can have a positive effect on inhibiting the production of neurotoxic reactive oxygen species.



2021 GLRM 184

Enzyme immobilization via crosslinking to a metal-organic framework for pharmaceutical drug synthesis applications

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A leading biotechnological advancement in the field of biocatalysis is the immobilization of enzymes onto solid supports to create more stable and recyclable systems. Metal-organic frameworks (MOFs) are nanocomposite materials that have been explored as solid supports to facilitate enzyme immobilization. Composed of organic linkers and inorganic nodes, MOFs have a porous structure with large surface areas and have the ability to be modified postsynthetically. Our target enzyme system for immobilization is glucose oxidase (GOx) and chloroperoxidase (CPO). Glucose oxidase is a commercially available enzyme that catalyzes the oxidation of glucose used for many applications in biosensing, biofuel cells, and food production. Chloroperoxidase is a fungal heme enzyme that catalyzes peroxide-dependent halogenation, oxidation, and hydroxylation. These two enzymes work sequentially in this enzyme system by GOx producing peroxide which activates CPO that reacts with a suitable substrate. This study focuses on using a zirconium-based MOF, UiO-66-NH_2, to immobilize the enzyme system, via crosslinking with the MOF's amine group. This study investigates the use of enzyme/MOF crosslinked composites for pharmaceutical drug synthesis applications that are more stable and recyclable than traditional free enzyme biocatalysts.

2021 GLRM 185

Preparation of gold nanoparticles with the plant secondary metabolite (epi)catechin

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Gold metal nanoparticles have found applications in various fields, including catalysis and biosensing. Easily accessible “bottom-up” synthetic methods require a reducing and capping agent that may involve toxic chemicals. Recent interest has focused on the use of biomolecules as an eco-friendly alternative, with the ultimate goal of producing biocompatible gold nanoparticles. In this work, we successfully prepared gold nanoparticles in aqueous solution using the flavonol (epi)catechin as reducing and capping agent. We monitored the reaction progress by following the nanoparticles’ surface plasmon resonance with UV-visible spectroscopy under different concentration and pH conditions. The resulting gold nanoparticles were characterized with UV-visible spectroscopy, scanning electron microscopy, atomic force microscopy, and dynamic light scattering.

2021 GLRM 186

Metal-organic Frameworks for Drug Delivery Vehicles for Photodynamic Therapy

***Ashley Barrera**[1], barreraashley831@gmail.com, Anthony Baudino[4], Kari L. Stone[2], Daniel Kissel[3]. (1) Chemistry, Lewis University, Romeoville, Illinois, United States (2) Department of Chemistry, Benedictine University, Lisle, Illinois, United States (3) Chemistry, Lewis University, Brookfield, Illinois, United States (4) Biology, Lewis University, Romeoville, Illinois, United States*

Photodynamic therapy (PDT) is a phototherapy where light activates photosensitizers and produces oxygen in the triplet state. At this triplet state, photochemical reactions can be done in the presence of oxygen to destroy microbial cells as well as cancer cells. Some photosensitizers used for PDT are chlorins, bacteriochlorins, and phthalocyanines. Many of these photosensitizers can be encapsulated in nano-drug carries due to their insolubility and hydrophobicity. In recent years, metal organic frameworks (MOFs) have been used as potential drug delivery vehicles for photosensitizers in PDT. This study explores how the metal organic frameworks MIL-68-NH_2 and MIL-68 can be used with the photosensitizers’ phycocyanobilin and phthalocyanines in photodynamic therapy. UV/vis spectroscopy data is used to observe the absorption of the photosensitizers in the metal organic frameworks. Furthermore, pH release studies can be done to observe the release of the phycocyanin and phthalocyanines photosensitizers from the MIL metal organic frameworks. The information gained from this study will provide direction into the use of the photosensitizers with the potential to kill microbial cells after being released from its

drug delivery vehicle. In this case, the drug delivery vehicle is the MIL metal organic framework.

2021 GLRM 187

Functionalization of C(sp^3)–H Bond with a Copper(II)/(III) Redox Couple

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Despite the growing interest in the synthesis of fluorinated organic compounds, few reactions are able to incorporate fluoride ion (F^-) directly into alkyl C–H bonds. In this presentation, I will discuss the C(sp^3)–H fluorination reactivity of a formally copper(III) fluoride complex. The C–H fluorination intermediate, **L**CuF, along with its chloride and bromide analogues, **L**CuCl and **L**CuBr, were prepared directly from halide sources with a chemical oxidant and fully characterized with single-crystal X-ray diffraction, X-ray absorption spectroscopy, UV–vis spectroscopy, and ^{1}H NMR spectroscopy. Multireference theoretical calculations reveal significant halide radical character for all complexes, suggesting their ability to initiate and terminate a C(sp^3)–H halogenation sequence by sequential hydrogen atom abstraction (HAA) and radical capture. The capability of HAA by the formally copper(III) halide complexes was explored with 9,10-dihydroanthracene, revealing that **L**CuF exhibits rates 2 orders of magnitude higher than **L**CuCl and **L**CuBr. In contrast, all three complexes efficiently capture carbon radicals to afford C(sp^3)–halogen bonds. The capability of **L**CuF to perform both hydrogen atom abstraction and radical capture was leveraged to enable fluorination of allylic and benzylic C–H bonds and α-C–H bonds of ethers at room temperature. The application of **L**CuF as catalyst in electrochemical fluorination will also be discussed.

2021 GLRM 188

Radical approach to aryne formation

***Jenna Humke**, jennahumke789@gmail.com, Courtney Roberts. Chemistry, University of Minnesota Twin Cities, Minneapolis, Minnesota, United States*

Arynes and heteroarynes are a valuable reactive intermediate used to access functionalized arenes. Despite promising applications in total synthesis, aryne chemistry has been largely underutilized due to lack of a general and convenient method for generating (hetero)aryne intermediates. Existing methods for forming these intermediates typically involve elimination processes which rely on harsh reaction conditions. Furthermore, many existing aryne precursors are not commercially available, therefore require additional prefunctionalization steps prior to the desired transformation.

In order to address these challenges, a new route for aryne formation is being investigated using radical processes. Arynes are typically depicted as aromatic rings

containing a triple bond, however they can also be represented as 1,2-diradical species. Therefore, we are working to apply methods for single aryl radical formation twice in order to form arynes as diradical species. Specifically, we have investigated the decarboxylation of benzoic acid derivates using oxidants. In addition, we are working to trap these radical species with the use of transition metal complexes in order to expand the scope of accessible.

Initial screens using phthalic acid and a variety of oxidants have been conducted and products of protodecarboxylation have been observed, showing that double decarboxylation is possible using these oxidants. First row transitional metals such as Ni and Cu have been screened in order to trap the radical intermediates to form the desired metal-aryne complex. Initial attempts using [Cu^{I}] have shown promising results, and work is ongoing to identify the product of these reaction.

2021 GLRM 189

Superseding substrate control in aryne difunctionalizations

***Erin Plasek**, plase018@umn.edu, Courtney Roberts. Chemistry, University of Minnesota Twin Cities, Minneapolis, Minnesota, United States*

Arynes have long been recognized as powerful intermediates en route to substituted arenes. However, difunctionalizations of unsymmetrical arynes are currently limited due to a lack of controlled regioselectivity. Of particular note are heteroarynes, which are also unsymmetrical and underutilized, likely because of this regioselectivity problem. The research described herein seeks to utilize transition metals to bind and catalyze selective difunctionalization reactions of unsymmetrical arynes. We hope to supersede impractical *substrate controlled* regioselectivities with *ligand controlled* regioselectivities in these difunctionalizations by employing ligands that are sterically and/or electronically unsymmetrical. Preliminary results show a deviation from the inherent regioselectivity of unsymmetrical arynes when a C1 symmetric metal complex is introduced to the system.

2021 GLRM 190

Mechanistic Investigations on the Protodemetalation of Ni(II)-Aryl Complexes

***Paige Piszel**, pep8qn@virginia.edu, Amanda M. Spiewak, Daniel J. Weix. Chemistry, University of Wisconsin - Madison, Madison, Wisconsin, United States*

Protodemetalation of arylnickel intermediates is a key side reaction in nickel-catalyzed cross-coupling and the microscopic reverse of electrophilic C-H activation, yet there are few systematic studies on the topic. We have recently undertaken studies on various arylnickel(II) complexes to better understand how aryl electronics, ligand identity, acid strength, and acid identity influence the rate of this step. Our latest results in this area will be discussed along with implications for improving nickel-catalyzed cross-coupling and C-H arylation reactions.

2021 GLRM 191

Development of a thiazole-containing ligand for use in organometallic transformations

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The five-membered thiazole ring contains a pyridine-like nitrogen; as such, it has the potential to replace pyridine in a variety of ligand scaffolds. As a five-membered ring, the bite angle is likely to be different than a pyridyl; as an electron-rich ring (also containing sulfur), the donor ability is also likely to be different than a pyridyl. Therefore, in this talk we will present results on the synthesis of thiazole-containing organometallic ligands for use in organometallic chemistry and catalysis.

2021 GLRM 192

Node-and-spacer metal-organic frameworks with functional groups in the bridge: synthesis and characterization of zirconium-bipyridyl and -bithiazole porous materials

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The zirconium(IV)-dicarboxylate supramolecular synthon can be used to create robust metal-organic frameworks (MOFs) with pore sizes varying as the length of the bridging unit between the two carboxylates. When the bridge also contains a functional group, chemical and/or chemical sensing of a guest molecule can take place. For example, in the case of aminobiphenyls, the resulting MOF can be used to detect and neutralize certain nerve gases of the "G-series" (sarin, tabun, etc.) chemical warfare agents. We are investigating the robustness of this supramolecular synthon by replacing the aminobiphenyl bridge with other functional groups, results of which will be presented.

2021 GLRM 193

Spatial distribution of low molecular weight BPEI and PEG-BPEI within *Pseudomonas aeruginosa* biofilms

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Chronic wound healing is often exacerbated by infections and about 90% of chronic wounds have biofilms. Bacterial biofilms are communities of microorganisms enclosed in a protective extracellular polymeric substance. Biofilm formation is one of many

resistance mechanisms that pathogens employ to evade existing therapeutics. Furthermore, it is reported that wound healing is delayed by biofilm formation. Among the biofilm-forming pathogens is *Pseudomonas aeruginosa*, a Gram-negative bacterium that easily spreads in healthcare settings. Multidrug resistant (MDR) *P. aeruginosa* infections are among the most serious threats that the Centers for Disease and Prevention (CDC) listed in their 2019 Annual Report. However, previous findings from our laboratory demonstrate that against MDR *P. aeruginosa*, the potency of β-lactam antibiotics can be restored with 600 Da branched polyethylenimine (BPEI). In addition, evidence suggests that 600 Da BPEI can also disrupt pre-formed biofilms. The hydrophilic nature of 600 Da BPEI and its cationic charge likely cause it to interact with anionic targets in the biofilms. However, 600 Da BPEI still creates toxicity concerns that cannot be overlooked. As a result, 600-Da BPEI was modified by attaching a low-molecular-weight polyethylene glycol (PEG) group, resulting in PEG-BPEI. In this study, PEG-BPEI was found to also have an antibiofilm activity against *P. aeruginosa*. In addition, the antibiofilm activity of 600 Da BPEI and its derivative was further characterized via fluorescence studies and microscopy imaging. Data collected via crystal violet assay suggest that biofilm biomass reduction is dose dependent. Furthermore, a biofilm model more suited for wound healing analysis was applied in this study to move the potential therapeutic use of these molecules forward. We envision 600 Da BPEI as a topical agent applied to acute and chronic wounds to combat susceptible and resistant pathogens and reduce the bacterial burden in wound infections.

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600-Da branched polyethyleneimine (BPEI) as a potential adjuvant to neutralize E.coli LPS and biofilm virulence factors.

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Escherichia coli (E.coli) is a Gram-negative bacterium with certain strains that are responsible for mortality and morbidity in medical device-related infections. Due to formation of biofilms, *E.coli* infections are difficult to eradicate. These biofilms protect the bacteria from severe environmental conditions by embedding the microbes in extracellular polymeric substances (EPS) matrix. The *E.coli* biofilms result in formation of stubborn and chronic wound infections due to the development of antibiotic resistance. Current antimicrobial agents are narrow-spectrum macromolecules with restricted efficacy against biofilms. Likewise, *E.coli* lipopolysaccharide (LPS) causes excessive inflammation in wounds and delays wound healing. Toll-like receptor 4 (TLR4) primarily recognizes, and is activated by bacterial endotoxin, leading to signaling events that eventually culminate with the release of inflammatory cytokines. In humans, uncontrolled production of inflammatory responses induced by bacterial endotoxin develops severe physiological responses and causes endotoxin shock and impaired wound repair. There is a need for new therapeutic adjuvants with effective drug delivery

mechanism to disrupt *E.coli* biofilm growth, alleviate wound infection, and improve healing activity. Recent studies in our lab show that 600-Da BPEI is able to facilitate the uptake of drugs and lower drug influx barrier as a potentiator in bacteria and bacterial biofilm. Additionally, it has been shown that BPEI can suppress interleukin-8 (IL-8) production in response to endotoxin induction and reduce inflammation. Inflammation reduction helps prevent many acute ulcers from becoming chronic wounds and alleviates the risk of recurrent infection and tissue necrosis. In the current study, the ability of BPEI to neutralize *E.coli* lipopolysaccharide (LPS) and disrupt *E.coli* biofilms has been demonstrated. Also, we show the effect of BPEI treatment on the expression profile of *E.coli* virulence genes involved in biofilm formation. Overall, we propose that BPEI is a multi-functional agent that can reduce biofilm formation, lower LPS-induced inflammation, eliminate *E.coli* pathogenicity, and eventually speed up wound healing.

2021 GLRM 195

Antimicrobial properties of Ginkgo Biloba

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As more bacteria and diseases are being discovered and spread throughout the human population, there is a larger need than ever for new antibiotics, which have caused many drug manufacturers to turn to alternative sources of potential antibiotics, such as natural products. The purpose of this study was to examine and determine whether the herbal medicine, Ginkgo Biloba, has any antimicrobial properties. The results varied as we used different combinations and methods of extraction and testing procedures. However, through our data, we determined that methanol extracts of Ginkgo leaf and ethanol extracts of Ginkgo produced the best results for this study. Our procedure included extracting the organic compounds from gingko leaves and pill concentrates with grinding and mixture with ethanol and methanol. Then we used the extract to test it against different ESKAPE pathogens: the most successful cases being *Bacillus subtiliis* and *Acinetobacter baylyi*. Our results show that Ginkgo Biloba has some medicinal properties that could help in killing certain types of bacteria.

2021 GLRM 196

Design of COVID-19 antivirals using computer modeling

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The discovery and development of effective antiviral drugs for COVID-19 are urgent and ongoing. An initiative to contribute to this process is COVID Moonshot project. The aim

of the project is to rapidly develop easily manufacturable antiviral drugs that can inhibit the SARS-CoV-2 main protease. To provide leads for the intractable biological target in COVID, we used fragment-based drug discovery which identifies low-molecular weight ligands that bind to biologically important macromolecules. Our group started with the fragment x1086 from the COVID Moonshot Consortium and successfully designed new molecules in SeeSAR, a 3D modeling software platform. We designed the molecules from different bonds from the fragment and calculated their estimated affinities and other physicochemical properties. We selected the compounds with the best estimated affinities from the 341 compounds we designed in SeeSAR from each bond and entered them into swissADME and ADMETSAR, websites that predict physicochemical descriptors and absorption, digestion, metabolism, excretion, and toxicity (ADMETox) parameters. These websites allowed us to see if our best binding affinity molecules were druglike and had good ADMETox properties. Specifically, we looked at Lipinski's rules and human ether-à-go-go related genes (hERG inhibition). We submitted our best eight compounds, which demonstrated the best affinity and drug-like properties, from the 341 molecules that were designed to the COVID Moonshot Initiative for further testing and drug development.

2021 GLRM 197

Design of SARS-CoV-2 main protease inhibitors by computer aided drug design

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In early December 2019, a novel coronavirus pandemic broke out in the city of Wuhan, China Hubei Province. As of the end of February 2021, nearly 114 million people have been infected worldwide, and over 513 thousand have died in the United States alone.. SARS-CoV-2 is a positive-sense, enveloped, single-stranded RNA Betacoronavirus and is the disease-causing agent for Covid-19. Of many SARS-CoV-2's proteins, its main protease (MPro) is the primary target for drug discovery efforts. The COVID Moonshot project focuses on inhibitors for mPro using the crowdsourced medicinal chemistry insights of companies and chemists around the world. A fragment from the COVID Moonshot database (x2600) was selected as a starting point to design new compounds. Using molecular simulation software such as SeeSAR, new compounds were designed and their binding affinities computed. ADME prediction websites such as AdmetSAR and SwissADME, were utilized to compute the new compounds' pharmacokinetic and physicochemical properties. The newly designed compounds improve on aspects such as binding affinity, torsion angles, ligand lipophilicity efficiency, and pharmacokinetic properties.

2021 GLRM 198

Towards Chemical Probes for APOBEC DNA Cytosine Deaminases

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The APOBEC family of enzymes facilitate the hydrolytic deamination of cytosines to uracils in single-stranded DNA substrates. These enzymes usually function to restrict foreign and pathogenic DNA in cells as part of the innate immune response. However, the activities of certain APOBEC enzymes, such as APOBEC3A, APOBEC3B, and APOBEC3G, facilitate genomic mutations that confer a growth and survival advantage for viruses and tumors. Therefore, the development of chemical modulators of APOBEC enzymes may ultimately confer therapeutics for multiple indications. Our laboratory has contributed to the development of nucleic acid- and small molecule-inhibitors of multiple APOBEC enzymes using a variety of discovery approaches. Our recent work to develop potent and selective chemical probes for discrete APOBEC enzymes will be presented.

2021 GLRM 199

Impact of Rng Size on the Biological Activities of Ipomoeassin F

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To date, several macrocyclic natural products, including ipomoeassin F, have been discovered to inhibit Sec61-mediated translocation of many membrane and secretory proteins in mammalian cells. Apparently, a ring scaffold seems to be the most pronounced common structural feature among these compounds; however, the ring size varies significantly, ranging from 12- to 30-membered ring. This raised an intriguing question about whether the nature has already selected the optimal ring size for each family of these molecules. To address this question, two ring-size-varying analogues of ipomoeassin F were synthesized and evaluated for their biological activities. Although decreasing the ring size from 20 to 19 caused more than 20-fold loss in cytotoxicity, increasing the ring size by 2 improved cytotoxicity by ~3-fold and in vitro protein translocation inhibition by ~2-fold. This delivers the encouraging message that there is unexplored chemical space in the binding pocket of Sec61α. Incorporation of new peripheral functionalities around the macrocyclic core of the ipomoeassin family of resin glycosides may lead to new chemical entities with further enhanced potency and even selectivity.

2021 GLRM 200

Synthesis of open-chain analogue of Ipomoeassin F

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Most resin glycosides exhibited only moderate inhibition activity against cancer cell growth. However, ipomoeassin F is exceptionally cytotoxic. To accelerate ongoing

chemical biology research on ipomoeassin F, research in our group is focused on the total synthesis of a novel simplified open-chain analogue **1** from commercially available D-glucose and L-arabinose based on previous SAR studies. It is expected that biological assessment of the analogue **1** would direct future design of ipomoeassin - derived chemical probes for studying biological pathways related to protein biogenesis.

2021 GLRM 201

Universal agent for wounds infected with drug-resistant *Pseudomonas aeruginosa* and Carbapenem-resistant *Enterobacteriaceae* (CRE), including those possessing metallo-beta-lactamases.

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Healing wounds infected with bacteria requires agents that (1) overcome drug-resistant pathogens, (2) disrupt biofilms, and (3) reduce inflammation from pathogen associated microbial molecules (PAMPS). We show data that one molecule -- 600 Da BPEI that is PEGylated to improve safety -- accomplishes these 3 goals. PEG-BPEI potentiates common antibiotics against drug-resistant *Pseudomonas aeruginosa, Escherichia coli, and Klebsiella pneumoniae*. These pathogens both intrinsic and acquired antibiotic resistance, making clinical management of infection a real challenge, particularly when these bacteria are sequestered in biofilms. Against *Enterobacteriaceae* and their

biofilms, the potency of β-lactam antibiotics is restored with 600-Da branched polyethylenimine (600-Da BPEI). Checkerboard assays using microtiter plates demonstrate the potentiation of piperacillin, cefepime, meropenem, imipenem, and erythromycin antibiotics. Growth curves demonstrate that a combination of 600-Da BPEI and piperacillin produces bacteriostatic effects. Scanning electron microscopy (SEM) was used to confirm that the combination treatment leads to abnormal morphology. Data collected with isothermal titration calorimetry and fluorescence spectroscopy demonstrate a mechanism of action in which potentiation at low concentrations of 600-Da BPEI reduces diffusion barriers from lipopolysaccharides without disrupting the outer membrane itself. LPS also stimulates pattern recognition receptors, leading the release of pro-inflammatory cytokines. BPEI and PEG-BPEI bind to LPS to reduce cytokine production. Coupled with the ability to overcome reduce antibiotic activity and biofilms exopolymers, PEG-BPEI provides new opportunities to counter the rise of multidrug-resistant infections.

2021 GLRM 202

Synthesis and *in-silico* analysis of azo-dye inhibitors of low molecular weight protein tyrosine phosphatase

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Low molecular weight protein tyrosine phosphatase (LMW-PTP) is an enzyme that acts on many phosphotyrosine-containing cellular proteins involved in signal transduction, including aberrant growth factor signaling. Recent studies have assessed the role of LMW-PTPs in malignant cell transformation and have shown that the expression of LMW-PTP mRNA and protein is significantly increased in human breast, colon, bladder, and kidney tumor samples. Moreover, its enhanced expression is generally prognostic of a more aggressive cancer and reduced survival rate. Small molecule inhibitors of LMW-PTP have been investigated for their anti-cancer properties by inhibiting dephosphorylation of certain receptors. Twenty-three azo dye analogs of (4Z)-4-[[4-(carboxymethyl)phenyl]hydrazono]-3-keto-2-naphthoic acid, a lead compound from a previous study in our lab, were synthesized and their binding to LMW-PTP isoform B was examined *in silico*. Multiple potential inhibitors demonstrated promising computational affinities, indicative of therapeutic potential which will eventually be further examined using *in-vitro* assays.

2021 GLRM 203

Synthesis of Potential Anti-parasitic Heterocyclic Compounds

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Schistosomiasis is a disease caused by parasitic worms of the genus *Schistosoma,* which can cause severe problems to the digestive tract in humans. Currently, there are only two drugs available to treat schistosomiasis, praziquantel and oxamniquine, which is problematic because the schistosomes might build up resistance to these drugs, which will decrease their effectiveness. Previous work has identified an antimalarial quinoxaline as a potential lead compound for anti-schistosomiasis drug development. Here, we present progress toward the synthesis of analogs of this lead compound with different amine substituents (e.g., 1,2-ethylenediamine, N,N-dimethylethylenediamine, and propargylamine). Once synthesized, these compounds will be tested for antiparasitic activity as well as cytotoxicity.

2021 GLRM 204

It's the items that make the assessment: Studies of test and item properties including item environment effects

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For over 85 years, the American Chemical Society, Division of Chemical Education's Examinations Institute (ACS Exams) has developed and produced chemistry tests utilizing exam committees of expert instructors. Similarly, instructors regularly write, administer and grade assessments ultimately to assign a grade for a course. These classroom assessment efforts can be valuable measurements of the progress of students through the program, and efforts to associate measurements between multiple courses in a program are routinely included in programmatic assessment requirements. But, how are tests developed, and, once written, what processes are in place to evaluate the test? Because tests are commonly used as a measurement for the degree to which a student understands the content, it is important that they are psychometrically sound instruments. Considerations as to what is the best measure of performance and how to capture this is important. This leads into item-level investigations including classic test statistics, item content, and item fairness. Item environment effects must be examined to understand and accommodate for item-order effects. Methods for examining for item fairness and the results of these analyses will be also presented.

2021 GLRM 205

Longitudinal hierarchical linear modeling of the impact of a transformed general chemistry curriculum on student performance in organic chemistry 1

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Since 2013, the transformed general chemistry curriculum CLUE—Chemistry, Life, the Universe, and Everything—has been implemented at Michigan State University, leading to full implementation in Fall 2015. Its conception, design, and evidence have been published extensively. Building on the theoretical alignment and design process, the transformed organic chemistry curriculum OCLUE—Organic Chemistry, Life, the Universe, and Everything—has been developed and implemented starting in Fall 2016. In this poster, we explore the impact of the transformed general chemistry curriculum CLUE on student performance in first-semester organic chemistry curricula (OCLUE and traditional).

Previous literature has suggested a strong connection between math preparation and general chemistry achievement for traditional general chemistry curricula. A previous exploratory analysis using multiple linear regression (MLR) suggested that general chemistry 2 course grade, high prior cumulative GPA, and enrollment in the transformed organic curriculum OCLUE have significant positive effects on the organic chemistry 1 course grade earned, whereas advanced academic standing (sophomore, junior, etc) has a negative significant effect. Math preparation scores (math ACT, math SAT, or MSU's math placement exam) did not have a significant coefficient in the MLR model. However, given the nested nature of this student data, we utilize a three-level hierarchical linear model (HLM) to model the variation and influence of student covariates, general chemistry 1 and 2 course grades, and whether the student took fully transformed or fully traditional general chemistry courses.

2021 GLRM 206

Using molecular modeling to teach visual-spatial reasoning

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Many types of imagery are used in teaching scientific information and they require that students possess visual-spatial cognitive abilities that are not explicitly taught in preparation for or during science classes. This NSF funded study used the program Jmol to help students learn about the 3D structure/function relationship of different hemoglobin molecules. Students chose hemoglobin molecules from the Protein Data Base and used the Jmol program to highlight important amino acids in the proteins and/or other important parts of the molecules chosen. This included original research into these hemoglobin molecules, by reading the primary scientific literature, and was followed by a poster presentation at a local Undergraduate Research Conference. The Jmol information was then made into physical models by the Center for BioMolecular Modeling at Milwaukee School of Engineering and used as teaching tolls in classes.

2021 GLRM 207

Gamified Process Oriented Guided Inquiry Learning Activities (gPa)

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Poor academic performance and high student attrition rates in general chemistry courses have resulted in the perception of chemistry courses as gatekeepers for students in pursuit of STEM areas. POGIL has shown promising results in both lecture and laboratory teaching on student performance in chemistry, while gamification has been used to enhance student learning experiences, and to help students grasp chemistry concepts in an engaging manner. In this presentation, some gamified POGIL activities (gPa) will be presented along with findings on the impact of these activities on student engagement and performance in chemistry.

2021 GLRM 208

Engaging Students in Inquiry of Snow Chemistry Processes Informed by Local and Traditional Knowledge

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Temperatures are rising faster in the Arctic than anywhere else on Earth. The resulting sea ice loss and permafrost melt are threatening the traditional knowledge practices and culture of the Iñupiat residents of Utqiagvik, Alaska, the northernmost community in the United States. The intersection of traditional knowledge and western science in Utqiagvik makes this a unique place for understanding how students utilize traditional knowledge to inform their inquiry of snow chemistry processes. The Iñupiat people have lived in Utqiagvik for thousands of years and rely upon subsistence hunting for survival. More recently, climate scientists have established research facilities in Utqiagvik to study the changing Arctic. We designed and constructed a culturally responsive science unit to engage students in developing a research project focused on changing climate patterns in the Arctic. In this snow chemistry unit, students interviewed community members to gather local and traditional knowledge, learned about snow chemistry through a Process-Oriented Guided-Inquiry Learning (POGIL) activity, and developed research questions and snow sampling protocols with an environmental chemistry researcher. In this presentation, we will report student reflections about how important it was for them to learn about the traditional knowledge of the Iñupiat people as it informed their research questions and methodology. In future iterations of the course, we plan to continue to engage students in inquiry of snow chemistry processes informed by

local and traditional knowledge by incorporating flexibility in the timing of snow collection and designing a new protocol for quantitating chloride ions in snow.

2021 GLRM 209

Examination of the impact of a success coach on student success in STEM through intrusive advising

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In August 2016, College of DuPage initiated a STEM Student Success program funded by a grant from the National Science Foundation's S-STEM program. The program's objectives are to (1) increase the number of financially needy and academically talented students who graduate or transfer in a STEM program and (2) improve the retention and completion rates of STEM students through individualized and group support systems. A central feature of the program is the use of a STEM Student Success Coach as the first line of support for participating STEM scholars. The use of the Success Coach provides a testing ground for the "intrusive advising" method used in the Guided Pathways model that is currently being implemented at numerous two-year and four-year colleges, including College of DuPage. We will present our most recent results from an evaluation of the academic performance of the S-STEM cohort compared with a non-scholarship cohort, selected for similar academic preparedness, in a range of common STEM classes.

2021 GLRM 210

Considering student perspectives to advance educational transformation, diversity, and inclusion in chemistry

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National calls for the transformation of undergraduate chemistry education have not yet led to widespread advancements in diversity, equity, and inclusion (DEI). Consequently, the severe underrepresentation of Black, Latinx, and other racial minority student populations in chemistry remains a pressing problem. Given this troubling reality, the main goal of this presentation is to discuss research-based recommendations that chemistry departments should consider enacting to advance systemic educational transformation, particularly to better facilitate the success of underrepresented racial minorities (URMs) in chemistry and STEM broadly. The recommendations are based on findings from qualitative studies involving 1) interviews with high-achieving 16 URM chemistry majors largely focused on eliciting rich insights on motivations and perceptions of the learning environment; and 2) 1092 general chemistry students' responses to an open-ended survey question centered on teaching practices. Drawing

on the anti-deficit achievement framework, self-determination theory, and theory of affordances, preliminary analysis revealed the following: 1) URM students are autonomously motivated to major in chemistry; 2) Departmental barriers including *ineffective teaching practices, lack of mental health resources, and lack of diversity in faculty and students* impeded URM student success in chemistry; 3) 29 teaching-related affordances were identified as supportive of learning in general chemistry. The 29 affordances were organized within four main categories-*instructor personality traits* (e.g., approachable), *engagement strategies*(e.g., demonstrations), *teaching methods* (e.g., interactive class discussions), *instructional resources* (e.g., practice exams), and *out-of-classroom support* (e.g., office hours). The 29 affordances taken together describe teaching as a complex, multidimensional practice. Collectively, the research findings call for departmental responsibility to advance DEI and student success in chemistry. Key recommendations for chemistry educational transformation will be discussed.

2021 GLRM 211

Early authentic research across the educational spectrum

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This presentation describes development and implementation of an early authentic research program for students at multiple education levels. Early research is defined as authentic research conducted sooner than traditionally done; specifically, by high school students, community college students, and college underclassmen. We have also coined the term ‘interlevel’ for research projects and programs that are done collaboratively and or synergistically across multiple education levels. This innovation arises from simultaneously teaching both high school and college chemistry on the campus of Andrews University over the last twenty-five years. In addition, while historically underrepresented groups (HUGs) are generally and conventionally classified in STEM on the basis of race, gender, socioeconomics and disability, our early research definition introduces the cross-demographic classification of age. Interlevel research across the educational spectrum is rare, undefined and untapped in contrast to interdisciplinary research and collaborations which are well known, defined and commonplace.

2021 GLRM 212

Diversity and Inclusion in Science Teaching and Learning (DISTL): A focus on undergraduate chemistry courses

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Students in Science, Technology, Engineering and Mathematics (STEM) come with a wide range of experiences and educational backgrounds. There is high attrition rate and low academic achievement among students in STEM areas, specifically in college chemistry courses that are prerequisites for many STEM majors. Hence it is important to look at diversity and inclusion in the first- and second-year college chemistry courses to address the challenge of student attrition in STEM. Diversity can be understood as the differences each student brings along the dimensions of prior knowledge, skills, race, ethnicity, sexual orientation, gender, socio-economic status, age, ability, religious or political beliefs, or other different ideologies that makes students individually unique. This presentation will focus on student and GTA understanding of DISTL, the design and use of DISTL modules to draw student attention to diversity in chemistry, and the impact of these modules on student understanding of chemistry.

2021 GLRM 213

Molecular Pedal Motion as a Means to Control Thermal Expansion Within Organic Solids

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The ability of stilbene and its derivatives to undergo molecular pedal motion in crystals is a common and often overlooked phenomenon in the area of organic solid-state chemistry. This type of dynamic motion is important in the realm of the light induced [2 + 2] cycloaddition reaction. In particular, a photostable conformation of a pair of carbon-carbon double bonds can undergo this motion to yield an orientation that is suitable to undergo a photoreaction. In a similar manner, this dynamic motion will influence the thermal expansion parameters of crystalline solids due to the inherent ability of these molecules to undergo this type of movement. In this presentation, the role of molecular pedal motion as it effects the thermal expansion within hydrogen-bonded co-crystals will be discussed. Special attention will be given to not only the overall structure of the co-crystals, but how the tendencies of each co-crystal to undergo pedal motion influences the observed thermal expansion will be addressed.

2021 GLRM 214

Everything Solid-state in Three Weeks: CHEM296 in January Term 2018

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“CHEM296: Organic Chemical Crystallography” was a first-time attempt in January of 2018 to bring this topic to undergraduate students at an especially early stage of their academic careers. With one semester of organic chemistry being the only prerequisite for the course, the class included a mix of sophomores, juniors, and seniors. Only two students had previously encountered symmetry in previous coursework (physical

chemistry). In addition to being intended to reach the widest possible audience, the course was intended to cover as broad a range of solid-state topics as possible, including not only the basics of X-ray crystallography but also some of its history and its broader application in solid-state organic chemistry. Over a period of fifteen two-hour class meetings, topics addressed included X-ray diffraction and practice, point-group and space-group symmetry, Weissenberg and precession photography, solid-state photochemistry (both historical and contemporary), conventional and non-conventional hydrogen bonding in crystals, graph sets, and polymorphism. Extensive use was made of the Cambridge Structural Database. Students used the Olex2 program package to refine structures provided by the instructor and the Mercury program to analyze the results. Although student feedback was generally positive, the course will require refinement before it is offered again, and the question of whether it would be more effectively offered as a semester-long course rather than concentrated into three weeks remains to be answered. As offered that January, the course did effectively provide a group of undergraduate students a window into a world of chemistry that they might not have encountered otherwise.

2021 GLRM 215

X-ray crystallography at Georgia Southern University – A tale of teaching and research

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The purchase of the Rigaku XtaLAB Mini X-ray Diffractometer in 2012 allowed for an expansion of teaching and research in the department of chemistry and Biochemistry at Georgia Southern University. The authors developed a team-taught course in X-ray Crystallography for undergraduate and M.S. graduate students that has taken various forms since its advent in 2014. The course is designed to bring theoretical and experimental aspects of crystallography to the students as well as access to the instrument in the course as well as in research activities. The diffractometer has allowed for the faculty to expand scholarly output as well as the collaborative web of faculty within and external to GSU. To date 40 peer-reviewed publications with undergraduate co-authors and trained 32 undergraduate students to grow and mount crystals, run data collection, and at times solve crystal structures using the most current Olex2 software. This talk will highlight the teaching and research that has been realized since the acquisition of the Rigaku XtaLAB Mini.

2021 GLRM 216

Visualization tools for teaching crystal packing and crystallography in the undergraduate curriculum

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The arrangements of atoms and the symmetry relationships between the atoms and molecules in crystalline materials are difficult to visualize, even with sophisticated virtual and physical models. We have created both computer and 3D-printed models of unit cells, molecules, and decorated solids that work together to help students understand these basic structures.

For General Chemistry, we have created 3D-printed models of the unit cell contents of simple cubic, body-centered cubic, face-centered cubic, and hexagonal close-packed structures. These models (along with a companion website) emphasize the relationships between the close-packed atomic layers and the unit cell contents and the structures of related ionic materials. We have incorporated these materials into our laboratory course enhancing a model-building exercise with computer representations and 3D building blocks to demonstrate lattice-point sharing, packing efficiency, and coordination number.

Web-based materials for teaching symmetry have been extended to include crystallographic point groups and the symmetry-relationships found in selected space groups and are suitable for use in upper-level courses. While students may have been introduced to symmetry in other courses such as Inorganic or Physical Chemistry, these resources emphasize crystallographic symmetry and the notation used within crystallography. Additionally, we have developed an interactive 2D Fourier transform website that demonstrates the reciprocal relationships found in diffraction. This site serves as a natural extension to the popular optical transform demonstration.

A 3D-printed model of a body-centered unit cell.

2021 GLRM 217

Using Powder X-ray Diffraction in a Solid-state Chemistry Course

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Students obtained powder X-ray diffraction data on metals, solid solutions, yttrium barium copper oxides and metal organic frameworks during the laboratory component of a solid-state chemistry course. By doing multiple labs students were exposed to the importance of sample preparation, instrument maintenance, and data analysis. This talk will focus on skills student developed and challenges encountered. The speaker seeks input from the audience on how labs might be modified to emphasize course concepts more clearly.

2021 GLRM 218

Using powder XRD system to probe single crystals

Nenad Stojilovic, *stojilovicn@uwosh.edu. University of Wisconsin Oshkosh, Oshkosh, Wisconsin, United States*

Powder X-Ray diffraction (XRD) system is one of the most widely used analytical instruments in chemistry, physics and materials science research, and can be a very valuable tool in undergraduate student education. In this presentation, I will discuss how powder XRD system can be used to probe single crystals, and what students can learn through inquiry-based activities. In particular, I will discuss activities which mimic real research and some challenges that instructors and students may face during implementation of proposed activities in the undergraduate curriculum.

2021 GLRM 219

Sweet video presentation for practical crystallography education

***Alain Beauparlant**, beauparlant@etsu.edu, Cassandra T. Eagle. Chemistry, East Tennessee State University, Johnson City, Tennessee, United States*

At ETSU, we teach a first year General Chemistry II x-ray crystallography experiment and a senior level analytical x-ray crystallography experiment. To assist in teaching the practical crystallography aspect of the experiments, we wrote a script and filmed a twenty-minute video that teaches students how to run a single crystal X-ray crystallography experiment using table sugar. The video guides students in selecting a suitable crystal, mounting it on a fiber, centering it inside the diffractometer, running the experiment, reducing the data, solving the structure and preparing an ORTEP. The video may be used either as a stand-alone background material for a virtual lab, or as preparation for a live experiment. Although currently used in the asynchronous labs we are teaching, this video builds on ongoing work since 2019 in developing live single crystal X-ray crystallography experiments for the undergraduate curriculum using table sugar and Epsom salt.

2021 GLRM 220

X-ray Crystallography at a Primarily Undergraduate Institution: Teaching, Research, and Collaborations

***Daron E. Janzen**, dejanzen@stkate.edu. Department of Chemistry and Biochemistry, St. Catherine University, St. Paul, Minnesota, United States*

As accessibility to both crystallographic data and instrumentation have increased, so too has the need to incorporate aspects of crystallography in the undergraduate chemistry curriculum. X-ray powder diffraction and single crystal diffraction represent modern structural methods that are key to student preparation in all areas of chemistry study, from biochemistry to solid-state materials. Though many Primarily Undergraduate Institutions (PUIs) have traditionally relied on research intensive universities for crystallographic access, more opportunities now exist for PUIs obtaining, operating, and maintaining their own crystallographic equipment in-house. Our story at St. Catherine University of how we obtained our crystallographic instrumentation, a Rigaku XtaLAB Mini, through a collaborative grant will be shared. Our subsequent work on integration of

crystallography teaching in our chemistry curriculum, including incorporation into projects in advanced labs and a stand-alone topics course will also be described. Undergraduate research projects focused on inter- and intramolecular interactions will be highlighted as well as the impact of external collaborations on the expansion of research opportunities to faculty and students provided by in-house crystallography.

2021 GLRM 221

C–C Bond Formation from Redox Active d^0-Metal Complexes

***Roman Belli**, rbelli@uvic.ca, Courtney Roberts. Chemistry, University of Minnesota Twin Cities, Minneapolis, Minnesota, United States*

This presentation describes our efforts to develop new catalytic C–C bond forming reactions using d^0-metals. Common organometallic reactivity that enables bond breaking and forming steps are oxidative addition (OA) and reductive elimination (RE), respectively. These steps are not traditionally observed with d^0-metals that lack the valence electrons to undergo these two electron processes. Herein we report the synthesis and characterization of new Sc and Zr complexes containing redox active trisamido ligands; examples of Sc complexes containing redox active ligands are scarce in the literature. These ligands are able to undergo two electron oxidation/reduction in lieu of the metal, which allows for redox processes at these d^0-metals. In the context of C–C bond formation, we investigated oxidation addition at these complexes with alkyl and aryl halides to generate metal-alkyl/aryl complexes where the oxidation occurs at the ligand. Subsequently, our efforts to exploit this reactivity for C–C bond formation through ligand-centred reduction elimination was explored.

2021 GLRM 222

Computational exploration of the turnover-limiting step in Re-catalyzed monoalkylation and monoalkenylation of phenols

***Ashton S. Havens**, ahavens2@emich.edu, Maria-Clelia Milletti. Chemistry, Eastern Michigan University, Detroit, Michigan, United States*

Renewed interest in a $Re_2(CO)_{10}$ catalyzed ortho-directed monoalkylation and monoalkenylation of phenols has led to the recent publication of two independent mechanistic studies. These studies both point toward a rate-limiting-step involving the cleavage of a catalyst resting state into an active form, though each come to separate conclusions regarding the exact catalytic species involved in the transformation, as well as the nature of C-C bond formation. In this work, we use DFT methods to further investigate the mechanism of this catalytic cycle. Specifically, we examine the energetics of resting-state cleavage among various organo-rhenium complex candidates, and explore the possibility of C-C bond formation resulting from, or occurring in parallel, with ring slippage events.

2021 GLRM 223

Multi-Electron Redox Chemistry with Thorium(IV) Iminoquinone Complexes

Ramitha Rupasinghe*, rdissana@purdue.edu, Suzanne C. Bart, Makayla Baxter. Department of Chemistry, Purdue University, West Lafayette, Indiana, United States*

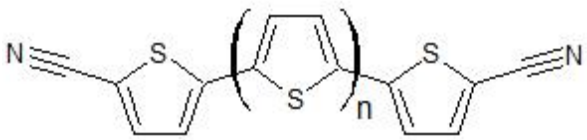
Thorium complexes primarily exist in the thermodynamically stable (IV) oxidation state with only a few low-valent thorium(III) complexes having been isolated. As a result, redox chemistry with thorium at the metal center is challenging without carefully designed ligand environments. This redox-restricted nature of thorium(IV) makes redox-active ligands an attractive option to facilitate multi-electron redox chemistry with thorium. In this work, a series of thorium(IV) complexes featuring the redox-active iminoquinone ligand and its derivatives, including the iminosemiquinone and amidophenolate species, were synthesized and isolated. Spectroscopic and structural characterization of each derivative established the +4 oxidation state for thorium with redox chemistry occurring on the ligand. Further spectroscopy, including SQUID, is underway. Preliminary reactivity studies of the amidophenolate complexes with azides, chalcogens, and oxidizing agents are ongoing.

2021 GLRM 224

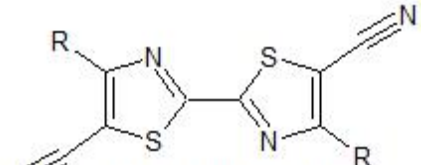
Node-and-spacer metal-organic frameworks using the silver(I)-nitrile supramolecular synthon and sulfur-containing heterocyclic oligomers as ligands

Craig D. MacKinnon[2]*, craig.mackinnon@lakeheadu.ca, Abdeljalil assoud*[1]*, Kaitlyn T. Kelly*[2]*, Nicholas R. Andreychuk*[2]*, Jamila S. Marroush*[2]*. (1) Chemistry, University of Waterloo, Waterloo, Ontario, Canada (2) Chemistry, Lakehead University, Thunder Bay, Ontario, Canada*

The silver(I) cation as a particular affinity for organic nitriles, binding in a linear fashion to the lone pair on the nitrogen. Because Ag(I) has a d^{10} electronic configuration, it has no particular geometric preference. Therefore, the resulting metal-organic framework (MOF) generated from combining Ag(I) with bridging organic ligands depends on the solvent of crystallization, the size and donor ability of the anion, and/or the shape and steric properties of the ligand. We have been specifically exploring off-axis linear ligand bridges, especially those that contain heteroatoms, to determine the structural effect, if any, of binding between the metal nodes and the heteroatoms in the bridge. This talk will present our recent findings for the sets of ligands shown in the picture, *i.e.* bi- and terthiophenes **1** and bithiazoles **2**.



1 (n = 0, 1)



2 (R = Me, Et, Ph)

2021 GLRM 225

Quantitative structure and property study of Iridium based organometallic complexes for optical properties

anas karuth[1]*, anas.kk@ndsu.edu, levi lystrom*[2]*, Wenfang Sun*[2]*, Svetlana Kilina*[2]*, Bakhtiyor Rasulev*[1]*. (1) Coating and Polymeric Materials, North Dakota State University, Fargo, North Dakota, United States (2) Department of Chemistry and Biochemistry, North Dakota State University, Fargo, North Dakota, United States*

Transition metal complexes display a rich array of photophysical properties where substituted ligands play a critical role in determining their emission and absorption properties. A cheminformatics-based machine learning (ML) approach has been employed to investigate the optical properties of a set of Iridium organometallic complexes. Specifically, a set of 46 Iridium organometallic complexes was used to build quantitative structure-property relationship (QSAR) models. By applying a combination of genetic algorithm and multiple linear regression (GA-MLRA) method several predictive models were developed for predicting the nonlinear optical absorption and near-IR emission properties. The developed best predictive model is based on a three-parameter model and can successfully predict the emission and absorption properties of an investigated set of Iridium organometallic complexes. The best-developed model identified several significant descriptors responsible for near-IR optical properties of organometallic complexes with a predictive coefficient of $R^2 = 0.84$. The developed model illustrates that the tailor-made photophysical properties can be achieved by tuning the nature of substituted ligands in investigated complexes

2021 GLRM 226

Measuring Physiochemical properties of Viruses Can Improve Downstream Processing of Viral Products

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Producing therapeutic viral vectors for vaccine and gene therapy applications is expensive and time consuming. First, production of the viral vectors happens in an

upstream bioreactor using cell culture. Then, the viruses are purified in the downstream to remove associated impurities formed during cell culture. The downstream makes up about 70% of the production cost. These purification methods are developed based on physiochemical properties differences between the viruses and impurities, such as hydrophobicity and charge. There are currently no reliable methods to measure these physiochemical properties that can help in predicting the behaviors of viruses and impurities when these solution conditions change. We have developed a method to measure how virus physiochemical properties change, and thus how absorption changes in different solution conditions using chemical force microscopy (CFM). CFM uses functionalized probes of an atomic force microscope (AFM) to measure adhesion of different chemistries to the viral surface. CFM results have shown changes in virus hydrophobicity and has been used in determining virus charge changes in different solution conditions. This demonstrates that the CFM can be used to select suitable buffers and processing parameters for virus purification with very small amounts of viral vector. This technique could revolutionize the development of downstream processing by decreasing the time and cost associated with buffer selection and optimization and increase the speed of getting viral products to the market.

2021 GLRM 227

An original biocatalytic synthesis of 3-hydroxypropionic acid

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Biocatalytic production of commodity and value-added chemicals is a research theme with enormous commercial and societal benefits. 3-Hydroxypropionic acid (3-HP) is an important chemical building block which serves as a precursor for acrylate, acrylamide, malonic acid and 1,3-propanediol synthesis. Inclusion of 3-HP on the U.S. DOE list of top value-added chemicals to be produced from biomass has resulted in a staggering body of research to develop efficient routes to this important molecule. In this talk, we offer acetylenecarboxylic acid (ACA) as a promising alternative to traditional feedstocks. Dehydrodimerization of methane to acetylene, followed by carboxylation yields C-1 derived ACA. We present the use of an engineered Cg10062, a tautomerase enzyme from *Corynebacterium glutamicum* which hydrates ACA to malonic semialdehyde. This step is coupled to NADPH-dependent YdfG from *E. coli* to produce 3-HP *in vitro.* In order for this pathway to be truly feasible in an industrial setting the cost of cofactor is an important consideration. Inclusion of a phosphite dehydrogenase allows utilization of phosphite as an inexpensive sacrificial substrate, resulting in quantitative conversion of ACA to 3-HP with as low as 0.001 eq cofactor.

2021 GLRM 228

One-pot reaction from cloning to validation coupling with a cell-free system

*Brock Cash, **Wakana Sato**, sato0055@umn.edu, Judee Sharon, Katarzyna Adamala. Department of Genetics, Cell Biology, and Development, University of Minnesota Twin Cities, Minneapolis, Minnesota, United States*

Cell-free transcription-translation (TXTL) is suitable for high-throughput screening due to the system's main advantage: enabling rapid small-scale protein expression. Here we present a streamlined bioengineering method of progressing from cloning to biological assay, which can be completed in a single-pot reaction. To eliminate unnecessarily sample preparation procedures, we engineered a cloning pipeline compatible with optimized buffer conditions for cloning, TXTL, and enzymatic assays. First, we demonstrated the proof of principle for the cloning platform using fluorescent proteins (GFP, CFP, YFP, and BFP.) A stop codon was inserted in the fluorophore center of the beta-barrel fluorescent protein sequence, and then active fluorescent proteins were successfully recovered after the one-pot cloning and expression scheme. Next, we used an antibiotic catalyzing enzyme to demonstrate the possibility of combining additional enzymatic assays in the same reaction mixture. By saturation mutagenesis of the single amino acid, we successfully showed that the antibiotics hydrolyzing enzyme changed its substrate specificities over four different penicillin analogs. We also demonstrated that it's possible to engineer brighter variants of the luciferase reporter protein in a similar one-pot scheme. Our entire scheme's simplicity will enable simpler automation of the design – build – test – learn pipeline. In the future, we hope to apply this method to a large number of samples with automation and machine learning platforms, enabling simplified directed evolution of proteins of interest to raise desired functions.

2021 GLRM 229

Cell-Free Biosensing for Environmental and Performance Monitoring

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Cell-free expression systems are an exciting platform for the detection of environmental hazards and human performance biomarkers. Once lyophilized onto paper, cell-free biosensors can be transported to austere locations and rehydrated onsite for field sensing applications. Here, we show the development of a cell-free sensor that detects bile acids in both environmental samples and human biofluids. Secondary bile acids, including deoxycholic acid (DCA) and lithocholic acid (LCA), are indicators of fecal pollution in water and biomarkers for certain disease states. Importantly, a cell-free bile acid sensor could potentially detect fecal contamination in water in less than two hours, an improvement over traditional approaches with fecal coliform cultures that require greater than 24 hours of incubation. Our bile acid sensor uses BreR, a TetR-like repressor from *Vibrio cholorae*, and was successfully transferred from whole cells to cell-free with an approximately ten-fold increase in DCA sensitivity. Further characterization of the sensor in cell-free showed a strong response to several

secondary bile acids. Therefore, we next explored the ability of this sensor to detect bile acids in human feces and wastewater samples. To further broaden the application space of our sensor, we also established strategies to mitigate the inhibitory effects of human blood serum on the functionality of the sensor for biomarker detection in blood. Ongoing work includes optimization of the sensor in a lyophilized paper-based assay. Additionally, we have shown that several biosensors can be transferred from whole cells to cell-free systems with an improvement in analyte sensitivity, this seems to be a common feature we are currently exploring. In summary, our bile acid sensor highlights the utility of cell-free systems for rapid onsite sensing of biomarkers and analytes for a variety of different applications.

2021 GLRM 230

Metformin (Glucophage) biodegradation: Relevance to water treatment and the human gut

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Metformin is the most prescribed type 2 diabetes medication in the United States and in many countries worldwide. In diabetes patients, this drug has been shown to alter the gut microbiome resulting in improved glucose metabolism. More recently, metformin has been proposed to have anti-aging and antiviral properties making the drug a potential candidate to treat other health conditions. Metformin and its proposed “dead-end” product, guanylurea, are not fully metabolized by humans and cannot be removed through conventional water treatment processes. These compounds have been detected in coastal waters around the world and are currently considered emerging pollutants. This study examined a bacterial consortium enriched from activated sludge which demonstrated the ability to utilize metformin as a sole source of nitrogen, as well as to degrade metformin to its transformation product, guanylurea. Metagenomic sequencing and bioinformatic analysis led to the identification of three relevant enzymes: guanylurea hydrolase, carboxyguanidine deiminase, and allophanate hydrolase. Biochemical studies revealed that these proteins catalyze the degradation of guanylurea to ammonia and carbon dioxide. Protein sequence analyses and structural modeling studies are currently in progress to identify a candidate gene(s) encoding the enzyme initiating the metabolism of metformin. This research presents the first evidence for a biochemical pathway associated with the microbial degradation of guanylurea. Significantly, it also advances understanding of the microbial capacity for metformin biodegradation. These findings could lead to the development of practical biotechnological applications to improve water treatment processes and provide insight into the effects of metformin on human microbiome metabolism.

2021 GLRM 231

Biochemical-characterization of a borosin RiPP system

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Ribosomally-synthesized and post-translationally modified peptide (RiPP) natural products often provide biosynthetic routes to unique peptide modifications not observed in primary metabolism. One such modification is α-*N*-methylation, which confers therapeutically useful properties to peptides that include membrane permeability, increased target specificity, and resistance to proteolytic degradation. α-*N*-Methylation was recently discovered as a post-translational modification in the omphalotin A biosynthetic pathway. This newfound α-*N*-methyltransferase was the first of its kind, and with its discovery founded a new class of RiPPs in fungi, called borosins. However, challenges associated with working with this fungal system motivated us to search for homologs in bacteria amenable to more rigorous characterization. A model bacterial borosin system was found in *Shewanella oneidensis* MR-1, a well-studied marine bacterium. Collective results from crystal structures as well as kinetic and tandem mass spectrometry experiments have offered insight into the process of substrate binding and catalysis. Moving forward, this model system will continue to further our understanding of how borosins catalyze chemically challenging peptide backbone α-*N*-methylations and inform our understanding of RiPP biosynthetic enzymes as a whole.

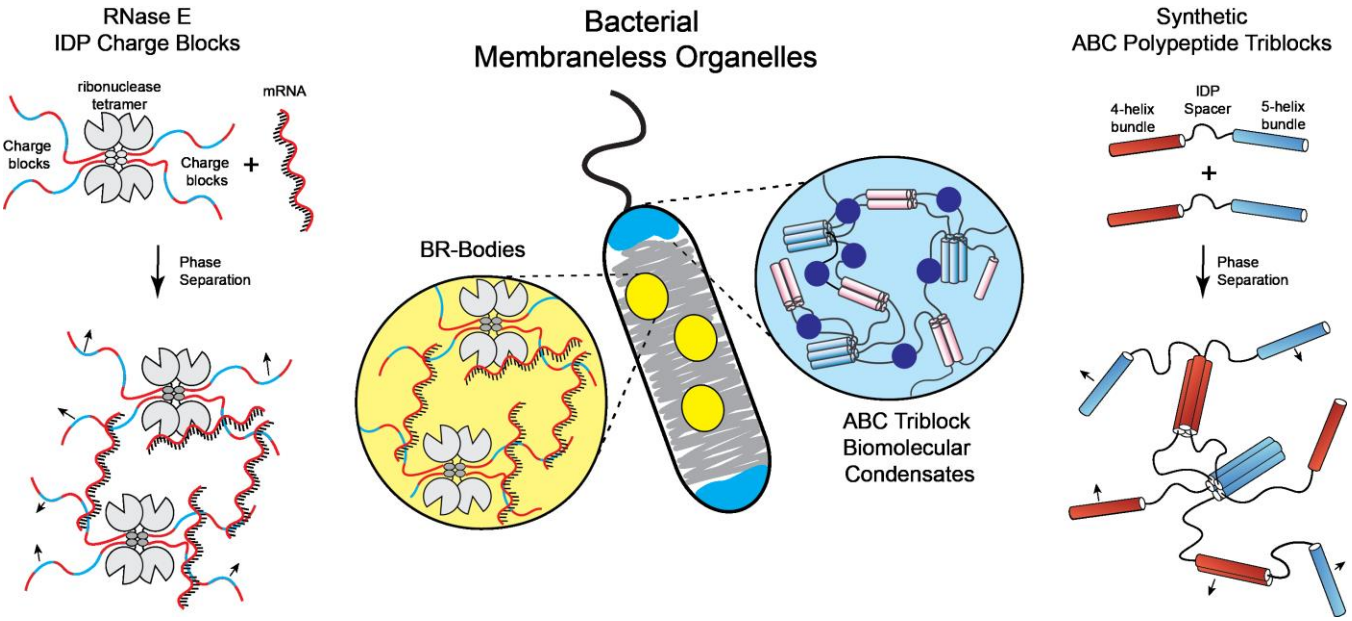
2021 GLRM 232

Block copolymers as biomolecular condensates to organize biochemistry in bacteria

Dylan T. Tomares[1]*, Sara E. Whitlock*[1]*, Nadra Al-Husini*[2]*, Nisansala Muthunayae*[2]*, Jared M. Schrader*[2]*,* ***William S. Childers***[1]*, wschild@pitt.edu. (1) Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania, United States (2) Department of Biological Sciences, Wayne State University, Detroit, Michigan, United States*

Liquid phase-separated droplets, termed biomolecular condensates, spatially organize biochemistry in eukaryotes. In the absence of organelles, we wondered whether bacteria also exploit phase separation to organize biochemical pathways. Towards this goal, we observed that the ribonuclease RNase E contained an intrinsically disordered C-terminus organized as alternating positively and negatively charged blocks. Such block organization is leveraged in the design of multi-block copolymers used in nanomaterials. *In vitro,* RNase E phase separates as liquid-like droplets that depend upon salt and protein concentration and selectively recruit RNA and protein clients. *In vivo,* we found that RNase E also phase separates as liquid-like assemblies that organize a multi-step mRNA decay.

Inspired by the multi-block co-polymer structure within RNase E, we revisited the phase properties of synthetic ABC triblock that serve as hydrogel nanomaterials. ABC triblocks contain coiled-coils in the “A” and “C” blocks that promote self-assembly that are connected by a “B” block composed of a disordered sequence that promotes water solubility. We observed that triblock polypeptides self-assemble at the cell poles as biomolecular condensates that depend upon block organization and valency. Thus, triblock polypeptides used as hydrogels in tissue engineering and drug delivery can be repurposed as membraneless organelles for synthetic biology applications. These natural and synthetic examples suggest that phase separation of proteins organized as block copolymers may provide a generalizable mechanism to compartmentalize biochemistry in bacteria that lack membrane-bound organelles.



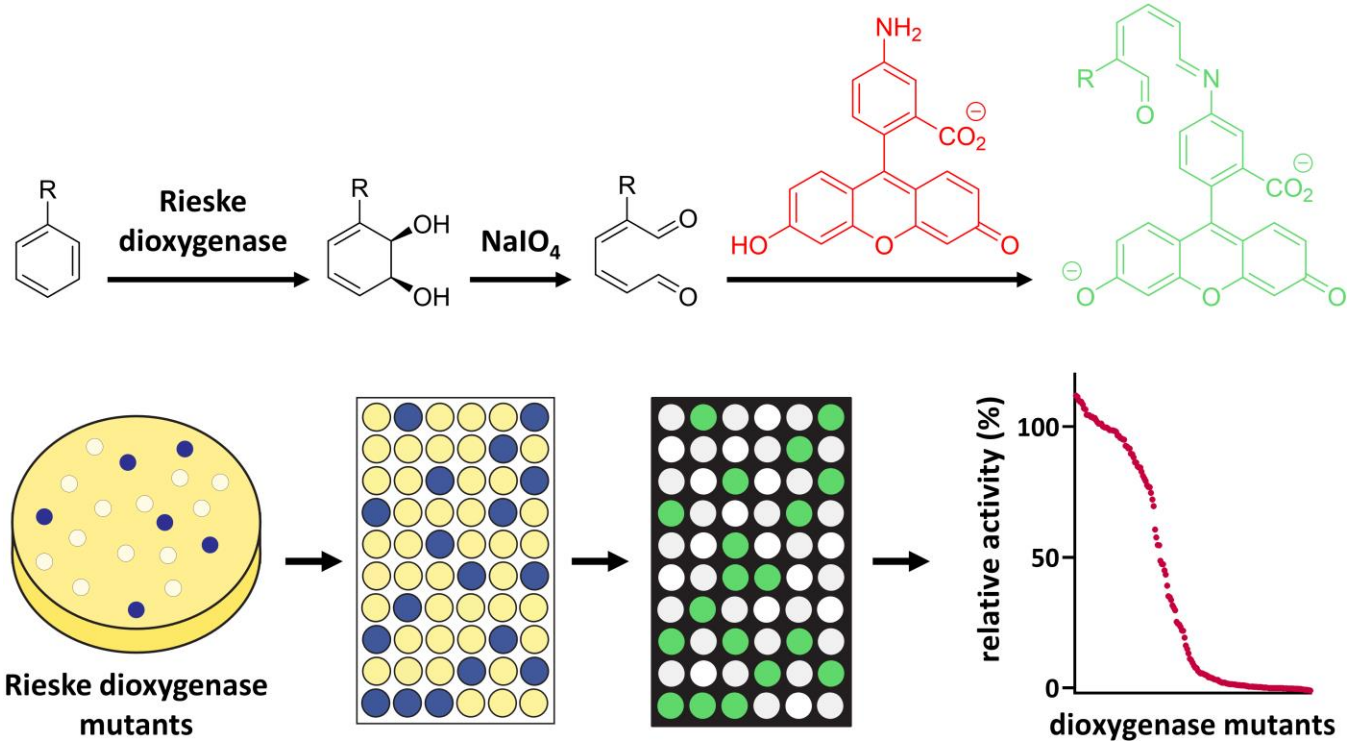
2021 GLRM 233

Rieske Business: Engineering Rieske Dioxygenases as Green-Chemical Catalysts

Jordan Froese*, jtfroese@bsu.edu. Chemistry, Ball State University, Muncie, Indiana, United States*

Today, fossil fuels are so commonly employed by the chemical industry as feed stocks for reactions, and as sources of the heat and pressure that drive them, that the chemical industry’s use of petroleum currently accounts for 14% of all greenhouse gas emissions, and the chemical industry is set to become the single largest driver of global oil consumption by 2030. In the Ball State Laboratory for Biocatalysis Research, we strive to develop new green-chemical tools that can contribute to alleviating the chemical industry’s reliance on fossil fuels.

With the recent advances in Synthetic Biology and Directed Evolution, the potential for engineering enzymes as robust, selective, and environmentally benign chemical catalysts has exploded. In the Ball State Laboratory for Biocatalysis Research, we have developed a novel periodate-based reactive assay system that has allowed us to pursue the engineering of Rieske dioxygenases. Rieske dioxygenases, with their unique ability to perform oxidative dearomatization to produce chiral *cis*-diol metabolites, have long been utilized as green-chemical catalysts in bioremediation efforts and by synthetic chemists, although their utility has been limited by their substrate scope and selectivity. By applying our novel assay system, we are developing new catalysts based on Rieske dioxygenases, which will expand the chemical utility of this class of enzymes. To this end, we have demonstrated the capacity of our novel assay system to screen for the *cis*-dihydroxylation activity of large Rieske dioxygenase variant libraries, and to identify Rieske dioxygenase variants with significantly altered reactivity.

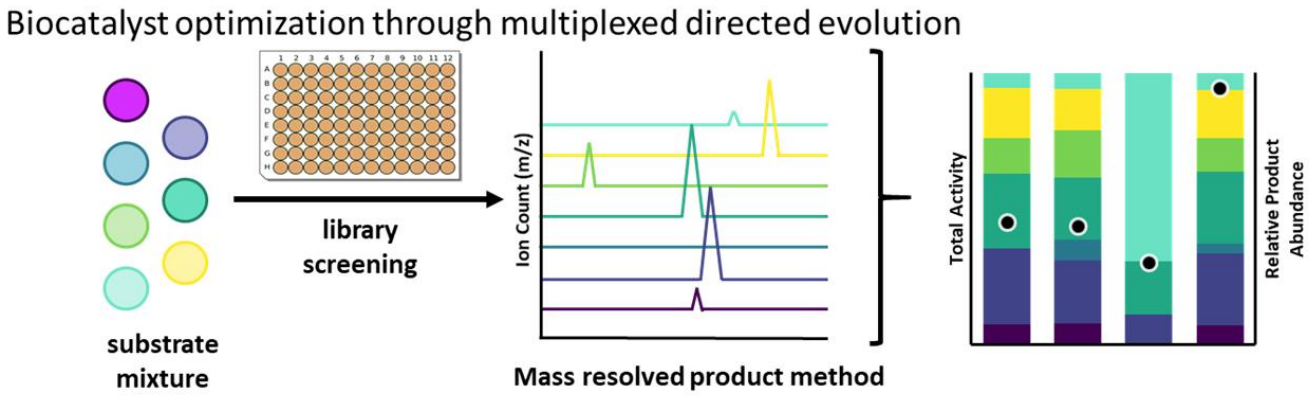


2021 GLRM 234

Controlling biocatalyst specificity through multiplexed substrate screening

Andrew Buller, *arbuller@wisc.edu, Allwin McDonald, Peyton Higgins. Chemistry, University of Wisconsin System, Madison, Wisconsin, United States*

Enzymes are often marvelled upon for their selectivity and catalytic efficiencies. However, applications in organic chemistry are often limited by unknown or poor activity with non-native substrates. This limitation can be overcome by directed evoltuion, but like its natural counterpart, directed evolution can also deliver 'specialist' enzymes that do not perform well on substrates that were not under selective pressure. We present a new approach to engineering enzymes for synthetic applications, Substrate Multiplexed Screening (SUMS). The approach can rapidly distinguish between generalists and specialists, as well as identify sites that influence catalytic activity, even if the distal mutation is deleterious. The method helps to solve a major limitation in biocatalysis and will facilitate the rapid evolution of enzymes for synthetic applications



2021 GLRM 235

Knowing the unknown: Chemical characterization of unknown leachables/extractables from medical devices

Ryan Espy, *ryan.d.espy@medtronic.com. Medtronic Inc, Minneapolis, Minnesota, United States*

Chemical characterization is an essential part of analytical testing for medical devices according to ISO 10993. This testing determines which chemicals, and the amounts, which may potentially be released by the device into the body. This talk will discuss how analytical testing, in particular mass spectrometry, is used to determine unknowns in leachables/extractables studies.

2021 GLRM 236

Thermal conductivity considerations in medical devices

Kendi Kebaara, *Kendi.Kebaara@bsci.com. Boston Scientific Corp, Arden Hills, Minnesota, United States*

Selecting materials used in medical device design, manufacturing controls, and hazard evaluation of devices and components that come into contact with the human anatomy invariably requires considering thermal properties such as thermal conductivity and transition temperatures such as glass transitions, melting and crystallization temperatures. The thermal properties of polymeric materials in particular can be related to the chemical and physical properties of the material of interest. Thermal conductivity by Differential Scanning Calorimetry (DSC) is a novel technique that allows for measurement of the rate at which heat is transferred through a material. By measuring heat flow in and out of materials as a function of time or temperature, DSC measures transition temperatures and associated heats of reaction in polymeric materials, which provides critical information for how materials will function in medical device processing and manufacturing.

2021 GLRM 237

Atomic spectroscopy analytical support in the life cycle of a medical device

***Jeff Zeske**, jeff.zeske@medtronic.com. Medtronic Inc, Brooklyn Center, Minnesota, United States*

Complex medical devices require a great deal of analytical chemistry support for engineering evaluation and risk management to manufacture these life sustaining products. Atomic spectroscopy techniques, specifically Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES) and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) play a critical role in the life cycle of medical devices from inspection to post-market evaluation. In the analytical chemistry lab these techniques provide valuable information for chemical and materials characterization in the research and technology phases. ICP-OES is used extensively for process and product support in design verification testing, manufacturing quality control, problem solving, packaging, and sourcing and supplier management.
The medical device world is heavily regulated and constantly evolving.With new EU Medical Device Regulations (EUMDR) and United States Pharmacopeia (USP) requirements for combination drug/device products, ICP-MS has become a crucial tool in the effort to show compliance with the regulations.Materials characterization through extractable/leachable testing has become the standard model for US Food and Drug Agency (FDA) and International Council for Harmonization (ICH) regulations to show safety and performance of new materials and devices.ICP-MS has is the gold standard for reaching the sensitivity needed to meet the requirements of USP chapters 232/233 for combination drug/device products and ISO 10993 Part 18 for materials characterization.

2021 GLRM 238

ISO 10993-18:2020- Chemical characterization of medical devices in a changing technical landscape

***Joseph Tokos**, Joe.Tokos@wuxiapptec.com. WuXi AppTec St Paul, Saint Paul, Minnesota, United States*

The long-awaited release of ISO 10993-18 (Part 18) took place in January, 2020 following the release of ISO 10993-1 in 2018. Both of these international standards emphasize the importance of chemical characterization studies, commonly referred to as extractables/leachables or E/L, for approval and re-registration of new and current medical devices. In this talk we will discuss regulatory updates, the importance of information gathering versus generation of new information, the calculation of the analytical evaluation threshold (AET), and critical details of Part 18 that need to be included in regulatory submissions.

2021 GLRM 239

Career panel in medical devices

***Ryan Espy**[2], ryan.d.espy@medtronic.com, Kendi Kebaara[1], Jeff Zeske[2], Joseph Tokos[3], Audrey Meyer[1]. (1) Boston Scientific Corp, Arden Hills, Minnesota, United States (2) Medtronic Inc, Minneapolis, Minnesota, United States (3) WuXi AppTec St Paul, Saint Paul, Minnesota, United States*

Join us for a career panel to ask your questions regarding careers in medical device. Learn critical experiences and opportunities from our panelists on their journey to their current positions in the medical device field. This is an opportunity to learn about their career path, critical experiences, lessons learned, and skills that can help you in your industrial job search

2021 GLRM 240

Novel 5-methylsubstitutedpyrrolo[2,3-*d*]pyrimidines as dual inhibitors of EGFR and AURK

***Sara LaForce**, laforcs@ferris.edu, Kyle DeJong, Sonali R. Kurup. Ferris State University, Big Rapids, Michigan, United States*

Simultaneous inhibition of EGFR and AURK has been suggested to provide synergistic effects on the inhibition of tumor growth and tumor resistance. Kurup et al. identified a series of 4-substitutedpyrrolo[2,3-*d*]pyrimidines as dual inhibitors of AURK and EGFR. Using these analogs as leads, we have synthesized a series of compounds that incorporate a 5-methyl moiety on the pyrrolo[2,3-*d*]pyrimidine scaffold. The 5-methyl substitution impacts the potency and selectivity of EGFR and AURK inhibition. The synthesis and kinase inhibitory activities of the target compounds will be presented and discussed.

2021 GLRM 241

The synthesis of small molecule inhibitors of microRNA-31

***John C. Getson**, john.c.getson@wmich.edu, Kelly A. Teske. Western Michigan University, Kalamazoo, Michigan, United States*

The biogenesis of microRNAs (miRNAs) can be successfully inhibited by small molecule drugs. In particular, miRNA-31 is overexpressed in metastatic colorectal cancer making it a potential target for the development of improved colorectal cancer treatments. A 3,4-dimethylisoxazole phenylsulfonamide compound was identified in the literature as an inhibitor of miRNA-31 expression. We are performing structure activity relationship studies using this compound as a scaffold to elucidate the structural features that drive inhibition. To simplify the synthesis, the methyl groups were moved to the 3- and 5-positions and various amines were explored. Herein, we discuss an efficient two-step synthetic route used to build a library of 3,5-dimethylisoxazole phenylsulfonamide analogues that were tested for miRNA-31 inhibitory activity in colorectal cancer cells using qRT-PCR. These compounds will be used for any future biological studies to determine the direct target engagement and downstream effects of these compounds.

2021 GLRM 242

Polyfluorosalicylic acids as antimycobacterial compounds

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Tuberculosis, caused by *Mycobacterium tuberculosis*, infects over ten million people every year. The salicylic acid derived small molecule siderophores, known as mycobactins, are essential for iron acquisition of *M. tuberculosis*. Mycobactin biosynthesis has been genetically and chemically validated as essential under iron deficient conditions. Herein, we explore polyfluorinated salicylic acid derivates as antimetabolites, designed to antagonize mycobactin synthesis. We performed enzymatic assays to evaluate whether the polyfluorinated salicylates were processed by MbtA, the first enzyme in the mycobactin biosynthetic pathway. While the tri- and tetra-fluorinated salicylic acid analogues were neither substrates nor inhibitors of MbtA, the difluoro analogues were found to be competent substrates of MbtA. Among the polyfluorinated derivatives, the 4,5-difluoro-salicylic acid exhibited the best antitubercular activity, with a microbial inhibitory concentration of 20 µg/mL. Further mechanistic analysis were performed using *M. tuberculosis* strains that differentially express MbtA, along with whole cell iron rescue and salicylic acid complementation. The results are inconsistent with an antimetabolite mechanism of action. In conclusion, we have identified polyfluorinated derivatives with moderate antitubercular activity, but further experiments will be required to delineate their mechanism of action.

2021 GLRM 243

Resistance to BPEI confers increased susceptibility to aminoglycoside antibiotics

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Antibiotic resistance is a global health emergency of increasing importance. Pathogenic microbes quickly find new ways of evading the effects of antibiotics which further drives home the importance of developing new therapies to combat these organisms. One such pathogen is the Gram-negative bacteria *Pseudomonas aeruginosa*. Several factors make targeting organisms like *P. aeruginosa* more challenging, like the presence of an outer membrane (OM) as well as the ability to form biofilms. We have previously identified 600-Da branched polyethyleneimine (BPEI) as a potentiator of several different classes of antibiotics against *P. aeruginosa*. If used in a clinical setting, it is inevitable that some organisms will eventually develop resistance to BPEI. We have generated BPEI-resistant mutants via a serial passage. Subsequent checkerboard growth inhibition assays demonstrate that BPEI-resistant mutants of *P. aeruginosa* are more susceptible to the aminoglycoside antibiotics tobramycin, gentamicin, and neomycin. The respective MIC values are 100 times lower than those observed in the wild-type strains. Thus, if BPEI resistant mutants arise in the clinic, they are likely to be more susceptible to aminoglycosides, giving BPEI increased value as a potential therapeutic agent.

2021 GLRM 244

Modifications of Nitro-Dihydroxyquinoxaline analogs of MMV007204 and axploration of their activities against Schistosoma mansoni

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In the past years groups from the Lawrence University Department of Chemistry, and the Department of Medical Parasitology and Infection Biology at the Swiss Tropical and Public Health Institute have been working on manipulating antimalaria quinoxaline derivative MM007204 from the Medicines for Malaria Venture Malaria Box into a promising candidate for an antiparasitic drug to combat *Schistosoma mansoni*, a parasitic worm known to cause Schistosomiasis in their hosts. In the original study, researchers developed several analogs of MM007204. These analogs were shown to have high in *vitro* activities against both larval and adult *S. mansoni*worms, however the in *vivo* activity was moderate at best. This prompted further modification of these MM007204 derivatives in an aim to maximize their in *vivo* performance. My goal within this project has been to learn more about the mechanism of action the drug takes when it encounters the *S. mansoni* parasites. The method for understanding more about this molecules mechanism of action was to replace the nitro compound on the 1 carbon of

the molecule with different electron withdrawing groups. The goal of this research was to understand weather the nitrogen itself was important to the effectivity of the drug, or weather similar results could be found using other electron withdrawing groups. This work is similarly a work in progress. Going forward I will mostly be focusing on the latter research question as it has ended up taking the most time. Currently, two derivatives of the starting material have already been produced, one with a fluorine and one with a chlorine. The chlorine will be further synthesized into a final product which will be tested against *S. mansoni*. The fluorine containing molecule will be reacted further and have the fluorine replaced with a different electron withdrawing group.

2021 GLRM 245

Using a Magnetic Field to Filter and Separate Compound Mixtures.

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Currently there is research in using magnetic fields to produce reactions and altering properties of compounds. This research has given promising results such as using a magnetic field to improve hydrocarbon fuel combustion. Results have shown better fuel efficiency and exhaust emissions reduction by using a magnetic field of varying strengths. It has shown that compound properties such as viscosity, surface tension, boiling point, can be altered with a magnetic field. Even IR and UV spectra can be enhanced by a magnetic field. Here the focus will be on potential magnetic field use in the separation sciences - stating current research/developments of magnetic field use in separating compounds.
Separation science deals with mobile and stationary phases to separate compound mixtures in HPLC/GC. Factors such as flow rate, temperature, stationary phase particle size, and mobile phase solvent play key roles. Other methods such as electrophoresis and dialysis use similar techniques. It will be shown how a magnetic field can be used in separating compounds.
Briefly discussing magnetic/electric field properties and then on organic/bioorganic compounds emphasizing on nucleophilic/electrophilic compounds, proteins, nucleotides, and microorganisms. Continued with examples of the research on using magnetic fields to filter and/or separate compounds and solution mixtures of aqueous/nonaqueous nature. Primarily emphasizing on the research of applying a magnetic field in oil spill clean-ups, blood dialysis and even space applications.
From there, it will be shown how this research can be applied to four main areas. In electrophoresis, it will show the advantages of a magnetic field over the electric one. The removing of deadly diseases such as the coronavirus and wastes from blood using magnetic dialysis. The use in sample preparation methods. HPLC/GC separations showing the advantages of using magnetic field in separation and advantages of a proposed magnetic stationary phases over the current ones.
The potential of magnetic field use in the separation sciences is great. Based on previous research such as improving fuel combustion has shown practical potential in other areas such mixture separations. By discussing the principals involved in this

shows how it is achieved. The potential feasibility in improving electrophoresis, dialysis, and HPLC/GC separations by using a magnetic field can help reduce costs and preparation time.

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How to Utilize Capillary Gas Chromatography with Electron Capture Negative Ion Mass Spectrometry (C-GC-ECNI-MS) to Achieve Sub-ppb Concentration Levels for Brominated and Chlorinated Organic Priority Pollutants.

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This presentation will discuss how to convert a conventional capillary gas chromatography-mass spectrometry (C-GC-MS) instrument that uses electron-impact (EI) single quadrupole mass spectrometry to one that uses both dissociative and resonance electron capture negative ion (ECNI) single quadrupole mass spectrometry to achieve sub-part per billion (ppb) concentration levels of various brominated and chlorinated organic priority pollutants.

2021 GLRM 247

Analysis of American negative ion consumer bracelets via geiger-muller counter, and gamma spectroscopy

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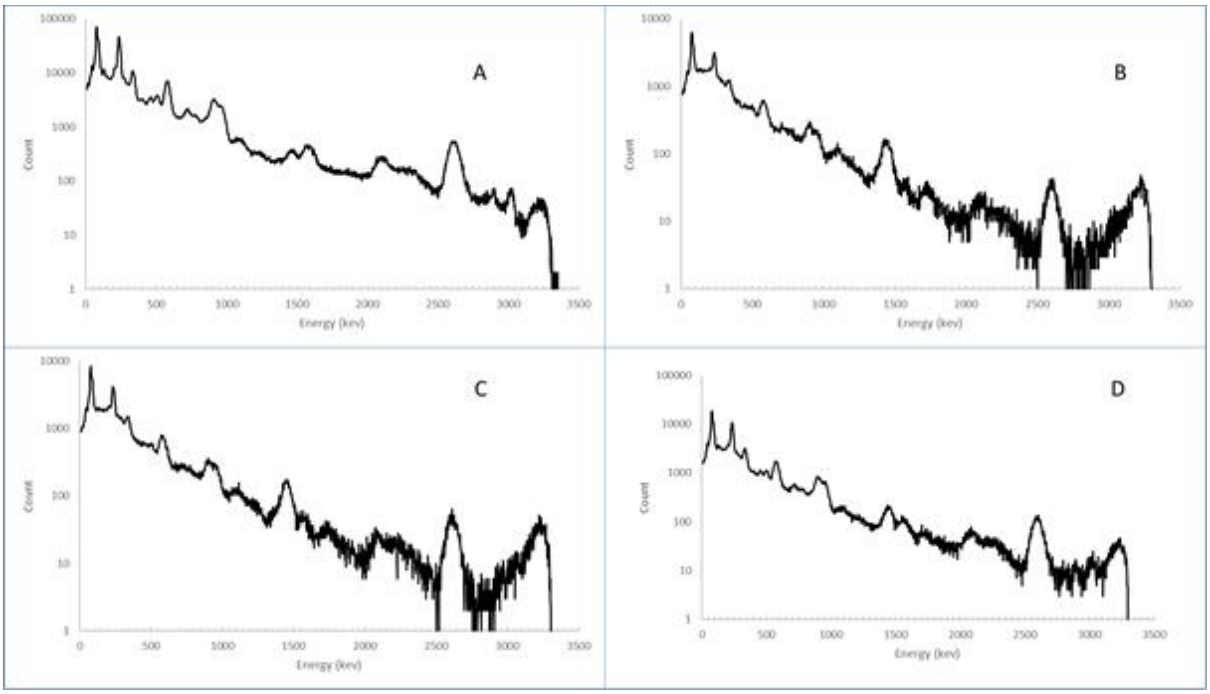
Negative ion bracelets are a commonly sold pseudoscientific product with dubious health claims. These products are advertised as emitting negative ions and have been determined to contain radioactive material. However, there is a dearth of information on the dosage and identity of the radionuclides contained in bands sold in america. In these study bracelets were purchased from seven random american companies across the United States and tested for radioactive material. Three out of the seven companies showed the presence of radioactive material under a geiger-muller counter. The bracelets were then subject to more rigorous dosage measurements via a geiger-muller counter revealing a dosage from 0.95 ± 0.04 to 2.45 ± 0.09 microseverts per hour. Further testing with gamma spectroscopy revealed bracelets contained isotopically pure Th-232.



Shown above are four gamma spectra corresponding to (A) thorium mantle, (B) bracelet 1, (C) bracelet 6 and (D) bracelet 7.Each spectrum was collected over one hour using a Gamma Spectacular GS-USB-PRO with a 2” CSI(Tl) scintillation detector.

2021 GLRM 248

Understanding the limits of paper in paper-based potentiometric sensors

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Point-of-care diagnostic tests are needed in order to increase access to medical care in rural and resource-limited areas. In transferring traditional laboratory instruments to a portable platform, paper is often used as a support substrate due to its low cost, wicking capabilities, and compatibility with ink-jet printing. Using a printer, one can print hydrophobic barriers with wax and the sensing elements with custom ink formulations, thus embedding sampling and sensing capabilities into the paper design. However, paper-based potentiometric sensors are plagued by non-Nernstian responses and worsened limits of detection when compared to conventional, rod-shaped ion selective electrodes. Here, we examine the composition and structure of commonly used filter paper in order to explain these deviations from optimal device performance. Contamination of the sample from the paper itself and adsorption of sample ions onto the paper are studied using ICP-OES and potentiometry. Taking into account possible transport mechanisms in the cellulose-based material, these results explain previously reported limitations of paper-based ion selective electrodes. By elucidating the interaction of paper with sample solutions, we explain previously found limitations of paper-based devices and suggest guidelines for choosing support substrate materials.

2021 GLRM 249

Using single particle inductively coupled plasma mass spectrometry to measure elemental chemical composition and number concentration of atmospheric nano- and micro-particles

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The number and elemental chemical composition of *individual* atmospheric nano-and micro-particles plays an important role in climactic processes (reflecting, scattering, or absorbing solar radiation; acting as nuclei for ice and clouds). The size distribution of atmospheric particles has been determined by Coulter counter, but only for particles greater than about 0.5 µm. Bulk elemental composition of particles has been determined by dissolving the particles and measuring the average signal of each element for around 1 second by inductively coupled plasma sector field mass spectrometry. In the last decade, single particle inductively coupled plasma mass spectrometry (spICP-MS) has been used to measure the number/mL and size of suspended engineered particles, such as Ag nanoparticles (1, 2). In the plasma, each particle produces an ion cloud with a signal resulting in an intensity peak ~0.2 to 1 ms wide. spICP-MS can measure thousands of individual particles by continuously collecting data every 30 to 100 µs for 1 to 5 minutes. Software identifies the peak produced from each particle; the total number of signal counts is proportional to the mass of that element (fg) in the particle. spICP-MS was used to measure individual atmospheric nano- and micro-particles entrapped in an ice core from Taylor Glacier (East Antarctica) spanning part of the last glacial-interglacial cycle (9,000-44,000 years BP). Two different instruments were used: spICP-Quadrupole MS (ICP-QMS) which measures one isotope at a time and spICP-Time of Flight MS (ICP-TOFMS) which acquires a complete elemental mass spectrum for every particle. Preliminary results indicate that individual atmospheric particles contained 1 to 15 different detectable elements (including Si, Al, Ti, Fe) in amounts from less than 1 fg to several hundreds of fg. Fifty different elements were detected among all the particles. Ultimately, these measurements will allow for a more comprehensive estimate of the number concentration and mineralogy of atmospheric particles. These data can be used to improve the accuracy of climate models by incorporating the chemical and physical properties of atmospheric particles into simulations.

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2021 GLRM 250

Developing Analyte Specific Probes for Inclusion onto Graphene-Based Sensor Arrays Through Monolayer Self-Assembly onto Graphene

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Graphene-based sensors have become attractive due to the quantum properties and conductivity of graphene and their ability to utilize many different sensing mechanisms. The use of graphene in electrochemical sensors has led to the development of diverse sensor arrays and devices that can be used to detect a wide range of analytes. In particular, using graphene-based sensors for the detection of volatile organic compounds in gas samples has resulted in limits of detection that reach the parts-per-billion range, making the development of graphene-based sensors for the detection of specific analytes in gases very attractive. Making analyte-specific graphene-based sensors requires functionalization of the graphene with a probe that can interact specifically with an analyte of interest. In this work, functionalization of graphene is accomplished through noncovalent monolayer self-assembly of probes resulting from π-π interactions between the probe and the graphene. This talk will focus on the analysis and synthesis of an analyte-specific probe that can be self-assembled onto graphene in the form of a monolayer. In particular, the screening of possible probes for interactions with specific carbonyl groups will be discussed, as well as an analysis of the chosen chemical's utility as an analyte-specific probe. Finally, the synthesis and self-assembly of the probe onto graphene for inclusion in graphene-based sensor arrays will be discussed.

2021 GLRM 251

All solid-state hydrogen ion-selective electrode using ionophore and ionic sites covalently attached to poly(methacrylate)

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Ion selective electrodes (ISEs) based on ionophore-doped polymeric membranes with a matrix such as plasticized poly(vinyl chloride) are widely used in a variety of analyses. However, membrane components such as plasticizer, ionophore, and ionic sites can leach out from the polymeric membrane phase into the sample solution over time. This leaching limits long-term durability and chemical stability of ISEs. Therefore, in the view of long-term use and monitoring, it is beneficial to use a plasticizer-free polymer with covalently attached ionophore and ionic sites. In this study, ISEs were prepared by using plasticizer-free poly(methacrylate) membranes to which either only the ionic sites,

only the ionophore, or both ionic sites and ionophore were covalently attached. The plasticizer-free polymer membranes containing covalently attached ionophore and ionic sites showed comparable or better potentiometric responses than conventional plasticized PVC-based ISEs doped with the free pH ionophore. To the best of our knowledge, it is the first time that a methacrylate-based alkyl sulfonate ionic site was covalently attached to the ion-selective membrane. In addition, by using hydrophilic ionophore and ionic sites, we confirmed for the first time that ISEs with both covalently attached ionophore and ionic sites give very long response times. Furthermore, due to the covalent attachment, ISEs with either covalently attached ionophore or ionic sites have high resistances to undiluted blood serum for at least 5 days, 90 °C heat for 2 hours, and 10% ethanol exposure for 1 day and showed good long-term stability (0.017 mV/h).

2021 GLRM 252

Ion-selective electrodes with hydrogel-based transducers using hydrophilic redox buffers

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Although the number of measurements performed using potentiometric sensors is large, the applications in which ion-selective electrodes (IESs) can be used are limited by the need for frequent recalibration and the large size of such electrodes, demanding both maintenance and skilled operators to obtain meaningful measurements. The size limitation is largely a result of the typically large volume internal filling solution. Sensors fabricated with miniaturized internal contacts that still retain a stable potential response and reproducibility in measurements, both over the long term and from one device to another, would expand the applications in which ISEs could be utilized. These expanded applications include both implantable and wearable medical devices, which would increase the availability of personalized medical treatment through the benefits of accurate long term and continuous monitoring of electrolyte concentrations in bodily fluids. The same advantages would be useful in environmental monitoring, where continuous data generation of ion concentrations would allow for both increased speed of detection of contamination in drinking water supplies, as well as data about ion speciation and relative concentration changes that take place during natural processes. Although a miniaturized inner filling solution is generally thought to result in unstable potentials as a result of ion activity changes in the inner filling solution, the issue has not been thoroughly investigated from the viewpoint of device-to-device reproducibility. Here, ISEs have been prepared using a miniaturized inner filling solution supported by a hydrogel, doped with a redox buffer composed of ferrocyanide and ferricyanide. Hydrophobic redox buffers have previously been shown to effectively control the phase boundary potential of solid-contact ISEs, although this demonstrates the first use of a dissolved, hydrophilic redox buffer to accomplish this. The longer-term stability of these

electrodes in terms of potential drift and loss of reproducibility has been also been investigated.

2021 GLRM 253

Functional group identification for FTIR spectra using image-based machine learning models

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FTIR is a ubiquitous non-destructive analytical method that provides information about chemical functional groups present in samples. Facile, streamlined analysis of FTIR spectra via a machine learning (ML) model would enable high-throughput applications of the method. The ML model will reduce the time required to evaluate spectra and determine present functional groups, while also eliminating subjectivity of interpretation. FTIR spectra from the NIST Chemistry WebBook are obtained via a web scraping method. Using Python scripts, each spectrum is converted from the downloaded file into a csv file. During the conversion, any spectrum not in units of absorbance or wavenumbers is removed. Spectra are normalized with respect to the most intense peak and saved as images. Spectra are sorted using the unique SMARTS key to determine the functional groups and image files are copied to corresponding directories. Many compounds have multiple functional groups and to address this, spectra are copied to each functional group directory that a compound contains. A convolutional neural network (CNN) is utilized to create a ML model for seventeen organic functional groups. The convolutions reduce data dimensionality over many nodes without reducing accuracy or specificity. Backpropagation is employed to improve model accuracy. Lastly, filters that are specific to features are used to direct spectral information throughout nodes. The implementation of filters reduces the reliance of the algorithm on one node and channels spectral information more efficiently. The trained functional group models are used to predict the functional groups present in unknown spectra to evaluate accuracy. All models are run simultaneously for an unknown spectrum. Fifteen of the seventeen models accurately predict functional groups of unknown spectra. The ML approach expedites analysis (15 seconds for a spectrum), without compromising accuracy or efficiency. The results aid in the application of ML to FTIR analysis because the model is generalizable and transferable without any computational or storage requirements. The described work is the first implementation of CNNs as a tool for spectral analysis and provides a platform in that future models can be pursued for specific FTIR applications or other spectral methods.

2021 GLRM 254

Protective Mechanism of Dried Blood Spheroids: Stabilization of Labile Molecules Stored under Ambient Conditions and Applications

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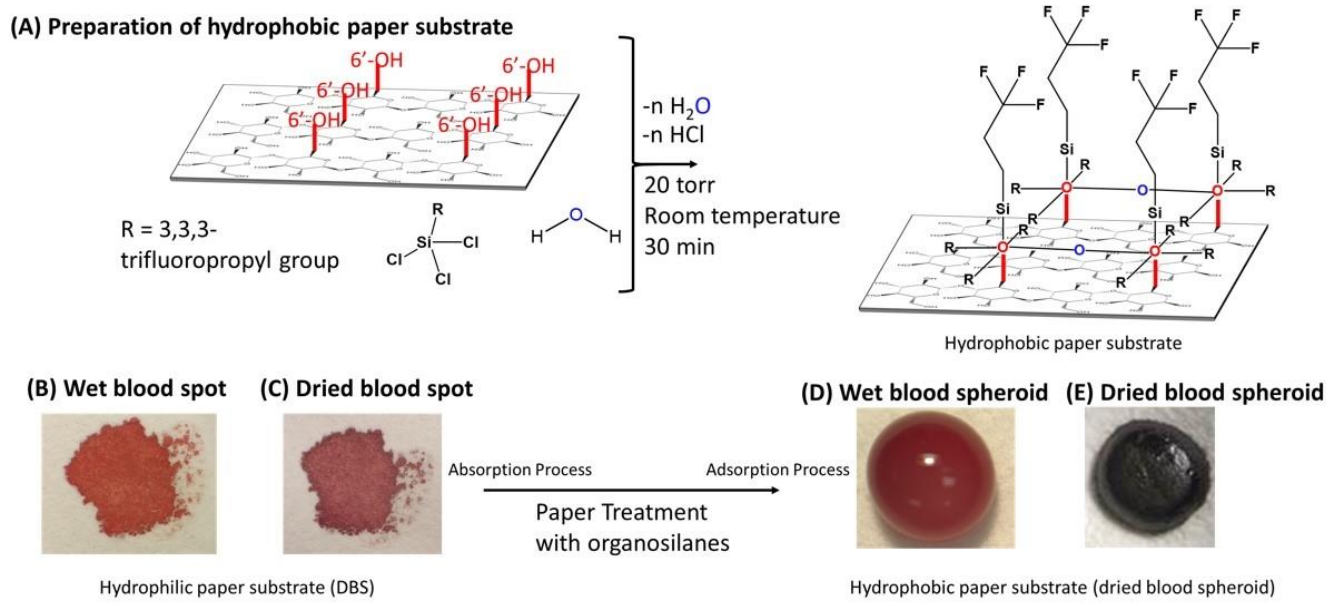
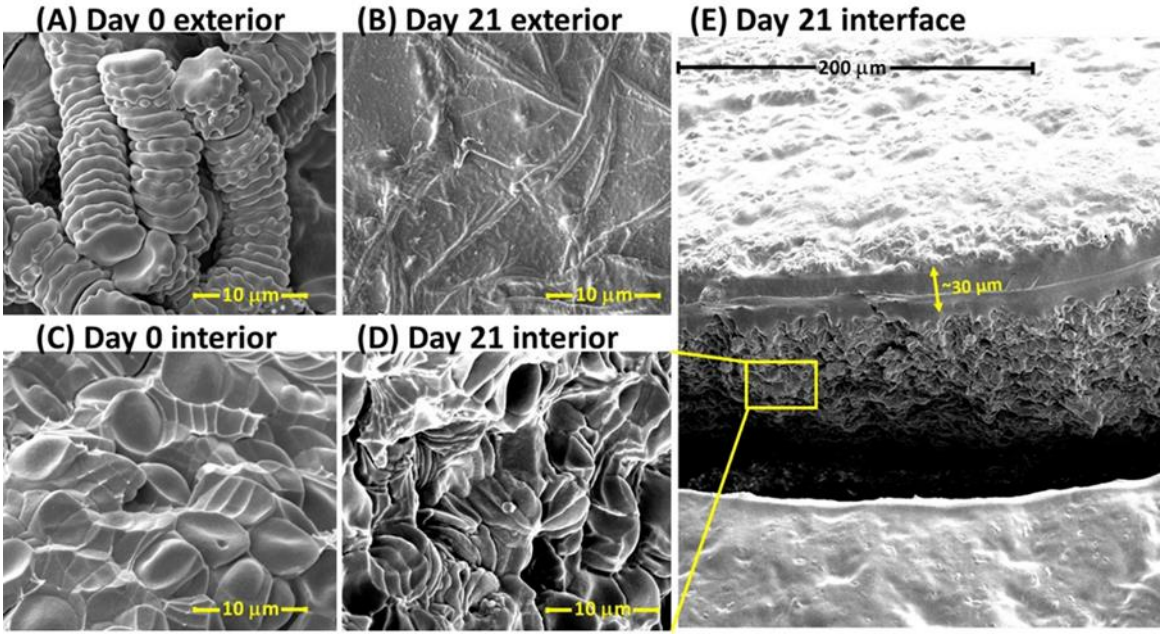
Ambient storage of biofluids on hydrophobic paper enhances stability of labile molecules through the formation of thin films or spheroids that form superficial barriers. Additionally, hydrophobic paper can act as a direct sample analysis platform with reduced sample preparation steps that are required for traditional dried blood spot (DBS) analysis workflows when coupled to tandem mass spectrometry (MS/MS). The protective film in dried blood spheroids has been determined to form from the self-assembly of red blood cells. In this study, the stability of illicit drugs and performance enhancer drugs in plasma, serum, and urine on hydrophobic paper stored at room temperature, as well as the introduction of an artificial barrier via polymer coating, was investigated. The stability, matrix effects, and ionization efficiency of the drugs in these matrices were investigated, and it was found that the drugs maintain stability on polymer-coated samples and samples deposited on hydrophobic-treated paper while poor stability was exhibited for samples on untreated paper without polymer coating. For performance enhancer drugs, matrix effects ranged from 55 to 98% for clenbuterol and 55 to 92% for trenbolone. The relative ionization efficiency for clenbuterol and trenbolone ranged from 71 to 92% and 70 to 93%, respectively. Increased signal-to-noise was observed for polymer-coated samples relative to non-coated samples.





2021 GLRM 255

Scaffolding towards Systems Thinking: Eliciting what Students Know through Evidence-Centered Design of a Case Study to Assess Students' Green Decision-Making

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In academic and industrial chemistry societies, long-standing professional interests in sustainability education are joined by emergent efforts to incorporate grand global challenges, such as those outlined by the United Nation Educational, Scientific and Cultural Organization (UNESCO) Sustainable Development Goals (SDGs). The phenomena posed by these SDGs and sustainability issues have enormous potential to inspire undergraduate science students. However, in the case of the undergraduate chemistry curriculum, integrating sustainability challenges--often the result of complex chemistry interacting at the boundaries of social or environmental systems--presents design challenges for curriculum developers working with novices' nascent knowledge base.

To meet this crucial need for sustainability education, successful integration of green and sustainable chemistry into the curriculum requires a deep knowledge of how people learn and an understanding of how to use this knowledge to design curricula and curricular materials to support learning. That is, there is an urgent need for (1) a theory of learning that can support students' green and sustainable thinking, (2) curricular

activities that are supported by theory and is informed by the results of assessment, and (3) assessments to measure students' knowledge-in-use. Our approach uses iterative case studies to introduce green chemistry metrics and tools for evaluation, followed by exploring life cycle thinking at beginning-of-life and end-of-life, and finally focusing on emergent behaviors between chemistry and environmental systems.

In this talk, we expand on this argument by illustrating the design process for a second-year organic course for STEM majors. Using a case study in which students evaluate synthetic routes to amide bond formation using green metrics for their argumentation, we outline the integration of evidence-centered design into the prompts of each case study element. The data presented will include the collection of two rounds of preliminary construct and response process validity data and subsequent revisions to prompt structures. This design process model serves as a template for curriculum designers with an interest in integrating socio-scientific issues in a chemistry course context.

2021 GLRM 256

Enzyme immobilization on metal-organic frameworks to facilitate greener chemistries

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The development of materials with co-immobilized enzymes that would advance new greener routes for the syntheses of pharmaceuticals and provide enantio-selectivity of substrates resulting in limited number of side products of biologically active compounds is the basis of this study. Successful entries into biocatalytic processes requires both biochemical and materials chemistry skill sets making this study highly collaborative focusing on creating new biocatalysts through co-immobilization of glucose oxidase (GOx) and chloroperoxidase (CPO) onto metal-organic frameworks (MOFs) to produce high-value pharmaceutical synthetic strategies. Creating robust and efficient biocatalysts of this nature could positively impact pharmaceutical organic syntheses by replacing hazardous solvents with greener chemistries.

2021 GLRM 257

From K-O2 to K-Air Batteries: Realizing Superoxide Batteries on the Basis of Dry Ambient Air

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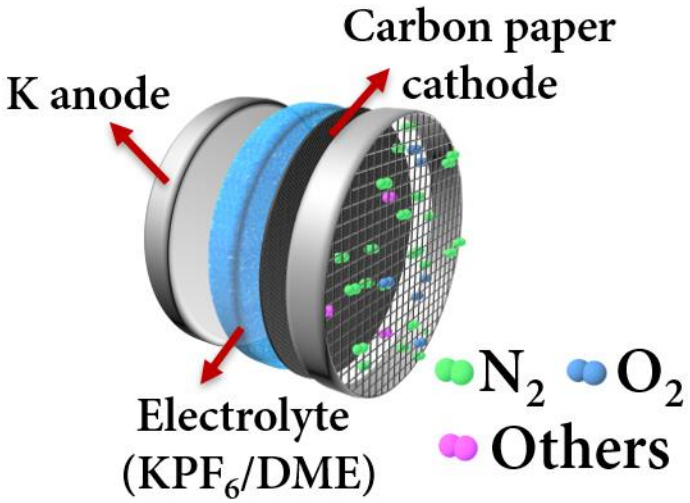
Although using an air cathode is the goal for superoxide-based potassium-oxygen (K-O2) batteries, prior studies were limited to pure oxygen. Now, the first K-air (dry) battery based on reversible superoxide electrochemistry is presented. Spectroscopic and gas

chromatography analyses are applied to evaluate the reactivity of KO2 in ambient air. Although KO2 reacts with water vapor and CO2 to form KHCO3, it is highly stable in dry air. With this knowledge, rechargeable K-air (dry) batteries were successfully demonstrated by employing a dry air cathode. The reduced partial pressure of oxygen plays a critical role in boosting battery lifespan. With a more stable environment for the K anode, a K-air (dry) battery delivers over 100 cycles (> 500 h) with low round-trip overpotentials and high coulombic efficiencies as opposed to a traditional K-O2 battery that fails early. This work sheds light on the benefits and restrictions of employing the air cathode in superoxide-based batteries.



2021 GLRM 258

Synthesis of a series of long chain, aliphatic, multi-dentate ligands as potential water remediators, and some complexes thereof

Jurlina Robinson, Destiny Proffett, Jiera Shears, Zeina Hachem, Dima Hammadi, Ayah Ismail, Evan Eding, Sameer Khan, Makalah McDougal, Ahmed Al-Hilali, Coryn Le, Kristian Arafat, Mena Morcos, ***Mark A. Benvenuto****, benvenma@udmercy.edu. Department of Chemistry and Biochemistry, University of Detroit Mercy, Detroit, Michigan, United States*

Several long chain, multi-dentate ligands have been produced, using only aliphatic starting materials. Amines such as tetraethyelenpentaamine, diethylene triamine, or ethylene diamine have been combined with aldehydes such as octanal, decanal, or dodecanal to produce ligands which should be highly hydrophobic, and that should be effective at removing metals ions from water. While smaller in chain length than established, defined macromolecules such as plastics, these ligands and their activity could be considered to function as lower molecular weight mimics of them. Complexes

using various transition metals or lanthanides have been made utilizing them, to determine how effectively these ligands extract metal ions from aqueous solutions.

2021 GLRM 259

Water treatment by a DC pin to water discharge plasma

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A pin to water DC discharge Cold Atmospheric Pressure Plasma (CAP) was used for water treatment. The plasma chemistry involved is a green chemistry as it eliminates the use or generation of hazardous substances in the design and application of this CAP to purify the water. Plasma was ignited in argon, argon + 20% oxygen, and air gases. A chemical “cocktail” of reactive nitrogen species and reactive oxygen species are produced within the gas to liquid interface during plasma ignition. Some of the long lived chemical species generated by the CAP were quantified. These include hydrogen peroxide, nitrates, and nitrites. Results indicate that all three gases are suited for generating hydrogen peroxide while argon and argon +20% oxygen generate very low amounts of nitrates and nitrites which are a known hazard for drinking water. OH radicals generated by argon and argon + 20% oxygen was quantified. OH radicals decompose a wide range of organic compounds, such as volatile organic compounds, pesticides, pharmaceuticals, and personal care products in water. Salicylic acid was used as a scavenger for OH radicals due to the fact that it reacts with the OH radical to produce 2,3-DHBA, 2,5-DHBA, and catechol. Quantification of OH radicals generated in the liquid water were obtained by using HPLC and adding the byproducts together. The chromatograms received from HPLC runs indicated that plasma treatment with argon + 20% oxygen produces more OH radicals than argon gas alone and that the amount of OH radicals increase with plasma treatment time. PFOA (perfluorooctanoic acid), the emerging contaminant in drinking and ground water was degraded using the CAP. Degradation of the PFOA was noted using mass spectroscopy. The peak areas for specific fragments of PFOA were seen to decrease after plasma treatment.

2021 GLRM 260

Uptake of radioactive ions from aqueous solutions by biopolymers

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The search for new adsorbents to decontaminate large bodies of water is a top priority for the scientific community. The presence of radionuclides like uranium and thorium in

the ecosystem has negative impacts in living organisms. Inexpensive biological waste such as spent green tea (GT), powdered yellow corn cob (YC), powdered chitosan (CH) and brown algae (AL) were evaluated as adsorbents of thorium and uranium ions from aqueous solutions. Equilibrium studies show that maximum adsorption capacities of 177 and 182 mg/g are achieved for thorium ions at pH 4 for GT and YC, respectively. Uranium ions are adsorbed at a maximum adsorption capacity of 68, 317 and 76 mg/g at pH 4 by GT, CH and AL, respectively. Salt effect demonstrated that the mechanism of adsorption is mainly driven by electrostatic and polar interactions for each radionuclide/adsorbent system. Desorption was optimized by using diluted HCl as eluting solvent. Time-dependent tests indicate that adsorption is complete in less than 10 minutes for thorium ions and less than 40 minutes for uranium ions. Scanning electron micrographs of the adsorbents display heterogeneous surfaces in agreement with their high adsorptive properties. Further studies are needed to scale up the process using these eco-friendly adsorbents for the decontamination of larger volumes of solution in column studies.

2021 GLRM 261

United States Water Quality as it Correlated to Consumer Socioeconomic Background

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Clean drinking water is a for granted necessity in the United States. Obtaining clean drinking water is a significant challenge for many countries around the world especially in developing countries where industrial waste finds its way into surface water source without much regulation from governmental agencies. However, in United States, potable water is regulated by the federal Environmental Protection Agency (EPA) to ensure public safety. The environmental protection agency has established standards for the maximum level of contaminants (MCLs) to regulate various contaminant levels in the public drinking water. Every five years, EPA publishes a list of contaminants to be considered for regulation known as the contaminant candidate list (CCL). Although there are many chemicals on the contaminant candidate list, only a handful will be considered for regulation. These contaminants are divided into six different groups: biological, organic chemicals, inorganic chemicals, radiological, disinfectants and disinfectant by-products. Copper and lead are strictly regulated by the EPA due to the harmful health concerns associated with elevated levels of these heavy metals. Heavy metals can enter water source due to erosion of household plumbing and their use in construction material. Recent improvements in construction materials have improved heavy metal levels in potable water however, some disparities remain in communities with lower household income. Although direct correlation was not observed, various lower income communities and states did display lower water quality.

2021 GLRM 262

Towards a greener synthesis of dibenzalacetone

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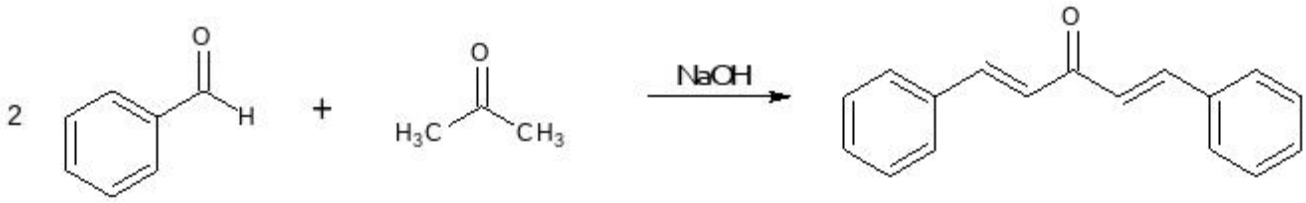
The synthesis of dibenzalacetone is a common experiment for undergraduate organic chemistry classes. The commonly used reaction conditions use a mixture of water and ethanol to solublize the reactants. Even though the product is not water soluble, the work up results in a filtrate that retains a considerable amount of product. The surfactants Triton-x and SPGS-550 were introduced to try to reduce the amount of ethanol needed to carry out the reaction, to improve the recovered yield and reduce the amount of waste produced.



2021 GLRM 263

Pretreatment and fiber content analysis of *Cannabis sativa*

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Cannabis sativa commonly known as hemp is one of the fastest-growing plants whose refined products have immense commercial value. Various products include refined hemp such as: biofuels, biodegradable plastics, textiles, dietary supplements, paper, clothing, and much more. Hemp fibers are also used in construction and manufacturing applications by strengthening their composite products. Hemp is a high yielding, sustainable, and environmentally friendly crop due to its various qualities, and has the potential to yield valuable raw materials for a great number of applications. Our research evaluates the pretreatment of hemp as well as the comparative analysis of the fiber content thereof. Our goal is to determine the suitability and the potential use of ionic liquid-based pretreatment (1-Butyl-3-methylimidazolium chloride) for the breakdown of hemp lignocellulosic biomass.

2021 GLRM 264

Biobased BPA Alternatives: a Search for Sustainable Synthesis

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Bisphenol A, or BPA, is a commonly used component in polymers. Unfortunately, this extensive use has resulted in widespread consumer concern over the pervasiveness of the diol in the environment and in human and animal tissues.
To avoid potential health concerns, we searched for an alternative. A furan core structure was chosen which we hypothesized could provide similar materials properties but not bind as well to estrogenic receptors. For proof of concept, these furanic diols were initially synthesized by stoichiometric means. However, as various uses for these diols have been explored, a need for a greener alternative synthesis arose. Catalytic methods of synthesis utilizing hemicellulosic furans has proven to be the best alternative thus far.

2021 GLRM 265

Green vitrimer chemistry for a teaching lab experiment

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In our continuing efforts to develop new experiments for the undergraduate laboratory modeling green chemistry and sustainable polymers, we noted there are limited education publications incorporating vitrimer chemistry. In this study, a recently published PLA-based vitrimer was explored as a potential teaching lab experiment using renewable feedstocks and novel benign catalysts. The vitrimers were prepared from an intermediate hydroxy-terminated star-shaped polymer using a variety of bismuth catalysts, replacing $Sn(Oct)_2$. Ethyl acetate and acetone were shown to be adequate alternative solvents to methylene chloride when precipitating and crosslinking the star-polymer. The resulting crosslinked polymers were subjected to breakage and then compression molding, which confirmed that the material was vitrimeric in nature; demonstrating dynamic properties for student engagement.

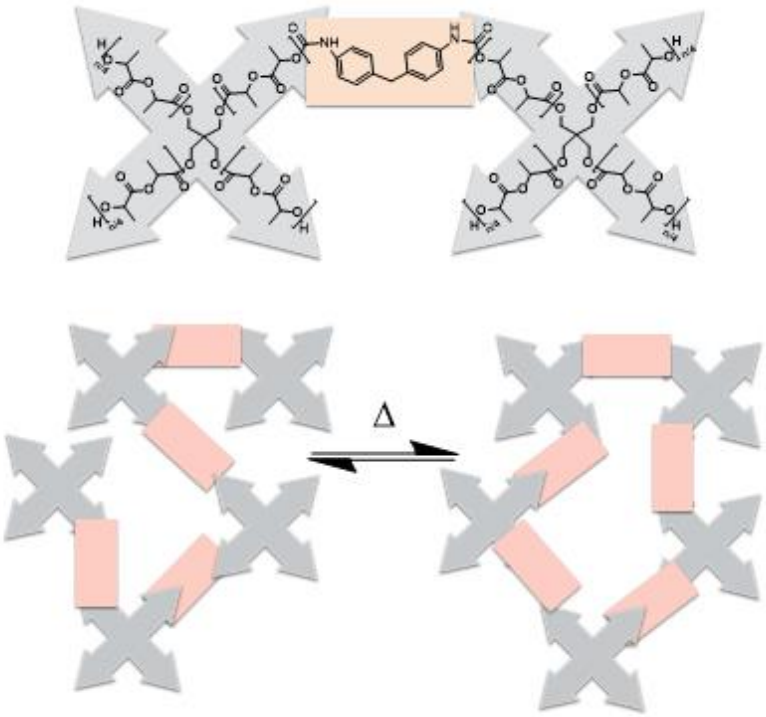

Illustration of the dynamic covalent network of PLA-based vitrimer.

2021 GLRM 266

Surface Monitoring of the Air-Seawater Interface during a Small-Scale Marine Algal Bloom

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The composition and lifetime of sea spray aerosols are driven by the molecular and biological complexity of the air-seawater interface. The changing biogeochemistry of algal systems throughout their bloom alters both the air-seawater interface and the mechanics of bubble bursting, giving rise to dynamic changes in sea spray aerosol composition. To understand the temporal change at the sea surface and subsequent sea spray aerosol production, we investigate the marine-relevant diatom *Skeletonema marinoi.* We explore in situ the temporal surface properties of small-scale *S. marinoi* monocultures by utilizing the surface techniques of Brewster angle microscopy (BAM) imaging, vibrational sum frequency generation (SFG) spectroscopy, and infrared reflection absorption spectroscopy (IRRAS). BAM images show morphological structural changes and heterogeneity in the interfacial films, revealing an ~5 nm thick surface

region in the late stages of the bloom. Our surface-specific SFG spectroscopy results show significant diminishing in the intensity of the dangling OH bond of water molecules consistent with organic species partitioning to the surface. Interestingly, we observe a new broad band appear between 3500 cm^{-1} to 3600 cm^{-1} in the late stages of the bloom that is attributed to weak hydrogen bonding interactions of water to the surface-active biogenic matter. IRRAS confirms the presence of organic molecules at the surface as we observe increasing intensity of vibrational alkyl modes and the appearance of a proteinaceous amide band. By coupling surface imaging and vibrational spectroscopies to complex, time-evolving, marine-relevant systems, we begin to unravel the complex role of algae as the “ocean’s elevator” which acts to transfer biogenics between bulk seawater and the air-seawater interface.

2021 GLRM 267

Development of Histidine Kinase Inhibitors as Anti-virulence Agents in Pseudomonas Aeruginosa

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Bacterial resistance to antibiotics is rapidly increasing and is projected to cause more than ten million deaths per year by 2050, surpassing cancer as the second leading cause of death. New strategies to combat resistant organisms are desperately needed. Two-component systems (TCSs) are the main signal transduction pathways used by bacteria to regulate a variety of processes including development, metabolism, virulence, and antibiotic resistance. TCSs consist of a homodimeric membrane-bound sensor histidine kinase (HK), and a cognate effector, the response regulator (RR). The high degree of sequence conservation in the catalytic and ATP-binding (CA) domain of HKs and their essential role in bacterial signal transduction make them an attractive target because inhibitors of this site could possess broad-spectrum antibacterial activity. Targeting virulence, as opposed to bactericidal or bacteriostatic compounds, has the potential to reduce the evolutionary pressure for acquired resistance. Additionally, compounds targeting the CA domain have the potential to affect multiple two-component systems that regulate virulence in a single pathogen, such as *Pseudomonas aeruginosa*, potentially minimizing acquired resistance further.
We will present structure-activity relationship (SAR) studies of 2-aminobenzothiazole-based inhibitors of the CA domain of three distinct HKs. Recently, we have shown that these compounds are effective in whole cells with anti-virulence activities in *P. aeruginosa*, reducing biofilm production, virulence-associated motility, and toxin production. To identify the direct protein targets of these inhibitors in live cells, we have generated a probe that contains both the 2-aminobenzothiazole scaffold, a sulfonyl fluoride electrophilic group to promote covalent tagging of the targeted proteins, and an alkynyl handle allowing for fluorescent labeling and biotin-avidin affinity isolation using click chemistry. Proteomic results indicate that these inhibitors target HKs in *P.*

aeruginosa, labeling a residue in the active site of the CA domain. These probes will ultimately be utilized to map the HK inhibition events that are most responsible for the observed anti-virulence activities in *P. aeruginosa* and myriad other gram-negative pathogens.

2021 GLRM 268

Development of selective BET bromodomain inhibitors as anti-inflammatory and anti-cancer agents

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Epigenetic therapies dynamically control dysregulated gene expression. My research focuses on the disruption of epigenetic complexes containing the protein BRD4 a member of the BET family proteins. Previous inhibitors have succeeded at inhibiting this entire family of BET proteins. Current BRD4 inhibitors in the clinic are being studied as anti-cancer and anti-inflammatory drugs, but lead to undesirable side-effects due to a lack of BRD4 selectivity. There is a need for more selective inhibitors to provide refined tool compounds to study the biological function of the individual BET protein, and to ultimately minimize side effects in the clinic. My research addresses the selectivity problem with inhibitors for improving our understanding of BRD4 function and seeks to reduce associated toxicities. By disruption of the conserved water network, a newly discovered halogen-bonding interaction and targeting a non-conserved amino acid Asp144 in the first bromodomain of BRD4 (D1), led to a unique selectivity profile and improved affinity for BRD4 D1. Currenlty, a BRD4 D1 selective inhibitor has been developed with 9- to 33-fold over other BET bromodomains. These inhibitors exhibit biological activity in cells and in preliminary anti-inflammatory experiments, in vivo. This research seeks to improve upon our BRD4-selective inhibitors to provide fundamental understanding of BRD4 biology and to treat disease.

2021 GLRM 269

Switchable electron catalysts modulated by the relative insensitivity of G-quadruplex secondary structures to destabilization by a chaotropic Hofmeister ion

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The Hofmeister ions are a series of ions categorized from their ability to increase biomolecular secondary structure stability (kosmotropes) to their ability to decrease biomolecular secondary structure stability (chaotropes). Despite extensive work on Hofmeister ions on proteins, comparatively less work has been done on the impacts of these ions on nucleic acid secondary structure. Here we show that the G-quadruplex, a noncanonical nucleic acid secondary structure, retains stability in solutions of anionic chaotropes relative to an array of other nucleic acid secondary structures including a duplex, triplex and i-motif. Additionally, we found that the relative insensitivity of G-quadruplex compared to duplex structures can enable a switchable nucleic acid electron transfer device using heat, dilution, or desiccation. The structure switching afforded by chaotrope coupled with the fact that G-quadruplexes, but not duplexes, catalyze electron transfer in the presence of the co-factor hemin enabled us to produce an electron transfer catalyst that can be switched by modulating the concentration of chaotrope in the presence of a strand of DNA that can form duplex or G-quadruplex structures.

2021 GLRM 270

Designing Peptidomimetic Antagonists of HIV-1 Envelope and SARS-CoV-2 Spike for Disease Therapy and Prevention

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With 38 million individuals worldwide infected by HIV-1 and no cure as yet for the disease, new options for prevention and therapy are needed in the global effort to end AIDS as a public health crisis. Cyclic peptides have arisen as a promising new class of peptidomimetic therapeutics to target the gp120 envelope glycoprotein on the HIV-1 surface by triggering gp120 shedding, causing irreversible inactivation of the virus and inhibiting host cell infection. The goal of our project is to synthesize different configurations of an existing cyclic peptide in order to identify those with optimized gp120 binding and infection inhibition potencies. This is done by modifying the three-residue pharmacophore region of the cyclic peptide with different functional groups. A series of molecular and virological assays are performed on these compounds to quantify their binding and infection inhibition properties. These new configurations help us learn about the mechanisms involved in the binding and inhibition by our cyclic peptides with HIV-1 Envelope. Understanding the mechanism enhances synthetic design, leading to the synthesis of better-performing cyclic peptides for viral envelope inactivation. Our work also consists of investigating the structural similarities between the receptor-binding envelope glycoprotein complex of HIV-1 and the receptor-binding glycoprotein spike region on the surface of SARS-CoV-2 virus. Our understanding of the makeup of the glycoprotein for HIV-1 and how to target this virus entry complex has been instrumental in our fight against the novel coronavirus, which contains a similar surface glycoprotein region for its cell entry and infection.

2021 GLRM 271

Synthesis of a Norbornene-Containing for the Enzyme Geranylgeranyltransferase

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Geranylgeranyltransferase (GGTase) plays a significant role in regulating cell signaling between cells by inducing hydrophobicity on cell signaling proteins that end in a CAAX amino acid sequence present on their C-terminal. This allows them to associate with the cell membrane. The primary function of GGTase is to attach a “membrane anchor” or a non-polar geranylgeranyl group to proteins. The significance of research on prenyltransferases such as this one is the dramatic affect their inhibition could have on cancer cell development. Ras proteins, for example, upon activation are responsible for regular cell growth and proliferation. However, mutations to the Ras oncogene can induce irreversible activation leading to uncontrollable cell growth and division. This is incredibly significant as roughly 20% of tumors are induced by Ras mutations. This study focuses on the synthesis of a probe that is similar to the GGTase substrate geranylgeranyldiphosphate (GGPP) which can be used in conjugation with a tetrazine molecule for the selective inactivation of Ras proteins.

2021 GLRM 272

Chemical probe development for BPTF reader domains utilizing biophysical assays

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In many disease states epigenetic protein complexes, such as the Nucleosome Remodeling Factor (NURF), have aberrant levels and/or function, which can result in dysregulation of gene expression. Bromodomain and PHD-finger containing transcription factor (BPTF), the largest subunit of NURF, is overexpressed in several cancers. The structurally characterized bromodomain and c-terminal PHD finger of BPTF bind chromatin via interactions with acetylated and methylated histone tails respectively to facilitate chromatin remodeling into an accessible state for gene transcription. While BPTF is a promising anti-cancer therapeutic target, the relevance of its individual domains in disease function is unclear. Currently, there are several reported BPTF bromodomain inhibitors, but there is a significant need for improved potency and selectivity to develop useful chemical probes. In our lab we have a promising new pyridazinone scaffold with improved potency for BPTF and selectivity over the BET family of bromodomains (>350-fold). We have utilized Protein-Observed Fluorine (PrOF) NMR, AlphaScreen, and x-ray crystallography to rationally design and expand the pyridazinone scaffold into a potent lead against the BPTF bromodomain (IC_{50} = 70 nM) that has shown preliminary on-target effects in synergistic cellular studies

with chemotherapeutics. For the BPTF PHD finger, there are no reported small molecule binders. Recent progress in our lab towards assessing the ligandability of the PHD finger by computational analysis, as well as method development for future NMR-based fragment screening will also briefly be discussed.

2021 GLRM 273

Manipulating Sugar-Driven Cellular Cytokine Production via Photocaged Glucose

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As a method of studying the cellular effects in hyperglycemic conditions, photocaged carbohydrates are being synthesized to control cytokine production. O-linked N-acetylglucosamine (O-GlcNAc), a monosaccharide derived from Glucose, is crucial to a multitude of metabolic processes (i.e. transcription, translation, nuclear transport, etc.). The post translational modification of O-GlcNacylation adds O-GlcNAc to a signaling protein at a serine or threonine site. In strained cell conditions, such modifications have a direct impact on internuclear cytokine levels. As the field develops greater knowledge of O-GlcNAcylation and its effects, stronger connections between cytokine overproduction and fatalities from hyperglycemia, a toxic event in conditions like diabetes mellitus, can be made. Currently, there is little known about what initiates unrestrained cytokine production as a response to cellular stress. In order for an inflammatory response of cytokines to occur it can be suspected that transcription factors are altered by O-GlcNAcylation to persuade its movement to the nucleus. Such nuclear translocation catalyzes cytokine production. This project identifies a chemical strategy to control GlcNAc elevation, effecting transcription factor nuclear relocation and cytokine levels. Specifically, transcription factor, NF-kB, serves as a model cytokine promoting protein that responds to hyperglycemia. Photocages, are light sensitive synthetic molecules used to harness reactivity of biological components. Once chemically bound to sugars, like O-GlcNAc or Glucose, it is of interest to determine their ability to control nuclear translocation of transcription factors, followed by nuclear cytokine synthesis. This will be accomplished by successfully synthesizing Glucose photocages, determining its decaging capabilities, then applying them to a variety of cell lines. Since Glucose is the predecessor of O-GlcNAc, we must gauge its photocage abilities to widen our scope of understanding towards these tools. Gaining depth in the versatility of photocaged carbohydrates, necessary for cellular maintenance, will encourage new directions of medicinal treatments.

2021 GLRM 274

Profiling Parkinson's Disease-related Antigens via Epitope Surrogate Technology

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While the pathogenesis of Parkinson's disease (PD) remains unknown, mounting evidence is showing that adaptive immunity plays an important role in processes leading to motor dysfunction. Specifically, humoral immune responses against PD-related proteins correlate with symptom severity, suggesting that IgG will be valuable biomarkers for tests that diagnose early stages of PD. Unfortunately, uncovering disease-relevant antigens needed as biomarker targets a priori has been challenging. To characterize novel antigens that elicit IgG responses in Parkinson's disease, we utilized an unbiased chemical approach to profile the immuno-proteome of PD, but not healthy control plasma donors. We hypothesized that epitopes on the complex autoantigens in PD patients could be represented by small-molecules capable of binding the same IgG binding site as the native epitope, so such small molecules are termed 'epitope surrogate.' Epitope surrogates were discovered by screening plasma from PD patient against libraries containing 250,000 unique peptidomimetic compounds after counter-screening the library against non-PD plasma. We identified one compound which was recognized exclusively by PD patient-derived antibodies. We affinity-purified PD plasma-specific IgG using the epitope surrogate as a capture agent and subsequently after immunoprecipitation. We identified potential autoantigens via proteomic analyses. our analyses revealed both apolipoprotein A-I (APOAI) and α-synuclein, presumably as a complex, is a candidate PD-specific autoantigen. Indeed, competitive binding analyses revealed specific binding only in the presence of a 4:1 mixture of the two proteins, but no competition of IgG binding was observed with either protein alone. Our current work is focused on validating the disease specificity of this complex and characterizing its role, as well as the role of IgG in Parkinson's disease with the hope that the it will serve as diagnostic markers for PD in the future.

2021 GLRM 275

Molecular Modeling of Penicillin Binding Proteins: Mechanism Elucidation and Probe Design

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The Penicillin Binding Proteins (PBPs) are a ubiquitous family of enzymes found in most bacteria and are quintessential drug targets for β-lactam antibiotics like penicillin derivatives and cephalosporins. However, the study of these enzymes has been limited due to a lack of tools to characterize the function and interactions of these proteins in bacterial systems, and the tools currently available have poor selectivity between isoforms and therefore are not useful as probes. Selective β-lactone probes targeting PBP isoforms 1b and 2x in *Streptococcus pneumoniae (Spn*) have been recently reported by the lab of Dr. Erin E. Carlson at the University of Minnesota. We have utilized available X-ray crystallography and experimental activity data in our molecular modeling techniques, including[CMM1] covalent and non-covalent docking methods

along with molecular dynamics. Here we report the relationship between structure and selectivity of PBP probes, which will be used in the future design of selective tools for the study of the PBPs.

2021 GLRM 276

BPEI otentiation restores multidrug resistant KPC to β-lactam antibiotics

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Pathogenic microorganisms rapidly and readily adapt to overcome threats. This evolutionary arms race between ourselves and such microbes has led to a global health emergency spanning decades. These microbes quickly develop solutions to evade treatments, such as antibiotics, to continue growth; the cause of increased infections, death, and financial strain on healthcare systems. Development of new therapeutics aimed to combat such microbes are needed to overturn this arms race in favor of human health. Gram-negative bacteria, *Klebsiella pneumoniae* and *Escherichia coli*, gained resistance to carbapenem antibiotics. Utilizing the *Klebsiella pneumoniae* carbapenemase (KPC) enzyme, these bacteria have the ability to withstand last-resort carbapenem antibiotics in addition to already being multidrug-resistant. Our lab has demonstrated 600 Da branched polyethyleneimine (BPEI) as a potentiator for other bacterial species, effectively lowering the minimal inhibitory concentration (MIC) of β-lactam antibiotics. This application carries forward aimed to demonstrate BPEI's capabilities as a potentiator for β-lactam antibiotics when treated against KPC *K. pneumoniae* and *E. coli*. Success in this area grants greater value of BPEI as a means to answer and maintain the use of carbapenem antibiotics.

2021 GLRM 277

Thromboxane Synthase (CYP5A1) Interactions with Small Molecule Ligands

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Thromboxane A_2 synthase (CYP5A1) is a membrane-bound cytochrome P450 enzyme which initiates platelet aggregation in humans. Through an unusual P450 mechanism, CYP5A1 isomerizes prostaglandin H_2 (PGH2) to the potent vasoconstrictor and clotting factor thromboxane A_2. CYP5A1 is a viable drug target for the treatment of hypertension, atherosclerosis, ischemia, and other cardiovascular diseases, but initial inhibitors have not shown strong clinical efficacy, suggested in part due to incomplete CYP5A1 inhibition *in vivo*. In the absence of structural information to support drug design**, this project probes how CYP5A1 interacts with diverse small molecules**

through ligand binding analysis. Recombinant human CYP5A1 has been expressed in *E. coli* and purified. The binding of substrate analogs and inhibitors in CYP5A1's active site have been characterized and the dissociation constants determined. Two stable PGH_2 analogs, which differ only at the position of the endoperoxide moiety, display substrate-like Type I binding modes when analyzed via UV-visible spectroscopy, but resulted in a 50-fold difference in dissociation constants. A series of Type II inhibitors were also explored to probe the overall size and shape of the active site in lieu of a structure. This work is expected to identify features of diverse small molecule ligands that correlated with binding affinity, a first step in the design of specific therapeutics for CYP5A1 inhibition for the treatment of cardiovascular diseases.

2021 GLRM 278

Protein/protein interactions in the human cytochrome P450 system

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Cytochrome P450 enzymes are the major superfamily of enzymes involved in xenobiotic metabolism and steroid biosynthesis. Human P450 enzymes are membrane proteins requiring a redox partner protein for catalysis. This study focuses on P450 enzyme interactions with the redox partner cytochrome P450 reductase. Reductase accepts electrons from NADPH via its FAD domain, transfers them to its FMN domain, and then supplies those electrons to the P450 heme to support P450 catalysis. The reductase FMN domain binds directly to the proximal face of P450 enzymes, but this interaction is transient, and little is known about the details of the interactions of the FMN domain with 50 different human P450 enzymes. Thus, this study sought to better define the structural interactions and the functional implications of the reductase FMN domain binding to multiple human P450 enzymes, including P450 enzymes responsible for both steroidogenic and xenobiotic metabolism.
To facilitate interactions of the reductase FMN domain and the different P450 enzymes, artificial fusion proteins were generated. The fusion proteins for xenobiotic CYP3A4, CYP2D6, CYP2E1, and CYP2A6, and steroidogenic CYP17A1 and CYP21A2 were successfully expressed in *E. coli* and purified. Ligand binding studies and substrate metabolism assays were used to compare the functions of these fusion proteins with the respective isolated P450 enzyme. The presence of the FMN domain fusion does not appear to change the ligand binding mode for any of the enzymes. However, fusion of the FMN domain can affect the percentage of the P450 population capable of ligand binding and the dissociation constant (K_d) in different ways for different P450 enzymes—either increasing or decreasing it. For some of these P450 enzymes, the effect of the FMN domain varies for different ligand types. These results reveal intricate communication between the proximal P450 surface where the FMN domain binds and the buried active site some 15-20 Å away. This variability suggests that different P450 enzymes do interact with the same reductase FMN domain in different ways, which might provide an orthogonal route to modulating drug metabolism and steroidogenesis.

2021 GLRM 279

Structure and Function of Human Cytochrome P450 8B1

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Human Cytochrome P450 8B1 (CYP8B1) is involved in the conversion of cholesterol to bile acids. CYP8B1 hydroxylates the steroid ring system at C12 to produce the bile acid cholic acid. As such, this enzyme controls the ratio of cholic acid over another bile acid called chenodeoxycholic acid. The ratio of these two bile acids controls the overall hydrophobicity of the bile pool and signaling through the farnesoid X receptor (FXR). Recent knockout studies implicated CYP8B1 as a good drug target for nonalcoholic fatty liver disease and type 2 diabetes. However, there are no selective inhibitors known for this enzyme, and no structures of CYP8B1 to guide their development.

Herein the CYP8B1 protein was generated recombinantly in *E. coli* from a synthetic engineered gene, purified to homogeneity, and characterized structurally and functionally. This protein displayed spectral features characteristic for P450 enzymes and was catalytically active. Changes in the absorbance spectra were used to evaluate the binding of ligands, to identify the tight-binding non-selective small molecule tioconazole. This ligand was then used to solve the first X-ray structure of CYP8B1 (at 2.6 Å resolution). This structure reveals the *(S)*-tioconazole imidazole nitrogen forming a coordinate covalent bond to the CYP8B1 heme iron, consistent with enzyme inhibition. The ligand is positioned towards the B' helix due to the spatial hinderance of W281 and N286 of I helix on the opposite side of the active site. The availability of the CYP8B1 active site architecture should aid structure-based design of inhibitors that selectively bind CYP8B1 vs. other closely related P450 enzymes, such as CYP7A1. Selective inhibitors should promote a better understanding of the role of CYP8B1 inhibition in normal physiology and disease states and provide a possible treatment for nonalcoholic fatty liver disease and type 2 diabetes.

2021 GLRM 280

New copper(II) complexes derived from anthranilamide Schiff bases: Insights into mode of action and antiproliferative study

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Development of new compounds with potential therapeutic activity is receiving much attention in response to disease-causing agents in the world. Herein, we report new copper(II) complexes synthesized from anthranilamide and salicyaldehyde (B1) and 5-

bromosalicyaldehyde (B2). The compounds were characterized by ^{1}H NMR, ^{13}C NMR, FTIR, mass spectrometry, cyclic voltammetry, UV-vis and fluorescence spectroscopy. The ESI-MS of the Schiff base ligands and complexes in acetonitrile were in good agreement with the calculated m/z values. Redox potential measurements confirmed quasi-reversible one-electron transfer for complexes under aerobic and anaerobic conditions. The complexes exhibit fluorescence, while UV-vis spectra show both *d-d* and charge transfer transitions. DNA cleavage studies revealed reactivity toward supercoiled at varying concentrations of the complexes. Oxidative degradative mechanism *via* ROS were evaluated for each compound. The complexes were also evaluated for antiproliferative activity on breast and cervical cancer cell lines and dose-dependent cytotoxicity toward cancer cell lines was determined from cell viability experiments.

2021 GLRM 281

Investigation of cytochrome P450 2J2 ligand binding modes

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Human cytochrome P450 2J2 (CYP2J2) is expressed primarily in the heart where it is thought to play a multifaceted role in cardioprotection and possibly also xenobiotic metabolism. CYP2J2 oxidizes endogenous polyunsaturated fatty acids, including arachidonic acid and linoleic acid, to various epoxyeicosatrienoic acids (EETs). These EETs are implicated in vasodilation and protection against hypoxia-reperfusion, but also promote tumor growth and metastasis, where their inhibition may be a clinical advantage. Recently, it has been reported that CYP2J2 is inhibited by anti-hypertensive drugs including manidipine, azelnidipine, and telmisartan. In its drug metabolism role, CYP2J2 metabolizes xenobiotics including anti-histamine and anti-cancer agents. While kinetic and metabolic parameters for many of these endogenous and xenobiotic compounds have been reported, it remains to be elucidated how such a wide variety of ligands are accommodated by the CYP2J2 active site.
This study determined the binding modes of a catalog of CYP2J2 ligands for the purpose of better understanding their interactions with CYP2J2. These compounds include substrates, inhibitors, xenobiotics, and a broad panel of azole-containing compounds. The binding modes and affinities were determined by monitoring the spectral shift of the P450 heme Soret absorbance, which is indicative of perturbation of the heme environment. Such spectral shifts indicated varying responses: displacement of the heme-coordinated water (type-I binding mode), compound coordination to the heme iron (type-II), a red-shifted type-I binding mode, compound coordination to heme coordinated water (reverse type-I binding mode), or no spectral shift. As the latter result can be consistent with no binding or binding in the active site in a way that does not perturb the heme center, these latter compounds were investigated via a luminescence-based inhibition assay to verify their interaction with CYP2J2. Overall, this study

expands our understating of different ligand scaffolds compatible with CYP2J2 binding, ultimately supporting the development of CYP2J2-targeted therapeutics. Supported by NIH R37 GM076343.

2021 GLRM 282

IONiC's Recent Virtual Approaches to Engage the Chemistry Community During the Time of COVID-19

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IONiC, the Interactive Online Network of Inorganic Chemists, is a community whose goal is to elevate, modernize, and disseminate information to increase student-centered learning using visible teaching and community engagement. The Virtual Inorganic Pedagogical Electronic Resource (VIPEr) has been the primary means of interacting with the inorganic chemistry community for the last 13 years, along with various workshops and social events at American Chemical Society and other Meetings. However, with the advent of the COVID-19 pandemic in 2020, and nearly all instruction moving to fully remote or hybrid formats, IONiC has tried to pivot to better support the teaching community during these unprecedented times. To this end, starting in July of 2020, we began hosting over Zoom sessions called SLiTHErs (Supporting Learning with Interactive Teaching: a Hosted, Engaging Roundtable). These presentations and discussions allow faculty to come together remotely and discuss approaches to their teaching, particularly with respect to moving to remote learning. The overall process for creating SLiThErs will be described and several specific lessons learned from them will be highlighted, as well as the future schedule for SLiThErs. IONiC has also been using a lively Discord server to interact with the community and further discuss topics similar to those in the SLiThErs during the pandemic, as well as creating short recorded discussions called nanoCHAts. The nanoCHAts are an opportunity for community members to critically reflect on their teaching practices and learn about the experiences of their peers.

2021 GLRM 283

Photoactivatable Pt(IV) Prodrugs Harnessing CD36 for Ovarian Cancer Therapy

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Targeting CD36 is a new therapeutic approach in cancer therapy. CD36 is a member of the class B scavenger receptor family of cell surface proteins that facilitates the uptake of free fatty acids for lipid metabolism. CD36 promotes tumour growth by fueling cancer metastasis, supporting drug resistance, and modulating tumor immunity. Recent studies indicate that CD36 is upregulated in ovarian tumors. We hereby engineered photoactivatable Pt(IV) prodrugs that harness CD36 to target ovarian cancer cells. The

Pt(IV) prodrugs mimic the fatty acid structure and act as “Trojan horse” to exploit CD36 to facilitate their cell entry. CD36-dependent cell entry of the Pt(IV) prodrugs was validated by graphite furnace atomic absorption spectroscopy using ovarian cancer cells with different expression levels of CD36 and a CD36 inhibitor, SSO. Upon entering cancer cells, these Pt(IV) prodrugs are activatable by light. Photoactivation of the Pt(IV) prodrugs was achieved via the attachment of fluorophores. Light irradiation enhances cytotoxicity of the Pt(IV) prodrugs up to 20 times against ovarian cancer cells *in vitro*. Our computational analysis indicates that the photoactivation process is driven by photoinduced electron transfer from the attached fluorophore to the Pt(IV) center. The resulted Pt(III) species is then rapidly reduced in aqueous solution and generates the cytotoxic Pt(II) product.

2021 GLRM 284

Electronic Structure of Actinide Oxide Nanoclusters

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Low valent actinide ions in the aqueous solution aggregate through the complex network of reactions such as hydrolysis, olation, and oxidation reactions. The study of An(IV) nanoclusters has potential applications in nuclear waste reprocessing, storage, and disposal. The Pu_{38} nanocluster contains a $[Pu_{38}O_{56}]^{40+}$ core stabilized by inorganic capping ligands. Interestingly, Pu_{38} species exhibits the rapid change of the aqueous spectral signature through acidification and dilution upon altering the ratio of water and chloride in the cluster surface while leaving $[Pu_{38}O_{56}]^{40+}$ inner core structurally unaltered. This phenomenon confirms a dependency of the cluster’s physiochemical properties on its surface speciation. Here, we present a density functional theory study of the electronic structure of $[Pu_{38}O_{56}Cl_{42}(H_2O)_{20}]^{2-}$ and $[Pu_{38}O_{56}Cl_{54}(H_2O)_8]^{14-}$ to explain the $[Pu_{38}O_{56}]^{40+}$ stability and physiochemical properties with different surface speciations.

2021 GLRM 285

Ligand effects on decarbonylation of Palladium-acyl complexes

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Linear α-olefins are widely used in industry as feedstocks for consumer products such as surfactants, lubricants, and polymers. However, current dependence on petrochemical sources for these commodity chemicals have long-term sustainability and environmental implications. Bio-derived carboxylic acids and their derivatives have

attracted great interest as potential feedstock due to their ready availability in nature, relatively cheaper cost, and ability to generate valuable olefins. Using combined experiment and theory, we have studied the influences of supporting phosphine ligand structure on the dehydrative decarbonylation of (L*n*)Pd^{II}(Cl)-hydrocinnamoyl complexes (L = P^tBu_3, *n* = 1; L = PPh_3, *n* = 2; L = dppe, *n* = 1) to yield styrene. Abstraction of chloride from the complexes by silver, and sodium salts enhances the efficiency of styrene formation, according to the following trend in L: P^tBu_3 > dppe > PPh_3. A stable intermediate forms after chloride abstraction, from which β-hydride elimination is most affected by ligand choice. Density functional theory calculations revealed β-hydride elimination from the stable intermediate to be rate-determining for the overall dehydrative decarbonylation. The *trans* disposition of the two phosphine ligands for L = PPh_3 contributes to the low efficiency for styrene production in that case. Overall, coordinative desaturation through chloride removal and use of the highly sterically hindered P^tBu_3 greatly facilitate dehydrative decarbonylation. We hope that our findings will inform future efforts to design new catalysts for the generation of olefins from bioderived carboxylic acids.

2021 GLRM 286

Iron (II/III) Halide Complexes Promote the Interconversion of Nitric Oxide and *S*-nitrosothiols through Reversible Fe-S Interaction

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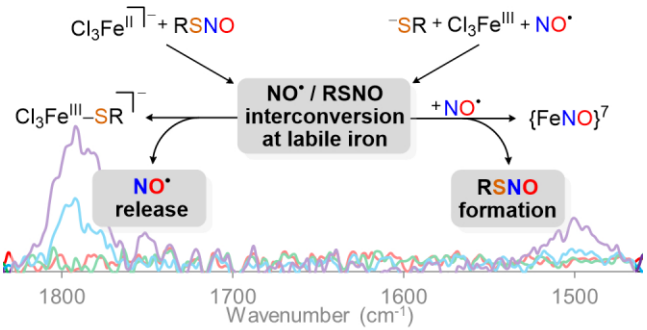
Heme and non-heme iron in biology mediate the storage/release of nitric oxide (NO) from *S*-nitrosothiols as a means to control the biological concentration of NO. Despite their importance in many physiological processes, the mechanisms of N-S bond formation/cleavage at Fe centers have been controversial. Herein, we report the interconversion of NO and *S*-nitrosothiols mediated by Fe^{II}/Fe^{III} chloride complexes. The reaction of two equivalents of *S*-nitrosothiol (Ph_3CSNO) with $[Cl_6Fe^{II}_2]^{2-}$ results in facile release of NO and formation of iron(III) halothiolate. Detailed spectroscopic studies, including in situ UV-vis, IR, and Mössbauer spectroscopy, support the interaction of the S−atom with the Fe^{II} center. This is in contrast to the proposed mechanism of NO release from the well-studied “red product” k^1-N bound *S*-nitrosothiol Fe^{II} complex, $[(CN)_5Fe(k^1\text{-N-RSNO})]^{3-}$. Additionally, Fe^{III} chloride can mediate NO storage through the formation of *S*-nitrosothiols. Treatment of iron(III) halothiolate with two equivalents of NO regenerates Ph_3CSNO with the Fe^{II} source trapped as the *S* = 3/2 $\{FeNO\}^7$ species $[Cl_3FeNO]^-$, which is inert towards further coordination and activation of *S*-nitrosothiols. Our work demonstrates how labile iron can mediate the interconversion of NO/thiolate and *S*-nitrosothiol, which has important implications towards how Nature manages the biological concentration of free NO.



2021 GLRM 287

Intricate new materials in K-Zn-Sb ternary system featuring novel clathrate XI

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Discovery of new crystalline materials is of utmost importance in solid state and materials chemistry. However, synthesizing new compounds is often serendipitous process requiring tedious optimization of syntheses conditions. Crystal structure prediction algorithms combined with theoretical calculations have greatly enhanced the search of new compounds. Nevertheless, complex crystal structures with large unit cells still cannot be predicted. Using the knowledge gained from the discovery of $K_{8-x}Zn_{18+3x}Sb_{16}$ and using compositions guided by heats of formation predicted by machine learning, a new material with a complex crystal structure, novel clathrate XI $K_{58}Zn_{122}Sb_{207}$, was produced using our rapid synthesis using hydride precursors. Early screening of the K-Zn-Sb ternary system resulted in the discovery of $K_{8-x}Zn_{18+3x}Sb_{16}$. The *P4₂/nmc* structure features the K cations residing in large channels in the framework made of covalently bonded Zn and Sb. In addition to K cations, Zn_3 triangles reside within the channels acting to block the diffusion of K resulting in uncommon air stability. Throughout this process, yet another unknown phase made its appearance. The composition and ultimately bulk preparation of the new clathrate was achieved using maps created by machine learning predictions and in-situ characterization to guide subsequent reaction compositions and conditions. Different from the channels formed in the Zn-Sb framework of $K_{8-x}Zn_{18+3x}Sb_{16}$, $K_{58}Zn_{122}Sb_{207}$ features an intricate structure of Zn-Sb cages with the K cation encased within. Of the four types of cages in this structure, two of them have never been seen in any clathrate structure. The new 24 vertex $[5^{10}6^3 4^1]$ and 23 vertex $[5^{12}6^1 4^1]$ cages appear to be modifications of the better known 24 vertex $[5^{12}6^2]$ cages that are seen in clathrate type I, III, and IV. The crystal structure was solved in the *I-42m* space group utilizing single crystal x-ray diffraction as a 6-component twin due to pseudocubic symmetry and racemic twinning. This solution was further confirmed using high resolution synchrotron

powder diffraction as well as state-of-the-art scanning transmission electron microscopy. This intricate framework as well as the “rattling” K cation results in an extraordinarily low thermal conductivity.

2021 GLRM 288

Solution phase and solid state analysis of dihedral angles in (halobiphenyl) chromium tricarbonyl complexes

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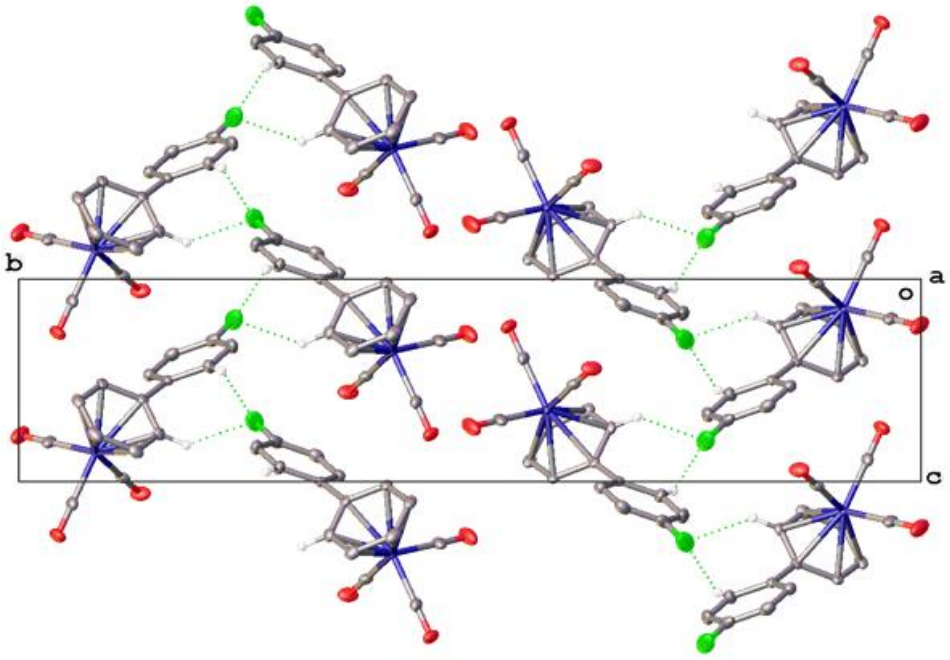
A series of halogen-substituted (biphenyl) chromium tricarbonyl complexes have been characterized by single-crystal X-ray diffraction. Syntheses of these compounds involved heating (2-X-biphenyl), (3-X-biphenyl), or (4-X-biphenyl) (X = F, Cl, Br) with $Cr(CO)_6$. These conditions led to formation of (biphenyl) chromium tricarbonyl complexes where the non-halogenated ring became ligated to the metal center. A series of solid state structures of (2-X-biphenyl)$Cr(CO)_3$ (X = H, F, Cl, Br) shows a trend in increasing arene-arene dihedral angles that may be rationalized through combination of halogen size and carbon-halogen bond length. Special emphasis was placed on single-crystal X-ray diffraction characterizations of the fluorinated derivatives and their respective free ligands. In the solid state [(η^6-C_6H_5)(2-F-C_6H_4)]$Cr(CO)_3$ exhibits a 55.77(4)° dihedral angle, [(η^6-C_6H_5)(3-F-C_6H_4)]$Cr(CO)_3$ exhibits a 32.50(4)° dihedral angle, and [(η^6- C_6H_5)(4-F-C_6H_4)]$Cr(CO)_3$ exhibits a 52.4(5)° dihedral angle. While the angle for the *ortho*-fluoro complex is not unexpected, the angles for the *meta*- and *para*-fluoro complexes are surprisingly large, since their free ligands are almost completely planar in the solid state. Packing diagrams reveal the presence of intermolecular C-H…F non-classical hydrogen bonding, which may be the basis for the observed large dihedral angles in the solid state. Variable temperature and variable concentration ^1H and ^{19}F NMR spectroscopy reveal no evidence for C-H…F hydrogen bonding in solution.



2021 GLRM 289

Advanced NMR (2D and Multinuclear) Study of Various Phthalocyanine Compounds

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This research investigates the NMR specta of Silicon Phthalocyanine Derivatives. This work includes 2D proton NMR techniques (NOESY and COSY), carbon NMR techniques (DEPT and ATP), as well as multinuclear proton-carbon techniques. Due to the large ring currents in these compounds, certain ^{1}H NMR peaks are observed below 0 ppm. These phthalocyanine compounds are of interest due to their optical properties.

2021 GLRM 290

Dual EGFR and AURK inhibitors for multi-resistant lung cancer

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Epidermal growth factor receptor kinase (EGFR) inhibitors are targeted cancer therapies that constitute the recommended treatment approach for EGFR-positive non-small cell lung cancer (NSCLC). Resistance develops rapidly to EGFR inhibitors and therapeutic outcomes for NSCLC expressing T790M/C797S EGFR (mEGFR+) or

mutant KRAS (mKRAS+) are poor. The aurora kinases, aurora kinase A (AURKA) and B (AURKB) are mitosis-related kinases that play a role in cell division and in pathways that drive tumorigenesis and metastasis in NSCLC. A combination of an aurora kinase inhibitor with an EGFR inhibitor has demonstrated enhanced anticancer effects in mEGFR+ and mKRAS+ NSCLC while either EGFR inhibitor or aurora kinase inhibitor alone has limited efficacy. Despite their promise, the effectiveness of dual-targeted EGFR/AURK inhibitors for NSCLC is unknown. Kurup et al. have investigated various molecules as dual EGFR/AURK inhibitors and anticancer agents. The synthesis, kinase inhibitory activities, and antiproliferative effects of these compounds in NSCLC cells will be presented.

2021 GLRM 291

Identifying small molecule probes for the pri-microRNA-18a – hnRNP A1 interaction

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microRNAs are short, noncoding RNAs (~22-25 nucleotides) that negatively regulate translation by binding to the 3' untranslated region of mRNA. Mature microRNAs are generated post-transcriptionally, starting with cleavage of the basal end of their initial transcript, primary microRNA (pri-microRNA). This is mediated by the enzyme Drosha to create a shortened stem-loop structure called preliminary microRNA (pre-microRNA). Recently, heterogenous nuclear ribonucleoprotein A1 (hnRNP A1), a RNA binding protein involved in many RNA related processes such as mRNA splicing, was found to play an essential role in the Drosha-mediated processing of pri-microRNA-18a. microRNA-18a belongs to the polycistronic *mir-17 – 92* cluster which is instrumental in physiological processes commonly dysregulated in cancer, such as proliferation, cell cycle, apoptosis, and differentiation. Additionally, mature microRNA-18a is overexpressed in numerous cancers such as lung cancer. Herein, we report a high throughput screening approach to identifying a small molecule inhibitor of the pri-microRNA-18a – hnRNP A1 interaction that will serve as a probe to better understand its role in cancer, as well as, serve as a starting point for drug development.

2021 GLRM 292

High throughput screening for the identification of small molecule inhibitors of the hnRNP A1—pri-miR-18a interaction

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The Human Genome Project revealed that most of the transcriptome contains non-coding RNAs (ncRNAs) that do not directly code for protein. These ncRNAs regulate cellular protein expression and many disease states, including cancer, demonstrate

aberrant ncRNA expression. MicroRNAs (miRs) are short (19-25 nucleotides) ncRNAs that bind at the 3' untranslatable region of target mRNAs, blocking translation and post-transcriptionally repressing protein expression. The biogenesis of functional, mature miR requires a pathway in which the primary and precursor miRs undergo cleavage by two RNAse III enzymes, Drosha and Dicer. Additional proteins are required in the canonical biogenesis pathway. Specific, auxiliary RNA-binding proteins (RBPs) are required for the maturation of some miRs—such as miR-18a and heterogenous nuclear ribonecleoprotein A1 (hnRNP A1). MiR-18a is overexpressed in many types of cancer, reducing proapoptotic protein expression and increasing tumorigenesis. hnRNP A1 is a RBP that has a diverse range of cellular functions, including binding to the primary-miR-18a (pri-miR-18a) transcript to facilitate its biogenesis to functional, mature miR-18a. The knockdown of hnRNP A1 greatly attenuates the expression of mature miR-18a. We hypothesize that high-throughput screening (HTS) of a library of pharmacologically active small molecules will yield an inhibitor of the hnRNP A1—pri-miR-18a interaction, halting the maturation and reducing the expression of miR-18a. A fluorescence polarization (FP) assay used for the HTS campaign, coupled with orthogonal cell-based assays and structure activity studies, will be used to identify small molecule inhibitors of the hnRNP A1—pri-miR-18a interaction. This small-molecule inhibitor will be used to probe the role of the hnRNP A1—pri-miR-18a interaction in various types of cancer and provide a potential starting point for anti-cancer therapeutics.

2021 GLRM 293

Development of small-molecule inhibitors of the epigenetic protein BPTF

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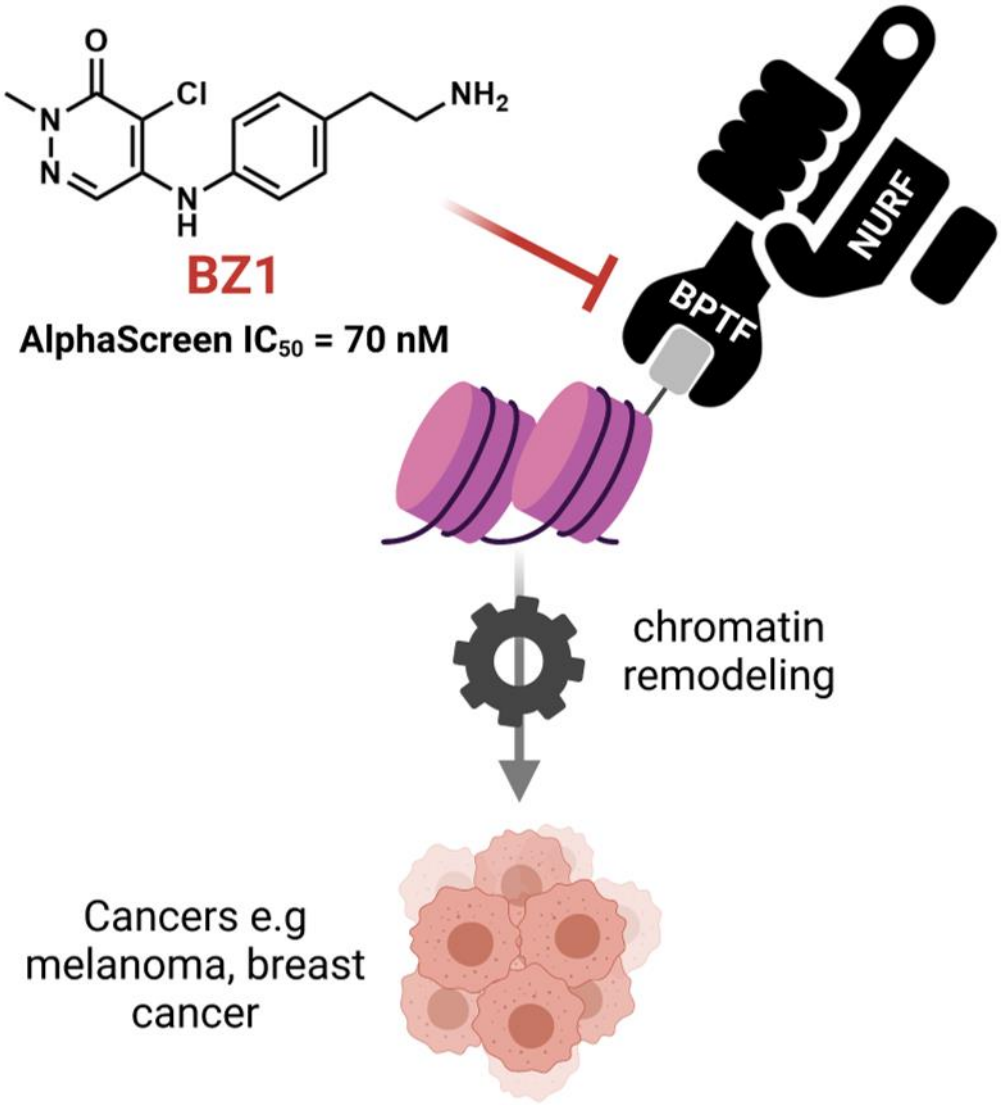
The identity of various cells in our body and their disease states is determined by mechanisms which turn genes on or off. Proteins involved in these processes are targets for drug discovery and their activity can be modulated by small molecules. Bromodomains are protein-protein interaction modules involved in epigenetic regulation of gene expression, typically through the recognition of acetylated lysine residues in histones. Bromodomain-containing proteins are involved in several diseases, including cancer, inflammation and viral replication. While numerous small molecule probes have been developed for the well-studied BET (bromodomain and extra terminal) family, few have been reported for the 53 non-BET bromodomains. Potent and selective chemical probes are, therefore, required to enhance our biological understanding of the non-BET bromodomain family. Among them, BPTF is known to play an important role in chromatin remodeling and has been identified as a target for anticancer therapy. My research uses structure-based design to develop chemical inhibitors that bind to BPTF with high affinity and are selective over other proteins. Biophysical assays, including Protein-Observed Fluorine (PrOF) NMR and AlphaScreen, are used to study the in vitro interaction of small-molecule inhibitors with the bromodomain of BPTF and to quantify their binding affinity. Several cocrystal structures of the synthesized compounds are also obtained with BPTF, providing insight into key interactions with the protein and

guiding future medicinal chemistry efforts. These inhibitors are being used to study the role of BPTF in cancer cells and may be optimized as future therapeutics.



2021 GLRM 294

Synthesis and Evaluation of Porphyrin-Capecitabine and Porphyrin-Gemcitabine Derivatives for Photodynamic Anticancer Therapy

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Photodynamic therapy (PDT) has attracted significant attention as an alternative approach to traditional cancer therapies such as radiotherapy, chemotherapy, and surgery. PDT involves irradiating a drug (the photosensitizer) with a photon of light to generate cellular oxygen that then proceeds to kill cancer cells. Porphyrin-based photosensitizers have been widely used in PDT. Porphyrins have significant absorption in the visible region (400-700 nm), little dark toxicity, and long-lived triplet states that can lead to high singlet oxygen production. Porphyrins are known to accumulate in tumor cells in high concentrations. Capecitabine (Xeloda) and Gemcitabine (Gemzar) are standard chemotherapeutic agents for pancreatic cancer patients. However, capecitabine and gemcitabine are highly water-soluble drugs; so, they are rapidly removed from the blood circulation in addition to being rapidly metabolized to inactive intermediates. So, they have a poor accumulation in tumor cells because of high hydrophilicity. In our study, two novel porphyrin-capecitabine and porphyrin-gemcitabine derivatives were synthesized for use as photosensitizers in the photodynamic treatment of different types of cancer. The introduction of the porphyrin ring makes capecitabine and gemcitabine more hydrophobic and thus enhances the accumulation in tumor sites, in addition to the added advantage of being photochemically active. When the modified drugs accumulate in the tumor site, they will be irradiated by the light of proper wavelength matching absorption maxima of porphyrin, generating a diradical that is expected to abstract H-atoms from biological molecules generating free radicals that disrupt cell replication and thereby kill the cancer cells. The photophysical properties of those derivatives were evaluated and the fluorescence and singlet oxygen quantum yields were calculated. The cytotoxicity of those derivatives was evaluated, under dark conditions and after light irradiation at 640 nm, against A549 lung cancer cells and AsPC-1 pancreatic cancer cells.

2021 GLRM 295

Pre-clinical screening of plasma membrane citrate transporter inhibitor SAP-165 using the NCI-60 human tumor cell lines.

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The mammalian plasma membrane citrate transporter (PMCT) catalyzes a sodium-coupled citrate import and is expressed predominantly in the liver where it functions in a variety of critical metabolic pathways that include fatty acid, triacylglycerol, and cholesterol biosyntheses, ATP production, and also is a key regulator of glycolysis. The hallmark of cancer is cell proliferation and a requisite of escalated membrane biogenesis is optimized lipid biosynthesis. Recent studies have demonstrated that inhibition of PMCT reduces cancer development and metastasis. We were the first to identify PMCT inhibitors and, in continuation of our effort to discover potent PMCT inhibitors, we identified the novel chromenopyridine analog **SAP-165** as a lead PMCT

inhibitor. In order to test **SAP-165** for anti-cancer activity, we used the National Cancer Institute's 60 human tumor cell lines (NCI-60) *in vitro* screen. Data from the NCI-60 assay indicated that our PMCT lead compound has consistent anti-proliferative activity against sixteen major cancer cell lines. **SAP-165** showed low micromolar range growth inhibition towards the following cell lines: CCRF-CEM and MOLT-4 (GI_{50}: 0.31 μM); HL-60(TB) (GI_{50}: 0.34 μM); K-562 (GI_{50}: 0.44 μM); RPMI-8226 (GI_{50}: 0.35 μM); SR (GI_{50}: 0.27 μM); HCT-116 (GI_{50}: 0.68 μM); HCT-115 (GI_{50}: 0.97 μM); U251 (GI_{50}: 0.95 μM); LOX IMVI (GI_{50}: 0.58 μM); UACC-62 (GI_{50}: 0.44 μM); IGROV1 (GI_{50}: 0.76 μM); 786.0 (GI_{50}: 0.49 μM); RXF 393 (GI_{50}: 0.74 μM); MCF7 (GI_{50}: 0.45 μM) and MDA-MB-468 (GI_{50}: 0.32 μM). In conclusion, our pre-clinical screening suggests that the new chromenopyridine pharmacophore has proven to be a very promising cancer therapeutic via PMCT inhibition.

2021 GLRM 296

Reasoning about mechanisms when considering multiple representations: Analysis of students' writing and peer-review interactions for a writing-to-learn assignment

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Organic reaction mechanisms are often represented by the electron-pushing formalism and reaction coordinate diagrams. Working with these representations poses a challenge to students because valuable information is encoded within each representation, and students must know how to reason about mechanisms using both. Hence, it is important to understand whether and how students consider these two representations when reasoning about reaction mechanisms. To study students' reasoning, we have collected responses to a writing-to-learn assignment administered in a second-semester organic chemistry laboratory course. The assignment was designed to elicit students' reasoning about the most likely of two pathways for a catalyzed intramolecular aldol reaction when given the electron-pushing scheme and reaction coordinate diagram for both pathways. As part of the assignment, students submitted initial drafts, participated in content-focused peer-review, and submitted revised drafts. Using a mixed methods approach, we analyzed each component to identify students' reasoning about the most likely reaction pathway and how their reasoning changed as a result of peer-review. This poster will include a quantitative overview of changes students made about their decisions for the most likely reaction pathway and how these changes are related to providing and receiving feedback. Additionally, the presentation will provide a qualitative analysis of the features of representations students use to reason about the likelihood of alternative reaction pathways. These analyses provide implications for implementing peer-review processes and teaching students to reason about reaction mechanisms using multiple representations.

2021 GLRM 297

Fink's taxonomy and the impact of assessment on student achievement in Organic Chemistry

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Organic Chemistry has a reputation of being a gate keeper course for students pursuing Science, Technology, Engineering and Mathematics (STEM) majors. The content of organic chemistry is heavily conceptual and also, abstract which offers a considerable challenge for student success in organic chemistry courses. In addition to the teaching of organic chemistry, and student engagement with learning activities, the use of assessments may also impact student success in organic chemistry. In this study the impact of the construction of assessment questions that were based on Fink's taxonomy was examined. A series of quizzes and exams in a second-year organic chemistry course were analyzed using the Legitimation Code Theory (LCT). This presentation will highlight the correlation of assessments with student success in organic chemistry and also identify knowledge gaps and strength areas of students participating in this study.

2021 GLRM 298

Developing expertise in ^{1}H NMR spectral interpretation

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Advancements in organic chemistry depend upon chemists' ability to interpret NMR spectra, and the organic chemistry curriculum aims to cultivate such expertise, though with variable success. Insight into how this expertise develops is thus needed to design instruction that better supports learning. This study investigated undergraduate and doctoral chemistry students' conceptual understanding and information processing during the interpretation of ^{1}H NMR and complementary IR spectra. Eighteen undergraduate and seven doctoral chemistry students at a research-intensive university evaluated the outcome of a series of syntheses using spectra corresponding to the products. Eye movements were measured during spectral interpretation and analyzed to identify differences in cognitive processes between undergraduate and doctoral participants. Retrospective think-aloud interviews were then conducted to elucidate the chemical assumptions that guided participants' thinking. Results suggest five areas of understanding are necessary for interpreting spectra, and progress in understanding corresponds to increasing knowledge of experimental and implicit chemical variables. Undergraduate participants exhibited uninformed bidirectional processing of all information, whereas doctoral participants exhibited informed unidirectional processing of relevant information. These findings imply the community can support novices' development of expertise by cultivating relevant understanding and encouraging use of informed interpretation strategies, including preliminary evaluation of relevant variables,

prediction of expected spectral features, and search for complementary data across spectra.

2021 GLRM 299

Graduate teaching assistants' knowledge for teaching organic chemistry mechanisms

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Many recent studies document the difficulties that students experience when learning organic chemistry, often due to the complex visualization and reasoning skills required to successfully understand the ways molecules interact in specific environments. Many of these studies call on instructors to improve their teaching strategies to support students' learning of organic chemistry mechanisms, but investigations of the instruction of this content at the college level remain scarce. To capture university instructors' knowledge for teaching organic chemistry mechanisms, we developed and implemented a task-based think-aloud interview protocol covering three fundamental organic chemistry reactions—substitution, acid-base, and addition. We qualitatively analyzed interviews with seventeen graduate students and three faculty members to describe topic-specific pedagogical content knowledge for organic chemistry mechanisms. Results presented will include a description of this knowledge and GTAs' strengths and limitations. Implications for understanding student difficulties in organic chemistry and designing graduate student instructor training will be discussed.

2021 GLRM 300

Factors that impact the difficulty of organic chemistry exam items: Item order and item environment effects

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There are a variety of features in assessment items that can influence the difficulty of the item. Some of these are intrinsic to the item itself, such as item complexity. Others can be artifacts of the test construction and the presence of these artifacts can lead to examinee ability estimates being dependent on the test format. IRT (Item response theory) statistical analysis has shown that students perform differently on certain items on an ACS first semester organic chemistry exam when multiple versions of the test are formed with questions and answered scrambled. The current work examines which

effects have the largest effect causing differential item functioning (DIF) on items between different test forms. Effects that were examined were answer placement, difficulty of the preceding questions and both material and process contained within the preceding questions (priming effects). Knowing which effects make the greatest change to student outcomes can aid in developing new assessments from existing item pools to capture student ability best.

2021 GLRM 301

Course-based undergraduate research (CURE) as means for increasing diversity and inclusion in organic chemistry courses

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Literature data demonstrate an incontrovertible impact of undergraduate research on the achievement of deep understanding of material by students. The development of course-based undergraduate research experiences (CUREs) that bring research aspects into the classrooms have, in large part, focused on assessment of metacognitive development.
Another important aspect of incorporating a research experience or applying a CURE model is a potential impact on the diversity and inclusion of students in chemistry courses. In this research project along with assessment of metacognition we investigated *the impact of a CURE on the diversity of the student population engaged in research*.
In chemistry, undergraduate students often follow an apprentice model to gain necessary research experience. These research opportunities are essential for successful applications to graduate schools and industry jobs upon graduation. However, the availability of those seats is strictly determined by number of faculty members doing active research and their willingness to take on new members of their group each semester. As a result, only few students every year get a chance to participate in faculty-mentored research projects. This also limits abilities of students to obtain REU positions as they are highly competitive and often require prior hands-on or research skills. Therefore, the availability of a limited number of research opportunities year after year provides only few selected students with a crucial experience. This problem can have a long-term impact on ability of graduating seniors to secure jobs or graduate school positions upon graduation.
In my continuous efforts to increase diversity and inclusion in my courses I incorporated research projects in organic laboratory for the last four years at the University of Wisconsin, La Crosse (UWL). The organic laboratory is an essential course for the science majors at UWL and traditionally was taught by a "cookbook" approach. Here, I present how incorporation of CURE practices into our organic laboratory course promoted collaboration and enhanced inclusion between members of the group. Findings on the potential impact of a CURE on engaging a diverse group of students in chemistry courses will be highlighted. The use of technology to achieve an increase in

inclusion and transparency during group work in both lecture and laboratory chemistry courses impacted by the COVID-19 restrictions will also be introduced.

2021 GLRM 302

Rational design of a ligand-activated fluorinase

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Challenges in current synthetic C-H fluorination methods include: poor chemo/regioselectivity outcome, the use of precious metals, and utilizing HF as a fluoride source. Typically, rational design of proteins typically entails leveraging structural and computational data to make mutations that increase protein stability, substrate scope, or activity. SyrB2 is an Fe/2-oxoglutarate(2OG)-dependent enzyme that catalyzes the chlorination/bromination of the methyl C-H bond of threonine. SyrB2 accomplishes this through a haloferryl (X-Fe(IV)=O) intermediate. To expand SyrB2's reaction scope to C-H fluorination, we propose a new form of rational design in which we modulate the electronics of the primary coordination sphere of the iron center. We do so by swapping the native 2OG ligand for a more electron-donating substrate mimic. This ligand swap allows for the binding of fluoride to the iron center and ultimately the production of fluorothreonine. This study constitutes the first example of C-H fluorination catalyzed by a metalloenzyme. Our rationally designed metalloenzyme platform offers a more sustainable solution for this challenging transformation.

2021 GLRM 303

Synthesis of a novel isoprenoid analogue for prenylomic analysis of geranylgeranylation and its role in Alzheimer's Disease

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Currently, 5.8 million people in the US live with Alzheimer's Disease (AD), and that number is only expected to increase in the coming years. The development of AD is complex and its relationship to specific biological processes is still being explored. One such process involved in the development of AD is prenylation. Prenylation is a post-translational modification of proteins with isoprenoid substrates that plays a key role in cellular signaling and regulation. There are three types of prenylation, each with a specific enzyme and protein substrates: farnesylation, geranylgeranylation type I, and geranylgeranylation type II. Initial experiments with AD mouse models demonstrated differences in cognitive recovery in a farnesyltransferase (FTase) knockout and a geranylgeranyltransferase I (GGTase I) knockout, indicating that the processes have different roles in AD. Recently, prenylomics has been a useful tool to identify prenylated proteins of interest in AD-related cells using an alkyne modified analogue of farnesyl

diphosphate (FPP). This process currently identifies substrates for all three types of prenylation. Consequently, to further elucidate the specific role of both farnesylation and geranylgeranylation in AD more selective methods are needed. Developed here is an alkyne analogue of geranylgeranyl diphosphate (GGPP) that is selective to the geranylgeranylation enzymes was made using convergent synthesis. Metabolic labeling experiments in COS7 cells demonstrated a difference in labeling between the GGPP analogue (C20AlkOPP) and the FPP analogue (C15AlkOPP) and prenylomic analysis of COS7 cells showed identification of geranylgeranylated proteins.

2021 GLRM 304

Shining a light on endogenous electrophiles: Releasing methylglyoxal with spatiotemporal control in biological systems

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Methylglyoxal (MGO) is an electrophilic glycolysis metabolite with promiscuous reactivity towards nucleophilic amino acid side chains on proteins. The stable adducts act as non-enzymatic post-translational modifications and are denoted collectively as a type of advanced glycation end-products (AGEs). AGEs are an important class of protein modifications and are implicated in numerous ageing-related diseases such as diabetes, neurodegeneration, cardiovascular disease and cancer. Thus, identifying proteins susceptible to MGO modification and conducting functional assays to understand the role of MGO protein-adducts in ageing and disease is critical in elucidating the role MGO plays in such diseases.
Unfortunately, chemical tools to study MGO protein modification remain limited due to the inherent reactivity of MGO, the plethora of AGEs potentially generated. Consequently, cellular studies require that cells be dosed at non-physiological concentrations of MGO or MGO derivatives, which may not accurately reflect intracellular conditions. Additionally, such doses are toxic to cells, constraining exposure times for long-term studies. Novel strategies that deliver controlled-release MGO intracellularly would overcome these issues. We developed such a controlled-release platform capable of raising intracellular MGO levels in particular subcellular locations. We first synthesized a photocaged MGO derivative, with a photolysis half-life of approximately 10 seconds. The caged MGO was modified further with a chloroalkane Haloprotein targeting element to yield our MGO probe molecule, which we call TMOP (targetable MGO precursor). We demonstrated that TMOP activation generates protein-AGEs in a spatiotemporally controlled manner in live cells. This work establishes TMOP (as a valuable tool for studying cellular responses resulting from increased MGO flux and resultant AGEs. We hope this strategy will inform important functions of MGO metabolic adducts and their roles in ageing and disease.

2021 GLRM 305

Construction of site-specific DNA-Histone conjugates in chromatin core particles and their effects on DNA transactions

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DNA-protein cross-links (DPCs) are bulky DNA lesions in which a protein becomes covalently bound to chromosomal DNA. Irreversible entrapment of cellular proteins on chromosomal DNA occurs following exposure to *bis*-electrophiles, transition metals, and free radical species. Subsequently, DPCs interfere with DNA-related processes, such as DNA replication, transcription, and repair. Recently, we discovered a novel mechanism of epigenetic regulation involving the formation of reversible DNA-histone cross-links between 5-formyl-2'-deoxycytidine residues (endogenously observed epigenetic marks) in DNA and lysine or arginine side chains of the proteins. The lysine side chains from histone proteins are known to undergo reversible acetylation, ubiquitylation, methylation, and other reversible posttranslational modifications that influence chromatin structure and control the levels of gene expression. There is currently poor understanding of how the DNA-histone cross-link affects chromatin structure, transcription and replication. To address this gap in knowledge, site-specific DNA-histone conjugates are constructed in a nucleosome core particle through the use of the unnatural amino acid amino-oxy lysine to form hydrolytically stable oxime linkages. We have previously incorporated this unnatural amino acid through solid phase peptide synthesis to synthesize the histone H3 tail, followed by Sortase-mediated ligation to the globular domain of histone H3 to afford a modified amino-oxy containing histone H3. Furthermore, primer extension assays using DNA polymerase η showed that oxime crosslinks between histone H3 and 5-formyl-2'-deoxycytidine containing DNA oligomers effectively block bypass of the lesion. These conjugates will serve as substrates in characterizing the biological function of DNA-histone cross-links and their potential role in epigenetic control of gene expression.

2021 GLRM 306

Single-cell Analysis of Prenylation in Mammalian Cells via Mass Cytometry

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Mass cytometry has become an important single-cell analysis tool due to its ability to measure over 40 parameters simultaneously through the detection of metal isotopes by ICP-MS. Traditional reporters for mass cytometry are antibodies linked with polymers that chelate metal isotopes often from the lanthanide series. Only using antibody reporters in experiments limits what targets can be detected in the cell. To expand the

questions that can be answered using mass cytometry, there is a need to develop additional reporters for important cellular components. In this work, a novel probe and reporter method has been established to track changes in prenylation with mass cytometry. Prenylation is an essential post-translational modification which is the enzyme mediated attachment of an isoprenoid to proteins to facilitate correct localization and signaling. Disruption of prenylation has been indicate in multiple diseases such as progeria and Alzheimer's. To track changes in prenylation, a farnesyl diphosphate analog containing a terminal alkyne is incorporated into cells during culture. After harvest, fixation and permeabilization the cells then undergo a copper catalyzed click reaction to attach a reporter containing a terminal azide and chelating a terbium ion. The intensity of terbium after the cells go through the mass cytometer can then be related back to level of prenylation in each cell. A non-specific binding reporter similar in structure to the terbium reporter has also been included in this method to track non-specific binding in the cells. To demonstrate applicability, the method has been successfully applied in two cell culture models of reduced autophagy function. In the future, this novel method can be used to investigate changes in prenylation levels in cellular models of disease, aging and after pharmaceutical treatments. Development of this technique has expanded the available cellular targets that can be investigated by mass cytometry and opened the door to expansion of similar reporters for other post-translational modifications or functional measurements.

2021 GLRM 307

Embedded genetic recorders in *Streptomyces* to 'listen in' on chemical signals that trigger antibiotic production in soil

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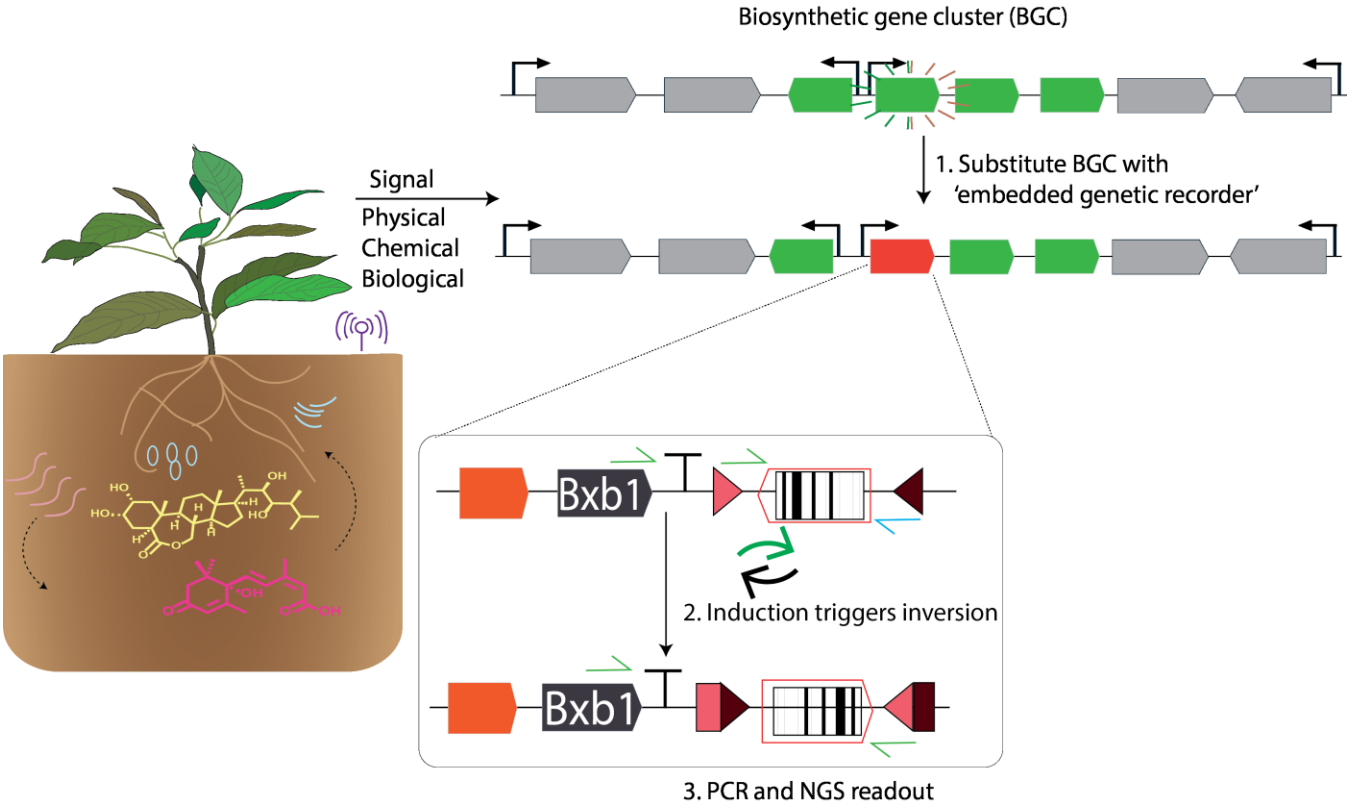
Disease Suppressive Soils possess antagonistic microbial interactions which are responsible for their effects on crops. *Streptomyces,* Gram-positive soil bacteria known for their prolific production of bioactive secondary metabolites and antibiotics, have been implicated as key functional members in disease suppressive soils. However, lab cultivation conditions fail to activate ~80% of the natural product biosynthetic potential of *Streptomyces* spp., making it difficult to characterize the influence these molecules have in nature. Understanding signals that lead to antibiotic production would allow for rational engineering of improved agricultural soil with beneficial microbes leading to improvements in crop production yields. It could also resuscitate the dwindling supply of new antibiotics entering drug discovery pipelines. Our approach for investigating signals that give rise to antibiotic production is to create a novel tool, an embedded genetic recorder (EGR), that permits in *situ* characterization of microbial signals interactions in soil. This tool will allow for permanently recording gene expression events, even if the elicitor is unknown. While other techniques exist for discovering new signaling molecules in *Streptomyces* spp., our method is the first that can function in a complex environment like soil.



2021 GLRM 308

Synthesis of functional bioprobes based on cyclohexanyl-polyamino carboxylate scaffolds

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Noninvasive techniques for disease imaging and targeted therapy allow for personalized treatment regimens. Radiometal-based imaging and therapeutic agents are expanding due to the increasing availability of ^{64}Cu, ^{89}Zr, ^{55}Co, and other isotopes. When coupled to an antibody or other targeting group using an appropriate *bifunctional chelator*, clinicians can view the localization of the radiopharmaceutical and monitor disease progression using Positron Emission Tomography. Each isotope requires a different chelator to properly bind the radiometal. When translating a compound from the benchtop to the clinic, any change in chelator requires a completely new set of tests to determine safety and efficacy. With this work, our goal will be to develop a panel of chelators capable of binding radiometals used in both imaging and therapeutics. Development of multi-use chelators will allow a single compound to be used for both cancer detection and targeted therapy, thereby speeding clinical development and enhancing patient outcomes.

2021 GLRM 309

Monitoring ligand-mediated helix transitions within the human estrogen receptor α using bipartite tetracysteine display

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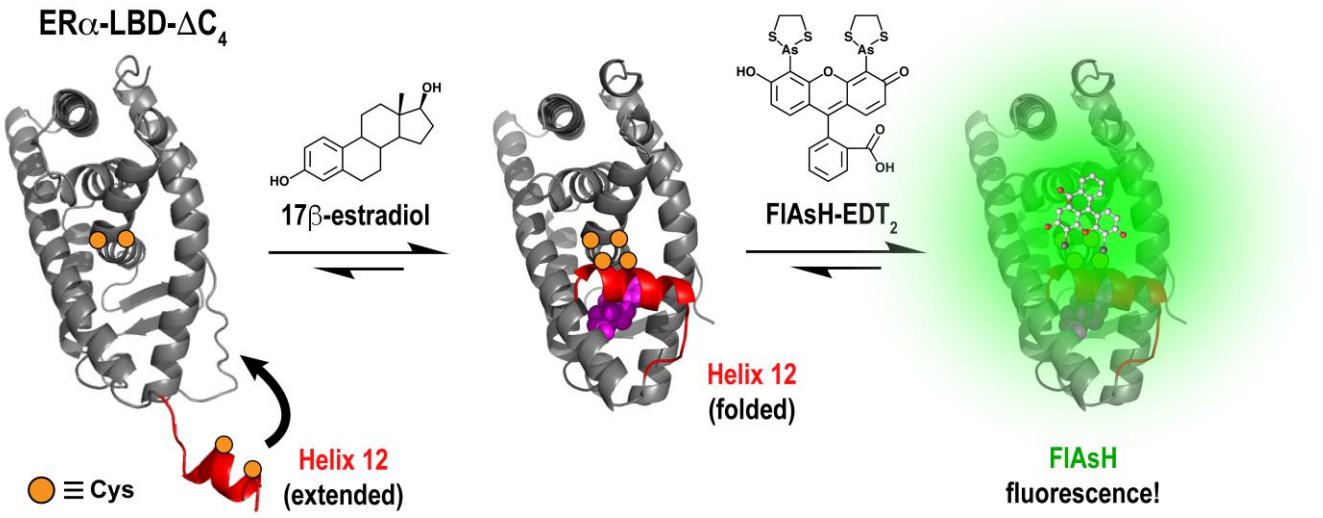
Strategies that inform on protein structural dynamics enhance our understanding of protein function and facilitate development of new therapies to treat disease. The human estrogen receptor α (ERα) is a ligand-mediated transcription factor that is modulated by the natural steroid hormone 17β-estradiol (E2). Through its interaction with E2, the ERα regulates cellular processes including growth, differentiation, transcription and apoptosis. Structurally, the ERα ligand-binding domain (ERα-LBD) adopts a well-folded globular structure comprised of 11 α-helices and a short β-strand. The globular portion of the ERα-LBD is believed to be relatively static, however, the C-terminal helix 12 (H12) is dynamic and can adopt different configurations depending on what ligand occupies the LBD. For example, binding of E2 causes H12 to tightly associate with the LBD in an 'active' conformation that facilitates binding of transcriptional co-activators. Alternatively, binding of selective ERα modulators such as tamoxifen forces H12 to associate with the coactivator-binding site of the LBD in an 'inactive' conformation that prevents transcriptional activation. In this study, we applied bipartite tetracysteine display to surveil ligand-mediated helix H12 transitions within the ERα-LBD. Wild-type ERα-LBDs were mutated to express a tetracysteine (C4) motif that binds to a biarsenical pro-fluorescent dye (FlAsH) upon transition of H12 to a folded state. Interestingly, binding of an agonist was accompanied by a reduction in FlAsH fluorescence, indicating that the C4 motif becomes occluded when H12 is tightly associated with the LBD. Our results also indicate that H12 remains flexible in unliganded receptors and receptors bound to pure antagonists, allowing for significant increases in FlAsH fluorescence. Such observations made it possible to determine association rates and equilibrium binding constants for FlAsH to the ERα-LBD in the presence and absence of estrogenic ligands. We anticipate that this genetically-encodable assay will be useful for studying how other estrogenic compounds influence structural organization of the ERα-LBD and may be applied to studying helix transitions within other members of the nuclear receptor superfamily.



2021 GLRM 310

Urinary N7-(1-hydroxy-3-buten-2-yl) Guanine Adducts in Humans: Ethnic differences and associations with lung cancer risk

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Lung cancer is the leading cause of cancer-related deaths in the United States. Cigarette smoking is a major risk factor for lung cancer development, with 82% of lung cancer cases being attributable to smoking. This risk varies among individuals, with 11-24% of smokers developing lung cancer in their lifetime. Identifying smokers at higher risk is critical for early-stage cancer prevention efforts. Additionally, the risk of lung cancer development among smokers varies by ethnic group. African Americans and Native Hawaiians are at greater risk for lung cancer development as compared to whites, while Japanese Americans and Latinos are at a lower risk. These differences cannot be explained by differences in smoking amounts. Of the 69 known carcinogens in tobacco smoke, 1,3-butadiene (BD) is one of the most abundant. Exposure to BD also occurs through automobile exhaust, wood burning smoke, and occupational exposure in the polymer industry. BD is metabolically activated by cytochrome P450 monooxygenases (CYP) 2E1 and 2A6 to 3,4-epoxy-1-butene (EB). Cellular detoxification of EB occurs through GST-catalyzed glutathione conjugation to form monohydroxybutenyl mercapturic acid (MBHMA) and dihydroxybutyl mercapturic acid (DHBMA). If not detoxified, EB can form covalent adducts at nucleophilic sites in DNA. We have previously employed EB-DNA adduct N7-(1-hydroxy-3-buten-2-yl) guanine

(EB-GII) as a biomarker of smoking-related BD exposure. In the present work, we investigated the associations between urinary EB-GII, ethnic groups, and lung cancer development. Urinary EB-GII adducts were first quantified in 600 smokers and non-smokers belonging to three ethnic groups with different risks of lung cancer development: white, Japanese American, and Native Hawaiian. We found that Japanese American smokers excreted significantly higher amounts of urinary EB-GII adducts than whites. Levels of urinary EB-GII in Native Hawaiian smokers were not different from whites. There were no ethnic differences in urinary EB-GII adduct levels in non-smokers. Urinary EB-GII adduct levels in smokers were significantly associated with DHBMA, but not with MHBMA. To investigate the association of urinary EB-GII with lung cancer risk, urinary EB-GII adducts were quantified in 520 smokers with lung cancer and the corresponding smoker controls. Our results provide important information regarding lung cancer risk assessment, which is crucial for the identification of high-risk smokers.

2021 GLRM 311

Novel 4-hydroxybenzyl adducts in human hemoglobin: structure and formation mechanisms

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Humans are continually exposed to electrophilic compounds in the form of environmental pollutants, dietary sources, and normal endogenous byproducts of metabolism. Within the body, electrophiles react with cellular biomolecules such as DNA, RNA, and proteins, potentially triggering health problems including neurotoxicity and cancer with extended exposure. By monitoring the formation of electrophilic adducts in long-lived proteins such as serum albumin and hemoglobin, human exposure to potentially hazardous electrophiles can be reliably assessed. Previous work in our group has revealed the presence of 4-hydroxybenzyl adducts (+ 106.042 Da) at the N-terminal valine of human hemoglobin. In the present work, we used mass spectrometry-based proteomics to determine whether this adduct could also be formed at internal nucleophilic amino acid side chains of hemoglobin. Our data provide evidence for the presence of 4-hydroxybenzyl adducts at αHis20, αTyr24, αTyr42, αHis45, βSer72, βThr84, βThr87, βSer89, βHis92, βCys93, βCys112, βThr123, and βHis143 residues in hemoglobin treated with para-quinone methide. These adducts were also found in untreated blood samples, suggesting that they are formed endogenously. These residues show variable propensity towards adduct formation, with LIST being most reactive. We also investigated alternative sources of 4-hydroxybenzyl adducts in the human blood in the form of 4-hydroxybenzaldehyde and UV-induced reaction of hemoglobin with tyrosine.

2021 GLRM 312

Impact of Acyclic Amine Leaving Groups on Quinone Methide Precursors for Resurrection of Organophosphorus-aged Acetylcholinesterase

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Acetylcholinesterase (AChE), responsible for the normal hydrolysis of the neurotransmitter acetylcholine (ACh), is vulnerable to inhibition by organophosphorus (OP) nerve agents and pesticides. OP poisoning creates a buildup of ACh in the body leading to a cholinergic crisis and death, if not treated in time. Unfortunately, after the inhibition step, there is a subsequent aging process where the phosphylated serine residue of AChE undergoes a dealkylation reaction, leading to a negatively charged phosphylated oxyanion at the same serine residue. At present, there are no approved therapeutics that can reverse the effect of aging of AChE. In 2018, our lab first reported a quinone methide precursor (QMP) which was able to in vitro resurrect the aged form of AChE. This QMP, based on a 3-hydroxypyridine core with an alkyl amine leaving group at the benzylic carbon of position 2, was improved to a more active 6-methyl-3-hydroxypyridine core. Herein, this study focuses on modifications to the amine leaving group in order to provide more novel compounds that may be able to resurrect recombinant human AChE after exposure to two OP pesticides and a nerve agent mimic. Overall, several compounds were able to resurrect these poisoned forms of AChE to various degrees, depending on the OP toxicant. In short, amines with branched and bulky alkyl chains were less able to resurrect OP-aged AChE, whereas amines with diethyl moieties performed the best.

2021 GLRM 313

Differences in DNA modifications in *P. aeruginosa* biofilms versus planktonic cells

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Pseudomonas aeruginosa is a Gram-negative opportunistic pathogen found in both environmental and medical settings. It is the leading cause of death in patients with cystic fibrosis, and the CDC has determined multi-drug resistant strains of *P. aeruginosa* to be of serious concern. *P. aeruginosa* commonly transitions from free floating planktonic cells to biofilms posessing a substantial matrix consisting of polysaccharides, proteins, and DNA. The biofilm architecture provides increased resistance to both penetration of antibiotics and immune system derived components.

Environmental factors in biofilms such as nutrient variations and oxygen availability have been shown to lead to biofilm heterogeneity. Stress arising from oxygen limitations and metabolism can lead to the upregulation of genes associated with biofilm formation, and DNA mutation rates have been shown to increase in *P. aeruginosa* biofilm cells. Epigenetic modifications, such as N^6-methyl-2'-deoxyadenosine (N^6mdA), have also been linked to biofilm formation in *Burkholderia cenocepacia* a Gram-negative bacteria associated with severe lung damage in patients with cystic fibrosis. Thus, we hypothesized that epigenetic DNA modifications and DNA damage products could differ in a *P. aeruginosa* biofilm cells as compared to planktonic cells. We also hypothesized that increased oxidative stress in the extracellular matrix could also lead to oxidized DNA bases in the matrix that could potentially be taken up into cells or impact the extracellular environment. We developed a *P. aeruginosa* PA14 biofilm model and methods to isolate cells. Improved DNA extractions were developed in order to isolate both cellular DNA and DNA from the extracellular matrix. An LC-MS/MS method was developed to assess if environmental factors within a biofilm results in oxidative damage or epigenetic modification differences between planktonic and biofilm cells as well as the extracellular DNA.

2021 GLRM 314

Evaluation of NADPH Oxidase Inhibitors for Reduction of Ultraviolet Oxidative Damage in Skin

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Reactive oxygen species (ROS) are essential to cellular function but in diseased states elevated levels cause oxidative stress. Skin cancer, the most prevalent type of diagnosed cancer in the world, is caused by ultraviolet radiation (UVR). Studies show UVR exposure leads to overproduction of ROS through NADPH Oxidase (NOX) unique complex assembly. NOX inhibition is a key target for the prevention of cancers in the skin. This research examines the efficacy of several novel NOX1 inhibitors to decrease damage after UVR. Through in vitro studies in primary skin cell cultures, the project assesses the toxicity of the inhibitors and their ability to protect against DNA damage caused by UVR. Several methods including MTT, UVR recovery, and NADPH oxidase activity assays are used to evaluate the inhibitors in primary cultures.

2021 GLRM 315

Synthesizing the Inhibitor for NADPH Oxidase:

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Reactive oxygen species (ROS) are a heterogeneous group of highly reactive ions and molecules derived from molecular oxygen (O_2) and causing DNA damage. Low levels of ROS can activate various signaling pathways to stimulate cell proliferation and survival and high levels of ROS can promote cancer development, the survival of cancer cells, and resistance to chemotherapeutics. One of the most important sources of intracellular ROS is the enzyme NADPH oxidase (Nox), which is the only mammalian enzyme dedicated to ROS generation. NADPH oxidase enzymes share the capacity to transport electrons across the plasma membrane and generate superoxide and other down-stream reactive oxygen species (ROS). In order to function, the membrane-bound NADPH oxidase must assemble properly. My project goal is to synthesize NOX Inhibitors to inhibit ROS production by stopping the assembly of the NOX complex. I will be evaluating my inhibitors by using the biotin labeling technique which utilizes biotin to observe the enzyme ligand binding interactions.

2021 GLRM 316

Derivatives of diapocynin into small molecule NADPH oxidase I inhibitors, that suppresses reactive oxygen species production in skin cells.

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Reactive oxygen species are a group of highly reactive oxygen-containing entities that are important at a cellular level for multiple biological processes. Low concentrations of ROS can be beneficial as powerful signaling molecules in those biological processes, although excessive concentrations can promote high levels of DNA damage and a variety of diseases such as skin cancer. A newly identified sources of intracellular ROS production in skin cell are NADPH oxidases. In order to function the membrane-bound, NADPH oxidase p22phox must assemble properly with the cytoplasmic protein p47phox. Inhibition of these enzymes represents a catalytic approach toward reducing ROS for the prevention of ROS inducible diseases. Key disease states include melanoma induced by UV exposure. This study is focused on the investigation of new small molecule inhibitors of a key NOX enzyme to address these challenges. We designed a series of molecules by computationally optimizing the structure of diapocynin and have synthesized the series of target molecules for the structure-activity relationship studies. The molecules are currently being tested on two skin cell lines, keratinocytes, and fibroblast, to identify the potential of recovering cells from reactive oxygen species caused by UV light exposure. These molecules are then aimed at understanding the key interactions between the p47-p22phox complex and target molecules. While some research groups have studied the NADPH oxidase enzymes and NOX inhibitors, this work represents the first study of biophysical characterization of the p47-p22phox complex inhibition.

2021 GLRM 317

Development of ADA-SMRT methodology enabling genome-wide mapping of alkyl DNA adducts (ADA); *a gateway to understanding epigenomic basis of mutagenesis and carcinogenesis.*

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Alkyl DNA adducts (ADA) are cytotoxic, mutagenic, and carcinogenic DNA lesions induced by exposure to environmental agents (e.g., tobacco smoke or fuel combustion products) and common anti-cancer drugs (e.g., dacarbazine, procarbazine or temozolomide), as well as endogenous cellular metabolites. DNA adducts play significant roles in both the development and treatment of cancer. To understand how various alkyl DNA adducts contribute to mutagenesis, cancer development and treatment, it is imperative to be able to systematically examine complete, genome-wide profiles of these lesions and investigate how factors (such as modifications of chemotherapy agents, or the genomic and epigenomic landscape of the cell) influence initial adduct formation and repair. Current approaches used to quantify and map alkyl adducts in DNA rely mostly on indirect methods, which are limited in many aspects, and do not allow high throughput mapping of multiple types of alkyl adducts to specific genomic locations. Recent advances in single molecule real time (SMRT) high throughput DNA sequencing provide an unprecedented opportunity for direct and simultaneous detection of various modified DNA bases, including alkyl DNA adducts, based on modification-specific kinetic signatures. Our group is working on development of ADA-SMRT sequencing approach enabling direct and simultaneous, high throughput mapping of various alkyl DNA adducts in eukaryotic genomes. This powerful method will facilitate integrative research on associations between adduct profiles, capacity of DNA repair and mutagenesis within the native genomic and epigenomic context. These studies will have a major impact on understanding the molecular basis of environmentally-induced cancers, responses to chemotherapy and will facilitate development of new approaches in cancer risk identification, prevention, and treatment.

2021 GLRM 318

Gold nanoparticle delivery of fatty acid-binding protein 4-targeted agent inhibits leukemia growth through upregulation of DNA hypermethylation-silenced tumor suppressor genes

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Introduction: Gold nanoparticles (AuNPs) have emerged as attractive drug delivery vehicles, because AuNPs are biocompatible, non-toxic and highly tolerable. High density lipoproteins (HDLs) are dynamic natural nanoparticles transporting lipids and oligonucleotides throughout the body. Thus mimicking HDL-NPs have been used to deliver small molecules. Leukemia is an aggressive blood cancer with no curative regimens available. We showed that overexpression of fatty acid-binding protein 4

(FABP4) promotes AML expansion and invasion via upregulation of DNA methyltransferase 1 (DNMT1) and epigenetic silencing of tumor suppressor genes (TSGs). Treatment with FABP4 inhibitor BMS-309403 (BMS) downregulates DNMT1 and reduces DNA methylation. Given the high toxicity and off-target effects of BMS, we hypothesize that BMS delivery by HDL-NPs may enhance leukemia killing particularly in vivo.
Methods: HDL-AuNPs-BMS were synthesized using a gold nanoparticle as template to control conjugate size and ensure a spherical shape to engineer HDL-like nanoparticle containing BMS. The zeta potential and size of the HDL-AuNPs were measured by transmission electron microscopy (TEM). Gene expression was assessed by Western blot and qPCR. Global or TSG specific DNA methylation was measured by dotblot or bisulfite sequencing. The cell viability and apoptosis were assessed by CCK8 assays and Annexin V/Propidium Iodide staining.
Results: TEM examination discloses that HDL-AuNPs are electrostatically stable and 25 nm in diameter. Compared with free drug, HDL-AuNPs-BMS conjugates are more readily internalized by leukemia cells, display higher killing of leukemia cells in vitro, and have more pronounced effects on downregulation of DNMT1, reduction of global DNA methylation, and restoration of epigenetically-silenced TSG *p15*^{INK4b} coupled with leukemia cell growth arrest. Importantly, systemic administration of HDL-AuNPs-BMS conjugates into leukemic mice impairs DNMT1-dependent DNA methylation, induces leukemia cell differentiation and diminishes AML disease progression without obvious side effects.
Conclusion: Our findings suggest that HDL-AuNPs are an effective vehicle to deliver BMS into leukemia cells naturally targeted by HDLs. Our studies demonstrate proof-of-concept of the function of HDL-AuNPs-BMS to inhibit leukemia growth *in vitro* and *in vivo* through the deployment of BMS to restore normal DNA methylation profile, thus offering a promising therapeutic platform to treat leukemia.

2021 GLRM 319

Epigenetic regulation: the third pillar of nitric oxide signaling

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Nitric oxide (NO) production is deregulated in numerous types of cancers and is generally considered a negative prognostic indicator. Most biological functions of nitric oxide (NO) are attributed to its reactions with heme proteins and through modification of thiol residues. However, a significant number of transcriptional responses and phenotypes associated with NO still lack mechanistic understanding. The role of NO as an epigenetic modulator has recently emerged and has potentially important mechanistic implications in regulating transcription of oncogenes and tumor-suppressor genes. In this regard we found that cellular exposure to NO can change both histone posttranslational modifications (PTM) and DNA methylation (5mC) by directly inhibiting the catalytic activity of JmjC-domain containing epigenetic enzymes. We were able to link NO to modulation of gene-regulatory histone PTMs and DNA methylation with gene

expression changes that promote oncogenesis. Our results establish that NO functions as an endogenous epigenetic regulator of gene expression in cancers.

2021 GLRM 320

Nucleic acids toolbox

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Many questions still exist surrounding the connection between human genetic makeup and health. One area of interest that has evolved to answer these questions is the study of the “exposome”. The exposome has been defined as the measure of all the exposures of an individual in a lifetime and how these exposures relate to health. When we think of this concept, it is easy to begin to catalogue the many chemical entities encountered by an individual through the body’s exogenous environment, but what about the endogenous environment? The biological mechanisms that dictate life processes produce a multitude of chemical entities that can be catalogued as the endogenous exposome. These substances come in the form of reactive oxygen and nitrogen species, sugar fragments, nucleic acid damage products and lipid oxidation products. Through the use of analytical chemistry heavily supported with organic chemistry, our laboratory has developed a toolbox for the identification of biological molecules that can be attributed to the internal exposome. This work is based on the use of site specifically modified substrates that can be photochemically activated under biologically relevant conditions to decompose to small molecule fragments which are by-products of cellular respiration, metabolism and aging just to name a few. In this presentation the creation and utilization of this toolbox will be described.

2021 GLRM 321

Student-driven discovery of a solvatochromic effect propels the design of an undergraduate organic laboratory experiment

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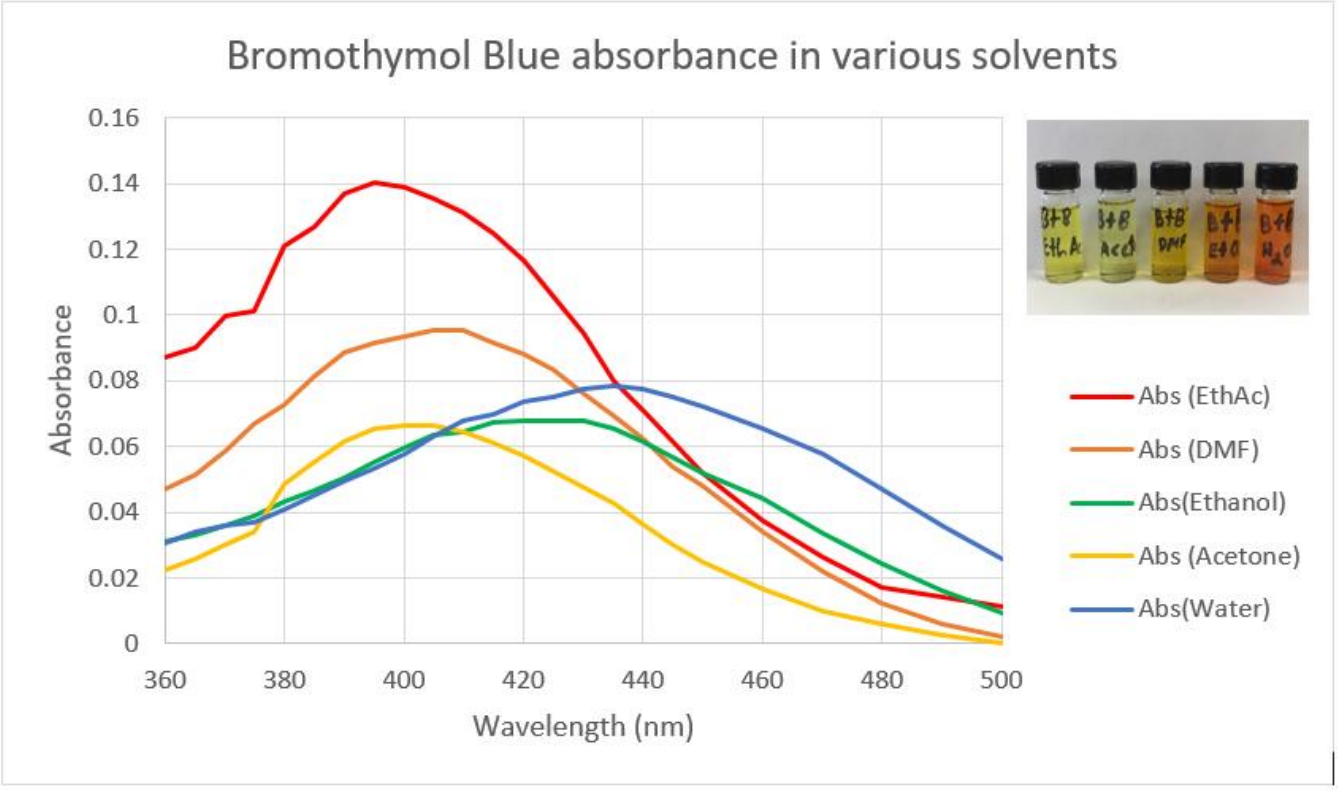
Solvatochromism is observed in compounds that exhibit a change in absorbance maximum when dissolved in different solvents. A pair of undergraduate researchers discovered a significant change in absorbance behavior of bromothymol blue (Btb), a common indicator dye. Btb was studied in a series of solvents, and five solvents were selected to design an experiment to be carried out in the first few weeks of Organic Chemistry I Laboratory. The experiment was designed to compliment lecture discussions of intermolecular interactions. The undergraduate research, experimental design, and results compiled from three semesters of student data shall be presented in this flash presentation.



2021 GLRM 322

Integrating writing-to-learn and project-based learning: Enhancing student knowledge of green chemistry through the creation of an open educational resource

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This presentation addresses the utility of a writing-to-learn activity in a majors' organic chemistry laboratory that resulted in the creation of an open educational resource (OER) on green chemistry. Because project-based learning has been shown to increase engagement, the writing-to-learn activity was specifically designed so that it would lead to the creation of an OER. Twenty students chose a reaction from a list of 39 key reactions provided by the instructor, who selected them from a second-semester organic chemistry textbook. Students then utilized free chemical drawing software to draw the mechanism. Then, using SciFinder, they researched the first report of the reaction and its current use with a bio-based molecule. Students reported their analysis of the reaction's adherence to the green chemistry principles findings on the OER website. Throughout the project, student work went through several cycles of peer

review, thus allowing for opportunities for feedback and engagement with classmate reaction and insight. Further details about this project will be presented at the meeting.

2021 GLRM 323

Tracking college chemistry instructors' teacher development through the evolution of their classroom document resources

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Many higher education chemistry instructors begin teaching with little or no formal training, and thus rely on their own experience and documents generated by other instructors (e.g. lecture notes, homework problems, learning management systems, videos etc.) to develop their teaching practice. To better understand how chemistry instructor's documentation practices evolve over time and thus how they evolve as teachers, we adapted and used a documentational approach from mathematics education, which captures the small changes that instructors make to documents over time. We conducted semi-structured interviews and observations to investigate how a faculty physical chemistry instructor create, utilize, and adjust their classroom documents. In the first interview of each participant, we asked instructors to present three important classroom documents and to describe the documents development. We collected copies of the documents and observed one teaching lesson in which the documents were used. We then conducted a post-observation interview for the instructor to reflect on the document's usage in the classroom. The data collected was qualitatively analyzed to describe the usage and evolution of the instructor's documents, and in turn their teacher development. Results presented will include a description of one physical chemistry instructor's document use and teacher development.

2021 GLRM 324

Analysis of chemistry students' conceptions of dissolving: The case of sodium chloride

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This presentation addresses the findings from a study that was designed to assess students' conceptions of the process of dissolving sodium chloride and the resultant properties of the solution. For students to truly understand science concepts, they must be able to link the three levels of representation (macroscopic, symbolic, and particulate). However, students often struggle to navigate between these levels. Therefore, this study sought to investigate students' conceptions about the process of

dissolving as represented by both the macroscopic and particulate levels. This study was conducted in a second semester General Chemistry (II) course at a Midwestern university (n=160). Students recorded their discussions while completing the worksheet in groups of 3-4, with a total of 46 groups. Worksheet responses were analyzed for correctness as well as patterns in conceptions. Audio recordings were used to further analyze student responses. Further details about the findings from this project will be presented at the meeting.

2021 GLRM 325

Experiment scaffolding for effective learning in the organic chemistry laboratory

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This pilot study examines the aspects of organic chemistry laboratory experiment and curriculum design and how they increase student learning. Two individual experiments, one assigned as a middle of the term experiment and another as a final exam experiment, were designed for first-semester organic chemistry students. Students were explicitly forewarned that their lab final practical exam would require the same techniques, but for that final experiment, they would be required to write their own procedure. Surveys to measure students' opinions on their laboratory learning experience were prepared based on literature examples; the studies use descriptive statistics to analyze student responses to labs. By examining student's laboratory experiences and expectations through this survey and descriptive statistics methodology, changes can be incorporated into the lab curriculum and experiments to meet learning outcomes.

2021 GLRM 326

Development of digital content on scientific writing for undergraduate and graduate students

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A component of undergraduate and graduate STEM education involves writing a scientific review paper. Students experience with writing in a scientific style widely varies and those students that have little background in writing often struggle. Graduate and undergraduate students from chemistry courses were surveyed on their experience with writing and perceived challenges of writing a scientific review paper. Based on the several years collection of surveys, challenges that students faced during the writing assignment were categorized and these categories were then used as the fundamentals for developing a digital online module on scientific review paper writing. The online

Canvas module introduces students to the structure and style of a review paper, how to find relevant literature, how to synthesize information into a review, and also how to manage the time and find an appropriate topic. This module was built in collaboration with a team from the School of Information, to enhance the modules design, and to improve user experience with the module. We will present the module and our approach in developing a digital content that will aid students in writing a scientific review paper.

2021 GLRM 327

Determination of pK^a of a Weak Monoprotic Acid from Equilibrium and pH Concepts: Alternative Method to Henderson-Hasselbalch Equation

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The pK_a of a weak monoprotic acid is usually determined using the half-equivalence point method in undergraduate laboratories in general chemistry curriculum. In this method, students estimate the pH at the half-equivalence point and that is the pK_a of the acid. The students are seldom taught to think about alternative methods to find the pK_a of a weak monoprotic acid. In this presentation, it will be shown how to calculate the pK_a using pH with an alternate equation derived from the dissociation equilibrium expression of the weak monoprotic acid. Also, the K_a and K_b relationship will be explored.

2021 GLRM 328

Incorporating Inquiry into General Chemistry Laboratory in a Feasible Way

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Open-ended and guided-inquiry based models for laboratory instruction allow students more opportunities to practice laboratory skill development in an environment that better mimics real world STEM workplaces. However, laboratory curricula with open-ended exercises are notoriously difficult to implement, especially on a large scale. Here, we elucidate an easy to implement approach for introducing some guided-inquiry exercises into a General Chemistry Laboratory curriculum. This model uses a two-week structure that first introduces students to a technique in week one before prompting students to create an experimental protocol to address an instructor-provided question for week two. With proper TA- and instructor support, this second week allowed students the opportunity to practice experimental design skills within the scope narrowed by the instructor-provided question and the technique introduced in week one. Such an approach was feasible while retaining the guided-inquiry experience for students. This model of laboratory was developed and piloted over two academic years, and student gains in experimental design skill and perception of confidence were assessed with an

in-house assessment administered before and after completion of a year of General Chemistry Laboratory (i.e. pre-post testing). Results of these assessments were compared for a pilot cohort who went through the new curriculum and a cohort of students who completed a traditional, unrevised curriculum. These comparisons showed that the students in the revised curriculum achieved slightly higher gains in experimental design ability and self-reported higher levels of confidence in their experimental design ability than their peers who completed the traditional curriculum. Moreover, the quality of students' explanations improved more for the cohort of students in the revised laboratory curriculum compared to those who completed the traditional laboratory curriculum. Overall, our results suggest that the two-week approach to implementing guided-inquiry exercises into General Chemistry Laboratory is not only feasible, but is also effective.

2021 GLRM 329

Development of student data analysis skills in the general chemistry laboratory

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We know that most students taking General Chemistry will not become a professional chemist. However, there are skills that they can develop in the chemistry laboratory that they can take with them into their new field of study. Most students will have to work with spreadsheets and/or evaluate numerical data in their studies and careers. Here we present a program integrating of Excel into the General Chemistry Laboratory sequence as a tool to properly present graphical data, to fit that data and extract useful information, and to interpret that data in terms of accuracy and precision.

2021 GLRM 330

Course-based undergraduate research experience (CURE) and Honors Program hybrid course on microplastic detection and analysis

Shaina Mattingly*[1], shaina.mattingly@und.edu, Alena Kubatova[2], Rebecca Simmons[3], Daphne Pedersen[3]. (1) Chemistry, University of North Dakota, Grand Forks, North Dakota, United States (2) Chemistry Department, University of North Dakota, Grand Forks, North Dakota, United States (3) University of North Dakota, Grand Forks, North Dakota, United States*

Undergraduate research gives students an opportunity to gain insight into the problem-solving strategies of a certain discipline. Scientific research can be a catalyst to spark a student’s interest in a career in science. When scientific research is embedded within the requirements of undergraduate coursework, students gain research experience that they may not have otherwise pursued. A Course-Based Undergraduate Research Experience (CURE) and Honors Program hybrid course was designed. The undergraduate course was taught as a co-disciplinary Honors and Chemistry course

and included a discussion component as well as a research component. The course was designed to increase interest in chemistry through research on a contemporary topic, and to add discussion-based curriculum to a chemistry undergraduate course.

Microplastic contamination is a rapidly increasing issue. An undergraduate course was developed to examine the extent of microplastic contamination in the environment. The course discussed social, political, and environmental implications of plastic and microplastic contamination. The research component of the course was designed to give students hands-on experience with techniques used to isolate and detect microplastics from their local environment. Student research involved testing multiple samples of varying matrices for microplastics. Analysis was done using the fluorescent dye Nile Red for detection and confirmation of microplastics.

Beyond research, student assessment included two presentations. One presentation involved the social, political, or environmental aspect of plastic and microplastic contamination. The final presentation was on their own microplastic research during the course. Results of student assessment suggest that student interest in chemistry was increased through participation in the course.

2021 GLRM 331

Bio-based hydrogels for green polymer teaching lab experiments

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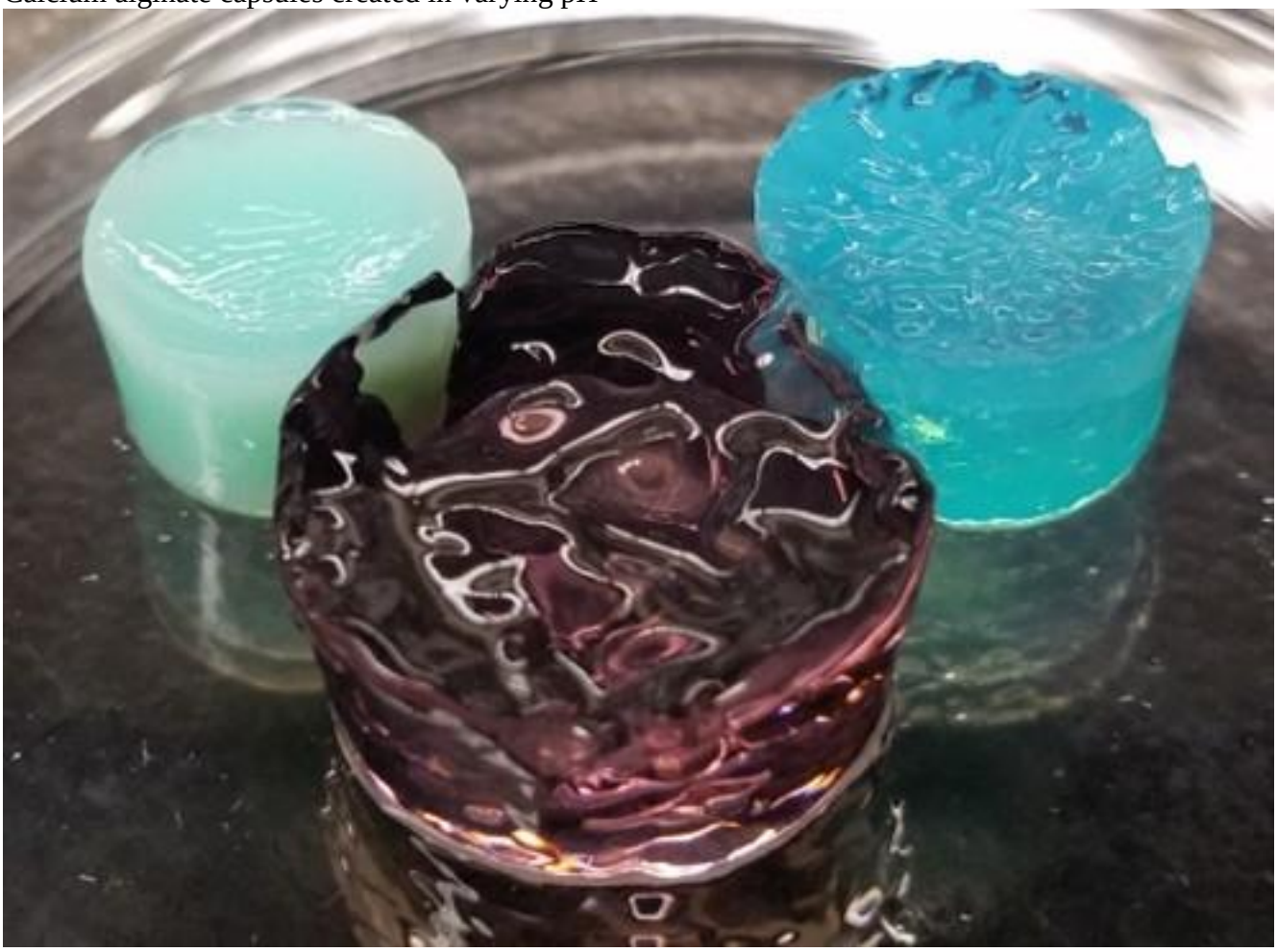
Hydrogels are cross-linked polymers known for their swelling behavior in retaining large amounts of water several times their weight. They have a wide array of applications as vehicles for drug delivery, tissue engineering, food industry, or smart materials. The tunable properties of hydrogels and their multitude of usage make them ideal model systems to engage students in learning about green methodologies, sustainable polymers, and core topics centered around chemical bonding and acid-base chemistry. This presentation will describe two recently developed teaching experiments for high school and undergraduate chemistry courses in an effort to integrate relevant research studies and technological developments into the classroom. To incorporate sustainable and green chemistry principles we focused on synthesizing biobased hydrogels derived from naturally occurring carbohydrates found in plants and dairy products as oppose to hydrogels that are sourced from non-renewable petroleum feedstocks. The first iterations of each experiment are scheduled for implementation this spring. A survey of student results and learning outcomes will be collected.

Calcium alginate capsules created in varying pH



Dyed dissacharide-based hydrogels varying in cross-linking density

2021 GLRM 332

Developing Undergraduate Lab Activity to Determine Quantum Efficiency of Visible Light Mediated Reactions

***Amandeep Arora**, aman.arora450@gmail.com. natural and applied science, University of Dubuque, Dubuque, Iowa, United States*

In any photochemical reaction, light is used as a reagent. One such example is Photosynthesis reaction used by plants in nature. The evaluation of light sources in terms of knowledge of the photon flux and light intensity is essential in designing any photochemical experiment. The photochemical reaction's quantum yield can be obtained using physical and analytical concepts, which provide valuable mechanistic details of the given reaction and provide a practical tool to improve the reaction's scaling process. However, very few publications reported about the photon flux of light source used in their photochemical setup. This work detailed an easy-to-performance undergraduate lab activity of finding quantum yield (on chosen blue LEDs (wavelength of 365 nm) using the NMR actinometer method. A well-known chemical actinometer o-nitrobenzaldehyde has been utilized to understand the light intensity of the chosen light Blue LEDs. Further, the method has been used to measure the quantum yield of several recently published photochemical reactions.

2021 GLRM 333

Design of Potassium Solid-contact Ion-selective Electrodes for Blood Sensors Using Polydimethylsiloxane and Colloid-imprinted Mesoporous Carbon

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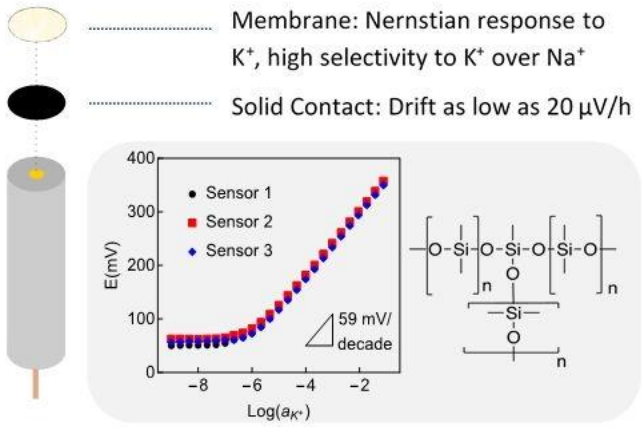
Quantifying potassium levels in blood serum is an important clinical test, as abnormal levels can indicate cardiovascular or kidney disease. Therefore, there is a demand for biocompatible devices to measure potassium activity in blood. Solid-state potassium ion-selective electrodes (ISEs) show great promise, as they have a predictable response to potassium ions, stable signal over time, and high selectivity to potassium over sodium. Currently, commonly used ISEs with polyvinyl chloride (PVC) exhibit these qualities, but the PVC membranes contain a toxic plasticizer that can leach from the ISE into the sample, making them poor candidates for biological testing. Therefore, the current challenge is to develop a silicone-based ISE which exhibits ideal functionality as a potassium sensor and does not contaminate the sample. In our work, fluorosilicone-based ISEs had Nernstian responses to potassium, detection limits near 10^{-6} M KCl, and selectivity to potassium over sodium equal to that of industry sensors. However, after storage in an aqueous solution for one week, the same ISEs displayed sub-Nernstian responses, losses of selectivity to potassium, and Donnan failure. In comparison, polydimethylsiloxane-based ISEs had excellent functionality, as they retained their ideal responses to potassium and high selectivity values after weeks of storage in 1 mM KCl solution. Furthermore, the signal stability of the ISEs was increased by using colloid-imprinted mesoporous (CIM) carbon as a solid contact between the ion-selective membrane and the electrode, reaching drifts as low as 20 μV/h that significantly decrease the need for recalibration. Overall, we propose that this polydimethylsiloxane-based design with CIM carbon films is a viable option for clinical blood testing.



2021 GLRM 334

Comparative Analysis of Polyphenols in Raw Elderberries and Commercial Products

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Elderberries have been used as a natural health remedy for a variety of ailments. The health benefits have been linked to the presence of polyphenols.This study specifically isolates the polyphenols in Sambucus canadensis (American Elderberry) as compared to Sambucus nigra (European Elderberry). Both varieties are easy to grow and are found in fertile moist soils in roadside ditches and at the edge of fields and pastures. Local berry samples (Sambucus canadensis) were compared against 4 separate commercial products of which, three originated from outside the US. The overall objective of this project is to identify the specific targeted compound that contributes to the health benefits. More specifically, concentrations of Rutin (flavonol) and Chlorogenic Acid (phenolic acid) were analyzed in multiple samples and the difference between berries and syrups were compared. Methodology was adapted from Mudge et al with slight variations in sample preparation and extraction. Analysis was performed using High Performance Liquid Chromatography and UV Spectroscopy. Final analysis and results are pending and will be completed by March 3rd..

2021 GLRM 335

Comparing the role of ion exchange sites in Nafion 117 versus Nafion EW 1100 in the cyclic voltammetry of lanthanide (III) trifluoromethanesulfonates at Nafion-modified platinum electrodes

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The electrochemical analysis of lanthanide trifluoromethanesulfonates (triflates) using Nafion® EW 1100 and Nafion® 117 compares the two ion-exchange membranes. This contributes to the understanding of Nafion® film characteristics and the current knowledge of lanthanide group properties and electrochemical mechanisms. Evaluation of lanthanide compounds is enabled by a recently discovered method using a Nafion film modified platinum electrode with lanthanide triflate redox molecules and tetrabutylammonium tetrafluoroborate electrolyte in acetonitrile. Cyclic voltammetry of this system reveals a complex and fascinating mechanism comprising of at least two distinct reduction reactions as well as a possible chemical disproportionation reaction followed by at least three oxidation reactions in the reverse direction. Part of the current theory to explain why this method allows observation of the three redox behavior of lanthanide triflates is Nafion® solubilizes the lanthanide compounds, possibly by replacement or equilibrium of a ligand with a sulfonate group. Nafion® is a cation-exchange polymer with unique properties due to the incorporation of perfluorovinyl ether groups terminated with sulfonate groups onto a tetrafluoroethlyene backbone. Trifluoromethanesulfonate is a ligand that closely resembles Nafion® perfluorosulfonate side chains. Experiments are conducted with bench top electrochemical cells using a three-electrode system involving the two kinds of Nafion® film modified platinum working electrode, silver/silver^{+} quasi-reference electrode, and platinum wire/mesh counter electrode. Our group predicts if the lanthanide triflate interacts with the ion exchange sites on the Nafion® membrane, the membrane with more sites will have a higher current density because there are more molecules near the film. Future research projects involve potential applications of lanthanide triflates and understanding the effects of a Nafion® film modified working electrode on the mechanism.

2021 GLRM 336

The Development of a Method for the Identification and Quantification of Calcitroic Acid in Biological Samples with Liquid Chromatographic Mass Spectrometric Detection.

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Our research is focused to provide insight into the biological role of calcitroic acid, the final metabolic product of vitamin D. Vitamin D metabolites are important molecules to regulate cellular proliferation and calcium homeostasis, especially 1,25-dihydroxy vitamin D_3 (calcitriol). The vitamin D metabolism has previously been investigated and reported using radiolabeling methods. While calcitroic acid has been identified in these studies, the activity of this molecule is still not well understood. Our group has developed a method for the identification and quantification of calcitroic acid in native tissue and biological samples using liquid chromatography paired with triple quadrupole mass spectrometry (LC–MS/MS). This method improved the limits of detection without

the need for derivatization of the analyte. Using the developed method, we were able to monitor levels of calcitroic acid in biological samples with a limit of detection of 1.0 nM. Samples underwent a workup that included a strong anion exchange solid phase extraction to further simplify the matrix of the samples before LC–MS/MS detection. The incorporation of a size membrane filter was implemented to prevent proteins and other large molecules from interfering with the strong anion exchange cartridge.

2021 GLRM 337

RP-HPLC method development to determine DL-amino acid ratios in eggshells for geochronological applications

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This research uses OPA-IBLC derivatization and HPLC-FLD parameters to validate lower limits of detection (LOD) and quantitation (LOQ) for eggshell amino acid ratio analysis. Published methods have used 240 or 340 nm excitation wavelengths for OPA-IBLC amino acid fluorescence. A 3-dimensional fluorometric scan in pH 4 sodium acetate-boric acid buffer showed peak OPA-IBLC derivatized histidine and glutamate fluorescence occurs at 334- to 440-nm and 336- to 442-nm excitation-emission, respectively; though less intense emission occurs at 260 nm excitation. Planned experiments will validate these results with systematic HPLC-FLD analysis of pre-column derivatized amino acid standards. Derivatization reaction completion will also be tested by increasing OPA-IBLC-amino acid mixing time until peak integration stabilizes. These FLD and mixing parameters will be applied to an enantioselective RP-HPLC method developed by Agilent Technologies to create amino acid calibration curves, allowing quantitative determination of eggshell DL-amino acid ratios for geochronological applications.

2021 GLRM 338

Characterizing ancient perfume residues in the double unguentaria from the Michael C. Carlos Museum

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Unguentaria are ancient ceramic or glass vessels thought to have once held oils, perfumes, ointments, balms, or cosmetics. These vessels are commonly found in archaeological sites across the Mediterranean region. Double unguentaria, the focus of this research, are generally small with two elongated barrels, and are thought to have held perfumes. Perfumes of the Greco-Roman period have two main components: the

matrix or base, commonly an oil or balsam, and the aroma element derived from herbs or flowers. By identifying the composition of residues left inside these artifacts, we can infer how the unguentaria were used. We report here on the results of analyses of the residual contents of several double unguentaria from the collections of the Michael C. Carlos Museum at Emory University. Mass spectrometry, either with direct analysis in real time ambient ionization or coupled to gas chromatography, is a powerful approach to determining the composition of these degraded ancient samples. Headspace solid-phase microextraction (HS-SPME) allows us to focus primarily on the aroma compounds. We report here on the results of our characterization of the unguentaria contents by use of GC-MS and DART-MS to determine the nature of the perfume bases and aroma compounds, and scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS) to investigate inorganic components that may have also been incorporated.

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Development of Lanthanide Enhanced Methanol Dehydrogenase Electrodes for Improved Bioelectrocatalysis Applications

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Methanol is a commonly used solvent that is a potential solution to creating more eco-friendly automobiles, as well as used in many biological processes. However, exposure to methanol can lead to many toxic effects from headaches, blindness, or even death. Therefore, it is imperative to both improve methanol sensors and advance methanol-based energy technologies (such as methanol biofuel cells). *Methylobacterium radiotolerans* is a methylotroph that feeds off of methane, methanol, and other methylated species. This bacterium has been found to exchange the calcium cofactor in some of its enzymes for rare earth metals when grown in lanthanide-rich environments. These REE modified enzymes show higher catalytic activity than their calcium counterpart. Here, the change in bioelectrocatalytic activity that lanthanide cofactors have on methanol dehydrogenase (EC 1.1.1.244) is investigated, by immobilizing the bacteria (*M. radiotolerans*) containing the lanthanide cofactor methanol dehydrogenase enzymes (Ln-MDH) onto a glassy carbon electrode with the goal of optimizing an enzyme-modified electrode system. Work done to date has developed methods for immobilizing the bacterial cells and improving the scans through the use of the methylene blue redox mediator. Deciphering the electron transfer kinetics between the bacteria, modified membrane, the redox mediator and electrode are necessary parts of developing bioelectrocatalytic applications, such as methanol biofuel cells and alcohol sensors. The system will consist of the whole bacterial cell entrapped on the membrane. Tetra-n-butylammonium bromide modified Nafion® will immobilize the Ln-MDH on the surface of the electrode. Once a functional Ln-MDH electrode has been made, testing will be done via cyclic voltammetry and the electrode performance will be compared to a calcium cofactor MDH electrode.

2021 GLRM 340

Plasma oxidation and AMS radiocarbon dating of archaeological textile fragments: Pretreatments for removing contamination

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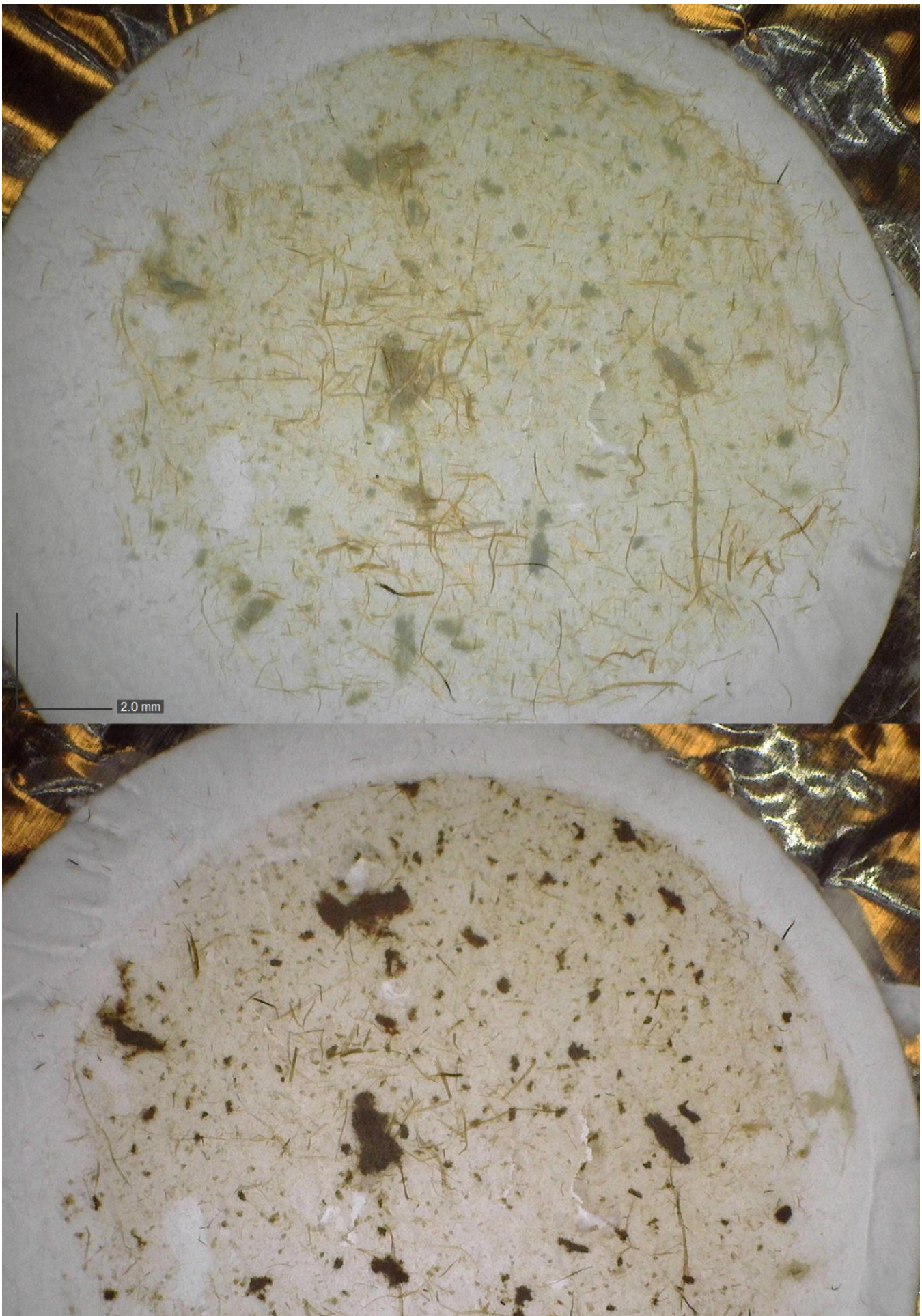
Tiny fragments shed by larger archaeological textiles can provide a way to directly radiocarbon date these precious and rare objects. Contamination can be present from the burial environment or from other aspects of the sample, including the presence of mineral pigments or even radiocarbon-free bitumen coatings, as is sometimes the case with linen from Egyptian mummies. These contaminants can lead to erroneous dates, and so they must be removed prior to dating, usually through a series of wet chemical pretreatments, some of which may be significantly destructive to the sample.

Radiocarbon analysis by accelerator mass spectrometric radiocarbon dating requires converting what remains from the pretreatment to carbon dioxide through combustion at high temperatures, consuming the entire prepared sample. Plasma oxidation is an alternative to combustion, wherein a low temperature oxygen gas discharge reacts with the surface of the prepared sample to generate CO_2 instead, preserving the object for redating in the future. Our group is developing appropriate and minimally destructive pretreatment protocols for plasma oxidation sample preparation and subsequent AMS radiocarbon dating. Calcium carbonate purportedly does not decompose under the plasma oxidation conditions, as it does not affect the dates for organic materials associated with carbonates. Copper carbonate pigments, however, exhibited unusual behavior under the plasma conditions, and modern plant fibers with malchite pigment yielded ages shifted by as much as 1200 years before present. Removing this contaminant will be an important step in obtaining reliable dates for copper-stained textile fragments excavated from the Seip Mound complex in Ohio.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2021 GLRM 341

Insights into the Nucleation of Mixed-Valent Polyoxovanadate-Alkoxide Clusters

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The synthesis of novel tunable electroactive species remains a key challenge for a wide range of chemical applications such as redox catalysis, energy storage, and optoelectronics. In the recent years, polyoxovanadate (POV) alkoxide clusters have emerged as a new class of compounds with highly promising electrochemical applications, however, our knowledge of the formation pathways is rather limited. Here, we present a computational study on the nucleation chemical space of mixed-valent POV alkoxide species.

2021 GLRM 342

Sulfur-Containing Analogs of the Reactive [CuOH]2+ Core: Theoretical Studies

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Copper-oxygen complexes comprising of the [CuOH]2+ core supported by dicarboxamide ligands are notably reactive, attacking C-H and O-H bonds via proton-coupled electron transfer (PCET). Present research was performed to study analogs that contain sulfur instead of oxygen (LCuSR R=H, Ph) to determine how the replacement of O by S influences structure, properties, and function of these complexes. In addition to experimental studies detailed theoretical investigation was carried out. DFT optimized geometries and UV-Vis spectra obtained from TDDFT studies were compared with experimental results. In addition to this, multiconfigurational studies were also performed on a series of complexes LCuR (R = OH, SH, SPh, F, Cl, Br) using CASSCF and localized CAS-CI calculation and similarities and differences in comparison to previously reported literature were reported in detail.

2021 GLRM 343

Understanding electronic structure and bonding in a Bis-Anthracene Uranium Dimer

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Actinide-arene complexes are interesting due to the unique bonding between the actinide and arene. Actinides have both *d* and *f* orbitals that are nearly degenerate and often participate in bonding with ligands and understanding the electronic structure of these new compounds is of fundamental interest. The actinides differ from the lanthanide and transition metals since the 5*f* orbitals can engage in covalent bonding; however, most of the time, the 6*d* orbitals dominate the bonding with the ligands while the 5*f* orbitals hold the unpaired electrons. This leads types of bonding that are not available in the rest of the periodic table. Specifically, we studied the electronic structure and bonding of a bis-anthracene uranium dimer, $[U(\eta^6\text{-}C_{14}H_{10})(\eta^4\text{-}C_{14}H_{10})(\mu\text{-OMe})]_2$**, 1** and $K_2[U(\eta^6\text{-}C_{14}H_{10})(\eta^4\text{-}C_{14}H_{10})(\mu\text{-OMe})]_2$, **1-K**, using both density functional and multireference methods. Both species present quintet ground states, consistent with experimental results. Bonding analysis shows that the U 6*d* orbital is the major contributor to the bonding orbitals with the anthracenide ligand with small participation of 6*p*, 5*f*, and 7*s* orbitals in some instances.

2021 GLRM 344

A novel reaction mechanism for the ring-opening polymerization of $[PCl_2N]_3$ revealed by quantum mechanical (DFT) calculations

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As the largest group of inorganic backbone polymers, phosphazenes are molecules with alternating phosphorus and nitrogen backbones. Despite major drawbacks (such as irreproducibility and high polydispersity index, PDI) the most popular method to prepare the parent, $[PCl_2N]_n$, has been through ring opening polymerization (ROP) of $[PCl_2N]_3$. To achieve better control over the polymerization process, different Lewis acids including MCl_3 (M = B, Al, Ga) and PCl_5 have been added to the reaction. Because some experimental facts cannot be well explained using the previously proposed SN1 mechanism, a deeper understanding of the ROP mechanism of $[PCl_2N]_m$, can be achieved by applying quantum mechanical (DFT) calculations to investigate the inter- and intramolecular re-arrangements between two or more $[PCl_2N]_3$ molecules. Our calculations also take into account how different Lewis acid additives, such as MCl_3, might act as initiators/catalysts in ROP, and how PCl_5 might inhibit the chain propagation. Based on the analysis of ROP potential energy surface, which describes the reactants, predicted reaction intermediates, and transition states of the reaction, we report here a novel SN2 reaction mechanism for the interaction between $[PCl_2N]_3$, which initiates the ROP in one concerted step.

2021 GLRM 345

Magnesium Alkoxide Complexes in Achiral and Chiral Ligand Environments for Polymerization of Lactide and Epoxide/Anhydride Copolymerization

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My research focuses on the synthesis of non-toxic and sustainable main group catalysts for polymerization of lactide and copolymerization of epoxide and anhydrides. Both polymerization and copolymerization processes are investigated with main group alkoxide catalysts featuring achiral and chiral ligand environments. Lactide is a renewable precursor for synthesis of polylactic acid (PLA), a biodegradable and recyclable polyester that can replace non-biodegradable petroleum-based polymers. There is a significant interest in the copolymerization of epoxide and anhydride to produce polyesters. Due to the availability of the large library of epoxides and anhydrides, copolymerization of epoxides and anhydride provides structurally diverse polyesters. Both polymerization processes proceed via Lewis acid catalysis in which the monomer inserts into the metal-alkoxide bond. Therefore, main group Lewis-acidic alkoxide complexes are commonly used as pre-catalysts for both processes. I will describe the synthesis of novel $Mg(OR)_2(THF)_2$ complexes, that contain a combination of a non-toxic metal with simple achiral and chiral alkoxide ligands. Achiral $Mg(OR)_2(THF)_2$ (OR = OC^tBu_2Ph) complex shows very high reactivity for polymerization of lactide, as well as in copolymerization of various epoxides and anhydrides. Tacticity of the polymer plays an important role in the macroscopic properties of the polymer including its crystalline, semi-crystalline and amorphous state. It is anticipated that the C_2-symmetryc chiral catalyst can exhibit enantiomorphic side control polymerization to produce tactic polymers. Therefore, I synthesized two chiral alkoxide ligands (OR = OC(Ad)(^{t}Bu)Ph and OR= OC(Ad)(Me)Ph) and their Mg alkoxide complexes to study both processes. Synthetic, structural and reactivity studies in the polymerization of lactide and in the copolymerization of maleic anhydride and propylene oxide will be presented and discussed.

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Synthesis and reactivity of a bis(phosphinoamide) Zr/Co heterobimetallic complex featuring an unprecedented dinitrogen binding mode

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Lewis acidic early transition metals and electron-rich late transition metals can be brought into close proximity by using a phosphinoamide ligand scaffold, resulting in polar metal-metal bonds. The synthesis of a bis(phosphinoamide) zirconium/ cobalt tetrametallic dinitrogen complex has been accomplished, featuring an unprecedented dinitrogen binding mode and extreme N-N bond elongation. The complex features a

novel side-on binding of dinitrogen to a late transition metal, which lends support to some models of dinitrogen binding in nitrogenase. The capability of this complex to cleave the dinitrogen bond under catalytic conditions will be discussed.

2021 GLRM 347

Development of selective CK2 alpha prime probes

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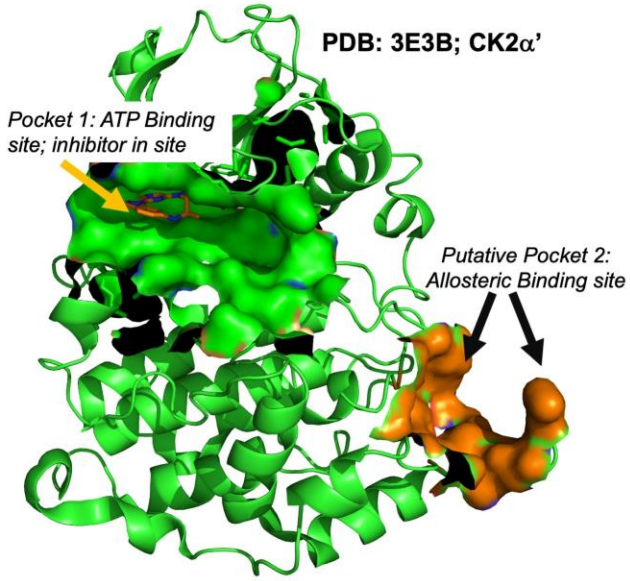
Protein kinase CK2 holoenzyme contains two catalytic subunits, CK2 alpha (CK2α) and CK2 alpha prime (CK2α'). CK2α' is involved in protein homeostasis and neuroinflammation, expressed primarily in the brain and testes of adults. In contrast, CK2α is a ubiquitously expressed, essential protein with hundreds of substrates. CK2α' KO mice are viable and very few substrates for this protein have been identified. Previous work has shown that only CK2α' is inappropriately upregulated in cellular and animal models of Huntington's Disease (HD) and in human patients with HD. However, prior research has not addressed the translational potential of targeting CK2α' due to the lack of specific inhibitors for this subunit. Different CK2 inhibitors based on ATP analogues are commercially available and are currently in human clinical trials for several cancers. Unfortunately, these inhibitors do not discriminate between CK2α and CK2α' subunits and impose deleterious effects in *in vitro* models of neurodegenerative diseases. We have embarked on a high-throughput screening (HTS) campaign to develop new probes that selectively target protein kinase CK2 alpha prime (CK2α') based on allosteric inhibition as a potential intervention in HD. Details of HTS assay development, validation, and any preliminary results will be presented.



A putative type IV allosteric binding pocket on CK2α', highlighted in orange, as computed using CASTp and visualized using PyMOL.

2021 GLRM 348

Computational Approaches to Fragment Selection and Screening for Protease Inhibitor Design

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Caspase-2 has been shown to be linked to synaptic dysfunction. This synaptic dysfunction is mediated by the tau fragment (delta-tau314) that is formed by cleavage of tau by caspase-2. We have embarked on a project to prepare non-canonical, non-proteinaceous inhibitors of caspase-2 that are suitable for delivery to the brain. Known caspase-2 inhibitors are typically too large and too polar to easily cross the blood-brain barrier. In order to find suitable small-molecule inhibitors of caspase-2, we have begun an exploration of fragment- and electrophilic-fragment screening approaches to novel chemical matter. In this presentation, we will discuss our findings in this area and our excursion into virtual fragment screening, examining and characterizing both non-covalent and covalent fragment-protein interactions.

2021 GLRM 349

Can ferricyanide core complexes be used as drug delivery systems for cisplatin?

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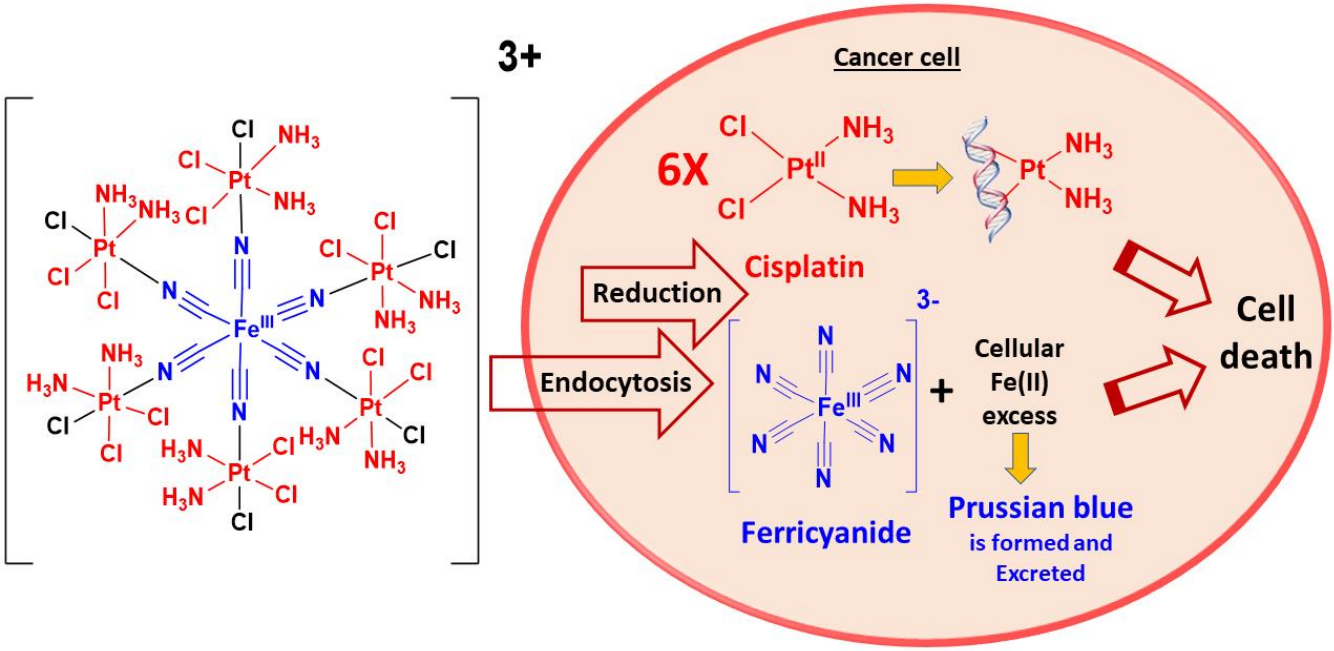
Design principles of a dual function prodrug that can, upon reduction, dissociate and release concurrently six cisplatin units and a ferricyanide anion per prodrug unit are presented. The prodrug molecule is a unique complex of hepta metal centers consisting of a ferricyanide core with six Pt(IV) centers each bonded to the Fe(III) core through a cyano ligand. The prodrug presents three desirable features for a delivery agent: 1. It is positively charged. 2. It is of a nanoscale size. 3. It releases upon reduction six active cisplatin molecules and a ferricyanide that synergizes the potency of the drug. The functionality of the prodrug is addressed through density functional theory (DFT) calculations.



2021 GLRM 350

Fractionation design of hemp (*Cannabis*) products for analysis and bioassay

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Preparations originating from *Cannabis* are reported to produce numerous favorable therapeutic outcomes. However, much confusion exists in the chemical characterization of herbal products referred to as *Cannabis* extract, hemp extract, hemp oil, CBD oil, full spectrum CBD, broad spectrum CBD, cannabinoids, or cannabidiol. This study was aimed at developing a comprehensive separation method to isolate high purity CBD as well as fractionate congeneric cannabinoids for further separation, isolation, and analysis. A liquid-liquid separation method was employed to separate cannabinoids from hemp seed oil. The rational chemical and biological assessment of hemp-derived natural products was facilitated by the DESIGNER approach of Depleting and Enriching Select Ingredients to Generate Normalized Extract Resources. Countercurrent separation (CCS) methodology allowed for cannabinoid fractionation with minimal sample loss and high reproducibility. NMR analysis of both purified cannabinoids and complex fractions provided quantitation as well as the structural identification of cannabinoids and other constituents. CCS of commercial “CBD oil” yielded high purity cannabidiol, a polar cannabinoid fraction containing cannabigerol and cannabidivarin, in addition to a nonpolar cannabinoid fraction containing cannabichromene, *trans*-Δ9-tetrahydrocannabinol, and *cis*-Δ9-tetrahydrocannabinol. Further separation of the polar and nonpolar fractions yielded purified cannabinoids and additional features of the chemical residual complexity present in the sample. Chemical characterization of these materials utilized ^{1}H(q)NMR, 2D-NMR, and HPLC to confirm chemical composition, assess residual complexity, and assign purity. The newly developed *Cannabis* DESIGNER extracts are distinctive natural product preparations, which may be tested individually or in combination. The biological testing of these materials will help fill the gap between chemical composition and possible biological and therapeutic applications of materials derived from *Cannabis*.

2021 GLRM 351

Synthesis of Novel Quinone Methide Precursors as Potential Resurrectors and Reactivators of Aged and Inhibited Acetylcholinesterase.

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Organophosphorus (OP) nerve agents serve as deadly chemical warfare agents and pesticides. Although typically colorless and odorless, these agents are capable of inducing respiratory, cardiovascular, and central nervous system symptoms by inhibiting the critical enzyme acetylcholinesterase (AChE) and can lead to death. AChE is

responsible for the hydrolysis of acetylcholine in post-synaptic junctions, and when deactivated by OP intoxication, acetylcholine results in overstimulation and cholinergic crisis.

Current treatments for organophosphorus poisoning are futile after a very short time-window, during which, the inhibited acetylcholinesterase undergoes an aging process where the phosphylated serine residue of AChE is dealkylated. As a result, it is no longer reactivatable via the current FDA approved treatment methods, thereby necessitating a novel treatment that can react with the OP-aged form of AChE. Previous work by our team has shown that quinone methides can serve as resurrectors and reactivators of OP-aged and OP-inhibited AChE. The precursors of these alkylating agents contain an aromatic framework with varying benzyl amino moieties, which serve as leaving groups in the formation of the hypothesized quinone methide in vivo. Previous studies have investigated the effect of changing the amine leaving group on multiple aromatic pyridine frameworks; however, the effect of changing the aromatic ring to a phenol scaffold has yet to be fully established.

Mannich reactions were used to synthesize a library of phenol-based quinone methide precursors, all with differing alkyl and O-alkyl substituents at the para and meta positions, and with 5 different benzyl amino substituents at the ortho position of the phenol core. This library was screened against OP-inhibited and OP-aged human AChE to test reactivation and resurrection potential with the intent of identifying a robust compound that can resurrect and reactivate aged and inhibited AChE.