ACS Local Section
Dallas-Fort Worth

53rd Virtual Meeting-in-Miniature

Saturday, May 1st, 2021

Technical Program
and
Abstract Booklet

Organized by

The Department of Chemistry and Biochemistry

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MATHEMATICS

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3:40 – 4:30 pm Break
4:30 pm – 5:00 pm Awards Ceremony

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Organic Section

Entry	Time	Activity
Greetings	9:30 am – 9:40 am	***Greetings***
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02	10:00 am – 10:15 am	David T. Hoang
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04	10:30 am – 10:45 am	Shashini D. Diwakara
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Break	12:25 pm – 1:00 pm	***Lunch Break***
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Break	2:00 pm – 2:10 pm	***Intermission***
15	2:10 pm – 2:25 pm	Olatunji Ojo
16	2:25 pm – 2:40 pm	Su Yang
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19	3:10 pm – 3:25 pm	
20	3:25 pm – 3:40 pm	
Break	3:40 pm – 4:30 pm	***Break***
Awards Ceremony	4:30 pm – 5:00 pm	***Awards Ceremony***

For questions about scheduling for Organic Section, e-mail:
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Total Synthesis of Bioactive Indole-Imidazole Alkaloids and Pyrrole-Imidazole Alkaloids

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Classification: Graduate

Natural products and their derivatives inspire a large fraction of FDA-approved drugs and are often referred to as privileged frameworks due to their structural diversity and biological endorsement. However, the process of isolating organic molecules from their natural sources can be expensive in terms of committed time, material expense and availability (access due to adverse political issues or disappearing ecosystem of the source organism). These issues can make it hard to explore their complete biological profile of these natural products. Furthermore, despite the development of advanced analytical tools, such as multidimensional NMR spectroscopy, high-resolution mass spectrometry and X-ray crystallography, the approach of establishing the structure of natural products is often proved to be tedious and can lead to errors. Total synthesis of natural products continues to play a vital role in structural elucidation and remains among the most exciting and dynamic areas of organic research. Interest in natural products synthesis has inspired incredible advances in the development of new synthetic methods and strategies for the construction of heterocycles. Indole-imidazole alkaloids (IIA) and pyrrole-imidazole alkaloids (PIA) are two classes of nitrogen-rich natural products, which have attracted considerable attention from synthetic chemists largely due to their intricate structural complexity and wide range of potential biological activities. The research described in this presentation explores the development of methodologies for the total synthesis of several of these IIAs (haploscleridamine, villagorgin A and lissoclin C) and PIAs (ageliferin and nagelamide).

Design and Synthesis of Potent Histone Lysine Demethylase Inhibitors Containing 8-Hydroxyquinoline

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Methylation and demethylation of histone are important epigenetic processes that control numerous transcriptional activities. Histone lysine demethylase 4 (KDM4) is a member of the Jumonji domain 2 (JDJM2) family which is overexpressed in tumors including prostate cancer. We have previously identified 8-hydroxyquinolin-based compounds like B3 that showed high potency and selectivity on inhibiting KDM4B. In an attempt to improve their biological activities, we have designed a large number of novel B3 analogs with structural modification of the 3-phenylpropylamine moiety with various aminoacyl N-alkylamide. This modification not only increased structural diversity of the alkyl chain but also provided an efficient solid-phase synthetic route. 183 compounds were synthesized with Fmoc solid-phase synthesis employing the aminomethylated polystyrene resin along with a backbone amide linker. Then MTT assays were performed on these compounds with a 4 days treatment of 1 um concentration. Among numerous analogs synthesized and tested, A16 that contains Trp showed the strongest cell growth inhibition on prostate cancer cells (22RV1), showing a potential of the synthetic strategy to achieve strong biological activity.

Donor-acceptor conjugates derived from cobalt porphyrin and fullerene via metal-ligand axial coordination: Formation and excited state charge separation

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Two types of cobalt porphyrins, viz., meso-tetrakis(tolylporphyrinato)cobalt(II), (TTP)Co, and meso-tetrakis(triphenylamino porphyrinato)cobalt(II), [(TPA)4P]Co, were self-assembled via metal-ligand axial coordination of phenylimidazole functionalized fulleropyrrolidine, ImC60 for form a new series of donor-acceptor constructs. A 1:2 complex formation with ImC60 was witnessed in the case of (TTP)Co while for [(TPA)4P]Co only a 1:1 complex was possible to arrive. The binding constants K1 and K2 for step-wise addition of ImC60 to (TTP)Co were found to be 1.07 x 105 and 3.20 x 104 M-1, respectively. For [(TPA)4P]Co:ImC60, the measured K1 values was found to be 6.48 x 104 M-1. Although both cobalt porphyrins were non-fluorescent, they were able to quench the fluorescence of ImC60 indicating occurrence of excited state events. Electrochemistry coupled with spectroelectrochemistry, revealed formation of cobalt(III) porphyrin cation instead of cobalt(II) porphyrin radical cation upon oxidation of imidazole coordinated porphyrin. With the help of computational and electrochemical results, an energy level diagram was constructed to witness excited state photo-events. Competitive energy and electron transfer from excited CoP to coordinated ImC60, and electron transfer from Im1C60* to cobalt(II) porphyrin resulting into the formation of PCoIII:ImC60.- charge separated state was possible to envision from the energy diagram. Finally, using femtosecond transient absorption spectroscopy and data analysis by Glotaran, it was possible to establish sequential occurrence energy transfer and charge separation processes. Lifetime of the final charge separated state was ~ 2 ns. Slightly better charge stabilization was observed in the case of [(TPA)4P]Co:ImC60 due to the presence of electron rich, peripheral triphenylamine substituents on the cobalt porphyrin.

Hydrazone linked covalent organic frameworks (COFs) with enhanced crystallinity and porosity through supercritical carbon dioxide activation

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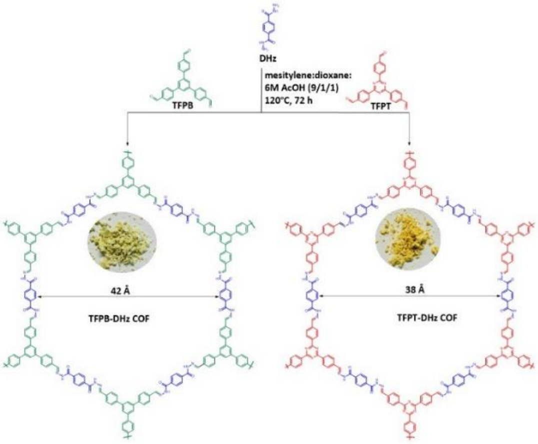

Covalent organic frameworks (COFs) are a class of crystalline, porous polymers which are synthesized from light weight elements (C, H, N, O) under dynamic control. These materials have been employed for different applications including gas storage, gas separation, sensing, and energy storage. Hydrazone linkages are formed through condensation between aldehyde and hydrazide linker. Among different COF activation methods super critical carbon dioxide (scCO2) activation provides milder conditions to process COFs without compromising their crystallinity and porosity. To this end, two hydrazone COFs (TFPB-DHz, TFPT-DHz) were synthesized with a hydrazide linker (DHz) without substituents. Synthesized COFs were characterized with FT-IR spectroscopy, powder X-ray diffraction (PXRD), and computer modeling. Surface area of COFs was determined using N2 adsorption−desorption experiments. scCO2 activated COFs were crystalline and porous. This study shows the significance of efficient, fast, mild scCO2 activation towards porosity and crystallinity of COFs.

Novel Benzothiazoles Derivatives for Musculoskeletal Applications

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Benzothiazoles, a benzene ring fused with a thiazole ring, are one of the most eminent heterocyclic classes due to its broad applications. The intriguing medical applications of benzothiazole derivatives include antitumour, antidiabetic, anticonvulsant, antiviral, anti-inflammatory, antitubercular, antimalarial, analgesic, and other activities. Although, there are number of approaches toward synthesis of benzothiazole scaffold, the yield and reaction steps are an issue with it. In this study, we are developing a simple and novel approach towards synthesis of novel benzothiazole derivatives from thioureas using hypervalent iodine reagents. The effect of the synthesized benzothiazoles as potential musculoskeletal agents has been targeted. Cell viability studies indicated that these compounds are safe at lower concentration of 5-10 µM. The differentiation studies revealed the potential use of five agents at low concentration of 5µM and one molecule is safe at higher concentration of 10 µM. Also the effect of two of these molecules using two different concentrations on gene expression is being studied.

Synthesis and characterization of B, B'-dithiophenyl-benzoporphyrins and naphtho[2,1-b:3,4-b']dithiophene-fused porphyrin

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In this report, the synthesis of B, B'-dithiophenyl-benzoporphyrins and naphtho[2,1-b:3,4-b']dithiophene-fused porphyrin is presented. B, B'-dithiophenyl-porphyrins were prepared using a Heck-based cascade reaction developed in our laboratory. Naphtho[2,1-b:3,4-b']dithiophene-fused porphyrin was derived from B, B'-di(thiophen-3-yl)-porphyrin through Scholl reaction. UV-Vis absorption shows red-shifted Soret bands compared to the starting materials for both π-extended porphyrins. The fluorescence spectra of B, B'-dithiophenyl-porphyrins show two peaks and the fluorescence lifetime for both compounds is around 10 ns. Crystal structures of the dithiophenyl-benzoporphyrins are also resolved.

Triple-tagged peptides utilizing orthogonal chemistries for intracellular targets

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Labeling peptides has been widely practiced in numerous applications in chemistry and biology. For example, fluorescent dyes make peptides both useful probes for in vitro and in vivo imaging and suitable substrates for determining enzyme activity; biotinylation has vast applications including affinity-based protein purification; PEGylation enhances plasma half-life and protects against metabolic degradation; radiolabeling offers in vitro and in vivo molecular imaging agents and targeted radionuclide therapy; and cell permeable peptides allow access to intracellular targets. Thus, peptides bearing such multiple labels may serve as powerful research tools as they become available for diverse biomedical studies. For labeling peptides, several coupling methods have been reported, such as alkyne-azide click chemistry, thiol-maleimide Michael addition, Staudinger ligation, and oxime-hydrazone formation. Despite the versatility of and broad use in traditional organic reactions, Suzuki-Miyaura coupling has been rarely practiced in peptide labeling. In addition, while each of these methods has been efficiently used alone in peptide conjugation, their combination for orthogonal coupling reactions has not been well studied. Therefore, we developed an efficient synthetic strategy for multiple labeling of peptides via various orthogonal coupling reactions, described herein utilizing Suzuki-Miyaura cross-coupling, thiol-maleimide reaction, and alkyne-azide cycloaddition. The potential of these orthogonal chemistries was demonstrated by a peptide with multiple labels of a cell-penetrating peptide, fluorescent dye, and biotin. The triple-tagged peptide was conjugated via thiol-maleimide addition to a BAK peptide and incubated with HCC95 lung cancer cells. Cellular uptake was confirmed by fluorescent microscopy, and biotin-streptavidin pulldown assay confirmed the interaction between the conjugated BAK peptide and its target protein, Mcl-1.

Development of a highly-sensitive CO_2 sensor for biological applications

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A eurhodin dye which has been popularly used as a biological stain is now being studied for its CO_2 sensing properties. Neutral red (NR) has been established to be a pH-sensitive dye based on the change in the absorption properties in aqueous media. Our studies demonstrate that at very low concentrations, the molecule exhibits change in fluorescence properties with respect to changes in pH and dissolved CO_2 concentrations (dCO_2) in a phosphate buffer medium at pH 7.3. Benchmark studies with pyranine (8-hydroxypyrene-1,3,6-trisulfonic acid trisodium salt or HPTS) provides functional information of NR related to sensitivity and response times. The calibration studies using six different concentrations of CO2 gas provide minimum limit of detection (LoD) information of the sensor in buffer media. Understanding the LoD, NR has been applied to study CO_2 levels in the exhaled air from various human participants. Further studies are to be done in vivo to apply the NR molecule for detecting changes in pH/CO2 levels in different biological systems.

Structure-Activity Relationship and Bioactivity of 8-Hydroxyquinoline Derivatives as Highly Potent KDM4/JMJD2 Histone Demethylase Inhibitors

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Inhibition of KDM4B has shown excellent therapeutic efficacy against castration-resistant prostate cancer (CRPC) due to its epigenetic roles in transcriptional activation and repression. Previous high throughput screening identified B3 (IC50: 0.74 µM) that features an 8-hydroxyquinoline pharmacophore with potent coordination ability to selectively inhibit KDM4 proteins through 1,4-bidentate chelation of active-site Fe(II). We investigated the structure-activity relationship for the 3-phenylpropyl modifier group of B3 using 55 analogues that revealed 9e, which demonstrated a seven-fold increase to 22Rv1 CRPC (IC50 = 0.10 µM) inhibition, as well as potent KDM4B inhibition (IC50 = 4.74 nM) in vitro. Further evaluation in vivo using xenografted murine models showed significant inhibition to tumor growth and little change to body weight, suggesting remarkable potential to target KDM4B inhibition for treatment against CRPC.

Attitudes Towards Organic Chemistry (ATOC) Survey: An Instrument for Measuring Students’ Attitudes Related to Learning Organic Chemistry

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Organic chemistry is known to be a challenging course for undergraduate students, with high rates of attrition. To address this, previous research has focused on students’ content knowledge, misconceptions that inhibit students’ understanding of abstract concepts, and students’ experiences in the lab. Previous work has also provided evidence for the importance of factors within the affective domain and the impact of those affective factors on undergraduate student learning in the general chemistry classroom. However, limited research has been conducted to investigate factors within the affective domain in the organic chemistry classroom. This research study aims to quantitatively and qualitatively assess undergraduate students’ attitudes related to their learning of organic chemistry and the origins of these attitudes, through the development and use of the Attitudes Towards Organic Chemistry (ATOC) survey as a measurement tool. An overview of the preliminary analyses and findings using data generated by the ATOC will be presented, including discussion of both the qualitative and quantitative analyses resulting in prevalent factors that influence undergraduate students’ attitudes towards learning organic chemistry.

Fluoride-Induced Cyclization of Oxazolones

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Five-membered heterocyclic ring systems have found wide application in natural products, total synthesis as well as serving as a major framework in pharmaceuticals. The biological versatility of five-membered rings with two or more heteroatoms have received great attention recently due to the challenges in their synthesis most especially in pharmaceutical industries. One of the most important heterocycles of this class is the oxazolone. Oxazolones are important precursors for dyes, amides, insecticides, pharmaceuticals (in known drugs such as fenozolone, thozalinone, cyclazodone, indolmycin etc). With these utilities, oxazolones have received wide attention lately. This work will investigate a new synthesis of the oxazolone motif starting from readily available aldehydes (aryl, aliphatic and heterocyclic) to generate chiral propargyl alcohols which are then treated with aryl isocyanates to furnish carbamates. The carbamates are then be cyclized under very mild conditions to afford the desired novel chiral oxazolones. We hope to study the mechanistic details of this project, perform biological studies which will involve anti-microbial activities and application in the synthesis of pharmaceutically relevant natural products.

In Situ Triggered Filamentous Cell Penetrating Peptides (FCPPS) For Tumor Cell Targeted Therapeutic Delivery

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Cell-penetrating peptides (CPPs) have been widely used for therapeutic delivery due to their unique ability to cross the cell membrane. However, the widespread application of CPPs was limited due to their low tumor specificity and limited retention in vivo. Peptide self-assembly offers an effective method to generate materials with dynamic control over both structures and bioactivity. We recently demonstrated a new family of Filamentous Cell Penetrating Peptides (FCPPs) based on the self-assembly of de novo designed multidomain peptides (MDPs). While FCPPs have potent cell penetrating activity, their tumor selectivity is poor. In this work, to construct tumor-selective FCPPs (TS-FCPPs), we append a cationic domain to the C-terminus of the optimal MDPs through a cleavable chemical linker. Under the physiological condition, the integrated peptide is unassembled due to electrostatic repulsion and has low cell penetrating activity. Under the tumor microenvironment, the cleavage of the chemical linker releases the cationic domain and restores the ability of MDPs to form FCPPs with enhanced cell penetrating activity. For proof of concept, we choose matrix metalloproteinase, MMP-2 as our initial target of the tumor microenvironment due to their overexpression by tumors. Biophysical characterization confirms the chemical and physical transformation from monomers to self-assembled nanofibers upon MMP-2 treatment. The in vitro cell uptake experiment showed enhanced cell penetrating activity of TS-FCPPs in cancer cells with high levels of MMP-2 compared to cancer cells with low MMP-2. MDPs with a non-responsive MMP linker exhibited low cell penetrating activity in all cell lines tested with different MMP-2 levels. Doxorubicin conjugated TS-FCPs demonstrated higher drug efficacy toward cancer cells with high levels of MMP-2 than cancer cells with low MMP-2 and healthy cells. The current results provide important insights into fundamental understanding of in situ triggered peptide self-assembly, which have great potential for the application of tumor-targeted therapeutic delivery with high selectivity.

Polymer Section

Entry	Time	Activity
Greetings	9:30 am – 9:40 am	***Greetings***
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02	10:00 am – 10:15 am	Alejandra Durand-Silva
03	10:15 am – 10:30 am	Jeri LaNiece Gill
04	10:30 am – 10:45 am	Uroob Haris
Break	10:45 am – 10:55 am	***Intermission***
05	10:55 am – 11:10 am	Ryan Patrick Madigan
06	11:10 am – 11:25 am	Ashele Kiwana Remy
07	11:25 am – 11:40 am	Erika Lopez Calubaquib
08	11:40 am – 11:55 am	John Michael Cue
09	11:55 am – 12:10 pm	
10	12:10 pm – 12:25 pm	
Break	12:25 pm – 1:00 pm	***Lunch Break***
11	1:00 pm – 1:15 pm	Masoumeh Tajik
12	1:15 pm – 1:30 pm	Sachini D. Perera
13	1:30 pm – 1:45 pm	Soheil Malekpour
14	1:45 pm – 2:00 pm	Abhi Bhadran
Break	2:00 pm – 2:10 pm	***Intermission***
15	2:10 pm – 2:25 pm	Khaled Shennara
16	2:25 pm – 2:40 pm	Chinthaka Mahesh Udamulle Gedara
17	2:40 pm – 2:55 pm	Juan Alexandro Garcia
18	2:55 pm – 3:10 pm	
19	3:10 pm – 3:25 pm	
20	3:25 pm – 3:40 pm	
Break	3:40 pm – 4:30 pm	***Break***
Awards Ceremony	4:30 pm – 5:00 pm	***Awards Ceremony***

For questions about scheduling for Polymer Section, please e-mail:
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Unipolar stroke, electroosmotic pump carbon nanotube yarn muscles

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Success in making artificial muscles that are faster and more powerful and that provide larger strokes would expand their applications. Electrochemical carbon nanotube yarn muscles are of special interest because of their relatively high energy conversion efficiencies. However, they are bipolar, meaning that they do not monotonically expand or contract over the available potential range. This limits muscle stroke and work capacity. In this talk, we will describe unipolar stroke carbon nanotube yarn muscles in which muscle stroke changes between extreme potentials are additive and muscle stroke substantially increases with increasing potential scan rate. The normal decrease in stroke with increasing scan rate is overwhelmed by a notable increase in effective ion size. Enhanced muscle strokes, contractile work-per-cycle, contractile power densities, and energy conversion efficiencies are obtained for unipolar muscles.

Dynamic Covalent Photoresins for Vat Photopolymerization 3D Printing

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Three-dimensional printing (3DP) is an advanced manufacturing process that builds successive layers of materials to create objects from digital models. Without the need of molds, 3DP enables the rapid fabrication of complex and customizable products at low cost. Several 3DP techniques are available, being extrusion and vat photopolymerization some of the most commonly used. Vat photopolymerization techniques, such as stereolithography (SLA) and digital light processing (DLP), stand out due to their efficiency in fabricating objects with minimal anisotropy and high resolution. However, only few photoreactive materials are compatible with the photopolymerization process. Inspired by the ability of natural systems to adapt to external conditions, several developments in polymer science emerged in recent decades, endowing them with the intrinsic ability to modify their properties under external stimuli. Specifically, the incorporation of dynamic covalent reversible bonds in polymeric materials imparts them stimuli-responsive properties. Polymer networks that include thermally reversible furan-maleimide (fmDA) Diels-Alder cycloadducts exhibit properties that improve their sustainability, such as self-healing or reprocessability. Thermoplastics and thermosets containing fmDA functionality have been 3D printed with extrusion techniques, but they exhibit poor thermal stability due to the reversible linkages. To address the shape instability of fmDA 3D printed materials, without affecting their self-healing properties, we have incorporated these reversible cycloadducts in photoreactive resins for SLA 3DP in a thermally stable polyacrylate network. We evaluated the self-healing ability and the shape stability of the printed parts when using fmDA adducts as crosslinkers in different concentrations, and demonstrated that only a 5% wt. concentration, provides the resins with a 99% self-healing efficiency, as observed in the recovery of mechanical strength, without affecting their detailed printed shape. In this presentation, I will discuss our results on the stimuli-responsive properties associated with the use of fmDA and other reversible cycloadducts in 3D printable polymers.

Removal of Microplastics from Water Using Plant Based Polysaccharides

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Microplastics are a new emerging contaminant that is becoming detrimental to aquatic environments globally. Scientists are developing new technologies to remove microplastics (Rachdi, 2017). In previous research in our laboratory, polysaccharides from plants such as Fenugreek, Cactus mucilage, Aloe Vera mucilage, Okra mucilage and Psyllium mucilage have been proven successful in the removal of microplastics as compared to synthetic polymers. Polysaccharides are non-toxic, biocompatible, biodegradable, polyfunctional, and highly chemically reactive (Pitkänen, 2018). They also have chelation and absorption capacities that allow them to better flocculate than synthetic polymers. The polysaccharide particle absorbs the microplastics and becomes heavy in weight and settles at the bottom, which is later filtered off (Dao, 2015). Simulated microplastic contaminated water will be prepared by spiking deionized water with commercially available microplastics in the laboratory. Live water samples will be collected from various surface water, in and around major cities in Texas. A polymer solution, combining two or more of the above organic polymers listed with varying concentrations, will be prepared. Qualitative and quantitative microplastic analysis will be performed using a hemocytometer by observing them under a dissecting microscope at 40X magnification. Fourier transform Infrared spectroscopy will be used to study the interaction and mechanism of the polymer with microplastics. Samples will be analyzed using Raman Spectroscopy to identify the types of microplastic found in the sample. The goal of the present research is to extract mucilage from the organic polymers Cactus, Okra, Fenugreek, Aloe Vera, and Psyllium, using them in the flocculation method. This will provide a better alternative to Polyacrylamide in the process of water treatment. The major focus of the present research is to study the efficiency of combining the polymers, listed above, in different ratios to remove microplastics more efficiently than the single polymer method.

High-resolution visible light photolithography

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Nanofabrication and precise manipulation of materials are increasingly setting the pace for continued improvement in emerging innovations including electronics, molecular machines, and nanorobotics. However, limitations of resolution, cost, and scalability in current lithographic nanofabrication methods hinder the large-scale realization of numerous possibilities. In order to achieve gentle and versatile chemical synthesis and lithography with high resolution and ultimately single molecule specificity, we combine photomediated chemical reactions with spatiotemporally controlled light microscopy. This presentation covers our research work on real-time observable photolithography with microscopic resolution and forms the foundation for achieving patterning with single molecule precision.

Modular Design and Self-assembly of Supramolecular Cell Penetrating Nanofibers for Therapeutic Delivery

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Cell penetrating peptides (CPPs) have great impacts on both fundamental and translational biomedical research due to their ability to transverse the cell membrane and deliver a range of therapeutics and imaging agents into cells. However, traditional CPPs suffer from proteolytic degradation and limited in vivo circulation half-life. Peptide self-assembly offers an effective method to generate peptide-based nanomaterials with improved stability, biological activity and biocompatibility. We present a class of peptide assemblies, termed supramolecular cell penetrating nanofibers (SCPNs), with intrinsic cell penetrating activity. SCPNs are generated through the self-assembly of de novo designed multidomain peptides (MDPs) containing both a beta-sheet self-assembling domain that forms nanofibers and an oligo-lysine membrane-binding domain, connected through an oligopeptide-based spacer. We synthesized a library of MDPs by varying the numbers of lysine residues in the membrane binding domain and the composition of amino acids involved in the spacer. The results showed nanofiber self-assembly is favored as the length of the spacer increases, possibly through reduction of the electrostatic repulsion between the oligo-lysine domains. While most MDPs formed nanofibers, their cell penetrating activity varied. Nanofibers with a longer membrane binding domain exhibited higher cell penetrating activity. Alanine in the spacer domain provided higher stability toward beta-sheet packing than spacers consisting of glycine. Alanine seems to provide the optimal conformational flexibility for the oligo-lysine membrane binding compared to MDPs with glycine or leucine residues in the spacer. An expanded library is being currently investigated to develop a more comprehensive structure-activity correlation. Given the increasing interests in the design of cell penetrating materials for vaccine development, in particular mRNA-based vaccine delivery, peptide nanofibers with intrinsic cell penetrating activity would be beneficial to the development of peptide-based immuno-and gene therapy.

Bio-based Materials for 3D Printing

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Recent advances in 3D printing have focused on sustainably sourced materials. One area of peak interest is a group of plant-based molecules called terpenes. This class of molecules is appealing because of its high abundance, ease of use, and functionality. In this work, geraniol acrylate was used to print a 100% bio-based material. From this base resin, various cross-linkers were added to improve the printed materials' durability and strength. Additionally, a dual mechanism system (acrylate and thiol-ene photopolymerization) and other terpenes (eugenol and vanillin) were used to improve the geraniol acrylate resin.

Design and Synthesis of Functional Polycaprolactones for Drug Delivery Applications

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Polycaprolactones (PCL) are widely used in various applications, particularly in the biomedical field including drug delivery, tissue engineering, and implants. To expand its scope, PCL is functionalized in the polymer backbone to tailor its physicochemical properties, such as wettability and degradation. Herein, we report functionalized PCL homopolymers and block copolymers that self-assembled to form micelles that could encapsulate hydrophobic molecules. Homopolymers of di-, tri-, and tetra-oligoethyelene-substituted caprolactones - poly(γ-2-(2-methoxyethoxy)ethoxy-ε-caprolactone) [PME2CL], poly(γ-2(2-(2-methoxyethoxy)ethoxy)ethoxy-ε-caprolactone) [PME3CL], and poly(γ-2(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)ethoxy-ε-caprolactone) [PME4CL] - of varying molecular weight were synthesized and characterized. Variation of the OEG chain allowed the tunability of the lower critical solution temperature. Block copolymers of hydrophobic γ-benzyl polycaprolactone and hydrophilic PMExCL (x =2,3,4) were used to co-load anticancer doxorubicin (Dox) and antioxidant quercetin (Que). Combination loading demonstrated improved loading of Dox and Que. Biological studies were performed using HepG2 human liver cancer and H9c2 rat heart cells.

$NdCl_3$·3TIBP-catalyzed Polymerization of Bio-based Dienes and Polar Vinyl Monomers: Bridging the Gap towards Sustainable Polymers

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Neodymium-based Ziegler-Natta systems are superior to traditional Ziegler-Natta catalysts for the polymerization of dienes and polar vinyl monomers. The inherent differences in reactivity between non-polar dienes and activated vinyl monomers prevents copolymerization using established polymer synthesis techniques. Herein, we demonstrated the polymerization of bio-based myrcene, farnesene, ocimene, limonene, acrylates, and methacrylates using discrete $NdCl_3$·3TIBP (triisobutylphosphate) with co-catalyst TIBA (triisobutylaluminum). The catalytic system is active for the stereospecific homopolymerization of myrcene (~200 kDa, Đ=1.6, 96% *cis*) and acrylates (~65% syndiotactic). The pseudo-*living* polymerization behavior of the system provides well-defined block copolymers from activated and non-activated monomers. We also provide a deeper understanding of the neodymium-catalyzed polymerization through end-group analyses, reaction rates, kinetics, thermodynamics, and reactivity ratios. These developments are focused on polymers derived from natural sources (e.g., plants) both to address sustainability objectives and to enhance function by generating new polymers with distinct or superior properties.

Age Reduction through crosslinking in Carbon Molecular Sieve Membranes

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Carbon molecular sieve membranes (CMSMs) have the ability to reform membrane-based gas separations, due to their unique porosity and surface chemistry. CMSMs are composed of both micropores (0.7-2.0 nm) and ultramicropores (<0.7 nm), which provides them with high flux and high selectivity allowing them to surpass commercially used polymeric membranes. Physical aging (collapsing of pores) is a property that impedes application of CMSMs and is often observed as a decline in permeability with a subsequent increase in selectivity. A proposed strategy for preventing aging involves crosslinking of the CMSM precursor polymers which would restrict the polymer chain movement and thus impeding the pore collapses. Thermal crosslinking which will cause decarboxylation in polyimides containing the carboxylic group have been proven effective in suppressing the aging and preventing the plasticization through making strong covalent bonds. In this study, the new copolymer of Matrimid which embeds diamino benzoic acid (DABA) with different ratios of 5 and 10 wt% were synthesized. These polyimides with different ratios of DABA which were thermally crosslinked at 450° C. the resultant CMSMs retained their selectivity while increasing their permeability, a desirable goal to achieve commercial viability.

Enhancing Mechanical Properties of Photoresins for 3D printing via Hydrogen Bonding

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3D printing is a process that produces complex structures from 3-dimensional model data. The AM process comprises of depositing or building successive layers of material on top of each other, and each 3D printing technique requires materials that can be processed according to the specific method to build the layers. Out of these techniques, vat photopolymerization plays a major role in producing fine structures with high resolution (25 µm) compared to other AM methods. One of the main limitations of the materials currently used in vat photopolymerization is that they possess poor mechanical properties which restrict their usage in applications. Herein we suggest a method to enhance the mechanical properties of printed nanocomposite, by incorporating interactions such as H bonds and dynamic covalent bonds which would directly improve thermal and mechanical properties of printed parts. By introducing aramid (p-phenylene terephthalamide) nano fibers (ANFs), we included additional intermolecular noncovalent interactions to 2-hydroxyethyl acrylate (HEA) and polyethylene glycol diacrylate (PEGDA) photoresins, to enhance the mechanical properties compared to the HEA/PEGDA control. The use of ANFs in 3D printing is an unexplored area that offers an alternative in the formulation of photocurable materials with improved mechanical properties and high thermal stability. This would allow to produce 3D printed objects as strong as molded parts with all the advantages of AM, including its low cost for customized manufacturing and high speed of prototyping. This approach offers a new method to enhance mechanical properties of other polymeric materials currently used in vat photopolymerization.

Hybrid Supercapacitors Using Electrodes from Fibers Comprising Polymer Blend – Metal Oxide Composites with Polymethacrylic Acid as Chelating Agent

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Hybrid supercapacitors made of carbon – metal oxide composites are devices which combine the advantages of electric double layer capacitors and pseudocapacitors viz. high energy density, high power density and high cyclability. Solutions of polyacrylonitrile (PAN) as the carbon source, cobalt (III) acetylacetonate as a metal oxide precursor, and polymethacrylic acid (PMAA) as a metal oxide precursor carrier, were electrospun into fibers, which were then carbonized at 1000 ºC and characterized as electrodes in coin cell supercapacitors. Fibers without the PMMA carrier were prepared for comparison. XRD and TGA showed conversion of the cobalt precursor to a mixture of cobalt and cobalt oxide (Co3O4). When the PMAA carrier was used, specific capacitance increased from 68 F/g in PAN-Co3O4 to 125 F/g in PAN-PMAA-Co3O4. Furthermore, the addition of PMAA to the system results in better uniformity, accessibility and dispersion of metal and metal oxide particles inside the fibers. Due to the relatively low surface area of carbonized samples, Co3O4 nanoparticles are the primary contributors to charge storage. The fabricated fibers show an energy density of 8.9 Wh/kg at 750 W/kg, which is twice that of the fibers made without PMAA.

Design and Synthesis of a Novel γ-Functionalized Poly(ε-Caprolactone) Grafted with Lipoic acid

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Poly(ε-caprolactone)s (PCL)s are among the most important classes of aliphatic polyesters for biomedical application due to their biodegradability, biocompatibility and synthetic versatility. The properties of this synthetic polymer can be easily tuned by introducing different functionalities. However, the difficulty in polymerizing functionalized ε-caprolactone (CL) monomers limits further applications. A major issue is the involvement of these functionalities in the polymerization process which results in unwanted side reactions. Herein, we utilized post-polymerization reactions as an alternative to introduce redox responsive lipoic acid to the side chain of PCL. We developed an ether linked γ-propargyl substituted PCL as the hydrophobic block of an amphiphilic diblock copolymer (AmDC). The propargyl group is used to couple the lipoic acid via click chemistry. The hydrophilic block is composed of an ether linked, thermoresponsive γ-tri(ethylene glycol) substituted PCL. The final AmDC can self-assemble in aqueous solution to form polymeric micelles with lipoic acid functionalized hydrophobic core and tri(ethylene glycol) functionalized hydrophilic shell. These polymeric micelles can be used as a drug delivery system for delivering the anticancer drug doxorubicin. The tri(ethylene glycol) containing hydrophilic shell is used to enhance the solubility of micelles, their circulation in the bloodstream, as well as thermoresponsive properties for triggering drug release. While the lipoic acid containing hydrophobic core can undergo reversible cross-linking to enhance the stability of the micelle and to prevent premature drug leakage.

Evaluation of Gold Nanoparticles for in vitro Biomedical Application via Plasmonic Photothermal Therapy

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Plasmonic photothermal therapy (PPTT) has a rising promise for treating different cancer cells, yet it has not yet been approved in the US as other radiation-based therapies like photodynamic therapy (PDT). There are major side effects from PDT related in part to the use of harmful UV light, and thus our team is interested in technique development of PPTT using metallic nanoparticles. The PPTT protocol will be developed upon a modification of the PDT irradiation therapy using two major changes. The first is using a less harmful visible light or a harmless near infrared light, and the second is using gold-loaded biocompatible nanoparticles without use of any chemotherapy drugs that usually require UV activation. Poly methyl methacrylate nanoparticles PMMA will be loaded with desired types of gold nanoparticles at different sizes. The gold-loaded gold nanoparticles will be conjugated to cancer cells. In this case, Jurkat cells (Hodgkin's lymphoma cancer) will be studied. By selectively delivering the gold nanoparticles into Jurkat cancer cells, irradiating a harmless near infrared light will achieve thermal ablation to these specific cells. Based on imaging spectroscopy, and cell viability assays, results showed significant reduction of gold loaded-normal cancer cells upon irradiating with a near infrared light, and no change in the number of cancer cells with irradiating with light only.

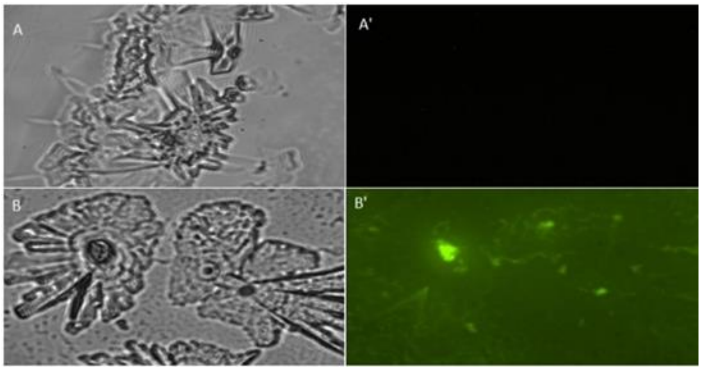

Figure 1 shows the uptake of PMMA nanoparticles of Fluorescent dye FITC under dark image A' and fluorescent microscopy B'

Effect of Furan Spacers in Thieno[3,2-b]pyrrole- and Diketopyrrolopyrrole-based Copolymers towards Thin-film Transistor Properties

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The structural alteration of semiconducting polymer backbones can be employed to improve the optoelectronic properties of organic semiconductors to enhance the field-effect mobilities. In our efforts towards enhancing the performance of organic field-effect transistors (OFET), we are reporting a thieno[3,2-b]pyrrole (TP) donors and furan-spacer substituted diketopyrrolopyrrole (DPP) acceptors containing donor-acceptor copolymer, poly(methylthienopyrrolo)furanyl)diketopyrrolopyrrol) **P(FDPP-TP)**, and its performance in OFETs. The introduction of the furan spacer group improved thermally induced crystallinity and molecular packing as confirmed by grazing incidence X-Ray diffraction (XRD) and tapping-mode atomic force microscopy (TMAFM), respectively. The tested OFET devices gave maximum hole mobility of 0.42 cm^2 V^{-1} s^{-1} with threshold voltages around 0 V for bottom-gate/bottom-contact device configuration. Compared to the thiophene-spacer-containing polymer previously reported by our group, the inclusion of furan generated a four-fold increase in hole mobility and 10^2 times increase in on/off ratios without sacrificing threshold voltages.

Microporous Carbon Microfiber Electrodes Derived From Polyacrylonitrile/Poly(Styrene-co-Acrylonitrile) Blends

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Supercapacitors and their electrode materials have received larger attention and demand in the current state of energy storage technology. Advancements will require devices that can deliver large quantities of energy quickly which electrochemical double layer capacitors (EDLCs) can achieve. EDLCs are capable of cycling thousands of times with minimal drop in total capacitance, and when used with an ionic liquid electrolyte they can deliver higher energy densities due to high operating voltages. Surface area, and pore size distribution play a critical role in the performance of EDLC devices due to their relationship to capacitance. Therefore, electrospun carbon nanofibers derived from polyacrylonitrile (PAN) are a promising EDLC electrode material due to their high surface area, conductivity, and cyclability. Their surface area can be tailored with the inclusion of in-situ porogens in the polymer precursor and activation during carbonization. The fiber morphology of electrospun PAN fibers can be tailored using immiscible polymer blends with sacrificial polymers like polystyrene (PS). The resulting carbons have high surface areas (>2,000 m2g-1), but a wide distribution of pore sizes. Altering the miscibility of the sacrificial polymer with the copolymer poly(styrene-co-acrylonitrile) (SAN) affords a unique fiber morphology with a high mesoporosity and capacitance.

Inorganic Section

Entry	Time	Activity
Greetings	9:30 am – 9:40 am	***Greetings***
01	9:45 am – 10:00 am	Waad Alharbi
02	10:00 am – 10:15 am	Alexander Brown
03	10:15 am – 10:30 am	Elamparuthi Ramasamy
04	10:30 am – 10:45 am	Kurt Bodenstedt
Break	10:45 am – 10:55 am	***Intermission***
05	10:55 am – 11:10 am	Kulatheepan Thanabalasingam
06	11:10 am – 11:25 am	Juan Vizuet
07	11:25 am – 11:40 am	Kapil Sayala
08	11:40 am – 11:55 am	Zhou Lu
09	11:55 am – 12:10 pm	Trent Kyrk
10	12:10 pm – 12:25 pm	
Break	12:25 pm – 1:00 pm	***Lunch Break***
11	1:00 pm – 1:15 pm	Daniel Tague
12	1:15 pm – 1:30 pm	Darshan Jayyasinghe Karunaranthne
13	1:30 pm – 1:45 pm	John Roque
14	1:45 pm – 2:00 pm	Marie Mortensen
Break	2:00 pm – 2:10 pm	***Intermission***
15	2:10 pm – 2:25 pm	Uyen Dang
16	2:25 pm – 2:40 pm	Hamid Firouzi
17	2:40 pm – 2:55 pm	Ashwin Ganesam
18	2:55 pm – 3:10 pm	Muhammad Abbas
19	3:10 pm – 3:25 pm	
20	3:25 pm – 3:40 pm	
Break	3:40 pm – 4:30 pm	***Break***
Awards Ceremony	4:30 pm – 5:00 pm	***Awards Ceremony***

For questions about scheduling for Inorganic Section, e-mail:
Mitchell Alexander Pope mitchell.pope@utdallas.edu

Mapping Basicity of 3d and 4d Metal Nitrides; A DFT Study

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A DFT study to map the basicity of 112 metal nitride complexes comprised of 3d and 4d transition metals: V, Cr, Mn, Nb, Mo, Tc and Ru. All complexes were gathered from the Cambridge Crystallographic Data Centre and have a single terminal nitride ligand. The levels of theory evaluated were B3LYP/def2-svp and b3lyp/6-311+G(d,p) with a SMD-acetonitrile continuum solvation model. Protonation of the metal-nitride complex resulted in the formation of a conjugate base (a cationic metal-imide). From the free energy of this protonation, the pKb(N–H) of the nitride group was calculated to assess the effects of metal identity, ligands, oxidation state, and conjugate base stabilization upon nitride basicity. In general, the basicity of the N–H bonds of transition metal-nitride complexes decreases from left to right across the 3d and 4d rows while it increases from 3d to 4d nitrides. Factors affecting the range in pKb for each metal are discussed.

Development of Novel Carbons for Lanthanide and Actinide Element Extraction from Coal Ash

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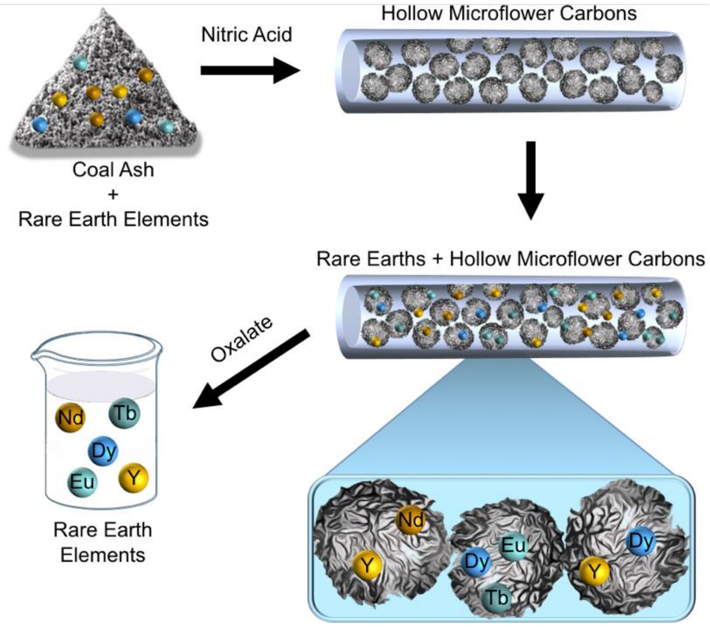
The U.S. consumes ~ 16,000 tons of Rare earth elements (REE) every year and REE are used in a variety applications; such as lighting, glasses, and electronics. The U.S. does not currently produce its own purified rare earth oxides and China dominates 89 % of the world supply. The U.S. fortunately has a semi-infinite supply of REE in waste coal ash. After burning coal, the concentration of REE increases ten fold. For decades, the U.S. has dumped 1.5 billion tons of coal ash into mostly unlined pits. The Department of Energy National Energy Technology Laboratory (NETL) is currently investigating coal ash as a domestic source of REE. We have prepared novel types of oxygen functionalized mesoporous carbons. The high surface area (> 1000 m^2/g) mesoporous carbons were functionalized with oxygen and tested as a solid adsorbents in acidic media for batch extractions of rare earth elements, uranium, and thorium. The carbons have outstanding extraction distribution coefficients (kd) up to 1 ×10^6 for lanthanide and actinide elements. The elements uranium and thorium can be selectively separated from the rare earth elements by adjusting the pH. Furthermore, the adsorption kinetics, pH variation, maximum adsorption, and recovery of elements are also reported.



Synthesis, Characterization and Photobiological Activity of NIR absorption pi-Expansive Ru(II)-Complexes for Photodynamic Therapy

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Classification: Postdoctorate

Photodynamic therapy (PDT) is a promising alternative technique offering advantages over conventional cancer therapy (i.e., surgery, chemotherapy, and radiotherapy) due to its capacity for spatial and temporal control. PDT combines a photosensitizer (PS), light, and oxygen to generate cytotoxic reactive oxygen species (ROS) such as singlet oxygen that destroy tumor cells. The production of ROS arises from interaction with a PS triplet state that follows from intersystem crossing (ISC) from an initial excited state. Therefore, PS design should target appropriate orbital energies for excitation and efficient ISC. However, the long wavelength light that is ideal for deep tissue penetration is not sufficiently energetic to excite many PSs. We have been designing PSs with pi-expansive ligands to produce low-lying excited states that promote NIR absorption in Ru(II) complexes, and this presentation will describe the design, synthesis, and testing of PSs that elicit PDT activity in this regime.

(O)LED Screening of Copper and Gold Mixed Ligand Complexes with S-/P-Donor Atoms

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Inorganic chemistry is one of the penultimate courses needed for an undergraduate degree in chemistry. Throughout this upper-division course, students develop an understanding of transition metal chemistry as well as inert atmosphere reaction chemistry. This research study is situated in the laboratory portion of an inorganic course at a large public university, where students were engaged in authentic research experiences directly related to concepts and theory taught in the lecture portion of the course and designed to mirror research in a graduate- and/or industry-level inorganic/materials chemistry laboratory. In this laboratory course, students are first presented with a research problem related to coinage metal (gold, silver or copper) chemistry. They are then asked to design a synthetic route using the literature, run the inorganic synthesis reactions for a few specific synthetic targets designed (some known but most are novel), and characterize products to ascertain their purity and molecular structure. Finally, they develop and acquire new skills and knowledge related to luminescence characterization techniques used in order to screen the new complexes made for potential application in inorganic (LEDs) and/or organic (OLEDs) light-emitting diodes (LEDs and/or OLEDs) -- as an example of the application screening from the Spring 2021 rendering of the discovery laboratory. The specific complexes synthesized in successive weeks were, for the Au group, as Complexes 1-4: Au(THT)Cl, Au2(dtp)2, Au2(dtp)2dppm, and Au2(dtp)2(dppm)2, respectively, whereas the analogous Complexes 1-4 for the Cu group were [Cu(CH3CN)4]BF4, Cu2(dtp)2, Cu2(dtp)2dppm, and Cu2(dtp)2(dppm)2, respectively. Only the precursor complexes of both metals and Au Complex 2 are known and adequately characterized in the literature whereas the rest of the targets are novel. We have screened all six Complexes 2-4 them for LED and OLED potential use based on the photoluminescence behavior of the powder respectively, and concluded that the Au complexes are suitable for both applications while the Cu complexes are more suitable for other applications such as temperature sensors. Details of the criteria for these conclusions will be presented.

A Spin ½ High Temperature Antiferromagnetic $Cu_3TeO_4SO_4{\cdot}H_2O$

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In our study of the spin ½ antiferromagnets with potential Mott insulating ground state, we have hydrothermally grown single crystals of Cu3TeO4SO4·H2O crystallizing in the orthorhombic Pnma space group with the lattice parameters of a = 15.974(2) Å, b = 6.3468(8) Å, and c = 7.2563(14) Å. The crystal structure contains corrugated layers of TeO4 units surrounded by four corner sharing CuO4 square planar units in the b-c plane. The corrugated layers are interconnected with the corner sharing SO4 and CuO4 units. An antiferromagnetic transition at TN = 67 K followed by a spin reorientation at 12 K were observed. A Θw = -137.2 K was obtained from a Curie-Weiss fit suggests magnetic frustration and can be rationalized from the exchange interactions. The effective magnetic moment μeff = 1.23 μB/Cu was obtained from Curie-Weiss fit, less than S = ½ spin state and can be attributed to the mix-valency. The crystal structure and magnetic properties of Cu3TeO4SO4·H2O will be discussed.

Structure Effects in Holmium-based MOFs: From Dimeric Clusters to Hexaclusters

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The crystalline, porous organometallic structures, commonly known as Metal-organic frameworks (MOFs), usually present high surface areas and defined pore structures. It is also due to their hybrid nature that their properties can be tuned by modifying one or more of their components. In particular, Lanthanide-based MOFs (Ln-MOFs) take advantage of the high coordination number of these elements, imparting MOFs with properties useful in areas such as drug delivery or chemical sensing. Ln-MOFs commonly present dimeric metal clusters in their structures, an effect derived from the solvothermal synthesis conditions. On the other hand, inclusion of multiatomic clusters in MOFs is an emerging field. To achieve the incorporation of these clusters in the structures, the synthesis conditions have to be tuned. These clusters usually result in improved stabilities. Specifically, the lanthanide Holmium can be neutron activated to form the radioisotope Holmium-166. This isotope has applications in radiotherapy and imaging since it emits both beta and gamma radiation, with a half-life of 26.8 hours. Combining the properties of MOFs and Holmium in one system, makes way for a new material in cancer therapy. The research to be presented focuses on a series of Ho-MOFs, from the most common structures presenting dimers, to newly developed structures containing hexaclusters. The mechanism of cluster formation will be discussed. Characterization of the MOFs, along with their potential as a radiotherapeutic materials will be covered as well.

Benziodazolotetrazoles as a Novel Class of Energetic Compounds

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Classification: Graduate

HV iodine(III) compounds comprising fused tetrazoles, and benziodazole(BIAT) rings, with various ligands(OH, Cl, OAc, OMe) coordinated to the I(III)center were synthesized and characterized by 1H and 13C NMR spectroscopy, ESI-HRMS, and X-ray crystallography. The structures, reactivities, and exothermic decomposition of these new compounds were studied and the results will be presented and discussed in detail.

Au3-toAg3 Coordinate-Covalent Bonding and Other Supramolecular Interactions with Covalent Bonding Strength

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Our group has studied cyclic trinuclear complexes (CTCs) of d10 coinage metal ions – cyclo-M3(μ-L)3 (M = coinage metal, L = anionic ligand) – bearing 9-membered rings. These d10 CTCs possess (near-)planar geometry and various properties that can be tuned by rational manipulation of metals (M), ligands (L), and ligand substituents (R), including acid-base chemistry, host/guest chemistry, supramolecular assemblies, luminescence sensing, and so on. This work here mainly focuses on the construction of π-acid/base stacked materials based on cyclic trinuclear d10-metal complexes and their potential ground-state charge transfer properties. Previously, we have described and predicted that the CTC π-basicity followed the trend of M3(μ-Imidazolate)3 > M3(μ-Pyridinate)3 > M3(μ-Carbeniate)3 > M3(μ-Pyrazolate)3 > M3(μ-Trizolate)3 for a given metal, and Au > Cu > Ag for a given ligand. Also, electron-donating groups gave rise to the π-basicity while electron-withdrawing groups gave rise to π-acidity. We designed and successfully obtained three different stacked CTC/CTC' materials by selecting the metal, ligand, and substituents, namely [Au(μ-Pz-(i-C3H7)2)]3·[Ag(μ-Tz-(n-C3F7)2)]3 (1), [Au(μ-Pz-(i-C3H7)2)]3·[Ag(μ-Pz-(CF3)2)]3 (2), and [Au(μ-Im-Et)]3·[Ag(μ-Pz-(CF3)2)]3 (3). All three stacked charge transfer binary complexes were structurally characterized by X-ray crystallography, confirming their unique Au3L3@Ag3L'3 conformation and extremely short intertrimer Au¬–Ag distances – among the shortest of any Au-Au, Ag-Ag, or Ag-Au intermolecular distances known in the literature. Previous attempts to make stacked CTC@CTC' adducts in the literature have failed, instead resulting in mixed-metal M2M' CTCs. Further computational work revealed the existence of abundant supramolecular interactions arising from a combination of M–M', metal–π, π–π interactions and hydrogen bonding in these charge-transfer complexes; the relative contribution of each such interaction type to stabilize the supramolecular structure has been evaluated. The calculated binding energy also reflected the strong bonding behavior between gold and silver (Ag→Au coordinate-covalent type) and gave rise to a bonding strength close to typical polar-covalent bonds.

It Runs In The Family: A Structural Comparison of BaAl4-Related Praseodymium Cobalt Germanides

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With the discovery of pressure induced superconductivity and suggested topological behavior in CeCoGe3, the interest in BaAl4 related intermetallic compounds is increasing. Here, we break down the structure relationships between three compositionally intermediate structures PrCoGe3, Pr2Co3Ge5, and PrCo2Ge2 and discuss their magnetic properties.

Templated Carbon Nanostructures Synthesis Catalyzed by Rare Earth Hydroxides and Group 2 Oxides

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There is a growing interest in porous graphitic materials with designed nanoarchitectures for applications ranging from catalysis to energy storage. The hydrophobic properties and high surface area of carbon-based materials offer advantages when used as catalyst supports; providing improved adsorption and diffusion of reactants. We have synthesized a variety of three-dimensional porous carbons using rare earth hydroxides and group 2 oxides as templates and catalysts to form graphitic carbon nanostructures. When combined with water and acetylene in a CVD tube furnace, large quantities of graphene-like carbon are formed. The carbons have different morphologies depending on the morphology of the catalyst, including crumpled carbon, nanotubes, wrinkled spheres, and hollow spheres. These porous carbon nanostructures make these materials desirable for supercapacitors and catalytic supports. The characterization was performed using, transmission electron microscopy, powder X-ray diffraction, simultaneous differential scanning calorimetry / thermogravimetric analysis, scanning electron microscopy, Raman spectroscopy, infrared spectroscopy, multipoint Brauner-Emmett-Teller surface area analysis, quench solid state density functional theory pore size analysis, and X-ray photoelectron spectroscopy. EDLC (JME) cells were assembled with the carbons as the electrodes in the ionic liquid electrolyte, 1-ethyl-2-methylimidazolium bis(trifluoromethylsulfonyl)imide.

Corrosion Inhibition Effect of pyridine-2-thiol for Brass in Acidic Environments

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In this study inhibitive performance of pyridine-2-thiol was investigated using potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and x-ray-photoelectron spectroscopy (XPS). Electrochemical experiments were performed using different inhibitor concentrations in 0.5M H2SO4 as the corrosive medium. The potentiodynamic polarization study indicated icorr values decreased significantly for the inhibited solutions in contrast to the uninhibited solution. Pyrdine-2-thiol had an optimum inhibition concentration of 0.25 mM, giving 1.86 µA/cm2 icorr value in comparison with 26.99 µA/cm2 icorr for the blank solution. Rp and Rct values calculated from EIS data increased substantially after the addition of the corrosion inhibitors and corrosion inhibition efficiencies increased more than 80% for the majority of the inhibitor solutions. Scanning electron microscopy images showed a defect free surface with lower scale formation for the inhibited surface but the bare brass surface had a larger amount of scale formation. X-ray photoelectron spectroscopy and UV-Vis spectroscopy was used to investigate surface chemical composition and inhibitor structural changes over time.

Exciting Metal Complexes for Hypoxia-Active Photodynamic Therapy

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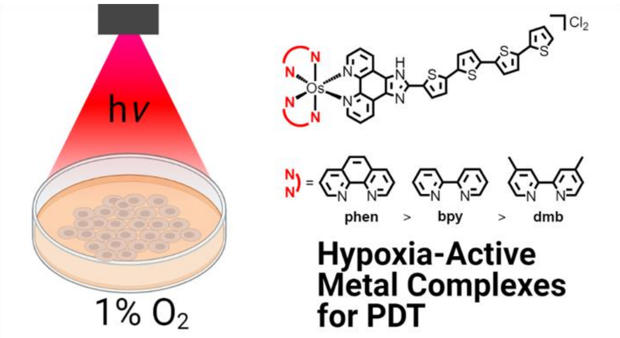
Classification: Graduate

The development of new treatment options for cancer is constantly in demand, despite ongoing progress in cancer research. Prodrug options like the light-based photodynamic therapy (PDT) offer much promise as complementary to traditional therapies, wherein light activates an otherwise nontoxic drug or photosensitizer to eliminate tumors and their vasculature. To date, the only US-based and FDA-approved photosensitizer for cancer therapy is Photofrin, an organic porphyrin-based mixture, which has limited PDT's mainstream adoption due to various drawbacks. On the other hand, metal-based coordination complexes are emerging as promising PDT agents that can be rationally designed and tuned for the optimal chemical, photophysical, and photobiological properties of a given application. Ruthenium- and osmium-polypyridyl complexes serve as examples, with our own TLD1433 currently undergoing a phase II clinical trial for bladder cancer. Herein, we report the development of photosensitizers active under hypoxia, one of the most challenging environments for both cancer treatment and PDT.



A Series of New Lanthanide Metal Organic Frameworks and Their Luminescent and Magnetic Properties

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Metal Organic Frameworks, or MOFs, are a class of crystal porous frameworks containing both a metal ion center and organic linker. By selecting different metals and organic linker, we can control topographies, magnetic, and chemical properties. As such, MOFs have many different applications including gas separation, gas capture, catalysis, sensors, and single molecular magnetics. Lanthanide MOFs are rarer and have the added benefit of enhanced luminescence, magnetic properties, and larger range of topographies. Lanthanides can also form extended clusters. These clusters have the added benefits of greater thermal and chemical stability and denser magnetic moments. As such, researchers have used modulators including 2-fluorobenzoic acid or fluorinated linkers to create lanthanide clusters in MOFs. In this research, a series of novel lanthanide MOFs containing clusters have been synthesized using the modulator 2-fluorobenzoic acid. These MOFs are studied for their potential applications as fluorescent sensors or for their magnetic properties. These structures are characterized by single crystal X-ray diffraction and powder X-ray diffraction. The thermal stability was determined through thermogravimetric analysis and powder X-ray diffraction.

Lattice Anharmonicity of Sterochemically Active Lone Pairs Controls Thermochromic Band Gap Reduction of $PbVO_3Cl$

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Stereochemically active lone pairs of electrons play an important role in a diverse range of physical phenomena in many materials, ranging from semiconducting halide perovskites to thermochromic inorganic-organic hybrids. In this work, we demonstrate the importance of 6s2 lone pair in the reversible thermochromic transition in the mixed-anion inorganic compound, PbVO3Cl. This 6s2 stereochemically active lone pair results in subtle structural distortions upon heating while the high symmetry orthorhombic structure is maintained. These distortions result in competing interactions with the Pb 6s2 lone pair and ultimately, a pronounced change between yellow and red at ~200 °C. X-ray diffraction analyses of PbVO3Cl demonstrates two-dimensional features in contrast to the three-dimensional network in isostructural BaVO3Cl. X-ray and neutron pair distribution function experiments reveal that Pb–O interatomic distances decrease upon heating, while Pb–Cl distances are only affected by thermal motion. X-ray photoelectron spectroscopy measurements provide experimental evidence of the presence of the 6s2 lone pair at the valence band maximum, which are corroborated by first-principles calculations. The results demonstrate a broadly generalizable mechanism for using repulsions between lone-pair electrons of p-block cations to drive discontinuous changes of local symmetry and electronic structure.

Novel Schiff-Base bisimidazole Ligand for Synthesis of Metal Organic Frameworks

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Metal-Organic Frameworks (MOF) are the crystallin structures with the highest surface area and largest pores among other porous solids. One subgroup of these crystalline structures is zeolitic imidazolate frameworks in which imidazole has a zeolitic connection with metals and brings about a higher stability structure. So far, many different derivatives of imidazole and corresponding MOFs have been synthesized and recently, the new generation of these linkers, bisimidazole, have been developed to form a new highly porous, and stable MOF structure. In this work, we have synthesized the novel Schiff base bisimidazole linker with benzene spacing group and have it reacted with zinc metal. Two different crystal structures have been formed at 45 and 80 Celsius degrees. The growth of the MOFs is followed through electron microscopy (SEM), infrared spectroscopy, and powder x-ray diffraction. The thermal stability analysis with TGA and chemical stability analysis with different solvents and single-crystal structures have revealed that the structure formed in 45oC is less stable, dense, and porous than the MOF formed in 80 oC. N2 adsorption isotherm shows that the structure formed in 80 oC just has one pore in its unit cell with a surface area of 824 m2/g and structure formed in 45 oC does not adsorb any significant amount of N2 thus resulting in a BET surface area of 21 m2/g and pore volume of 0.0071 cc/g as calculated by DFT method.

Electrochemical Reduction of N_2 to Ammonia by Vanadium Oxide Thin Films at Neutral pH

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The conventional production of NH 3 from N 2 via the Haber-Bosch process is an effective yet energy intensive method with environmental concerns. An alternative approach through the electrochemical reduction of NH 3 to N 2 facilitated by active sites on vanadium oxide thin films is an environmentally friendly technology and worthy alternative. In this work, reactive sites on earth abundant oxides and oxynitride surfaces responsible for the reduction process are examined. Here, we report N-free V III/IV -oxide films, created by O 2 plasma oxidation of polycrystalline vanadium, exhibiting N 2 reduction at neutral pH with an onset potential of −0.16V vs Ag/AgCl. DFT calculations indicate that N 2 scission from O-supported V-centers is energetically favorable by ∼18 kcal mol −1 compared to N-supported sites. Fundamental insights towards the metal oxophilicity supported by experimental results and theoretical calculations make the work promising for wider applications.

Step-by-Step Design of 3D Metal Organic Frameworks

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Metal-organic frameworks (MOFs) are porous crystalline materials with surface areas ranging from 1000 to 10,000 m2/g, better than traditional porous materials such as carbons or zeolites. These materials can possess high surface areas, open compartments for guest substrates, functional linkers, active catalytic sites, and tunable metal nodes. These advantages allow MOFs to be used for gas storage, gas separation, catalysis, sensing, drug delivery, radiotherapy, and other biological applications. There is plenty of room to tune the properties of MOFs that may enhance the ultrahigh porosity, thermal and chemical stability, and gas capture selectivity. Synthesis of the possible theoretical structures is not always straightforward and may need multiple routes to reach the target. Metal-organic polyhedra (MOPs), also called nanoballs, are porous zero-dimensional high symmetry discrete units. These are composed of metal paddlewheel clusters M2(RCO2) and organic linker. MOPs could serve as high connectivity supramolecular building blocks for 2D and 3D MOFs synthesis. Uncoordinated points of extension could be connected with a ditopic linker having active functional groups. Using predesigned building blocks offers better control over the pores topology and introducing required functional groups. We explore the strategies that involve step-by-step multivariate frameworks design by linking supramolecular building blocks and functional organic linkers. Precise control and targeted introduction of organic functionalities may yield sophisticated and smart materials for future technologies.

Materials Section

Entry	Time	Activity
Greetings	9:30 am – 9:40 am	***Greetings***
01	9:45 am – 10:00 am	Baowin Li
02	10:00 am – 10:15 am	Sujata Mandal
03	10:15 am – 10:30 am	Jennifer England
04	10:30 am – 10:45 am	A K M Nur Alam Siddiki
Break	10:45 am – 10:55 am	***Intermission***
05	10:55 am – 11:10 am	Samia Rifat
06	11:10 am – 11:25 am	Rajitha Parrera
07	11:25 am – 11:40 am	Malsha Udayakantha
08	11:40 am – 11:55 am	
09	11:55 am – 12:10 pm	
10	12:10 pm – 12:25 pm	
Break	12:25 pm – 1:00 pm	***Lunch Break***
11	1:00 pm – 1:15 pm	Alireza Aminifazl
12	1:15 pm – 1:30 pm	Shan Li
13	1:30 pm – 1:45 pm	Yafen Tian
14	1:45 pm – 2:00 pm	Jacob Fripp
Break	2:00 pm – 2:10 pm	***Intermission***
15	2:10 pm – 2:25 pm	Olatomide Omolere
16	2:25 pm – 2:40 pm	Syed Fahad Bin Haque
17	2:40 pm – 2:55 pm	
18	2:55 pm – 3:10 pm	
19	3:10 pm – 3:25 pm	
20	3:25 pm – 3:40 pm	
Break	3:40 pm – 4:30 pm	***Break***
Awards Ceremony	4:30 pm – 5:00 pm	***Awards Ceremony***

For questions about scheduling for Materials Section, e-mail:
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2-Dimensional Cu(II) Coordination Polymer Distance Modified by Substituted Functional Groups

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Metal-organic frameworks (MOFs) are crystalline porous materials with high surface areas composed of inorganic metal nodes as well as organic linkers. The pore size and thermal stability of MOFs can be modified by interchanging linkers through post-synthetic modification (PSM). Functionalized MOFs are desirable because of their controllable surface area. These copper-based layers are exploitable due to their potential to adjust the hydrogen bond strength and the distance between the sheets by applying substituted H2BDC linkers. The research to be presented will be the focus on the structures of the Cu2(BDC-X)1.5(L1) MOFs and their PXRD, TGA, and FTIR characterization.

Exploring the potential of biomass based activated carbon for the efficient removal of Lead (Pb) metal and fungicide from aqueous solution

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Contamination of the water resources by industrial and agricultural activities is a major threat to human health and the ecosystem. Atrazine (2 chloro-4 ethylamino-6-isopropylamino-1, 3, 5 triazine) is one of the most widely used herbicides. The extensive use of atrazine in agricultural production has caused increasingly serious environmental risks. The stable chemical properties and a slow degradation rate of atrazine are known to have drastic effect on aquatic and human life. Lead (Pb) is a common heavy metal found originating from wastewaters of mining, electrical, electroplating, and smelting industries. Long-term exposure to lead metal can cause severe damage to the nervous system, reproductive system, kidney, brain, and liver. So, the removal of herbicide and lead from contaminated water is essential. Adsorption has been identified as an effective, fast and, economical technique to eliminate organic and inorganic pollutants in water. The present work demonstrates an environmentally benign solution to effectively remove atrazine as well as lead metal from polluted water. Activated carbon derived from the hemp hurd without the use of any harsh chemicals is evaluated for its ability to remove toxic lead metal and herbicide atrazine from aqueous solution in a batch process. Surface area and pore volume and average pore size are determined by the BET method (Brunauer-Emmett-Teller). Surface morphology and porosity information are obtained using Scanning Electron Microscopy data. The basic chemical information regarding functional groups presents in the biomass-based activated carbon is determined using Fourier transform infra-red (FTIR) spectroscopy. Equilibrium studies are conducted in the range of 10 –50 mg/L of the pollutant. The effect of adsorption with respect to solution pH, temperature, and contact time are evaluated. This work will provide a promising protocol for the effective removal of toxic lead and atrazine from contaminated waters by simple adsorption using naturally available, biologically benign, mesoporous hydrophobic sustainable biomass.

Mechanical and Corrosion Studies of Additive Manufactured Stainless Steel

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The 3D printing of metals is a growing industry for creating desired shapes from either a bed of powder or the introduction of powder with a laser. Selective laser melting (SLM) is a type of laser powder bed fusion (L-PBF) additive manufacturing (AM) where a laser is used to melt a bed of powder. An investigation into the relation between the processing parameters and the mechanical characteristics and corrosion resistance was done. The volumetric energy density (VED) applied for melting of the samples ranged from 45.24 J/mm^3 to 83.33 J/mm^3. The micromechanical properties were characterized using nanoindentation, areal roughness, and electron back scattering diffraction (EBSD). Effect of the various VED processing parameters on corrosion of the AM materials were investigated using open circuit potential (OCP), linear polarization resistance (LPR), electrochemical impedance spectroscopy (EIS), and potentiodynamic polarization tests. The sample with the best micromechanical and corrosion properties had a VED of 56.67 J/mm^3. This sample also had the lowest surface roughness and smallest grain size. Further tuning of the SLM processing parameters is needed to create more uniform materials with more competitive mechanical and corrosion properties.

Encapsulation of semiconductor quantum dots into the hollow core of wrinkled mesoporous silica

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Mesoporous silica nanoparticles have gained attention as drug delivery vehicles for cancer therapy due to the potential high loading capacity of anticancer drugs. Semiconductor quantum dots have emerged as a substitute for organic dyes for in vivo imaging. In contrast to fluorescent dyes the quantum dots are brighter and more stable therefore demonstrate greater potential in vivo imaging and diagnostics. In this work, semiconductor ZnO quantum dots are synthesized by the sonochemical method and then encapsulated in the hollow core of wrinkled mesoporous silica (ZnO@WMS). ZnO quantum dots and ZnO@WMS were characterized by UV-Vis, PL spectroscopy, XRD, and TEM. The particle size of pure hexagonal wurtzite ZnO quantum dots are 3-5 nm. The optical bandgap is estimated to be 3.34 eV and shows a broad emission centered at 541 nm. The particle size of ZnO@WMS particles are ~300 nm and can accommodate ~50 ZnO quantum dots in its core. Encapsulated ZnO quantum dots in the core of hollow wrinkled mesoporous silica will fluorescence while the outer mesopores can be loaded with cancer drugs. The ZnO@WMS will help to understand the biodistribution of cancer drugs delivered by mesoporous silica nanoparticles in animal and cell models.

Encapsulation of CrN nanoparticles into immiscible PAN/PMAA polymer blends derived carbon nanofibers for supercapacitor application

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Various approaches are being utilized to enhance the performance of Supercapacitors. The incorporation of nanoscale transition metal nitrides (TMN) into Porous carbon nanofibers (PCNFs) has demonstrated superior performance because of their high specific surface area and low electrical resistivity. Electrospun PAN/PMAA polymer blends have gained prominent recognition as the precursors of CNFs because of their excellent spinnability and high carbon yield (>50%), mechanical stability. In our present work, electrospun fiber mats were prepared with immiscible PAN/PMAA polymer blends and CrCl3.6H2O as a source of Cr followed by the stabilization, carbonization & activation with NH3 at 900 ºC. Here, Polyacrylonitrile (PAN) was employed as the carbonizing material and Poly(methacrylic acid) (PMAA) as a sacrificial material. The inclusion of PMAA improved the uniform in situ dispersion of the CrN all over the fibers. Additionally, its carboxylic moiety formed porogen by decarboxylation upon heat treatment. Furthermore, an activation process was employed, which increased the surface area and introduced CrN nanoparticles on fibers. It was the gateway to the introduction of a faradic redox materials (CrN) for increasing the electrode's capacitance. In a preliminary investigation, single electrodes' electrochemical properties were examined using a three-electrode system with 0.5 H2SO4 as electrolytes. Consequently, two reversible redox peaks were observed on the CV for CrN within the 1.2V maximum working potential.

An “On-Off” Eu(III)-based Optical Sensor for Quantitative Detection of Dissolved CO2 towards Practical Applications

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Detection of carbon dioxide (CO_2) is very important to industrial and medical fields. An increment above 0.04% of CO_2 in the atmosphere, can be fatal for living beings. A higher concentration (>5%) can cause the development of hypercapnia and respiratory acidosis in humans, whereas CO_2 levels above 10% may cause convulsions, coma, and death. From an environmental perspective, CO_2 being a renowned greenhouse gas, its contribution towards global warming and climate change is significant. Even other industries such as food packaging, beverages, biotechnology, medicine, and marine sciences have been identified as crucial areas for CO_2 level monitoring. Non-dispersive infrared (NDIR) and gas chromatography (GC) are the most common methods to analyze gaseous carbon dioxide and Severinghaus electrodes are considered to be the standard method for detecting dissolved carbon dioxide. But IR and GC-based methods are limited by water interference and expensiveness of the instrument. Severinghaus electrode methods suffer from electromagnetic interference and low sensitivity. Optical CO_2 sensors offer a higher advantage over conventional non-optical methods due to reduced noise-to-signal ratios, no water interference, possible miniaturization of the instrument, remote sensing, cost-effectiveness, etc. Here, we report the development of a photoluminescence- (PL)-based optical CO_2 sensor based upon a well-known europium dikentonate complex. The complex shows on-off PL switching in the presence vs absence of CO_2. The pKa was determined to understand the mechanism of CO_2 sensing and effect of pH on the sensor. The changes in CO_2 concentrations are quantified based on PL intensity variations of the 5D0→7F2 line in the Eu(III) complex at ca. 617 nm. Our sensor, K[Eu(hfa)4], exhibits PL enhancement with respect to increase in CO_2 concentrations, unlike many other sensors that exhibit fluorescence or phosphorescence quenching. In this study, the sensor's performance is optimized by interrogating with different solvents, and the limit of detection was determined by exposing the sensor to quantities that vary between 1-100% CO_2. The data are highly reproducible and studies to understand the applications of the sensor for breath analysis, fermentation and for other environmental and biological/biomedical applications are under investigation.

Hydroxyethylcellulose-functionalized Halloysite Nanotubes: An Insulating Recipe for Oilwell Cement Sheaths

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Mobilization of bitumen deposits using the injection of hot fluids in methods like steam-assisted gravity drainage (SAGD) and cyclic steam simulation (CSS) entails the use of cement sheaths encasing the steel pipes through which steam is injected to the bedrock. However, cyclic thermal stresses subjected to SAGD cement sheaths impose considerable strain gradients leading to crack formation and loss of energy efficiency. Hence, reliance on SAGD for accessing unconventional bitumen deposits heavily depends on ensuring thermal insulation while maintaining mechanical resilience upon prolonged exposure to cyclic thermal stress. However, the current palette of insulating cement is exceedingly sparse. Enriching the cement matrix with many disparate interfaces and enclosed void space by the inclusion of hollow yet robust fibrous fillers well dispersed in the cementitious matrix serves as effective barriers over phonon conduction within the cement sheaths. The incorporation of hollow carbon and halloysite nanotubes and cellulosic jute fibers well dispersed in the cementitious matrix aided by polymeric dispersants demonstrated effective modifications of the microstructure of oil well cement sheaths while maintaining the mechanical robustness and compositional profile essentially unaltered. However, the best insulation is attained by the incorporation of hydroxyethylcellulose- functionalized halloysite nanotubes (HEC-HNT) staying at a percolation threshold of 2 wt.% (per cement weight). This composition reduces the thermal conductivity of thermal cement from 0.856 W/m·K to 0.206 W/m·K without substantially altering the compressive strength. Annular cement sheaths encasing steel rings constructed from cement modified with 2 wt.% of HEC-HNTs subjected to cyclic thermal stresses characteristic of operando SAGD conditions (20 h at 250°C followed by 4 h at 25°C) for 20 days demonstrate the ability to maintain a higher temperature gradient as compared to unmodified cement. Even at the aggressive heating and cooling temperature ramps afforded in this study, a 4.5 cm thick cement sheath could maintain a 12°C increased temperature differential between hot and cold surfaces compared to unmodified cement.

Preparation and characterization of functionalized organic and inorganic modified Zn-Al LDHs

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Layered Double Hydroxides (LDHs) are two-dimensional materials that consist of cationic layers and intercalated anions. LDHs are very attractive additives used in polymer composites that drastically increase the composites' mechanical, thermal, and corrosion inhibition properties. Separation of strongly adhered the LDHs' plates and making the plates compatible with organic media is still a big challenge. In this work, Zn-Al LDHs are synthesized through the co-precipitation method and then modified via the anion exchange process using inorganic and organic anions. In the final step, a Silane coupling agent is added to LDHs' solutions in order for surface modification and their easy incorporation in the polymer matrix. The change in LDH basal spacing, anion incorporation, grafting of coupling agents on the LDH surface, structural morphology, and elemental analysis are studied using x-ray diffraction, thermogravimetric analysis, infrared spectroscopy, scanning electron microscopy, and energy-dispersive x-ray analysis.

Cyclic Trinuclear Gold(I) Pyrazolate: A New Bright Wide-band Phosphor for (O)LEDs

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A cyclic gold(Ⅰ) pyrazolate trimer, Au3[3,5-(COOEt)2Pz]3, is being evaluated as a promising candidate for inorganic or organic light emitting diodes (LEDs or OLEDs, respectively) due to its bright phosphorescence caused by intertrimer metal-metal interactions among the molecular stacks. Absolute photoluminescence quantum yield (PLQY) measurements attained extremely high values of 53% and 96% (close to unity) for the solid phase in powder and thin-film formats, which are the functional forms for LEDs and OLEDs, respectively. Phosphorescent radiative lifetime were ~ 15-20 microseconds in both forms. Thermal properties include melting and decomposition temperatures at 215 and 249 °C from TGA and DSC measurements, respectively, suggesting that $Au_3[3,5\text{-}(COOEt)2Pz]_3$ exhibits highly thermal stability suitable for thermal evaporation, a major method for small-molecule OLED deposition. CzSi and/or DPEPO are chosen as wide-band hosts with potential for efficient energy transfer from these hosts to the trimer dopant, upon high spectral overlap between the host's emission and dopant's absorption, in a suitable device structure for phosphorescent doped OLEDs. The photoluminescence and electroluminescence performance of red emissive $Au_3[3,5\text{-}(COOEt)2Pz]_3$ in the doped organic semiconductor films and/or OLEDs illustrated different luminescent and charge transfer mechanisms (e.g., whether exciton recombination/luminescence is realized directly in the trimer, its excimer, or at the interface of transporting materials; also whether the charge carriers in the emissive layer are those of the host with a high carrier mobility as normally the case or those of the dopant upon direct recombination in an inert host, which leads to poor carrier transport properties given $Au_3[3,5\text{-}(COOEt)2Pz]_3$ is designed as emissive not charge-transporting material). This work represents that the first report on cyclic trinuclear gold (Ⅰ)-based OLEDs. Ongoing further improvements in the device structure of OLEDs, utilizing the fundamental understanding of the device physics of the studies herein as a backdrop, as well as utilizing the same $Au_3[3,5\text{-}(COOEt)2Pz]_3$ molecule (but as powder instead of thin film) as down-conversion phosphor for LEDs, are under further development.

Mg(OH)2 templated carbon film as electrode material for supercapacitor

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Supercapacitor has many excellent advantages, such as large power density, wide application temperature scope, long life and so on. Therefore, tremendous efforts have been devoted to developing active electrode materials for supercapacitor applications. Electric double-layer capacitors (EDLCs) store energy based on the adsorption and desorption of anions and cations at the electrode surface to obtain high power densities. Carbons with designed nanoarchitectures to achieve high surface areas and appropriate pore distributions have been studied as EDLC electrode materials. Herein, carbon film with needle shape reservoir was synthesized via chemical vapor deposition with magnesium hydroxide as a template. A high surface area of 1542 m^2/g was achieved to enable large quantities of electrolyte adsorption. The symmetric supercapacitor using EMI-TFSI as electrolyte has a specific capacitance of 177 F/g which will have great potential to be used in supercapacitors.

Luminescent Metal Inorganic Framework Sensors: Chemo- and Baro-sensing

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FMIF-1 (fluorous metal-inorganic framework-1, aka FMOF-1) has been the subject of intense studies for the past 14 years mostly for its high volumetric guest molecule storage abilities coupled with its superhydrophobic nature. Through recent discoveries, three new polymorphs of FMIF-1 have been found: aFMIF-1, mFMIF-1, and mFMIF-2. Along with these new polymorphs, multiple unusual photoluminescence (PL) phenomena have been discovered: 1) water-stable PL in mFMIF-2 that is capable of detecting some toxins that are dangerous to the environment and human/aquatic organism health, and 2) pressure-dependent PL, herein referred to as baroluminescence, in aFMIF-1 and FMIF-1 that can accurately determine vacuum levels based of emission intensity. These PL sensing properties and the FMIF family's unique solubility rules, which enable facile creation of stand-alone thin films and membranes, are promising for the creation of inexpensive and easy point-of-access sensors for various real-world applications.

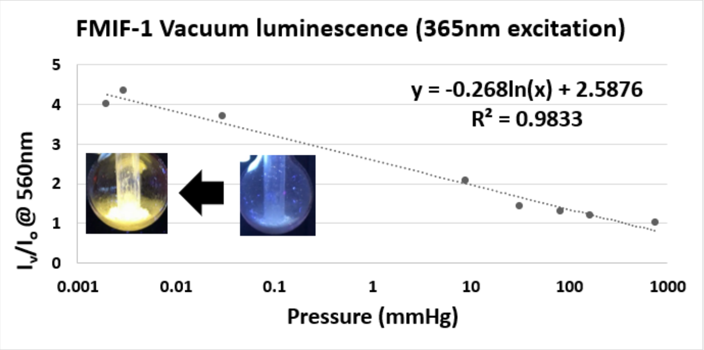

Figure 1. Tracking the relative intensities of FMIF-1's emission centered at 560 nm as a function of pressure in nitrogen atmosphere. Excitation at 365 nm. I_v = intensity of 560 nm peak at given vacuum level, I_o = intensity of 560 nm peak at STP. Photo on the left displays FMIF-1's luminescence under vacuum, right shows the diminished luminescence at 1 atmosphere nitrogen.

In-situ study on plasma cleaning of Lithium garnet substrate surface

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Category; Graduate

Li garnet solid-state electrolytes (SSEs) are of significant interest for future Li battery applications. A major issue in battery fabrication however, is the formation of lithium carbonate on the surface upon exposure to atmosphere, adversely impacting Li ion conduction. Because of this garnet property, plasma-based cleaning techniques are currently being pursued in general effort to increase in-situ processing capabilities. Here , we report in situ plasma cleaning/photoemission studies indicating that annealing an ambient-exposed sample to >1000k in UHV effectively reduced surface carbonate and oxygen leaving significant amounts of carbon in lower oxidation states. This carbon build-up was then subsequently removed by oxygen plasma. This method presents alternative approaches to lithium carbonate removal, which currently rely on heating or polishing in inert atmosphere—and are compromised by even momentary electrolyte exposure to ambient. Plasma methods are also compatible with both industrial processing and vacuum/ultra-high vacuum methods for electrolyte modification and electrode deposition.

MOP-18/Matrimid derived Cu–CNF nanocomposites for high-performance hybrid supercapacitor

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Climate change, fossil fuel's inevitable scarcity, and our modern way of life in general forcing society to change the way we produce, store, and consume energy. Renewable energy sources like the sun and wind are being a major contributors to electrical energy all over the world and as they are intermittent, the ability to store them is crucial. On the other hand, the rapidly growing electric vehicle industry is continuously pushing the boundaries of electrical energy storage system (EES) performances. To meet the need for ever-increasing performance demand from storage systems, research and development in this sector are crucial to make them sustainably mitigate our existing and future needs. Li-ion batteries have been the default EES for quite some time now and have a high energy density but suffer from low power density due to ion diffusion limitations. Supercapacitors (SC), also known as an electrochemical capacitor (EC), have some great advantages like high power density, long cycle life, flexible operating temperature, and environmental friendliness over Li-ion batteries but they suffer from low energy density in general. In this study, we are focusing on developing high energy density hybrid supercapacitor (HSC) electrode material that uses both electrochemical double-layer capacitance (EDLC) like supercapacitors and pseudocapacitance (PC) to store electrical energy. We are using Metal-Organic Polyhedra (MOP) as redox-active pseudocapacitive material for its impressive solubility and porous structure in our HSC electrode and Matrimid as carbon nanofiber source for its remarkable chemical and thermal stability. We are currently characterizing and fine-tuning our electrode setup and so far we have seen a lot of promising results from selected materials.

Physical/Computational Section

Entry	Time	Activity
Greetings	9:30 am – 9:40 am	***Greetings***
01	9:45 am – 10:00 am	Ajyal Zaki Alsaleh
02	10:00 am – 10:15 am	Sadisha Manendri Nanayakkara
03	10:15 am – 10:30 am	Shariq Haseen
04	10:30 am – 10:45 am	Lama Abu-Amara
Break	10:45 am – 10:55 am	***Intermission***
05	10:55 am – 11:10 am	Hao Tian
06	11:10 am – 11:25 am	Noura Dawas Alkhaldi
07	11:25 am – 11:40 am	George Curtis Rawling
08	11:40 am – 11:55 am	Megan Simons
09	11:55 am – 12:10 pm	Malgorzata Zofia Makos
10	12:10 pm – 12:25 pm	
Break	12:25 pm – 1:00 pm	***Lunch Break***
11	1:00 pm – 1:15 pm	Hanof Dawas Alkhaldi
12	1:15 pm – 1:30 pm	Bailey Michelle Raber
13	1:30 pm – 1:45 pm	Emmett Michael Leddin
14	1:45 pm – 2:00 pm	Avdhoot Shrikrishna Datar
Break	2:00 pm – 2:10 pm	***Intermission***
15	2:10 pm – 2:25 pm	Hussain J. Alathlawi
16	2:25 pm – 2:40 pm	Madison Brandi Berger
17	2:40 pm – 2:55 pm	Leonel Varvelo
18	2:55 pm – 3:10 pm	Ramesh Sapkota
19	3:10 pm – 3:25 pm	
20	3:25 pm – 3:40 pm	
Break	3:40 pm – 4:30 pm	***Break***
Awards Ceremony	4:30 pm – 5:00 pm	***Awards Ceremony***

For questions about scheduling for Physical/Computational Section, e-mail:
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Charge Stabilization via Electron Exchange: Excited Charge Separation in Symmetric, Central Triphenylamine Derived, Dimethylaminophenyl- Tetracyanobutadiene Donor-Acceptor Conjugates

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Photoinduced charge separation in donor-acceptor conjugates plays a pivotal role in technology breakthroughs, especially in the areas of efficient conversion of solar energy into electrical energy and fuels. Extending the lifetime of the charge-separated species is a necessity for their practical utilization, and this is often achieved by following the mechanism of natural photosynthesis where the process of electron/hole migration occurs distantly separating the radical ion-pairs. Here, we hypothesize and demonstrate a new mechanism to stabilize the charge separated states via the process of electron exchange among the different acceptor entities in multimodular donor-acceptor conjugates. For this, star-shaped, central triphenylamine derived, dimethylamine-tetracyanobutadiene conjugates have been newly designed and characterized. Electron exchange was witnessed upon electroreduction in conjugates having multiple numbers of electron acceptors. Using ultrafast spectroscopy, the occurrence of excited-state charge separation and the effect of electron exchange in prolonging the lifetime of charge-separated states in the conjugates having multiple acceptors has been successfully demonstrated. This work constitutes the first example of stabilizing charge-separated states via the process of electron exchange.

Hydrogen Bonding Networks in 2D and 3D Ice Polymorphs: A Periodic Local Vibrational Mode Study

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Ice come in many forms and so far, 10 thermodynamically stable and 6 metastable 3D ice phases along with square and hexagonal (bilayer) 2D ice phases have been experimentally resolved under different conditions. Accurate lattice energy data exist for the aforementioned structures which account for the cumulative strength of the hydrogen bond network. Nonetheless, the individual hydrogen bond strengths within the lattice has not been investigated so far which would provide means to identify different hydrogen bonds and their varying bond strengths. In this work we studied several experimentally resolved 2D and 3D ice polymorphs to assess the donor and acceptor hydrogen bond interaction strengths, using periodic local vibrational mode analysis to probe their intrinsic bond strength. The insights offered by this would further help to account for the credibility of several predicted ice polymorphs obtained by various approaches, even before experimental data become available.

ReaxFF for select Si-based polymer-derived ceramics

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Polymer-derived ceramics are a class of materials that exhibit many desirable properties such as high-temperature stability, oxidation resistance, and creep resistance. We develop a new reactive force field (ReaxFF) for large-scale simulation of the polymer-to-ceramic transformation of a subset of polymer-derived ceramics (PDCs) with density functional theory-like (DFT) accuracy. Taking advantage of our extensive library of hypothetical crystalline and amorphous structures, we first aim to reproduce energy differences between calculations in ReaxFF and calculations in density functional theory (DFT). We further optimize parameters by matching ReaxFF molecular dynamics energy and forces with those of DFT ab initio molecular dynamics. In order to evaluate and improve our parameters, we generate melt-quench (MQ) ReaxFF models and optimize these models in DFT in a “self-learning” loop that is used to augment the training set. Using our final set of ReaxFF parameters, we investigate the thermal conversion of polymers to PDCs.

Pressure-controlled Topochemical polymerization in Two-Dimensional hybrid Perovskite

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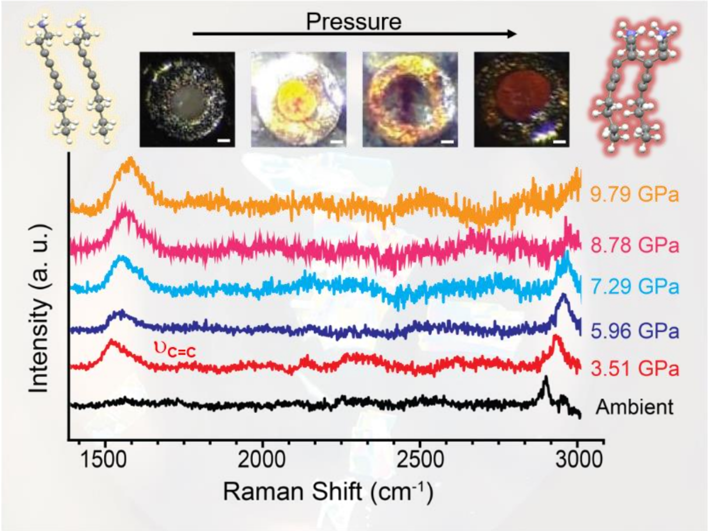
Mechanical pressure offers unique control over the energy landscape of chemical reactions, opening up pathways that are inaccessible through conventional thermochemistry. Pressure-driven reactions have been extensively studied in three-dimensional (3D) bulks, yet much less understood in low-dimensional systems. We hypothesize that the reduced dimensionality defines the conformational space of the high-pressure reaction, giving rise to new selectivity that is unavailable in 3D systems. Here, we demonstrate this concept through the pressure-controlled topochemical polymerization of the diacetylene molecule deca-3,5-diyn-1-amine (DDA) incorporated in the two-dimensional (2D) perovskite [DDA]2PbBr4. Compression at 3 GPa drives the first topochemical polymerization through 1,2 addition, forming a polyene product at room temperature. The reaction is initiated by the mechanical bending of the linear DDA molecule, a mechanism fundamentally different from the 1,4 addition in 3D solids. Importantly, pressure hinders the second 1,2 addition by disfavoring the gauche conformation between the remaining acetylene groups, allowing for the selective formation of polyene versus polyacene products. We characterize the reaction mechanisms and products using spectroscopies (Raman, X-ray photoelectron, ultraviolet-visible), X-ray diffraction and density-functional theory simulations. These results highlight the important role of dimensionality in high-pressure chemistry, and offers a new paradigm for creating low-dimensional functional materials.



Machine Learning Framework for Deciphering the Allosteric Process of Circadian Clock Protein

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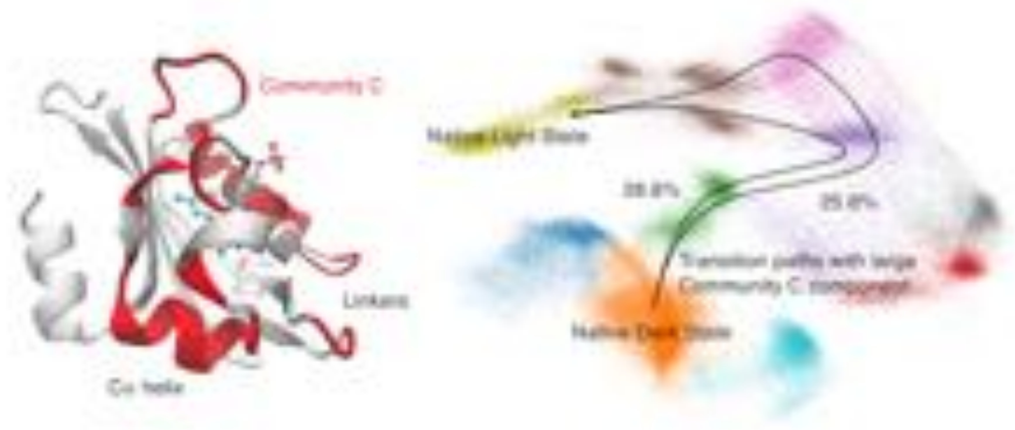
The circadian clocks play an important role in ecosystems by synchronizing biological processes to cycles of light and temperature. In nature, they are regulated by protein allostery, which is the process that regulates protein functional activities, together with conformational or dynamical changes, upon an external perturbation. Light, oxygen or voltage (LOV) proteins are a circadian clock family that are sensitive to blue light. The conformational-driven allosteric protein, diatom Phaeodactylum tricornutum aureochrome 1a (PtAu1a), belongs to this group, with certain differences from other LOV proteins for its uncommon structural topology. The mechanism of signaling transduction in the PtAu1a LOV domain (AuLOV) including flanking helices remains unclear because of this dissimilarity, which hinders the study of PtAu1a as an optogenetic tool. To clarify this mechanism, we employed a combination of molecular dynamics (MD) simulations, ivis dimensionality reduction method, Markov state models, one-vs-one random forest, machine-learning-based community analysis, and transition path theory to quantitatively analyze the allosteric process. Our results identified several experimentally reported residues that are vital in the allosteric process. We further revealed a previously overlooked Cα helix and protein linkers as important in promoting the protein conformational changes. This integrated approach can be considered as a general workflow and applied on other allosteric proteins to provide detailed information about their allosteric mechanisms.



Stability Study of Copper-Cysteamine Structures and Investigation of their Electronic and Optical Properties

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Copper cysteamine (Cu-Cy) is a molecular solid which has a strong luminescence that can be used in imaging, solid state lighting, and radiation detection. It is a photosensitizer that can be activated by visible light, X-rays, microwaves, and ultrasound to generate reactive oxygen species (ROS). This ROS can be used to treat the cancer and infection diseases. Hence, it is important to understand the electronic and optical properties of Cu-Cy. In this study, density functional theory (DFT) has been used to investigate the electronic and optical properties of Cu-Cy-X, with X= F, Cl, Br, and I. Stability of Cu-Cy structures have been studied considering different states as well spin-orbit-coupling (SOC) to understand the electron transition from the occupied to the unoccupied bands. Our theoretical data is in good agreement with the experimental results.

Studies of the kinetics and infrared spectrum of HC(O)Cl

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Halogenated compounds are of interest because of their interactions with the atmosphere, such as strongly absorbing infrared (IR)bands that influence global warming and the release of chlorine radicals that destroy ozone. One such compound is formyl chloride, HC(O)Cl, which is a degradation product of chlorocarbon molecules. HC(O)Cl is unstable at room temperature and, within minutes, decomposes into CO + HCl in the laboratory. By using IR spectroscopy to monitor the reaction in real time, the profiles for HC(O)Cl and all other species as the reaction proceeds is obtained. This leads to the ability to determine absolute IR cross sections for HC(O)Cl, which have been unavailable until now.

Transition-potential coupled cluster

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Coupled cluster (CC) is a numerical method used for describing many-body systems and is classified as one of the post-Hartree-Fock ab initio methods. The purpose of this method is to describe electron correlation in a wave function. The coupled cluster method is preferred due to its size-extensivity and implicit inclusion of higher-order excitation effects. The accuracy of the CC wave function can be controlled by truncating the cluster operator, T, at increasing levels of excitation; thus we use the coupled cluster singles, doubles, and triples method (CCSDT) as a benchmark for a range of x-ray absorption spectroscopy (XAS) calculations using only singles and doubles or with perturbative triple excitations. Our XAS benchmark involves transition of an electron from the 1s (K) orbital to a number of excited states in 14 small molecules. The problem of orbital relaxation in computational core-hole spectroscopies, including x-ray absorption and x-ray photoionization, has long plagued linear response approaches, including equation-of-motion coupled cluster with singles and doubles (EOM-CCSD). Instead of addressing this problem by including additional electron correlation, we propose an explicit treatment of orbital relaxation via the use of transition potential reference orbitals, leading to a transition-potential coupled cluster (TP-CC) family of methods. One member of this family in particular, TP-CCSD(1/2), is found to essentially eliminate the orbital relaxation error and achieve the same level of accuracy for core-hole spectra as is typically expected of EOM-CCSD in the valence region. These results show that very accurate x-ray absorption spectra for molecules with first-row atoms can be computed at a cost essentially the same as that for EOM-CCSD. Starting from TP-CCSD(1/2), we have further tuned the core electron fraction in order to improve spectroscopic agreement for all first-row atoms.

Prediction of the Transition State Geometry via Machine Learning

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Transition state (TS) is experimentally not observable but is important in computational chemistry because it is necessary to understand the reaction process of molecules, crystals, and material. Currently, the TS search is done using complex quantum chemical algorithms, that require many thousands of reaction rate coefficients and approximations. This motivates us to develop a deep learning algorithm that will predict TS geometry out of Cartesian coordinates of reactant and product. The proposed method efficiently maps the space between reactants and products and generates reliable TS guess geometries, and it can be easily combined with any quantum chemical software package performing geometry optimizations. The algorithm was trained and applied to generate TS guess structures for typical chemical reactions, such as hydrogen migration, isomerization, and transition metal-catalyzed reactions. The performance of our method was directly compared to classical approaches showing its high accuracy and efficiency.

Computing the Tungsten–Nitrogen and Ternary Lithium–Tungsten–Nitrogen Phase Diagram at High Pressure and High Temperature

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We compute the tungsten–nitrogen (W–N) pressure–temperature phase diagram through a combination of density functional theory and thermodynamic calculations. Augmenting standard enthalpy-pressure calculations by the chemical potential change of nitrogen at high pressure and high temperature conditions, we estimate Gibbs energies under nitrogen-rich conditions. The approach allows to predict temperature and pressure conditions necessary to synthesize W–N polymorphs and to locate optimum pressure/temperature conditions for successful syntheses. Our investigations include W2N3, W3N5, W2N2(N2), and correctly locates stability of recently synthesized WN6 and WN8-N2. We further investigate ternary lithium–tungsten–nitrogen (Li–W–N) structures that feature W in high oxidation states. Starting with Li6WN4, we explore feasibility to synthesize phases with high nitrogen content – Li6WN(2·n), with n=4 to 11 – as potential energy storage materials. Our study includes investigating thermodynamic stability of these ternary Li–W–N compounds at high pressures and temperatures relative to combinations of binary W–N and Li–N structures.

Gaining new insight on photoinhibition with a multiscale model of PSII

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Photosynthesis sustains life on Earth. Photosystem II (PSII) is a major light harvesting complex that initializes the conversion of sunlight to energy. The PSII reaction centers are highly susceptible to physical damage due to excess light, a process known as photoinhibition. When photodamage occurs, the reaction centers functionally adapt to dissipate the excess energy as heat. There is still debate on the mechanism of this quenching process; therefore, in this work we develop a membrane scale model to study the functional changes in PSII reaction centers upon photoinhibition. We show that experimental time-resolved fluorescence measurements and immuno-blotting data can simultaneously be described by a two-step damage model of PSII: initial damage to a reaction center forms quenchers, then these quenching reaction centers are slowly degraded. This work uses multiple experimental measurements to construct a kinetic model of photodamage, and provides new insight on the process of photoinhibition.

How Six Cancer-Related Mutations Affect the TET2-DNA Complex

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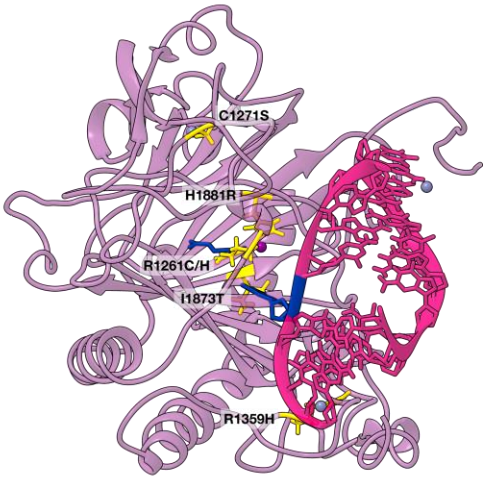
DNA methylation is an important epigenetic feature that most commonly results in 5-methylcytosine (5mC). The TET2 enzyme mediates the stepwise oxidation of 5mC to 5-carboxylcytosine (5caC) using Fe(II) and a-ketoglutarate as co-substrates. Somatic mutations in TET2 are implicated in a variety of myeloproliferative disorders, but not much is known regarding the impact these mutations have on the protein-nucleic acid complex structure. Molecular dynamics simulations of six TET2 variant systems (R1261C, R1261H, C1271S, R1359H, I1873T, and H1881R) have been performed with an everted 5-hydroxymethylcytosine (5hmC) nucleotide. The six variants are located in five different regions throughout the TET2 enzyme, which can provide insight into how mutations in these regions affect the overall function and dynamics of TET2 complexes. Simulation data reveal that these variants share characteristics with each other that are distinct from wild type simulations.



Dissociation dynamics of water molecule on the core-excited potential energy surface

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X-ray emission spectrum (XES) of water shows a doublet nature for 1b1 peak. Several explanations have been proposed for the splitting of 1b1 peak. The origin of the low energy 1b1 peak is attributed to either the intact water molecule or OH□ species arising from ultrafast dissociation of water molecule. Since the XES takes place after the evolution of the molecular wavepacket on the core-excited state, it is necessary to understand the topology of core-excited potential energy surface (PES). Thus, using equation of motion coupled-cluster (EOM-CC) method, PESs are calculated for lowest core-excited states along OH stretching mode of isolated water molecule, and water dimer. Initial investigation suggests that the lowest core-excited state is dissociative, while the higher energy states are bound along OH stretching coordinate. For water dimer, similar results are obtained for non-hydrogen bonded OH stretching. However, for hydrogen bonded OH stretching, transfer of hydrogen to the acceptor water molecule is observed. The vibrational overlap of ground and excited state wavefunctions are calculated using discrete-variable representation.

Electronic and magnetic properties of silicon-carbide fullerenes-like nanostructures

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Silicon carbide (SiC) is an important material for extreme environment applications, such as high temperature, high pressure, high power, etc. In its bulk phase it has more than 200 polymorphs. At the nanoscale, stabilized functional clusters are of particular interest. Experimentally, the C60 fullerene was found to be the most stable form of carbon. Si and C have similar valence electrons configurations, implying that Si and SiC could form similar fullerene structures. We will present our first principles investigations of the Si30C30 fullerene derived clusters. The calculation started from the Si60 fullerene, we studied different configurations of Si30C30 fullerene-like structures and relaxed them without any symmetry. The result has shown some Si-C and Si-Si double bonds in unpassivated structures. In addition, the endohedral doping of fullerene with W atom and the clusters' magnetic properties will be presented. Finally, these clusters' dynamical stabilities at high temperatures will be discussed briefly from the ab initio Molecular Dynamics calculations.

Molecular dynamics investigation on the Effects of Distal Mutations on DNA Polymerase III*

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DNA replication is fast and highly efficient due to the polymerases that carry out this process. DNA Polymerase III (Pol III) is the main replicative polymerase of E coli composed of over 10 proteins. A subset of these proteins, termed Pol III*, includes the polymerase and exonuclease domains alpha and epsilon the clamp, beta, and an accessory protein theta. Previous work has shown that a single mutation in the alpha subunit can impact the proofreading activity carried out by the exonuclease epsilon. In a separate work, it has previously been reported that the L82E and L82D mutations on both monomers of the beta dimer cause a destabilization of this subunit. We will present results for the molecular dynamics simulation of the whole complex of E. coli Pol III* wildtype, beta L82E, and beta L82D. These results provide insights into the effects of the mutations on the beta clamp and the proofreading activity of epsilon.

Simulating rare events in open quantum systems using transition path sampling

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Rare events in excited state dynamics, such as transport across grain boundaries, are difficult to simulate due to large time scales and high computational expense of quantum dynamics algorithms. We present a new method for extending timescales of quantum simulations using transition path sampling. Implementing the Hierarchy of Pure States method, a formally exact equation of motion for open quantum systems, we construct independent stochastic trajectories which are used to produce a quantum path ensemble. Using transition path sampling we can directly construct a reactive ensemble, where each member of the ensemble is a realization of the rare event in a non-Markovian system. With our new method we can efficiently study the dynamics of rare events in non-Markovian systems by calculating unbiased rate constants using short trajectories.

Infrared spectrum and Atmospheric chemistry of 1,1,2,3,3,4,4 heptafluorobut-1-ene

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Fluorinated alkenes, because they react quickly in the atmosphere, are potential low-global warming potential substituents for halocarbons. The relative rate method was used to determine the reaction rate of 1,1,2,3,3,4,4 heptafluorobut-1-ene (CF2=CFCF2CF2H) with chlorine atoms. A mercury UV lamp was used for generating atomic chlorine which initiated the reaction. The reaction was monitored by FTIR spectroscopy. Ethane was used as the reference compound for relative rate studies. Oxidation of 1,1,2,3,3,4,4 hepatafluorobut-1-ene initiated by chlorine atom creates carbonyl difluoride and 2,2,3,3 tetrafluoro-propanoyl fluoride (O=CFCF2CF2H) as the only two products. Anharmonic frequency calculations for 1,1,2,3,3,4,4 heptafluorobut-1-ene and 2,2,3,3, tetrafluoro-propanoyl fluoride based on density functional theory are in good accord with measurements, when all low energy conformations are taken into account. The GWP of 1,1,2,3,3,4,4 hepatfluorobut-1-ene and 2,2,3,3 tetrafluoro-propanoyl fluoride was calculated using the IR spectrum and atmospheric lifetime.

Biochemistry/Biological Chemistry Section

Entry	Time	Activity
Greetings	9:30 am – 9:40 am	***Greetings***
01	9:45 am – 10:00 am	Nisansala Sandamali Abeyrathna
02	10:00 am – 10:15 am	Andrea Gabriela Guedez Pena
03	10:15 am – 10:30 am	Olivia Rose Brohlin
04	10:30 am – 10:45 am	Anjala Wijayanthi Bulathge
Break	10:45 am – 10:55 am	***Intermission***
05	10:55 am – 11:10 am	Oladimeji Sunday Olaluwoye
06	11:10 am – 11:25 am	Yingyu Huang
07	11:25 am – 11:40 am	Niraj Verma
08	11:40 am – 11:55 am	Arezoo Shahrivarkevishahi
09	11:55 am – 12:10 pm	Weike Chen
10	12:10 pm – 12:25 pm	
Break	12:25 pm – 1:00 pm	***Lunch Break***
11	1:00 pm – 1:15 pm	Fabian Castro Herbert
12	1:15 pm – 1:30 pm	Noushin Akhavantabib
13	1:30 pm – 1:45 pm	Katherine Rose Smart
14	1:45 pm – 2:00 pm	Perouza Parsamian
Break	2:00 pm – 2:10 pm	***Intermission***
15	2:10 pm – 2:25 pm	Sameera Sandaruwan Abeyrathna
16	2:25 pm – 2:40 pm	Jenica Lumata
17	2:40 pm – 2:55 pm	Fatemeh Khashami
18	2:55 pm – 3:10 pm	Yalini Hansika Wijesundara
19	3:10 pm – 3:25 pm	Wirya Feizi
20	3:25 pm – 3:40 pm	
Break	3:40 pm – 4:30 pm	***Break***
Awards Ceremony	4:30 pm – 5:00 pm	***Awards Ceremony***

For questions about scheduling for Biochemistry/Biological Chemistry Section, e-mail: Laurel Mikaela Hagge laurel.hagge@utdallas.edu

A Biophysical Approach to Study in-vitro Real-time Substrate Translocation Kinetics and Mechanism of Transport in Cu(I)-translocating P-type ATPase pumps

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Copper is an essential trace element in all biological systems, playing a crucial role as a co-factor for cuproenzymes and in signaling processes. Maintaining correct cellular copper homeostasis is critical, as copper deficiency can lead to fatal phenotypes while excess results in cellular toxicity. Copper transporting P-type ATPases are a class of primary active transmembrane transporters which utilize the energy derived by the hydrolysis of ATP to drive Cu(I) translocation from cytosol to the extracellular space. These transporters play a gate keeper role in maintaining correct cellular copper homeostasis in all living organisms. In humans, mutations in the P-type ATPases ATP7A and ATP7B which are involved in Cu(I) homeostasis, lead to the Menkes disease and the Wilson disease respectively. Bacterial Cu(I) exporting P-type ATPases (CopA) are homologous to the human Cu(I) P-type pumps and act as virulence factors, allowing to overcome the Cu(I) stress which is generated by the host defense system as a response to pathogenic invasions. This makes these transporters excellent therapeutic targets in many pathogenic bacteria. Despite crystal structures are available for Cu(I) pumps in the metal released form, the data that can be derived to address kinetics and mechanism of substrate translocation is limited. In this study we recombinantly expressed, purified and encapsulated in artificial lipid bilayer vesicles (proteoliposomes) the model CopA protein from E. coli, to determine the kinetics and the mechanism of Cu(I) transport in real-time. To this end, we developed a novel biophysical platform centered on a diverse set of fluorescent detector probes (CTAP-3, Pyranine and Oxonol (VI)) responsive to different stimuli (Cu(I), pH change and electrogenic potential) to be encapsulated in the proteoliposome lumen. The platform allowed to study in real-time, kinetic parameters of Cu(I) ion translocation, the mechanism of transport and electrogenicity in Cu(I) P-type ATPase pumps. We reveal that that these transporters are primary active uniporters in which substrate ion translocation is not coupled to proton-counter ion transport. Also, we reveal that one Cu(I) ion is transported per a single ATP hydrolysis cycle and that CopA is an electrogenic transporter. This study further reveals mechanistic differences in substrate translocation in CopA proteins in comparison to other characterized P-type ATPase classes. The developed platform can be further extended to study the substrate and the mechanism of transport in uncharacterized transmembrane metal transporter classes.

Genetic selection of sarcosine-specific synthetic riboswitches from a glycine riboswitch

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The aptamer domain of a naturally occurring glycine riboswitches was randomized to generate a library containing billions of different variants. The dual genetic selection of this library was performed for sarcosine, a prostate cancer marker, and successfully led to the identification of sarcosine-specific synthetic riboswitches. When a chloramphenicol-resistance gene was expressed under control of these riboswitches, E. coli cells showed chloramphenicol resistance only in the presence of sarcosine. For a colorimetric assay, the sarcosine riboswitch gene was inserted upstream of the lacZ gene. When tested with various concentrations of sarcosine, the enzymatic activity of LacZ was proportional to the amount of sarcosine, clearly indicating the sarcosine-dependent gene regulation by the sarcosine riboswitch.

Zeolitic Imidazolate Framework 8 Provides Nuclease Resistance to CpG for Enhanced Immunoadjuvancy

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The DNA-based immunoadjuvant, CpG, has faced limited success in clinical trials for cancer immunotherapy because of its susceptibility to degradation by nucleases. To overcome this limitation, the phosphodiester (PO) backbone can be replaced with a phosphorothioate (PS) backbone, however, this modification has been found to reduce the binding affinity of CpG to toll-like receptor 9 (TLR-9), reducing the immunoadjuvancy of the oligonucleotide. As an alternative to the PS backbone, we propose using metal organic frameworks (MOFs) to improve the in vivo stability of PO CpG, in this way also retaining the innate immunoadjuvancy of the oligonucleotide. We have successfully encapsulated CpG within the MOF, ZIF-8, by biomimetic mineralization (76% EE). Upon incubation with in vitro splenocyte cultures, the CpG@ZIF displayed enhanced uptake and activation of B cells as compared to PS CpG by shielding the strong negative charge of the oligonucleotide and preserving TLR-9 binding affinity. Our study presents a new method for stabilizing DNA without altering the inherent properties of the nucleic acid through encapsulation within a crystalline framework. By protecting the DNA immunoadjuvant, CpG, from nuclease degradation, improving cellular uptake, and preserving TLR-9 binding affinity, we have out performed the commercial “gold standard” PS CpG in cellular immune activation.

Molecular mechanism of Pt(II)-drug Resistance via Metallothionein-Dependent MTF-1 Activation

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Cisplatin (cis-[Pt(NH3)2Cl2]) is one of the most successful and widely utilized Pt(II)-based chemotherapeutic drugs. Cisplatin demonstrated efficacy in the treatment of various human cancers, including testicular, ovarian, bladder, and lung tumors. Cisplatin's antineoplastic activity is caused by the formation of Pt(II)-DNA adducts that introduce lesions and distortion in the DNA structure that cannot be repaired, eventually leading to cancer cell apoptosis. Despite cisplatin’s therapeutic benefits, intrinsic and acquired resistance limit its efficacy. In pre-target resistance, molecular processes upstream of Pt(II) binding to DNA, prevent its reaction with its pharmacological target. One of predominant mechanism in pre-target resistance is cisplatin sequestration via covalent binding by intracellular thiol-rich molecules like metallothioneins (MTs). High MTs expression levels correlate with cisplatin drug resistance in preclinical and clinical studies, but the molecular mechanism of MT-mediated resistance remains still elusive. The transcriptional induction of the MT gene is mediated by Metal-Responsive Transcription Factor 1 (MTF-1). Upon zinc binding to its hexa-zinc finger domain, MTF-1 binds to specific DNA motifs termed Metal Responsive element (MRE) in the MT gene promoters, leading to transcriptional induction of MT expression. By biochemical and spectroscopic analysis we investigated the relative reactivity of cisplatin towards Zn(II)7MT-2, each of MTF-1 Cys2/His2 zinc fingers, and the entire MTF-1 hexa-zinc finger domain. By performing cis-[Pt(NH3)2Cl2] binding competition experiments between MT-2 and individual and apo-/holo- zinc fingers, we demonstrate that cisplatin preferentially binds to Zn7MT-2 over MTF-1. Preferential Pt(II) binding to MT cysteine thiolates result in Zn(II) displacement, release and subsequent Zn(II) binding to MTF-1 zinc fingers, thereby potentially activating MTF-1. Analysis of reaction kinetics reveal indeed that the rate of cisplatin binding to Zn7MT-2 is faster than its binding to each of the individual MTF-1 zinc fingers. Initial experiments confirm that similar processes occur with the entire MTF-1 hexa- zinc finger domain. The work substantiates that zinc release upon cisplatin binding to MTs leads to MTF-1 activation, which in turn induces apoMT expression. The consequent increased apoMT levels would lead to cellular cisplatin sequestration and promote MT-mediated drug inactivation. Overall, the work provide a molecular mechanism for metallothionein-mediated cisplatin pre-target resistance.

Identification of coronavirus antibody binding a conserved neutralizing epitope on the spike S2 subunit by hydrogen deuterium exchange mass spectrometry

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Severe Acute Respiratory Syndrome Coronavirus 2 (SARS-CoV-2) causes Covid-19 in humans and is responsible for millions of deaths worldwide. Disrupting the interaction between the receptor-binding domain (RBD) in the S1 subunit and its host cell receptor angiotensin-converting enzyme 2 (ACE2) is a powerful way to prevent coronavirus fusion. Particularly, most monoclonal antibodies developed target this interaction. Here we identify and report the discovery of a novel antibody epitope on the S2 subunit of the spike protein that potentially prevents conformational rearrangement needed for viral fusion by Hydrogen Deuterium Exchange Mass Spectrometry (HDX-MS). Our result shows antibody 3A3 binds conformational epitope at the apex of S2 subunit. We also identified residues 980-1006 located at the apex of the S2 subunit as the 3A3 epitope. This result suggests that antibody 3A3 prevents conformation rearrangement in the S2 subunit needed for viral fusion.

Salivary Excretion of Engineered Silver Nanoparticles

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Salivary elimination is an important pathway for the body to excrete small molecules and digestive enzymes. However, very few engineered nanoparticles can be excreted through salivary glands, which often host bacteria or viruses during infection and are involved in disease transmission. Herein, we report that ultrasmall glutathione coated silver nanoparticles (GS-AgNPs) can selectively accumulate in the submandibular salivary gland, followed by being excreted in its excretory duct. By conducting a head-to-head comparison on the in vivo transport and interactions of both GS-AgNPs and glutathione coated gold nanoparticles (GS-AuNPs) with the same size, we found that low-density GS-AgNPs showed much higher vascular permeability than GS-AuNPs and can rapidly penetrate into submandibular salivary glands, be efficiently taken up by striated and excretory duct cells, and eventually being secreted into saliva.

SSnet - Secondary Structure based End-to-End Learning model for Protein-Ligand Interaction Prediction

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Computational prediction of bioactivity has become a critical aspect of modern drug discovery as it mitigates the cost, time, and resources required to find and screen new compounds. Deep Neural Networks (DNN) have recently shown excellent performance in modeling Protein-Ligand Interaction (PLI). However, DNNs are only effective when physically sound descriptions of ligands and proteins are fed into the network for further processing. Furthermore, previous research has not incorporated the secondary structure of the protein in a meaningful manner. In this work, we utilize secondary structure information of the protein which is extracted as the curvature and torsion of the backbone of protein to predict PLI. We demonstrate how our model outperforms previous machine and non-machine learning models on three major datasets: humans, C.elegans, and DUD-E. We further investigate the inner workings of our model by visualizing heatmaps through Grad-CAM. This analysis is adapted to visualize the most important aspects of the protein that the algorithm has learned. We observed that the important residues highlighted by Grad-CAM are the ones responsible for non-covalent interactions with a ligand and is not just confined to the binding site as it also includes allosteric sites and other locations where a ligand interacts. Our new model opens the door in exploration of DNN based on the secondary structure which is not just confined to protein ligand interactions.

PhotoPhage: A Virus-based Photothermal Therapeutic Agent

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Therapeutic efficiency of available cancer treatment approaches are limited by the uncontrolled spread of cancer cells to distant parts of body.1 The tumor recurrence; low survival rates and therapeutic failures are typical outcomes following metastasis;2 therefore, there is an urgent need for new therapeutic strategies that simultaneously treats the primary tumor and while efficiently combating distant metastatic sites. Method: We developed a new combinational therapy based on the photothermal ablation and immunotherapy to enhance treatment efficacy by combining benefits of both methods compared to either therapy alone. For this purpose, we took advantage of the immunogenicity and site specific functionalizability of engineered phage nanoparticles to present an effective photo-immunotherapy system for primary breast cancer tumor destruction in BALB/c mice bearing 4T1 tumor while reducing metastasis. The immuno-photothermal agent design involves bioconjugation a next-generation organic near infrared photothermal dye to the exterior surface of an engineered version bacteriophage Qβ, the system called PhotoPhage. This formulation is administered intratumorally followed by irradiation of 808 nm laser light. Result: Upon laser irradiation of tumors containing the PhotoPhage, the temperature of tissue increases significantly and causes significant cellular cytotoxicity that prevents the progression of primary tumors in mice. It is found that PhotoPhage not only acts as a PTT agent that initiates anti-tumor immune response, but also simultaneously acts as an immunoadjuvant that promotes maturation of dendritic cells, triggers T lymphocyte cells (CD4+, CD8+) and reduces suppressive T regulatory cells leading to effective suppression of primary tumors, reducing lung metastases, and increasing survival time. Conclusion: Our study presents a new in situ photo-immunotherapy agent that successfully suppress primary breast cancer tumors and reduces lung metastases. We attribute these results to the synergistic effect of PTT and immunotherapy.

Combined Tumor Environment Triggered Self-Assembling Peptide Nanofibers and Inducible Multivalent Ligand Display for Cancer Cell Targeting with Enhanced Sensitivity and Specificity

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Many tumor active targeting strategies, such as tumor microenvironment-triggered cell targeting and multivalent ligand approach for cell surface receptors, have been widely employed to construct nanocarriers as molecular imaging probes and therapeutic delivery vehicles for targeted tumor therapy. While the principle of each strategy has been well illustrated, due to the large macromolecular scaffold, most systems have difficulty in deep penetration of solid tumors, resulting in low tumor-targeting specificity and sensitivity. To overcome this problem, herein we develop a new family of tumor microenvironment-responsive supramolecular peptides with the combination of both strategies to simultaneously improve tumor-targeting specificity and sensitivity. Specifically, we append a cationic domain to the C-terminus of the targeting ligand conjugated self-assembling monomer precursor (SAM-P) through a cleavable chemical linker. Under the physiological condition, the SAM-P is unassembled due to electrostatic repulsion and has good tissue penetrating ability. At the tumor site, SAM-P undergoes tumor-triggered cleavage to release the active form of self-assembling monomer capable of forming supramolecular nanostructures with multivalent display of targeting ligands. Biophysical characterization confirms the chemical and physical transformation of SAM-P from unimers or oligomers with low ligand valency to supramolecular assemblies with high ligand valency under a tumor-mimicking reductive microenvironment. The in vitro fluorescence assay shows the importance of supramolecular morphology in mediating ligand-receptor interactions and targeting sensitivity. Enhanced targeting specificity and sensitivity can be achieved via tumor-triggered supramolecular assembly and induced multivalent ligand presentation toward cell surface receptors, respectively. The results support this combined tumor microenvironment-induced cell targeting and multivalent ligand display approach, and have great potential for use as cell-specific molecular imaging and therapeutic agents with high sensitivity and specificity.

Stabilization of Supramolecular Membrane Protein-Lipid Bilayer Assemblies Through Immobilization in a Crystalline Exoskeleton

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Artificial native-like lipid bilayer systems constructed from unilamellar liposomes allow the reconstitution of transmembrane proteins into proteoliposomes, which mimic cellular membranes. Stabilization of these remains challenging because of their chemical composition, the hydrophobicity and structural instability of membrane proteins, and the lability of interactions between protein, detergent, and lipids within micelles and lipid bilayers. In this work we demonstrate that metastable lipid, protein-detergent, and protein-lipid supramolecular complexes can be successfully generated and immobilized within zeolitic-imidazole framework (ZIF). We describe a method for the thermal stabilization of blank 200 nm liposomes, purified transmembrane proteins, and 200 nm transmembrane protein-liposome supramolecular complexes (proteoliposomes) against chemical and thermal stressors through biomimetic nucleation in ZIF-L. We found that encapsulation of the proteoliposome complex generates thermodynamically stable bio-composites that can withstand exposure to high temperatures, aging, and common protein denaturants (Figure 1). Further, the ZIF-L coatings can be removed to afford pristine proteoliposomes, liposomes, and transmembrane protein micelle complexes of similar composition, morphology, structure, and catalytic activity to their native counterparts.

Vps75 promotes H3-H4 tetramerization by stabilizing the four-helix bundle

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Histone chaperones are structurally diverse class of histone-binding proteins that impact chromatin organization in an ATP-independent manner. Histone chaperones play key roles in many DNA-related processes, thereby regulate DNA replication, transcription and repair. Vacuolar protein sorting 75 (Vps75) and Nap1 (nucleosome assembly protein) constitute the Nap-family of histone chaperones in yeast. This family is characterized by a common fold that is capable of binding core histones H2A-H2B and H3-H4. We have utilized Hydrogen Deuterium Exchange coupled to Mass Spectrometry (HDX-MS) to gain understanding of the H3-H4 dynamics in dimeric vs. tetrameric form. Our histone HDX data shows that H3-H4 tetramer formation stabilizes the entire molecule through H3-H3' coming together to shape the four-helix bundle. Moreover, we assessed the Vps75-H3-H4 dynamics and identified potential histone binding sites. Apart from the expected stabilization effect on histones upon Vps75 binding, we have shown that Vps75 binding promotes tetramer formation. Comparing our HDX results with available Nap-histone structures further clarifies the distinct chaperoning role between Vps75 and Nap1.

Study of novel GLC-based methods for isomeric fentanyl analogs

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Synthetic opioids contributed to 446,032 deaths from 1999 to 2018 according to the Centers for Disease Control and Prevention. Fentanyl is a synthetic opioid of major concern since its use has become common in society. The analysis of fentanyl and its analogs is focused on identification and chemical profiling to aid law enforcement in decreasing their availability in society. Developing the rare analytical methods geared towards isomeric analogs will advance the capabilities of forensic laboratories in the detection of these compounds. In this study, we present a gas-liquid chromatographic (GLC) based method using an ionic liquid phase to analyze isomeric fentanyl analogs. In comparison to a traditional 5% phenyl/95% dimethyl stationary phase, the analogs exhibit lower retention times and a different elution order on the ionic liquid phase. The ionic liquid also exhibits better selectivity, aiding in identification of fentanyl and its analogs. This project was supported by NIJ Award No. 2019-R2-CX-0043, awarded by the National Institute of Justice, Office of Justice Programs, U.S. Department of Justice. The opinions, findings, and conclusions or recommendations expressed in this publication/program/exhibition are those of the author(s) and do not necessarily reflect those of the Department of Justice.

Enhanced nanobubble formation: Gold nanoparticle conjugation to QB virus-like particles

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In this presentation, we aim to discuss the formation of nanobubbles (a.k.a water vaporization) via the excitation of surface plasmons of gold nanoparticles (AuNPs) by ultra-short laser pulses (ps, fs) for biomedical applications in cancer cell destruction for the treatment of brain tumors. Gold nanoparticles excited with ultra-short laser pulses can generate nanobubbles through spinodal decomposition, or the spontaneous separation of one thermodynamic phase into two phases. As the AuNP is pulsed with ultra-short laser light, the heat generated from the surface plasmon of AuNPs surpasses the boiling point of the liquid phase of water molecules surrounding the AuNP, and phase changes from liquid to vapor, generating nanobubbles. To maximize this effect, the experimental design we propose is by synthesizing monodispersed 3.5 nm AuNPs attached to the surface of Qβ, a Virus-Like Particle (VLP) with 720 available amines through carbodiimide chemistry to examine their enhanced nanobubble formation in comparison to individual AuNPs.

MavN/IroT is a Legionella Transmembrane Fe(II) Transporter: Metal Selectivity and Translocation Kinetics Revealed by In-vitro Real-time Transport

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Iron plays a pivotal role in all kingdoms of life as a protein cofactor for a range of enzymatic activities in metabolic processes. Yet, due to its high reactivity and insolubility in oxidative environment, cells evolved a sophisticated protein network to tightly handle iron homeostasis, allowing iron acquisition and maintain iron cellular concentrations below toxic levels. As an essential trace element, iron plays a central role in growth, replication, and virulence in intracellular pathogens. Legionella pneumophila is an intravacuolar pathogen that cause the Legionnaires' disease in humans. During its growth and replication cycle inside host-derived vacuoles in macrophages, a putative metal transporting membrane protein, MavN/IroT is incorporated into the vacuole membrane at the host-pathogen interface. MavN/IroT facilitate iron acquisition from the host cytosol to the Legionella containing vacuole, but its molecular function remained elusive. In this study we developed a platform for in-vitro purification and functional reconstitution of MavN/IroT in artificial phospholipid bilayer vesicles, called proteoliposomes, for biochemical and biophysical characterization of its function at molecular level. By encapsulating the fluorescent probe Fluozin-3 in the liposome lumen and performing real-time substrate transport assays, we reveal that MavN/IroT is a high-affinity ferrous iron transporter that is highly selective for Fe(II) over other first- and second- row divalent transition metal ions. Key residues in the transmembrane region and soluble domains important for metal recognition and translocation were identified by mutational analysis. In addition, by encapsulating the pH sensitive fluorescent probe pyranine, we reveal that MavN/IroT is a proton-coupled secondary active antiporter. This work sets the basis to study substrate translocation events and mechanism of transport in novel transporter families involved in transition metal ion transport across phospholipid bilayers.

Nitroxyl-Modified TMV as Contrast Agent for in Vivo Superoxide Production in Lipopolysaccharide-induced Pancreatitis

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Studies have demonstrated the potential of organic radical contrast agent (ORCA) to sense reactive oxygen species (ROS) - the superoxides using magnetic resonance imaging (MRI).1,2,3 However, free ORCA has low proton relaxation rate or low contrast ability. Scientists have found a way to improve this by attaching it in high concentration to a synthetic, polymeric scaffold which has indeed improves its relaxation rate relative to free ORCA.3 Our lab has exploited the potential of a virus-like particle, the tobacco mosaic virus (TMV), to serve as a scaffold for ORCA molecules. TMV is a noninfectious, rigid, monodisperse, thermostable, and biocompatible4 which is very amenable as a scaffold for MRI contrast agent. Previous study from the group showed that about 4-5 orders of magnitude of relaxivity has increased as compared to free ORCA using this probe.2 This research sought to improve the relaxivity of the current MRI probe by exploring other organic radical molecules and to demonstrate its feasibility to map out superoxide. Two nitroxide radicals will be explored, the TEMPO and proxyl. In order to gather information about the rate of oxidation and reduction of each conjugate, kinetics analysis will be conducted using electron paramagnetic resonance (EPR). To demonstrate the efficiency of O2●− detection and redox sensing of the TMV bioconjugate, both relaxivity experiment and MR imaging in vitro via phantom imaging will be conducted. Relaxivity is a very important parameter of an efficient of contrast agent as it tells us the extent to which the TMV-nitroxide increases the relaxation rate of tissue water. The higher the relaxivity, the higher the contrast. On the other hand, phantom image gives us the physical extent of contrast. Since our goal is to show that the probe is feasible to living model, in vivo study will be conducted. To do so, mice will be subjected with pancreatitis induced by lipopolysaccharide. T1 and T2 experiments will be performed on a 9.4 T MRI. The collection of imaging following the administration of the reduced probe will help differentiate the normal to the superoxide-rich area in the body.

Intracellular and Extracellular Metabolism of High-Fructose Corn Syrup in Cancer Monitored by 13C NMR Spectroscopy

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Glioblastoma Multiforme (GBM) is an aggressive type of the Central Nervous System (CNS) tumor that grows within brain tissue. This type of tumor is fast-growing, characterizing it as one of the most malignant of all primary brain tumor. GBM tumors are made up of many different types of cells which are not responsive to the same type of treatment, making it notoriously challenging to cure. According to the Surveillance, Epidemiology, and End Results (SEER), about 23,820 will be diagnosed with primary brain and other CNS tumors and about 17,760 people will be dead of this disease in the only United States. People with a cancerous brain or CNS tumor have the 5-year survival rate of approximately 32.9% from SEER 18 2009-2015. In this study, we have used 13C NMR spectroscopy to probe metabolic effects of high-fructose corn syrup (HFCS), which is prevalent in Western diet, on the progression of GBM and another type of cancer (liver cancer) for comparison.

Biomimetically Mineralized DNA in ZIF-8 as a particulate carrier for Gene-gun Delivery of Genetic Material in Plants

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Biolistic transfection is becoming an increasingly popular method for incorporating DNA into cells that are otherwise difficult to transfect using traditional methods. This technique usually fires genetic material coated gold or tungsten “microparticles” which are microns in size directly into plant tissues using a pressurized gas. 1,2 These metal microparticles are efficient in gene transfection in cells but are expensive and has considerable cytotoxicity, thus limiting their potential day-to-day usefulness. Zeolitic imidazolate framework-8 (ZIF-8) is considered as the most ubiquitous Metal Organic Framework (MOF) using for biomimetic mineralization in drug delivery applications.3 It has proven that these plasmid DNA molecules are found to be well distributed inside ZIF-8 nanostructure and benefit from their protection against enzymatic degradation.4Our work will focus on investigation of DNA@ZIF-8 as a particulate carrier for gene gun gene delivery in plant gene transfection in place of metal microparticles.We will be investigating the gene transfection process in onion cells and intact plant leaves with the DNA@ZIF-8 nano and micron sized particles.

NMR Spectroscopic Study of Ethyl [1, 3-13C2] Acetoacetate Metabolism in Pancreatic Ductal Adenocarcinoma (PDAC) Cells

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Pancreatic Ductal Adenocarcinoma (PDA/PDAC) is among the most lethal of all cancer types, with approximately 48,000 new cases and 40,000 deaths annually in the United States. Tracking aberrant metabolism in cancer cells is one of the many applications of Nuclear Magnetic Resonance (NMR). Its high specificity and use of non-destructive RF waves are some reasons that we are using it in this study as a spectroscopic tool. The wide chemical shift dispersion of the 13C nucleus allows NMR spectral distinction of the specific metabolites or biochemical in cancer cells and tissues. In this study, we have investigated the metabolism of the amino acid [1, 3-13C2] ethyl acetoacetate in pancreatic ductal adenocarcinoma (PDAC). The NMR and biochemical properties of hyperpolarized Ethyl (1, 3-13C2) Acetoacetate were assessed to evaluate its potential as a hyperpolarized metabolic contrast agent. Ethyl (1, 3-13C2) acetoacetate is a liquid at room temperature. After being exposed to the magnetic field for about two hours [1, 3-13C2] ethyl acetoacetate, ample 13C signal was detectable, both for [1, 3-13C2] ethyl acetoacetate and its hydrolysis product [1, 3-13C2] acetoacetate. There are two picks for the labeled carbon atoms in the agent (EAA-C1, EAA-C3) (13C1 170.6, 13C3 208 ppm) and its product, metabolic product, is (1, 3-13C2) Acetoacetate (AA-C1, AA-C3) (13C1 175.5, 13C3 211.1 ppm). In the spectra, a small signal from 3-hydroxybutyrate (3-HB) could be detected. The much lower 3-HB product formation compared to AA is apparently due to a relatively lower activity of the ketogenic enzyme, 3-HB Dehydrogenase, which catalyzes the reversible reduction of keto-acids taking place in the mitochondria. Our results indicate that ethyl (1, 3-13C2) acetoacetate is metabolized quickly in PDAC cells thus it is a metabolic contrast agent that mainly reports on metabolism in vitro and could be a potential biomarker for early detection of PDAC.

Undergraduate Section

Entry	Time	Activity
Greetings	9:30 am – 9:40 am	***Dr. Ronald Smaldone***
01	9:45 am – 10:00 am	Raymond Wiliiam Brown
02	10:00 am – 10:15 am	Rohith Narra
03	10:15 am – 10:30 am	Yujin (Lisa) Kim
04	10:30 am – 10:45 am	Emily Boone Buchanan
Break	10:45 am – 10:55 am	***Intermission***
05	10:55 am – 11:10 am	Michelle K Bland
06	11:10 am – 11:25 am	Jacob Koehler Lynd
07	11:25 am – 11:40 am	Samantha Martin
08	11:40 am – 11:55 am	Andrew Duy Vu
09	11:55 am – 12:10 pm	Jonathan Coria
10	12:10 pm – 12:25 pm	
Break	12:25 pm – 1:00 pm	***Lunch Break***
11	1:00 pm – 1:15 pm	Abhinay Varma Adlooru
12	1:15 pm – 1:30 pm	Jongwook Mah
13	1:30 pm – 1:45 pm	Abigail Layne Lewis
14	1:45 pm – 2:00 pm	Lauren Quinn McCaghren (presented by Masoumeh Tajik Asl)
Break	2:00 pm – 2:10 pm	***Intermission***
15	2:10 pm – 2:25 pm	Maxwell Uddin Hyder
16	2:25 pm – 2:40 pm	Julie Nguyen
17	2:40 pm – 2:55 pm	Arun Kumar Raja
18	2:55 pm – 3:10 pm	Sindhoora Ponnam
19	3:10 pm – 3:25 pm	
20	3:25 pm – 3:40 pm	
Break	3:40 pm – 4:30 pm	***Break***
Awards Ceremony	4:30 pm – 5:00 pm	***Awards Ceremony***

For questions about scheduling for Undergraduate Section, e-mail:
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Removal of Escherichia Coli using plant-derived polysaccharides

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The research conducted focused on the capture of Escherichia coli (E. coli) coliform bacteria from contaminated sources. The research objective proposed for this study was the use of plant-based polysaccharide polymers in the place of synthetic polymers, using similar water treatment tests. The use of plant derived polysaccharides in flocculation using jar test method has shown some promising results in the coagulation of E. coli in river water. To conduct the experiments multiple doses & various kinds of polysaccharide polymers were sampled. Water was used from nearby rivers, and the Tarleton dairy lagoon and samples were collected within two hours prior to conducting experiments. To conduct the tests sample were tested against a standard at time intervals of 5 minutes, 15 minutes, 30 minutes, and 60 minutes after flocculation, in determination of proper timeframe for the polysaccharide to coagulate with the bacteria, and at which time frame has best percent capture. We are seeing results aa 2g/100ml polymer/D.I. water mixture. The best results have been seen at the 15-30-minute timeframe. For identification of the E. coli specimen the EPA 1603 modified mTEC method was utilized, as well as a new emerging method using photo spectrometry at a 600-nanometer wavelength. This technique can hopefully prove beneficial in identify & quantify the coliform bacteria, without killing the specimen directly. The Spectrophotometric method will be examined against the certified EPA 1603 mTEC method to test validity.

Computational Modeling of Interfaces in CsPbBr3 PeLEC

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I am working with my research advisor - Dr. Steven Nielsen - to utilize classical molecular dynamics simulations to model the LiPF6:PEO:CsPbBr3 composite material during the operation of a CsPbBr3 Light-Emitting Electrochemical Cell during device operation in order to gain insight from a theoretical standpoint of ion dynamics within the device to understand the physical phenomena underlying its operation. Once a bias is applied, there will be two different currents across the device – electronic current and ionic current. Specifically, we are modeling the device's ionic current which will help us understand how exactly the mobile ions (Li+, PF6-) are interacting with the perovskite (CsPbBr3) and polymer electrolyte (PEO) atoms. In my talk, I would like to provide a background about the system I am studying, define the goals of my project, explain what progress we have made since beginning the project in March 2020, and what next steps we are planning to take.

Using ELISA to detect levels of arginase activity in lungs

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In the lungs, nitric oxide plays a role in asthma, a chronic inflammatory disease of the airways. Nitric oxide is produced by activation of nitric oxide synthase (NOS), and NO exerts both beneficial and detrimental effects in the lungs. From previous studies on asthma, the beneficial effects of nitric oxide are greater than the detrimental effects, which indicates that asthma may be the condition due to a decrease in bioavailability of nitric oxide. The nitric oxide pathway in the lungs is highly complicated, and multiple endogenous and exogenous factors influence the production of NO. For NOS to be fully activated, one of the required substrates is arginine. Arginase and NOS compete for arginine as a common substrate. Therefore, high levels of arginase activity inhibit NOS and eventually cause NO deficiency in the lungs. Another factor that affects NO levels in the lungs is stress. Thomas Ritz's research lab performed an experiment on measuring exhaled nitric oxide in students during finals. With this study, he evaluated the relationship between exhaled nitric oxide and stress conditions in the body. The results showed that sustained stress over the final exam period caused a decrease in exhaled nitric oxide level, indicating low NOS activity. With this background information and previous studies, I am testing if low NOS activity in the condition of asthma and sustained stress is due to high activity of arginase. I use enzyme-linked immunosorbent assay (ELISA) technique to detect human arginase-1 in saliva samples from SMU students.

Hyperpolarized 15N NAD+/ NADH Mimetics as Redox- Active MRI Sensors

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Redox sensitive sensors are highly desirable for detection and assessment of a number of clinical conditions including hypoxic cancers, liver toxicity, and oxidative stress. The goal of this project was to develop 15N NMR probes that mimic the redox action of NAD+/NADH cofactor. We used hyperpolarized NMR technology (microwave driven dynamic nuclear polarization) to amplify the 15N NMR signal in order to facilitate the observation of this low sensitivity nucleus. As the hyperpolarized magnetization decays by T1 (spin-lattice) relaxation, the use of the 15N nucleus in hyperpolarized NMR/MRI is a promising due to its long T1 relaxation time. The oxidized form of the NAD+/NADH mimetic, [1-15N]-3-carbamoyl-1-methylpyridin-1-ium-iodide, was synthesized from 15N labeled nicotinamide as shown in the abstract figure. The compound was reduced with sodium dithionite to afford the reduced form, [1-15N]-3-carbamoyl-1,4-dihydro-1-methylpyridine. Conventional 15N NMR spectroscopy at 9.4 T revealed that there was a dramatic difference (124.2 ppm) between the 15N chemical shifts of the oxidized and reduced form. The oxidized form was hyperpolarized by dynamic nuclear polarization (DNP) in a commercially available clinical polarizer (SPINlab) using trityl OX063 free radical as polarizing agent followed by dissolution with superheated water. The hyperpolarized 15N signal was recorded at 1 T after dissolution. The decay of the hyperpolarized 15N magnetization afforded a spin-lattice (T1) relaxation time of 180 s at 1 T. The long T1 and the large chemical shift difference between the oxidized and reduced form suggest the viability of 15N labeled N-alkylated nicotinamide derivatives as 15N NMR redox sensors.

Novel synthesis of 2-(3H)oxazolones via fluoride-induced cyclization

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Oxazolones are five-membered heterocyclic compounds containing nitrogen and oxygen which display marked biological activity. Many are included in a wide variety of pharmaceuticals due to their antimicrobial and antifungal activities, among others. The high versatility of this class of compounds demands further methodological exploration for their preparation. Thus, a novel strategy for synthesis of 2-(3H)oxazolone from aldehydes is being developed using a fluoride source to induce cyclization of alkynyl carbamates to the heterocycle. Starting from 3-phenylpropionaldehyde, the propargyl alcohol was derived using an acetylenic Grignard reagent and was further subjected to an addition reaction using various isocyanates to furnish carbamate derivatives. Currently, optimization of carbamate cyclization is being investigated starting with tetrabutylammonium fluoride as the fluoride source by varying the equivalents, solvents, reaction times and temperature used, followed by exploration of alternative fluoride sources. From the results so far, the adduct has been obtained in high yields around 95% yield using a catalytic amount of fluoride source in a short reaction time.

Simulating Charge Separation in Organic Photovoltaics

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Charge separation is the process by which a tightly-bound electron and hole dissociate at a donor-acceptor interface in organic photovoltaics. Despite the strong coulombic binding between charges, which greatly exceeds thermal energy at room temperature, charge separation is both rapid and efficient in certain materials – a phenomenon that remains mechanistically controversial. Early-time delocalization of the electron (a “quantum-classical ratchet mechanism”) and the existence of an exponentially greater number of separated states than bound states in two and three-dimensional materials (a density of states gradient) have both been hypothesized to play a role in the unexplained kinetics and yield of charge separation. Confirming the roles of these phenomena is difficult, as any simulation involving both must account for a large number of states, quantum effects, and a complex thermal environment. The adaptive Hierarchy of Pure States (adHOPS), an ansatz for treating excited-state dynamics in large molecular aggregates that exhibits size-invariant scaling (i.e., O(1)), may prove capable of simulating the process. As a first step towards constructing these adHOPS simulations, we explore the importance of temperature-dependent vibrational modes (Matsubara modes) in a dimerized model system.

Arsenic (V) Removal via Plant-Based Polymers

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Arsenic is a contaminant found in water through both natural and anthropogenic sources. Anthropogenic inputs are largely due to agricultural and industrial processes. Natural inputs occur from weathering of geologic features. The Environmental Protection Agency (EPA) has set standards within the United States declaring water contaminated with 10 ppb of arsenic (As+5) as a health hazard. This research is set out to determine a natural plant-based polymer which removes As+5 at an economical and environmentally friendly concentration as an alternative to the widely used synthetic polyacrylamide. This study looks at polysaccharide polymers derived from Opuntia (cactus), Trigonella foenum-graecum (fenugreek), Abelmoschus esculentus (okra), psyllium hydrophilic mucilloid husks, sodium alginate, and Tamarindus indica L.(tamarind). The bridging mechanism proposed in this study utilizes London-dispersion. These forces allow As+5 to adsorb onto the polymer and work as a flocculant. The methodology employed involves the use of simulated and well water samples, incremental jar tests, HACH Arsenic Test Kit, Fourier-transform infrared spectroscopy (FTIR) and ion chromatography. Tamarind displayed the best percent removal (90%) with the lowest dose of 0.05g out of all the polymers tested including polyacrylamide. Further research efforts will continue to evaluate plant-based polymers as flocculants in the removal of As+5 at combined quantities and explore new arsenic determination methodologies.

Synthesis of Carbon Molecular Sieve Membranes with Organometallic Compounds to prevent Physical Aging

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Gas separation membranes are a highly attractive alternative to thermally driven processes like distillation which accounts for 10-15% of the world's energy consumption. This is because membrane separations have lower energy demands, lower costs, and higher scalability. Carbon molecular sieve membranes (CMSMs) represent a very promising development in the gas separation industry and are superior to traditional polymeric membranes and mixed matrix membranes (MMMs). CMSMs possess desired characteristics such as high selectivity, thermal stability, and chemical stability.

CMSMs are limited by the issue of physical aging where the carbon layers and pores structurally collapse over time. This in turn causes a loss in permeability and a gain in selectivity over time. This is not ideal because a constant permeability is desired when planning for scaled-up industrial applications. A potential solution to prevent physical aging in CMSMs is to introduce nanostructures throughout the CMSMs before the carbonization process. These solid structures will act as "pillars" that support the graphitic layers of the CMSM and prevent pore collapse. These pillars would allow CMSMs to maintain their high permeability and constant selectivity for longer periods of time, making them viable for large scale gas separation operations.

Our methods involve mixing a polymer precursor, divalent metal salt, and cyclic nitriles to create phthalocyanines to pillar the carbon layers. Once the CMSMs have been synthesized, the membranes will be put into a permeameter to test for gas.

Self-Diffusion of Nitrogen in 3-D Silicon Nitride

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Silicon nitride ceramics are highly sought after for their thermodynamic stability at high temperatures and their applications under harsh conditions. The chemistry of intergranular films (IGFs) between individual grains determines various properties of these ceramics including strength, toughness, and oxidation resistance. Through the use of molecular dynamic simulations, we are able to see the self-diffusion of Si and N in models of poly-crystalline Si_3N_4 at different temperatures. Five different potentials will be compared, each of which determine the strength of bonds between Si and N. The goal of these molecular dynamic simulations is to acquire a mean square displacement (MSD) and relate it to a diffusion coefficient D. By calculating the diffusion coefficient, we will be able to use its temperature dependency and find activation energies for the dominant migration processes. The activation energies for each of the five different potentials were extracted for the temperature ranges of 4000 K to 5000 K. Parameters we intend to change in the simulations over time are temperature, density of the silicon nitride, and bond strength potentials.

Photothermal Immunotherapy with Controlled Local Delivery of Checkpoint Inhibitors

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Tumor cells can evade an immune response by disabling T cells. To fight the tumor and prevent impairment of the T cell response, anti-CTLA-4 therapy as an immune checkpoint inhibitor can be administered. However, this therapy's effectiveness is limited by toxicity, low circulation time, and poor stability along with insufficient immunogenic cell death due to the lack of activated APCs and tumor-associated antigens in the tumor microenvironment. Therefore, a safe and selective formulation is needed to protect these molecules from the surrounding biological environment, prolong circulation half-time, and effectively deliver them to the tumor site while promoting immune cells into the tumor microenvironment.

A multiagent delivery vehicle based on a metal-organic framework (MOF) platform would be used for the concurrent delivery of a photostimulatory immunoadjuvant and an immunomodulator. Specifically, the anti-CTLA-4 drug would be implanted in a MOF called Zeolitic Imidazolate Frameworks-8 (ZIF-8). ZIF-8 allows for sustained release of the drug, and its surface would be decorated with a complex of the virus-like particle (VLP) Qβ and an NIR absorbing dye. VLPs, an immunogenic agent, can be recognized by the immune system as pathogen-associated molecular patterns and further trigger an immune response when irradiated with 808 nm light.

This combinational therapy has 3 methods of cancer ablation. Firstly, irradiating the tumor with NIR light induces apoptosis in the cancer cells. Furthermore, ZIF-8 dissociates when irradiated, releasing the anti-CTLA-4 drug into the tumor microenvironment. The drug then blocks the CTLA-4 receptor, prevents downregulation of the immune response, and allows T cells to kill cancer cells. Finally, the ZIF-8 platform allows for gradual release of the drug, which enhances the drug's efficacy and minimizes the chance of autoimmunity.

The combinational system, VLP, anti-CTLA-4@ZIF-8, and PBS will be injected intratumorally into 4 different groups of mice. After monitoring tumor volume over time, we expect to see high suppression of tumor growth in mice with the combinational system compared to other groups. It is also expected that the mice injected with the combinational system would show significant metastasis inhibition and a longer survival time compared to the other groups.

Investigation of PAN:PAA Binary Polymer Blend Porous Activated Carbon

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Supercapacitors have carved out a place in the energy industry over the years by providing strong advantages over conventional energy storage methods such as Li-ion batteries. Supercapacitors, compared to traditional energy storage devices, provide high power density, quick charge-discharge times, high longevity, as well as the potential to be much more environmentally friendly. An area of improvement for supercapacitors is in their energy density. To address this, activated carbons can be used as electrode material in supercapacitors. Their porous structure and surface area can be tailored to increase the overall energy density. The tailoring of the porous structure can be done by adding a pyrolyzing polymer to a carbonizing polymer to obtain specific morphology and increased surface area in the activated product. These porous activated carbons are prepared by electrospinning polyacrylonitrile (PAN) and poly(acrylic acid) (PAA) blends in various concentrations and activated under CO2 to increase surface area. PAN is a well-researched carbon precursor while PAA is used as a sacrificial polymer. PAN:PAA blends have a small solubility parameter difference resulting in small dispersed phases compared to blends such as PAN:PMMA or PAN:PS which form large pores and channels. When activated, these materials can achieve high surface areas which improve energy density in supercapacitors. The activated materials were characterized with spectroscopic and electrochemical techniques to determine their capabilities for energy storage devices.

Holmium Hexaclusters in Metal-Organic Frameworks for Cancer Therapy

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Metal-organic frameworks are crystalline structures that possess high surface area, stability, and porosity. In particular, lanthanide-based metal-organic frameworks are of increasing interest in research due to their high coordination numbers. This allows for the presence of open metal sites in the structures, since the metal centers bind to both the organic linker and the solvent, which can be removed. The lanthanide, Holmium (Ho), has unique characteristics as it is an element that can be neutron activated; the 100% naturally abundant holmium-165 isotope is converted to radioactive isotope holmium-166 (166Ho). 166Ho emits γ photons and β- particles, and the β- particles have the potential to damage the DNA of cancer cells, showing promise in applications for radiation therapy. With the addition of holmium as the metal center, the properties of MOFs along with the benefits of neutron-activated holmium demonstrate potential in applications of cancer treatment.

The research to be presented focuses on a novel hexacluster Holmium-based metal-organic framework (Ho-MOF). A preliminary single crystal structure was obtained. Analysis was performed on the framework through infrared spectroscopy, powder x-ray diffraction, thermogravimetric analysis, and surface area analysis. These findings support that the structure synthesized has the desired properties and shows promise in cancer treatment.

Pillaring Effect on Porous Carbon Molecular Sieve Membranes

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Research in Carbon Molecular Sieve Membranes (CMSM) has been expanding over the past few years. While various types of membranes have been made and tested, a common issue that still plagues researchers is the aging and subsequent decrease in their efficacy due to pore collapse and plasticization. In order to make CMSMs more commercially viable, research into anti-aging strategies is being conducted. A recent approach is pillaring the CMSM through the incorporation of metal nanoparticles to prevent pore collapse. Pillaring is based around the idea that if there is a way to support the pores and keep them from fully collapsing, the useful life of the membrane could be greatly expanded. Current research into creating this pillaring effect is centered around using small metal particles with sizes based on the approximate pore size of CMSM. Since the metal supports are of a similar size, as the membrane ages and the pores begin to collapse, the metal particles keep the pores open to almost the same size as they were originally. In this study, the effect of using MOP-18 as a pillaring agent in porous CMSM obtained from the carbonization of BTDA-BAF polymer has been investigated.

Transformation of a Novel 1-D Polymer

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Metal organic frameworks, MOFs, are porous crystalline materials formed from metal ions and organic linkers. They're a fairly recent class of compounds, having been discovered in the late 1990s. These materials has drawn immense interest due to their highly adaptable nature. The interchangeability of the metal centers and linkers allows for many different properties and applications. MOFs have high porosity, turnability, and versatility. Thus, these complexes are known for their uses in gas separation, gas capture, catalysis, sensors, and their intrinsic magnetic properties. The addition of different types of metals further diversifies their topographies, structures, chemical and magnetic properties.

Difficulties with synthesizing mixed metal MOFs occurs due to inherent issues with combining different metals with different reactivities within the MOF. This can be solved by reacting a 1-D homometallic polymer with additional metals and linkers, expanding to a 3-D framework. This can occur with a process known as a Facile Single Crystal to single Crystal Transformation, SCSC, which alters the molecular structure without losing crystallinity.

In this research, a novel 1-D copper polymer (Compound 1) was synthesized. This incorporated the linker 4-(3-pyridine)benzoic acid and copper ions. This research focuses on the transformation of this novel polymer, 1, from a 1-D polymer into a 3-D MOF. It is by this transformation we are attempting the addition of the either metal, gadolinium or holmium, and linkers such as isonicotinic acid. This would transform the Cu 4-3 pbz polymer into a Mixed Metal MOF. We have characterized the structure using single crystal X-ray diffraction and scanning election microscopy. The thermal stability was characterized through the use of thermogravimetric analysis and powder X-ray diffraction.

Iron Nanoparticles for Cancer Therapy

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One of the most commonly used methods of cancer therapy is radiation, but it is a long process that produces many harmful side effects. Our research is focused on a possible new method of cancer therapy using Holmium Metal-Organic Frameworks (Ho-MOFs) with encapsulated magnetic iron nanoparticles. With the presence of a magnetic core, the radiation from the Ho-MOF can be localized to the tumor site using an external magnetic field.

To accomplish this, our first step is modifying the surface of the iron nanoparticles to allow them to bind with the Ho-MOF itself. FTIR was taken before and after modification to confirm the presence of carboxylic acid groups on the iron nanoparticle surface.

Our next step is to encapsulate the modified iron nanoparticles inside of the Ho-MOF. This is done by combining a Holmium salt, the organic linker, and the nanoparticles together in a solvothermal reaction with DMF solvent. In the reaction, the Holmium ions bind to the surface of the nanoparticles and subsequent reaction with the linker leads to the MOF growing around the magnetic core. TEM along with other characterization methods will be used to confirm the encapsulation.

Encapsulation of Ovalbumin in Zeolitic Imidazolate Framework 8 Enhances Antibody Production and Overcomes Need for Booster Dose

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One of the main problems facing vaccines today is that they require multiple visits to the doctor's office for booster doses in order to maintain prolonged immunity. Booster doses serve to re-expose the immune system to an immunizing antigen after memory of that antigen has declined over time. In this project we wanted to encapsulate the common antigen ovalbumin in the ZIF 8 metal organic framework to provide a sustained release system and test the immunogenicity in order to see whether it overcomes the need for a booster dose. To start off, we encapsulated Cy7 labeled Ovalbumin in ZIF 8 using HMIM and Zinc. The resulting crystals were characterized by SEM to confirm ZIF-8 formation and the fluorescence of the supernatant was measured to determine the encapsulation efficiency of ovalbumin (>90%). Both Cy7-Ova and Cy7-Ova@ZIF were injected into mice and fluorescence was monitored over the course of a month where it was found that encapsulation of ovalbumin in ZIF extended the tissue residency from 7 to 28 days. After confirming the ability of ZIF-8 to provide a sustained release system, mice were given either 3 injections of Ova or a single injection of Ova@ZIF. Using an ELISA and serum collected from the mice at various time points, we determined that one injection of Ova@ZIF produced equal to higher levels of antibodies than 3 OVA injections.

In conclusion, the encapsulation of ovalbumin in ZIF 8 enhances the production of antibodies through a sustained release of antigen, leading to a strengthened humoral immunity, and ultimately overcoming the need for a booster dose.

Immunotherapy Against Tumor Growth Through the Injection of Metal-Organic Framework Encapsulated Tumor Cell Lysates

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Immunotherapy against tumor growth as a potential cancer vaccine is an effective solution in need of new solution developments. A potential antitumor cancer vaccine would be injecting lysed tumor cells as antigens into the tissues of the body, however, this method is normally ineffective for various reasons such as the injected lysed tumor cells could be attacked and degraded by the immune system, the release of lysed tumor cells into the tissues could be too quick and the body's immune system response may not be great enough for a positive effect to occur, or inflammation of the tissues could occur. However, injecting tumor cell lysates in a biocompatible capsule, or in this case, a metal-organic framework could be potentially effective immunotherapy against tumor growth which is the study we are conducting. Immunotherapy against tumor growth through the injection of metal-organic framework encapsulated tumor cell lysates could be a promising cancer vaccine.

The biocompatible capsule we will work with is a metal-organic framework called ZIF-8. ZIF-8 will be generated from the amalgamation of 3M HMIM and 1M Zinc Acetate. Tumor cell lysates, the proteins that are cancer markers and do not have the ability to proliferate, will be obtained from the B16F10 Melanoma cancer cell line. The vaccination groups of mice for the study would be those injected with PBS (Phosphate Buffer Saline), only the tumor cell lysates, only the ZIF-8, and the ZIF-8 encapsulated tumor cell lysates. The methodology of this procedure includes the generation, isolation, and characterization of tumor cell lysates, the preparation and characterization of the ZIF-8 encapsulation of tumor cell lysates, the analysis of the ZIF-8 encapsulated tumor cell lysate release after injection, and the immunization and tumor challenge.

The anticipated results of injecting ZIF-8 encapsulated tumor cell lysates would be: ZIF-8 would not be recognized by the immune system as an antigen, ZIF-8 would be slowly degraded by the body and dissolved into the body's tissues, and there would be sustained-release dosage of the tumor cell lysates as antigens, which could elicit a better response from the body's immune system. If the vaccination of mice through the injection of metal-organic framework encapsulated tumor cell lysates works and the mice are challenged with live cancer cells, the tumor should not grow. Memory T-cells should recognize the tumor cell lysates as antigens, triggering an immune response against the cancerous tumor due to the antitumor vaccine-like therapeutics.