ACS Local Section
Dallas-Fort Worth

54th Meeting-in-Miniature

Saturday, April 23rd, 2022

Technical Program
and
Abstract Booklet

Organized by
The Department of Chemistry and Biochemistry

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ACS Applied Materials & Interfaces

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Program Schedule

8:30a – 8:40a	Greetings by Dr. Mihaela Stefan & Dr. Gabriele Meloni (SCI 1.220)
8:40a – 9:25a	Keynote speaker (SCI 1.220)
9:25a – 9:40a	Break
9:40a – 12:15p	Presentations (Morning sections)
12:15p – 1:45p	Lunch Break
1:45p – 4:00p	Presentations (Afternoon sections)
4:00p – 4:30p	Break
4:30p – 5:00p	Awards Ceremony (SCI 1.220)

Technical Support

All of the presentations will be occurring in the Sciences Building, and lunch will be provided in Dining Hall West, both of which have been highlighted on the following map(s).

Additionally, free parking is available in Green parking spots, which can be found on the roof of the parking structures or in Lot T, highlighted on the following map.

Free Lunch at Dining Hall West (on campus). The tickets will be distributed after the morning sections before lunch.


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University

1st Floor
Sciences Building

2nd Floor
Sciences Building

3rd Floor
Sciences Building

Presentation Rooms

SCI 1.210—Physical/Computational section

SCI 1.220—Biochemistry/Biological Chemistry section

SCI 2.210—Inorganic/Analytical Chemistry

SCI 2.215—Organic Chemistry

SCI 2.225—Materials Chemistry

SCI 2.230—Polymer Chemistry (Morning)/ Undergraduate Section II (Afternoon)

SCI 2.235—Undergraduate Section I

SCI 3.230—Preparation room

Plenary Speaker

Dr. Kirk Schanze

Professor

Robert A. Welch Distinguished University Chair in Chemistry at UT San Antonio,

Editor in Chief for ACS Applied Materials and Interfaces.

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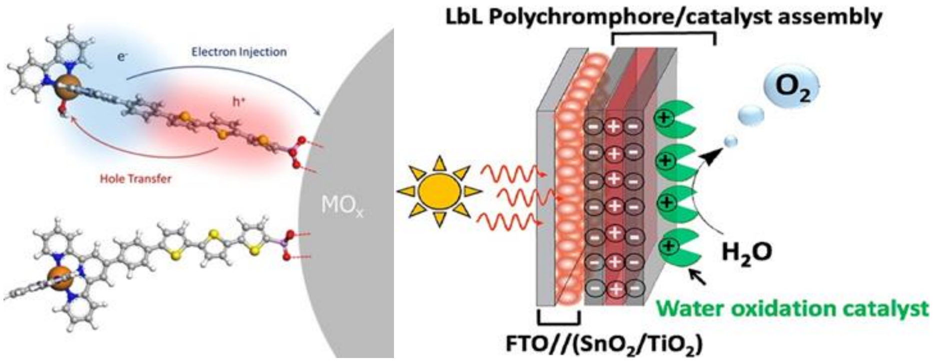
Title: Chromophore-Catalyst Assemblies for Solar Fuels

Abstract: The dye-sensitized photoelectrochemical cell (DSPEC) represents a novel approach to combining molecular chromophores and catalysts with semiconductors to effect light driven production of solar fuels. A multidisciplinary approach has been used to develop and study molecular and polymer assemblies for light driven water oxidation at a DSPEC photoanode and proton reduction at a photocathode. The work aims to understand mechanisms and dynamics for the photoprocesses occurring at the molecular/semiconductor interfaces. The talk will present an overview of work done during the past several years, involving the design, construction and study of molecular and polymer-based assemblies of light absorbing chromophores and catalysts, primarily aimed at water oxidation at the DSPEC anode.



Biochemistry/Biological Chemistry Section

SCI 1.220—Biochemistry/Biological Chemistry section

Entry	Time	Activity
Greetings	**9:40 am – 9:45 am**	***Greetings***
01	9:45 am – 10:00 am	Mitchell Pope
02	10:00 am – 10:15 am	Darby Ball
03	10:15 am – 10:30 am	Jenica Lumata
04	10:30 am – 10:45 am	John Michael Bustamante Tubije
Break	**10:45 am – 11:00 am**	***Intermission***
05	11:00 am – 11:15 am	Oladimeji Sunday Olaluwoye
06	11:15 am – 11:30 am	Ryanne Nicole Ehrman
07	11:30 am – 11:45 am	Daniel Lee Anable
08	11:45 am – 12:00 pm	Yalini Hansika Wijesundara
09	12:00 pm – 12:15 pm	Sydney Michael Schoellhorn
Break	**12:15 pm – 1:45 pm**	***Lunch Break***
10	1:45 pm – 2:00 pm	Jayoh Amurao Hernandez
11	2:00 pm – 2:15 pm	Asiye Asaadzade
12	2:15 pm – 2:30 pm	Weicheng Peng
13	2:30 pm – 2:45 pm	Fabian Castro
Break	**2:45 pm – 3:00 pm**	***Intermission***
14	3:00 pm – 3:15 pm	Cody Larsen
15	3:15 pm – 3:30 pm	Dr. Priyanka Basak
16	3:30 pm – 3:45 pm	Sneha Kumari
17	3:45 pm – 4:00 pm	Alexis Antoinette Ann Delgado
Break	**4:00 pm – 4:30 pm**	***Break***
Awards Ceremony	**4:30 pm – 5:00 pm**	***Awards Ceremony (SCI 1.220)***

For questions about scheduling for Biochemistry/Biological Chemistry Section, e-mail: Mitchell Pope Mitchell.Pope@utdallas.edu

Identification and Characterization of a Novel Human Transmembrane Cu(I) Binding Protein, hTMEM52B

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Transition metals are essential trace elements in all kingdoms of life, acting as structural centers in metalloproteins (e.g.: zinc fingers), as enzyme cofactors (e.g.: Cytochrome C Oxidase), or signaling ions (e.g.: zinc and copper in neurons). Among essential metals, copper plays critical roles in biochemical processes in light of its redox properties, thus efficiently catalyzing chemical reactions other chemical elements cannot. Despite the small amounts of copper present in the body (~100 mg total copper) copper homeostasis dysregulation results in severe pathologies, such as Menkes and Wilson's disease, and necessitates strict regulation of free metal ion concentration. Furthermore, the metabolic pathways associated with uptake, sequestration, and efflux of copper are poorly understood and incompletely characterized. hTMEM52B, an uncharacterized orphan transmembrane protein, was identified as a potential Cu(I) binding protein, due to the high content of traditionally Cu(I) coordinating amino acids (cysteine and methionine) and potential copper-binding motifs, thus representing a potentially uncharacterized piece of Cu(I) metabolism. A recombinant expression system was developed to express and purify hTMEM52B, in E. coli, for subsequent characterization by biochemical and biophysical techniques. Electronic absorption spectroscopy and ligand-metal charge transfer (LMCT) analysis were used to characterize Cu(I) binding to sulfur-containing amino acids (cysteine and methionine). The affinity of hTMEM52B for Cu(I) was then determined by competition experiments with spectrophotometric Cu(I) binding probes of known affinity and hTMEM52B. These results confirm that hTMEM52B is in fact a novel Cu(I)-binding membrane protein and highlights the need for further exploration of other "orphan" metal-binding proteins.

Dynamics and Interfaces of Core Histones and the Nucleosome

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The basic organizational unit of chromatin is the nucleosome, containing 146 bp of DNA wrapped around an octamer composed of two copies of histone H2A, H2B, H3 and H4. The stability of histone complexes is regulated in vivo by chaperones and/or extensive interactions with DNA. This can be mimicked in vitro using salt concentration. Despite the availability of histone and nucleosome structures, it is unclear how various factors regulate nucleosome assembly and disassembly. We developed a high-throughput, solution-based assay for measuring histone and nucleosome dynamics using hydrogen-deuterium exchange coupled to mass spectrometry (HDX-MS). The assay is a platform for an array of future experiments on chromatin and its regulatory factors. We include data on histones, nucleosome intermediates, and the mono-nucleosome. A protocol was developed for the efficient removal of DNA after labelling to enable HDX experiments on the nucleosome and its assembly intermediates. Analysis of the core histones across a range of salt concentrations demonstrated reliance on ionic strength for the stability of hetero-dimer interactions. Comparative experiments were performed with the linker histone H1 and myoglobin to demonstrate which behaviors were unique to the core histones. The interfaces of the histone octamer can be identified and compared by HDX, with additional protection from deuterium exchange by the histone octamer under conditions favoring octamer stability. Analysis of the tetrasome, a nucleosome intermediate, yielded novel insight on its solution conformation and stability. This work demonstrates the utility of our workflow for quantifying the dynamics and interfaces in nucleosomes and their intermediates.

TEMPO-Modified TMV as an MRI Contrast Agent for in vivo Superoxide Production

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The overproduction of reactive oxygen species (ROS) — such as the superoxide $O_2^{\bullet -}$ — is a sign of pathological disturbance. Studies have shown that REDOX-active nitroxide radicals can be used as a Magnetic resonance imaging (MRI) contrast agent to detect $O_2^{\bullet -}$. The MRI-inactive reduced form of nitroxide is oxidized by the $O_2^{\bullet -}$ into MRI-active nitroxide radical. However, the nitroxides have low relaxivity; hence low MRI signal. Previous studies from our group have shown that the relaxivity of nitroxide radicals, specifically TEMPO, has increased by 4-5 orders of magnitude after attaching to the exterior surface of Tobacco Mosaic Virus (TMV) via a copper-catalyzed click reaction. TMV is noninfectious in humans, thermostable, and biocompatible, making it very amenable as an in vivo agent. The improvement in relaxivity is largely based on two points: First, there is a very high concentration of TEMPO attached per TMV rod due to over 2000 functionalizable coat proteins in TMV. Second, the large, rigid, rod-like structure of the TMV leads to a slower rotational dynamic in solution, which helps increase the relaxivity. Our goal is to investigate the efficiency of TEMPO-TMV MRI probe in detecting $O_2^{\bullet -}$ in vivo. We determined the relaxivity to be 2.67 $mM^{-1}s^{-1}$, which is several-fold higher than the reported relaxivity of free TEMPO. We were also interested in how long it takes for the agent to oxidize. Since the agent is originally in oxidized form, we reduced it with sodium ascorbate and subsequently added potassium superoxide, after which the oxidation was monitored through electron paramagnetic resonance (EPR) spectroscopy for 1.5 hrs. EPR detects molecules with unpaired electrons like nitroxides. The initial rate constant, k', was found to be at 1.8×10^{-2} s^{-1}, which is very fast, and fast enough to detect superoxide in living tissue. In preparation for in vivo study, Lactate dehydrogenase or LDH assay was performed to determine whether the agent is cytotoxic. At 2 mg/mL TMV-TEMPO, the cell viability is almost 100% even after a 24h co-incubation. The next step is to study our sensor in vivo in a murine model that mimics oxidative injury using lipopolysaccharide or LPS-induced superoxide.

Investigation of the Pentose Phosphate Pathway in A549 Lung Cancer Cells using 13C-Ribose NMR Tracer

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The Hexose monophosphate shunt, commonly known as the Pentose Phosphate Pathway (PPP), is a metabolic pathway parallel to glycolysis. In the non-oxidative reversible phase of PPP, ribulose 5-phosphate can be isomerized into ribose 5-phosphate depending on the needs of the cell. Ribose 5-phosphate can be further converted into fructose 6-phosphate which is an intermediate in the production of ATP in the glycolytic pathway. In this study, ^{13}C-ribose was used a tracer to investigate the viability of ribose as an alternative energy source for A549 lung cancer cells using nuclear magnetic resonance (NMR) spectroscopy. Initial NMR results indicate that in the presence of glucose in the cell culture media, ^{13}C-ribose was metabolized into lactate. NMR data and results will be presented here in detail.

The Effect of Glycerol on WNK Kinase Activation

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Kinase domains are known to adopt active and inactive conformations and the switch between these conformations can be regulated by various factors. For WNK kinases, this switch is pressure and pressure may be mimicked in vitro by glycerol in solution. Here we set out to identify the molecular details of WNK kinase activation by performing hydrogen/deuterium exchange coupled to mass spectrometry in the presence of glycerol. We set out to do this for WNK1 and WNK3 kinase domains that have high sequence and structural similarity. Understanding the WNK molecular switch will facilitate the development of therapeutics as these kinases are involved in hypertension. This work led us to further investigate the impact of glycerol in a hydrogen/deuterium exchange experiment. To quantify the impact of glycerol on the intrinsic rate of hydrogen/deuterium exchange we performed an array of experiments using peptide standards Glu Fibrinopeptide, Leucine-Enkephalin, and Angiotensin II. We monitored the impact of various glycerol or D-glycerol concentrations at several pH values and time points of deuteration. We further monitored the impact of glycerol on the hydrogen/deuterium exchange of the kinase domains of WNK1 and WNK3. We quantified the effect of glycerol on the intrinsic rate of hydrogen/deuterium exchange using standard peptides as a model system. Under conditions of maximum deuterium uptake, glycerol seems to not participate in the exchange, but rather to increase the effective concentration of deuterium. Under conditions of sub-maximal exchange, the effect is more subtle and difficult to quantify at such low deuterium incorporation. Based on these results, we identify regions of WNK1 and WNK3 that are influenced by glycerol.

Exploiting the Protein Corona Through Photothermal Heating for Enhanced Cancer Therapeutics by Creating an *in situ* Cancer Vaccine

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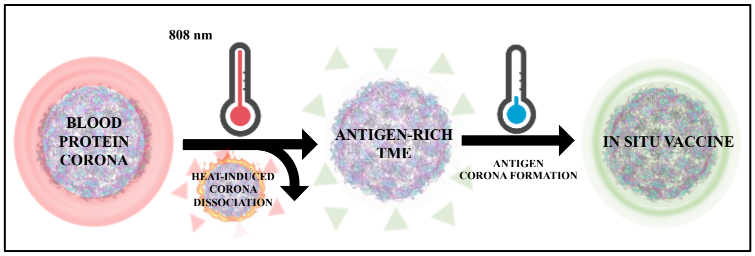
Traditional treatments against metastatic cancer—e.g. chemotherapy, radiotherapy, and surgery—are typical first line treatments in clinical settings; however, treatment efficacy, refractory, and post treatment side effects are major challenges in the oncology field. Immunotherapy has entered clinical space to treat metastatic disease, but response rates have been low, as many cancers are immunologically cold. Emerging cancer therapies, such as photothermal therapy (PTT) are promising as an approach to treat tumor sites, but they're not well suited for metastatic disease. PTT takes advantage of the increased heat-sensitivity of cancer cells by employing a photothermal agent (PTA) to locally convert light to heat upon near-IR irradiation. We have recently shown that a PTT agent, created from a non-infectious recombinant virus-like particle (VLP), not only ablates local tumors, but also can initiate a modest immunological response and reduce metastatic burden. I hypothesize that this modest reduction can be significantly enhanced through selective chemical modification to our nanoparticle system. Specifically, my research object is to create an anti-cancer vaccine in situ by taking advantage of protein-nanoparticle interactions that occur when a material undergoes a cycle of heating and cooling. When nanoparticles enter the body, especially the bloodstream, they interact with available proteins forming a nanoparticle-protein complex called 'protein corona'. Serum proteins electrostatically adhere to nanoparticle surfaces, which can significantly alter their therapeutic efficacy in vitro and in vivo. Common blood proteins—albumin, globulins, and fibrinogen—form the most notable coronas owing to their high concentration in blood. These protein–



nanoparticle interactions are known to be temperature-dependent; therefore, by increasing the temperature of the system, coronal proteins will dissociate from the surface of the nanoparticle. I hypothesize that coronal proteins formed in the blood can be exchanged with tumor neoantigens following photothermal heating within the tumor. This system is based upon Le Chatlier equilibrium—blood proteins are in low concentration in the tumor microenvironment (TME), whereas neoantigens are in high concentration following photothermal ablation. Upon TME cooling, neoantigen corona formation will dominant forming the *in situ* vaccine. Here, I will optimize the VLP surface coating to preferentially bind tumor neoantigens while maintaining high photothermal efficiencies. I will use calorimetry and surface plasmon resonance techniques to identify optimal surface coatings that will enable a high-yielding exchange of corona in the complex tumor environment. I will then incorporate this into 4T1 and MC38 murine models. I will show that serum protein-neoantigen exchange elicits an anti-cancer immune response.

Altered Metabolism in Cancers Cells under Hypoxic Conditions

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Hypoxia is a physiological condition, that is detrimental to normal cells, in which there is a lack of oxygen. Cancer cells however thrive even under hypoxic conditions. In this study, we have investigated the effects of total hypoxia (0% O2) and partial hypoxia (5% O2) vis-`a-vis normoxia (20% O2, normal oxygen conditions) on the metabolism of glucose in colo-205 colorectal cancer cells in vitro. In preliminary trials with two modular hypoxia chambers gassed with pure nitrogen gas and a 5% O2, 6% CO2, 89% nitrogen mixed gas, we found a significant increase in lactate production at total hypoxia and a near negligible change at partial hypoxia. After 24 hours, the total hypoxia cells have nearly consumed all glucose and by 48 hours in the incubator, all glucose has been consumed which led to significant and consistent cell death, while the other two have an equivalent consumption rate. These preliminary NMR results will be discussed together with other supporting data

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Carrier Gas Triggered Controlled Biolistic Delivery of DNA and Protein Therapeutics with ZIF-8

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Biolistic delivery—physically shooting DNA and protein therapeutics loaded onto a metal microparticle directly into a cell—is an established method for introducing genetic materials into cells that are otherwise difficult to transfect using traditional methods and to deliver other protein therapeutics directly into the targeted tissue. Commercial gene guns and the gold or tungsten microparticle “bullets” that carry the DNA and protein into the cells are expensive. Furthermore, there are concerns about their cytotoxicity, biopersistence, and potential for DNA degradation with the genetic material placed on the metal microparticle surface. We have developed an approach that biomimetically encapsulates DNA in Zeolitic Imidazolate Framework-8 (ZIF-8) as an efficient and stable gene carrier that can be used with a low-cost gas-powered “MOF-Gun” for direct delivery into living tissues of plants and animals. ZIF-8 is more economical, biodegradable, and affords protection to the DNA and sensitive proteins against degradation compared to metal microparticles. By using CO2 as a reactive carrier gas in the MOF-Gun system, we can cause a rapid local pH drop in the cell, dissolving of the ZIF-8, and subsequently releasing the DNA and encapsulated therapeutics in a controlled manner with respect to the amount of CO2 used for the delivery which otherwise has no control over the release profile of the therapeutic molecules with current biolistic delivery method with Helium gas powered gene gun. This innovation represents the first example of biolistic-mediated controlled delivery of biomolecules with ZIF-8 and provides a powerful tool for both fundamental and applied research of plant and animal sciences.

Examining the Viability of *Sarocladium zeae* to be used as Biocontrol Agent in Agricultural Production of Maize

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In the United States, agriculture remains a major contributor to the economy. Of all crops cultivated in the US, maize is the largest economic agricultural product – not only does corn make up a majority of feed grain content, but the US alone provides about one third of the global corn supply. As with all agricultural products, great consideration must be given to appropriate biocontrol agents that may protect the crop from exogenous threats while remaining safe for human and animal consumption. Some such exogenous threats to maize specifically are fungal pathogens such as *Aspergillus flavus* and *Fusarium verticillioides*. *A. flavus* and *F. verticillioides* are known to be major producers of aflatoxins and fumonisin, respectively. Pyrrocidines A and B, which have been found to selectively protect against these mycotoxins, were isolated from in vitro studies on *Sarocladium zeae*. This level of selectivity increased the interest in the possibility of using *S. zeae* as a biocontrol agent over the less specific, but currently commercially available fungicide, nystatin. When sequenced by a research group at UCLA, biosynthetic pathways for Pyrrocidines A and B within *S. zeae* were explored, but the remainder of the biosynthetic gene clusters (BGCs) were left unexplored. Hence, it is necessary to screen all possible metabolites produced by the remaining BGCs for potential toxicity to animals, including humans, to examine the viability of *S. zeae* for use as a biocontrol agent in corn cultivation. As mimicking every theoretical set of growth conditions to determine all possible metabolites is nonviable, instead genes will be over-expressed by DNA manipulation to increase their activity and, thus, generate higher concentrations of their natural products. Identification of these resulting metabolites may then be performed to evaluate any possible toxins.

Substrate Selectivity and Translocation Mechanism of NixA, A Nickel Transporter of the NiCoT family from *Helicobacter pylori*

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Nickel is essential for the survival and virulence of several pathogenic bacteria in humans including *Helicobacter pylori* (*H. pylori*), a pathogen that continues to be the main cause of gastric ulcers. To survive the harsh acidic conditions present in the human stomach, *H. pylori* utilizes Ni(II) as a metal cofactor that activates the enzyme urease. This enzyme catalyzes the hydrolysis of urea and ultimately releases ammonia and bicarbonate which are involved in creating a buffered environment that allow *H. pylori* to tolerate the acidic environment of the stomach. As regulation of Ni(II) homeostasis inside the cell proves to be a vital process for the growth and pathogenicity of *H. pylori*, unique transmembrane (TM) transporters that permit the selective translocation of Ni(II) across the cellular membranes evolved to control cellular Ni(II) uptake and efflux. NixA is a prominent Ni(II) transporter expressed by *H. pylori* when the bacteria experiences a drastic drop in pH in the extracellular environment. NixA is a Class I Nickel-Cobalt transporter (NiCoT) that strictly allows the transport of Ni(II) across lipid bilayers. In this study, we characterized NixA by using a platform where recombinantly expressed and purified NixA in detergent micelles could be reconstituted in artificial lipid bilayer vesicles (proteoliposomes). Several fluorescent sensors responsive to diverse stimuli (Fluozin-3-Zn(II), pyranine, and oxonol-VI were then encapsulated in the proteoliposomes to monitor in vitro real-time Ni(II) transport, lumenal pH changes and membrane potential, respectively. Kinetic transport assay analysis revealed that NixA is highly selective for Ni(II) and showed low substrate promiscuity towards other metal ion substrates of the NiCoT family. We also provided evidence that Ni(II) transport by NixA did not require proton counter-transport, thus generating a membrane potential inside the proteoliposome lumen and indicating that substrate transport is electrogenic. Mutational studies revealed that the conserved motifs at TM II (HAF/VDADHI/L) and TM III (G(Xaa)5GHSVV) were responsible and

essential for substrate recognition, selectivity, and transport. Overall, this work provides an approach to characterize these novel types of transporters responsible for Ni(II) acquisition in prokaryotes.

13C NMR Spectroscopic Studies of the Metabolism of 2-deoxy-d-glucose (2-DG) and its Effects on Glycolysis in Cancer Cells

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2-Deoxy-D-Glucose (2-DG), a glucose analogue inhibits glycolysis and induce cell death due to formation and intracellular accumulation of 2-deoxy-d-glucose-6-phosphate (2-DG6P), inhibiting the function of hexokinase and Glucose-6-phosphate isomerase. In this work, we have investigated via carbon-13 nuclear magnetic resonance the concentration dependence of 2DG on [U-13C] glucose metabolism in a variety of cancers including renal cell carcinoma (Caki-1, A498, and 786-O), breast cancer (MCF-7), and glioblastoma (SfXL cells). Our results reveal that even highest concentration of 2DG minimally affect lactate production however other glucose metabolites in these cancer cell lines e.g. glutamate and acetate have been altered. Intra- and extra-cellular metabolic products of glucose metabolism will be discussed in light of the metabolic vulnerability of the key glutamine metabolic enzymes to certain inhibitors.

Discovery, Characterization, and Cellular Application of a Monomeric Green Fluorescent Protein Sensor for Chloride

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Chloride is the most abundant physiological anion and is found in all living systems. Intracellular chloride concentrations are regulated by chloride channels to control cellular processes such as cell volume, pH regulation, cell division, epithelial fluid absorption and secretion, muscle contraction, and neuroexcitation. To study chloride in these biological contexts, the green fluorescent protein (GFP) derived from the jellyfish *Aequorea victoria* has been identified and extensively engineered as a chloride sensor. Beyond this starting point, limited advances have been made in the last two decades. Here, we introduce a structure-guided bioinformatic approach to mine the existing natural and engineered GFP sequences for the identification of new chloride-sensitive fluorescent proteins. For our goal, this approach affords unique starting points to engineering functional imaging tools. To this end, in this presentation, I will describe the discovery, characterization, and cellular application of a monomeric, turn-off fluorescent protein sensor for chloride.

Engineered Proteinaceous Materials: Applications in Vaccine Development

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The increasing rate of resistance of bacterial infection against antibiotics requires next generation approaches to fight potential pandemic spread. The development of vaccines against pathogenic bacteria has been difficult owing, in part, to the genetic diversity of bacteria. Hence, there are many potential target antigens and little a priori knowledge of which antigen/s will elicit protective immunity. The painstaking process of selecting appropriate antigens could be avoided with whole-cell bacteria; however, whole-cell formulations typically fail to produce long-term and durable immune responses. These complications are one reason why no vaccine against any type of pathogenic *E. coli* has been successfully clinically translated. As a proof of principle, we demonstrate a method to enhance the immunogenicity of a model pathogenic E. coli strain by forming a slow releasing depot. The *E. coli* strain CFT073 was biomimetically mineralized within a metal−organic framework (MOF). This process encapsulates the bacteria within 30 min in water and at ambient temperatures. Vaccination with this formulation substantially enhances antibody production and results in significantly enhanced survival in a mouse model of bacteremia compared to standard inactivated formulations.

Tracking The Effects of Lithium on the Glycolytic Pathway of Neuroblastoma Cells Using 13C NMR Spectroscopy

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Neuroblastoma is a childhood cancer typically found around the adrenal glands that impacts early nerve cells. Previous work performed upon patients with neurological ailments has found that phosphofructokinase pathways in glycolysis can be blocked by lithium. This work seeks to investigate the impact that various forms of lithium has upon the metabolic pathways of two cell lines of neuroblastoma, specifically in regard to lithium's influence on lactate production via glycolysis and pentose phosphate pathway. Preliminary results on the metabolic effects of lithium on [U-13C]D-glucose will be discussed along with other supporting data.

CtpV from Mycobacterium tuberculosis is a transmembrane Cu(I)-transporting P_{1B}-type ATPase pump

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Classification: Postdoctoral Research

Copper is a biologically essential, redox-active metal which is required in trace amounts by all organisms ranging from bacteria to humans. However, in light of its ability to redox-cycle and catalyze free radical production, copper becomes toxic when in excess. During microbial infection by intracellular pathogens, as one of the strategies to prevent infection, the host macrophages exploit the copper redox-dependent toxicity by mediating Cu-overload into the intracellular compartment (phagosome) where the pathogens replicate. However, the human pathogen *M. tuberculosis* (Mtb)

evades this process while in the phagosome by inducing the expression of genes in the copper sensitive operon (cso) that confers Cu-resistance. Among these genes, CtpV encodes a putative uncharacterized cation-transporter that is predicted to serve as a Cu-efflux pump. Deletion of CtpV results in increased sensitivity towards Cu-overload and decreased virulence in mouse models of Mtb infection, corroborating the potential role of CtpV as a Cu-exporter responsible for bacterial virulence. Sequence analysis suggests that CtpV is a P-type ATPase that shares significant sequence similarity to other Cu-efflux pumps, such as CopA from *E. coli*, but it lacks the typical Cys/His-rich N-terminal metal binding domain. However, putative Cu(I) transport by CtpV, its substrate selectivity and its mechanism of cargo translocation and putative interaction with Cu-chaperones in *M. tuberculosis* remain elusive. In our research, we have developed a strategy for recombinant expression and purification of MtbCtpV in detergent micelles to biochemically characterize CtpV function. Metal-dependent ATPase stimulation assays unambiguously revealed that CtpV is indeed a Cu(I)-translocating type ATPase pump, and we are currently dissecting the molecular mechanism underlying of Cu(I) recognition and translocation

Use of Zeolitic Imidazolate Frameworks for Mechanical Protection of Liposomes for Application in Biolistic Delivery of Vaccines

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Classification: Graduate

The goal of this project is to develop a vaccine delivery system that can provide comparable ease of use and immunological effectiveness of a needle-based injection using biolistic delivery. We use liposomes as a model for biomaterial-based nanocarriers that are used in the development of vaccines. Liposomal and other lipid-based vaccines – without any protective shell – are prone to aggregation and lipid fusion and need to be transported via an expensive cold chain. Furthermore, our preliminary experiments strongly indicate that liposomes themselves do not possess the mechanical robustness to penetrate the tissue barrier, and leak when subjected to shear stress. Encapsulation of liposomes in ZIF will not only provide protection to the formulation against heat and other stressors associated with transportation, but will also give it the structural rigidity required for facilitating penetration past the epidermis into the dermis when delivered biolistically. A library of liposomes were prepared to validate the proof-of-concept across a variety of lipid surfaces – cationic, neutral, anionic, and PEGylated. For calculating the encapsulation efficiency and for visualization, liposomes were prepared with Cy5 dye encapsulated inside the lumen. The liposomes were encapsulated in ZIF (Lip@Z) using several ligand/metal molar ratios – 32, 16, 8 and 4. Formulations with ratios of 32 and 16 were further investigated to due to their high encapsulation efficiency – even for cationic liposomes – on a 3h reaction setup. To ensure that the process of encapsulation is biofriendly and does not damage the liposomes, the ZIF coating from Lip@Z was removed using chelating agent EDTA and the exfoliated liposomes were characterized using TEM and DLS. Adding another level of mechanical stress, Lip@Z was biolistically delivered into a 5% gelatin-A ballistic gel, which was then melted at physiological temperature to recover the particles and subsequently exfoliated using EDTA to check the integrity of the recovered liposomes. It was exciting to observe that the ZIF coating protected the liposomes against the mechanical stressors originating from biolistic delivery and tissue penetration. We developed a model experiment to show that biolistic delivery can transport the Lip@Z particles into the dermis. Particles were delivered into a 2% agarose gel, which mimics soft tissue inside the body. A cross section of the gel was imaged via Z-stack and the fluorescence of the particles were integrated to obtain a density plot across the depth of the gel, showing that most of the particles were in the dermis depth range. The ultimate vision for our work is to apply this protection technique to commercially available liposomal vaccines, and eventually other sensitive vaccine platforms. These protected vaccines can then be packed as a dry powder, shipped across the world in an affordable manner, and delivered via a no-contact, low-cost biolistic delivery system through the skin without heavy reliance on trained medical staff.

Probing Base Pairing Effects of DNA via Vibrational Spectroscopy

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Deoxyribonucleic Acid (DNA), the molecule that carries the genetic information necessary for maintaining and constructing an organism, is a complex macromolecule that acquires two strands, each strand consists of a sugar-phosphate backbone and four bases: adenine(A), cytosine (C), guanine (G), and thymine (T). The two strands of DNA, complementary to one another, interact with one another via hydrogen bond interactions that are established between adjacent base pairs. According to traditional Watson–Crick base pairing, AT and GC base pairs are the only possibility. From infrared (IR) spectra chemists have obtained detailed information about the structure and function of DNA and have observed the formation of base pairs directly from spectra. However, a detailed understanding about the structural changes that occur before and after base pairing remains unclear. In this study we investigate methylated DNA bases and their base pairs via quantum chemistry computations, following appropriate modeling and appropriate computational methodology, to uncover details about structural changes that occur before and after base pairing. Our work shows that local mode analysis (LMA) can enable one to keep track of and probe the base pairing effects of methylated DNA bases and base pairs.

Inorganic/Analytical Section

SCI 2.210—Inorganic/Analytical Chemistry

Entry	Time	Activity
Greetings	**9:40 am – 9:45 am**	***Greetings***
01	9:45 am – 10:00 am	Hamid Reza Firouzi
02	10:00 am – 10:15 am	Cynthia Archambault
03	10:15 am – 10:30 am	Mojgan Gharaee
04	10:30 am – 10:45 am	Rhiza Villones
Break	**10:45 am – 11:00 am**	***Intermission***
05	11:00 am – 11:15 am	Simin Sheybani
06	11:15 am – 11:30 am	Phillip Arche
07	11:30 am – 11:45 am	Katherine Smart
08	11:45 am – 12:00 pm	Wirya Feizi
09	12:00 pm – 12:15 pm	
Break	**12:15 pm – 1:45 pm**	***Lunch Break***
10	1:45 pm – 2:00 pm	Husain Kagalwala
11	2:00 pm – 2:15 pm	Muhammad Abbas
12	2:15 pm – 2:30 pm	Jacob Fripp
13	2:30 pm – 2:45 pm	Marie Mortensen
Break	**2:45 pm – 3:00 pm**	***Intermission***
14	3:00 pm – 3:15 pm	Arslan Umer
15	3:15 pm – 3:30 pm	Baowen Li
16	3:30 pm – 3:45 pm	
17	3:45 pm – 4:00 pm	
Break	**4:00 pm – 4:30 pm**	***Break***
Awards Ceremony	**4:30 pm – 5:00 pm**	***Awards Ceremony (SCI 1.220)***

For questions about scheduling for Inorganic Section, e-mail:
Rhiza Villones rhizalyne.villones@utdallas.edu

Mechanistic study of direct extraction of fluorine from 2-Fluorobenzoic acid by Holmium Ion

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Rare-earth elements in metal-organic frameworks, or MOFs, are highly attractive due to their different coordination environments, providing the formation of many different topologies. These elements provide an opportunity to utilize them for optical, magnetic, and electrical applications. Recently, the modulator, 2-fluorobenzoic acid, 2, 6-difluorobenzoic acid, and other organoflourine structures have been used to form tri-, hexa-, and nona-clusters of these lanthanides in MOFs. These clusters were previously identified in Zr-MOFs such as Zr-UIO-66, but recently, it was determined that holmium could directly extract fluorine from these fluorinated modulators and form a μ3-fluorine-bridging tri- and hexanuclear cluster MOFs using 2 2'-bipyridine-4 4'- dicarboxylic acid and terephthalic acid, respectively. Holmium ions also formed holmium fluoride precipitation in presence of these modulators. In this work, the mechanistic pathway of direct fluorine extraction from 2-fluorobenzoic acid by holmium ions will be discussed. Different characterizations such as Nuclear magnetic resonance, Powder x-ray diffraction, and mass spectroscopy are used to reveal this pathway.

Dinitrogen activation through pressure-driven mechanochemistry

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The fixation of dinitrogen is pivotal for modern civilization. The state-of-the-art Haber-Bosch process, however, is energy intensive, consuming up to 2% of global energy. The fundamental challenge lies in the activation of the dinitrogen bond (N≡N) with an extraordinarily high dissociation energy (~1000 kJ/mol). Here we demonstrate activation of dinitrogen bond through mechanically induced hapticity switching. Our computations have predicted a zirconium-dinitrogen complex (Zr2N2) with irreversible N≡N activation through pressurization. Compression of the compound yields >6% selongation of the N≡N bond, corresponding to ~5% reduction of the dissociation energy. Furthermore, the bond activation is achieved through hapticity switching, a mechanism that has not been explored for nitrogen fixation so far. Here I will present this bond activation through the use of diamond anvil cell (DAC) techniques in combination with in situ spectroscopy and computations. The verification of this hapticity switch will establish the pressure-driven N≡N activation and its molecular mechanism, laying down the foundation toward N2 fixation via mechanical energy input.

Computational study of cobalt Oxynitrides Electrocatalysts for ammonia production

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One of the most important methods for the reduction of dinitrogen to ammonia is the Haber-Bosch process and this reaction is vital to agriculture and currently consumes ~2% of global energy. This reaction also produces a large amount of CO2 because of using of fossil fuels to run the reaction at high temperatures. Electrocatalytic reduction of N2-the nitrogen reduction reaction (NRR)- is an environmentally friendly replacement for producing NH3. A lot of Electrocatalysts such as noble and non-noble metal oxides and nitrides are being investigated for this purpose. Recently, interest in cobalt Oxynitrides and other Earth-abundant oxynitrides is growing For NRR. However, one important issue is still unclear, and it is the role of lattice N and O in this reaction. Base on DFT calculations, both lattice N and solvated N2 can be reduced to ammonia by cathodic polarization of cobalt Oxynitrides films. Both lattice N and N2 reduction mechanisms involve oxide-supported Co surface sites ([Co]O in preference to N-supported sites [Co]N). Moreover, the result demonstrates that the formation of CoN, Co-N=N-H, and other proposed reaction intermediates prefer [Co]O rather than [Co]N surface sites.

Pathway of assembly for the formation of metallothionein-3 $Cu(I)_4$-thiolate cluster proceeds through a long-lived, Cu-coupled, and oxygen-inert disulfide radical anion

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Human metallothionein-3 (MT-3) is a small (6-7 kDa), cysteine-rich metal-binding protein that plays essential roles in mediating the biochemistry of copper. Despite copper's inherent instability in the oxidizing extracellular environment that promotes its redox cycling, MT-3 remarkably binds and forms clusters with Cu(I) that are inert to oxidation in the presence of molecular oxygen. Using a combination of biophysical and spectroscopic approaches, we investigated the chemistry and pathway of assembly behind the formation of this uniquely redox-stable $Cu(I)_4$-thiolate cluster in the final $Cu(I)_4Zn(II)_4$MT-3 product formed upon the reaction of Zn_7MT-3 with Cu(II). The cysteine thiolate residues of MT-3 can reduce Cu(II) to Cu(I) in a concerted electron transfer process concomitant with the formation of intramolecular disulfide bonds. Stopped-flow electronic absorption spectroscopy revealed rapid formation and consumption of transient disulfide radical anion (DRA) species with absorption centered at 430-450 nm, which have lifetimes in the seconds regime. By rapidly freeze quenching the reaction intermediates, the DRA nature of the sulfur-centered species was confirmed by both Raman and Electron Paramagnetic Resonance (EPR) spectroscopies, with the EPR simulations revealing that the DRA intermediates are coupled to Cu(I). Overall, we were able to dissect and provide evidence that the pathway of assembly and formation of this unique Cu(I)-thiolate MT-3 cluster with short Cu-Cu distances (<2.8 Å), as verified by low-temperature luminescence spectroscopy, proceeds through the formation of long-lived, Cu-coupled, and oxygen-stable disulfide radical anion intermediates.

Difluorination of per- and polyfluoroalkyl substances (PFAS) by rare-earth ions and construction of fluoro-bridged metal-organic frameworks

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Rare-earth metal-organic frameworks with their unique optical and electronic properties have gained interest in recent years. Previously, the synthesis of fluoro-bridged RE metal-organic frameworks with the use of fluorinated modulators such as 2-fluorobenzoic acid or 2,6-difluorobenzoic acid has been reported. This research shows the cleavage of the C-F bond of perfluoroalkyl substances with rare-earth ions. Perfluoroalkyl substances (PFAS) as a large, complex, and ever-expanding group of manufactured compounds are used in a wide array of industrial and commercial products to make them more resistant to stains, grease, and water. Because the carbon-fluorine (C-F) bond is among the most chemically robust bonds; the degradation of fluorinated hydrocarbons in the environment is exceptionally difficult. Multiple fluorine atoms from perfluorooctanoic acid (PFOA) and perfluorhexanoic acid (PFHA) can be removed and bridge the lanthanide atoms in the lanthanide fluoride structure. For the first time, RE (Ho3+, Gd3+, Dy3+, Eu3+, Tb3+) fluoro-bridged nonacluster and tricluster of a highly connected known metal-organic framework with perfluorooctanoic acid and perfluorhexanoic acid as modulator have been synthesized. Additionally, the transformation of a 2-FBA dimeric lanthanide complex into the fluoro-bridged nonacluster and tricluster MOF will also be described. Characteristics studies such as single-crystal X-ray diffraction crystallography, powder X-ray diffraction (PXRD), X-Ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA), energy-dispersive X-ray spectroscopy (EDS), and Fourier-transform infrared spectroscopy (FT-IR) are performed to confirm the synthesis of fluoro-bridged nonacluster and tricluster metal-organic frameworks.

Iminopyridine-Based α-Diimine Nickel (II) Complexes in Direct C-H Bond Arylation of 4-methylthiazole

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Arylated five-membered (hetero)aromatics have attracted the field of organic electronics and drug discovery due to their unique physical and chemical properties. To synthesize biaryl moieties through a more atom-economic approach, the direct (hetero)arylation method does not need a pre-functionalization of either coupling arenes that conventional cross-coupling reactions do. Palladium and phosphine-free means of providing direct (hetero)arylation have been attempted to provide cheaper and more sustainable alternatives. To facilitate the coupling reaction, a bis¬-ligated iminopyridine nickel(II) catalyst was synthesized. The synthesis of the complex started with the condensation of 2-pyridinecarboxaldehyde and 2-ethylaniline, followed by the complexation reaction with NiCl2(DME). Direct (hetero)arylation with 4-methylthiazoles and aryl halides of various electronics and sterics was observed even at a catalyst loading of 0.2 mol% and the presence of oxygen in the air. The characterization of the Ni catalyst through X-ray diffraction showed an octahedral shape with the two chloride ligands trans with each other. The position of the two labile ligands is thought to inhibit the reaction, but density functional theory (DFT) calculations were done to show how the rearrangement of the complex can afford the coupling reaction.

Gas chromatographic separation of fentanyl analogues with an ionic phase

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The current opioid epidemic is driven by opioids such as illicit fentanyl and fentanyl analogues, often in combination or in adulterated forms. With a potency that is 50-100 times greater than that of heroin, and the ability to induce a euphoric high, fentanyl has readily gained recreational popularity. To meet demands and bypass federal regulations, clandestine laboratories have opted to create analogues of fentanyl that can induce similar effects. Illicit designer drugs often contain impurities and adulterants making such substances more concerning. Often the exact nature of these confiscated drugs goes unknown due to the lack of methods that provide cost effective results for forensic laboratories. As a result, the applicability of an ionic liquid phase for chromatographic separations is explored. A variety of synthetic routes can be used to synthesize analogues. In this study, the one-pot Gupta method[1] was used to synthesize fentanyl and 5 analogues (butyryl fentanyl, isobutyryl fentanyl, crotonyl fentanyl, cyclopropyl fentanyl and furanyl fentanyl). These analogues were successfully separated with a novel GC-FID method using an ionic liquid stationary phase. In addition, 24 fentanyl compounds were identified in one chromatographic run. These results using the ionic liquid phase were compared to a traditional 5% diphenyl/95% dimethylpolysiloxane phase using GC-MS. [1] P.K. Gupta, K. Ganesan, A. Pande, R.C. Malhotra, Journal of Chemical Research. 36(9) (2005) 452–453. doi:10.3184/030823405774309078 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.

X-Band Overhauser DNP setup for enhancing liquid state 1H NMR Signals at room temperature

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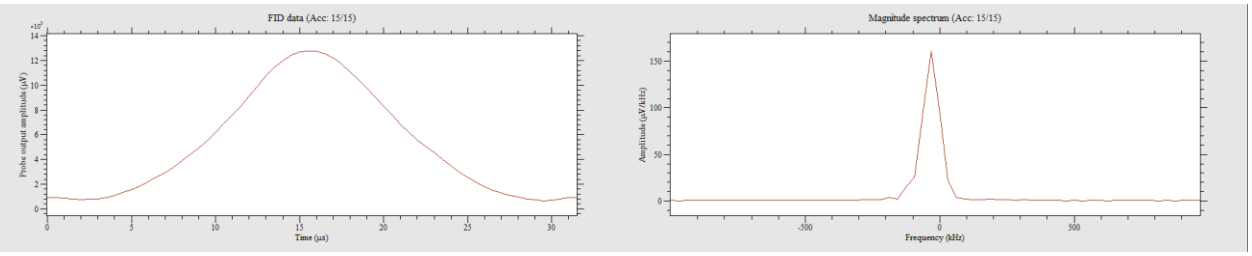
Overhauser effect (OE) dynamic nuclear polarization (DNP) is a method of enhancing the nuclear magnetic resonance (NMR) signals of samples by transferring the high electron spin alignment to the nuclear spin by microwave radiation at the electron paramagnetic resonance (EPR) frequency of the free electron source. Here we report the preliminary results of an experimental setup of an X-band Overhauser DNP polarizer for the purpose of enhancing the 1H nuclear magnetic resonance (NMR) signals of water doped with free radicals by tens or hundreds of times compared with the thermal NMR signal of the sample at room temperature. This research used different free radicals with different EPR linewidths. This technology's ability to enhance NMR signals can have practical applications for improving MRI signal sensitivity. This presentation will present preliminary 1H NMR results, EPR characterization studies, and the engineering challenges involved in the instrumentation.



Near-infrared emitting chemiluminescent iridium 1,2-dioxetane complexes for oxygen sensing

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Classification: Postdoctorate

Recent years have seen a rapid development of spiroadamantane 1,2-dioxetane chemiluminescent probes for imaging biorelevant analytes such as reactive sulfur, oxygen and nitrogen species, pH and hypoxia in tumors. A current focus in the field has been to shift the emission of such probes into the near-infrared region and beyond via synthetic modifications of the original scaffold. Here, we discuss our efforts to enable red-shifted chemiluminescence by appending spiroadamantane 1,2-dioxetane phenol scaffolds to red-emitting phosphorescent iridium complexes. Energy transfer from the resulting chemiexcited benzoate to the iridium complex results in oxygen-sensitive ratiometric responses which were gauged by Stern-Volmer quenching analysis. Furthermore, these responses enable in vitro oxygen imaging, as well as intraperitoneal, intramuscular and intratumoral imaging in live mice.

Fluoro-Bridged Hexaclusters in Rare Earth MOFs

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Metal-organic frameworks (MOFs) are porous crystalline materials constructed from organic linkers and metal ions (or clusters). Advances in MOFs applications include gas storage and separation, drug delivery, sensors, water capture, and catalysis, depends in part on new structures. We recently discovered a new methodology for the preparation of fluoro-bridged rare earth (RE) clusters (Figure 1). In this presentation a new series of RE MOFs synthesized using bicinchoninic acid (BCA) and lanthanides (Ln= Y, Eu, Gd, Tb, Dy, Ho, and Yb) will be discussed. 2D MOFs based on lanthanide dimer nodes are formed in the absence of organo-fluorine molecule. In contrast the addition of 2-fluorobenzoic acid (2-fba), 2,6-difluorobenzoic acid (2,6-dfba), or other fluoro-organic compounds results in μ3-F bridged hexaclusters (Figure 1a) and the porous 3D MOFs shown in Figure 1b. The presence of fluorine was verified by XRD, EDS and XPS analysis. Preliminary data shows these MOFs are selective for CO2. The Eu-MOFs are fluorescent, their fluorescence can be tuned using mixed metals for thermo or host-guest based sensing applications. This study will also help to explore how presence of μ3-F bridging could increase the fluorescence intensity in hexacluster MOFs.

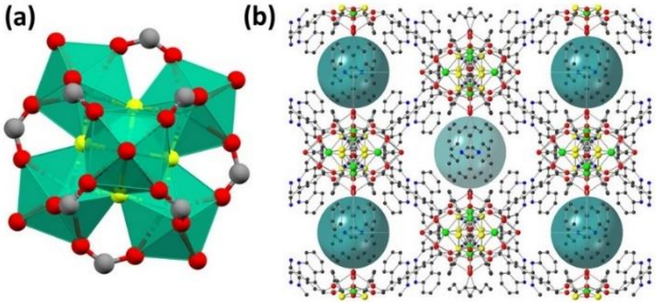

Figure 1. Crystal structure of (a) hexacluster containing μ3-F bridging in c-direction (b) 3D MOF network showing cavities (Ln=green, C=gray, N=blue, O=red, F=yellow)

Pressure dependent turn-on Photoluminescence in MOFs

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In this work two fluorous metal organic frameworks (FMOFs) have been found to exhibit an unusual turn on photoluminescent behavior in regards to pressure (herein called baroluminescence). While under vacuum these MOFs luminesce yellow, however a massive quenching event occurs when the pressure is increased, even with inert gasses. The rate or quenching is gas dependent however complete quenching is usually achieved before 0.1 atm. This phenomena in FMOFs may have a real world application as a cheap, low tech, baroluminescent barometer.

Several New Lanthanide Containing Metal Organic Frameworks exhibiting fluoro-bridged triclusters and their structural and luminescence properties

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Lanthanide containing metal organic frameworks or MOFs have unique magnetic and luminescent properties. In order to improve their stability and further increase the number of topologies formed, the modulator, 2-fluorobenzoic acid, was added to the synthesis to create lanthanide clusters. Recently, it was determined that the lanthanides are reacting with the modulator and extracting the fluorine from the compound. This results in lanthanide clusters that are fluoro-bridged instead of hydroxy-bridged. Using this method, a series of four lanthanide containing MOFs were synthesized from a DMF/water solution containing 2, 2'bipyridine 4, 4'dicarboxcylic acid, a fluorinated modulator, and lanthanide nitrate (Ho3+, Eu3+, and Gd3+). The synthesis of three isostructural MOFs, containing either Ho3+, Eu3+, or Gd3+, and two closely related isostructural MOFs, containing Gd3+ or Ho3+, will be described. The presence of the fluorinated clusters, as demonstrated in Figure 1, is shown through single crystal X-ray diffraction, energy dispersion X-ray spectroscopy, and X-ray photoelectron spectroscopy. The luminescence of the Eu3+ and Gd3+ isostructural MOFs will also be described.

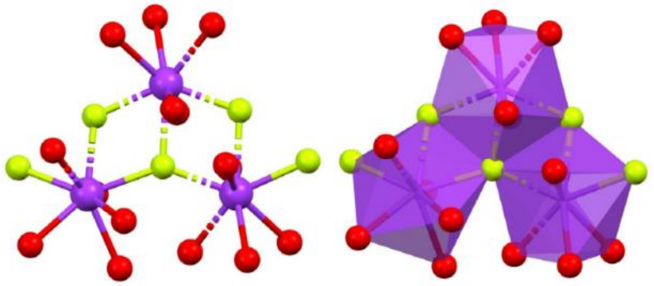

Figure 1: The fluoro-bridged tricluster of Eu 4,4'-BPDC MOF.

Redox-active Neodymium oxide templated-conductive carbon for supercapacitors

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Carbon-based materials with designed nanoarchitecture have been studied for energy storage applications due to their high surface area and conductivity. Many methodologies have been established to prepare these carbon materials. Among these, using a template-based synthesis by chemical vapor deposition (CVT) has been widely researched. In this method, different templates, such as zeolites and mesoporous silica, have been previously used to synthesize these carbons. Unfortunately, most of these methods produce amorphous carbons. This limits their use in energy storage as well as catalysis. Graphene-based carbon electrodes with high porosity have shown excellent performance in supercapacitors due to electrical double-layer capacitance (EDLC). Moreover, the use of a redox-active template for carbon synthesis further increases the performance of the capacitor due to their pseudocapacitance (PC) capabilities. Therefore, it is of great interest to make templated carbons from a redox-active material for energy storage applications. This work demonstrates the synthesis of graphene-like porous carbons using a redox-active Neodymium oxide as a template. This work focuses on the development of supercapacitors with synergetic effects between EDLC from conductive carbons and PC from redox-active Neodymium oxide.

Controlling pore size and interlayer distance by electron-withdrawing effects in 2d MOFs

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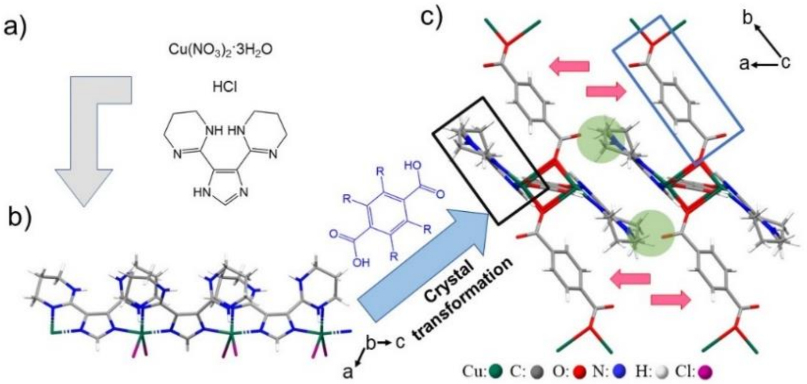
Classification: Graduate

Metal-organic frameworks (MOFs) are three-dimensional structures coordinating between metal nodes and organic linkers. They are attractive crystalline microporous materials with diverse energy-related applications ranging from gas storage, gas separation, catalyst, sensors, etc., due to their high surface area, permanent porosity, controllable structures, and stability. Two-dimensional MOF layers can be held by hydrogen bonds, van der Waals interactions, and π-π stackings. Three isoreticular hydrogen-bonded 2D MOFs were synthesized from a 1D polymer chain. The 1D polymer chain, Cu(L1)BDC(Cl)2, was constructed from copper(II) and 2,2'-(1H-imidazole-4,5-diyl)di-1,4,5,6-tetrahydropyrimidine, (H-L1). The three isoreticular 2D copper-based MOFs were constructed using different BDC analogs that react with the 1D polymer chain. The pore size of Cu(L1)BDC-F4 has been improved by rotating the tetrafluoro substituted aryl rings. The new perfluorinated copper-based MOF showed three times larger channel volume and six times faster argon gas adsorption with a slight increase of the interlayer distance. Meanwhile, the hydrogen bonding interlayer distance between the MOF layers was also elongated by the electron-withdrawing effect of o-nitro and o-bromo substitution on the aryl ring of the H2BDC linker.



Materials Section

SCI 2.225—Materials Chemistry

Entry	Time	Activity
Greetings	**9:40 am – 9:45 am**	***Greetings***
01	9:45 am – 10:00 am	Alireza Aminifazl
02	10:00 am – 10:15 am	John Alptekin
03	10:15 am – 10:30 am	Yafen Tian
04	10:30 am – 10:45 am	Thomas Howlett
Break	**10:45 am – 11:00 am**	***Intermission***
05	11:00 am – 11:15 am	Sheikh Islam
06	11:15 am – 11:30 am	Shailendra Koirala
07	11:30 am – 11:45 am	Steve Lan
08	11:45 am – 12:00 pm	Tengteng Lyu
09	12:00 pm – 12:15 pm	Perouza Parsamian
Break	**12:15 pm – 1:45 pm**	***Lunch Break***
10	1:45 pm – 2:00 pm	Ashish Shivaji
11	2:00 pm – 2:15 pm	Jatan Sharma
12	2:15 pm – 2:30 pm	A.K.M. Siddiki
13	2:30 pm – 2:45 pm	Masoumeh Tajik
Break	**2:45 pm – 3:00 pm**	***Intermission***
14	3:00 pm – 3:15 pm	Andrew Vavrinak
15	3:15 pm – 3:30 pm	Xiangyu Zhu
16	3:30 pm – 3:45 pm	Fahad Haque
17	3:45 pm – 4:00 pm	
Break	**4:00 pm – 4:30 pm**	***Break***
Awards Ceremony	**4:30 pm – 5:00 pm**	***Awards Ceremony (SCI 1.220)***

For questions about scheduling for Materials Section, e-mail:
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Preparation and characterization of organic modified and silane functionalized intercalated Zn-Al Layer Double Hydroxides (LDHs) as corrosion inhibitors for use in polymeric coatings

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Natural Sciences and Mathematics
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Classification: Graduate

Two-dimensional plate-like Layer Double Hydroxide materials are well-known as corrosion protective fillers used in polymeric coatings. How to intercalate, modify and disperse them in a polymeric matrix is still a challenging issue. In this work, first nitrate is intercalated into Zn-Al-LDH layers through an aqueous co-precipitation method, then different organic anions are intercalated through the anion exchange process to obtain nitrate and organic intercalated Zn-Al LDHs. In the last step, a silane coupling agent is added to functionalize LDHs' surface. The synthesized LDHs were characterized by X-ray diffraction (XRD) analysis, and infrared (FTIR) spectroscopy, which showed a successful anion exchange reaction and positive effect of using large organic anions which resulted in increasing the interlayer distance in LDH structure. Thermal analysis (TG-DTG) indicated high thermal stability of modified and factionalized LDHs which can be attributed to the reaction of silane alkoxy groups with LDH surface hydroxyls that lowers related hydroxyl weight loss. Scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) were also used to study all intercalated-LDHs' surface morphology and elemental analysis.

Enabling the Next Generation of High Reliability Electronics Utilizing Foundational Chemistry Knowledge

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Copper, with advantages of higher electrical conductivity, lower cost, and better mechanical strength, has rapidly replaced more expensive gold as the dominant (>60%) wire bonding material in integrated circuit (IC) packaging. However, corrosion-related failures, although at low ppm level, need to be carefully controlled to ensure the highest packaging reliability, especially under harsh conditions such as in automotive environments. Device failure rates as low as 1 ppb can have dangerous consequences for sensitive functions such as traction control, automatic braking, and power steering. And, the consequences of device failure turn even more catastrophic with the increasing use of 'self-driving' cars, LiDAR sensing, and lane-assist technology. In most wirebonding applications, the IC chip is connected by fine Cu wires via Al bonding pads microfabricated on chip and the contact pins that anchor on the printed circuit board. In the past 10 years, the corrosion related failures between the Cu wire and Al bond pad have been the most un-trackable reliability issue plaguing the IC packaging industry. Most prior studies hypothesized that intermetallic compounds (IMCs) like Cu_9Al_4, CuAl and $CuAl_2$ were responsible for the observed acute wirebond lift-off corrosion defects. However, utilizing a novel real-time corrosion screening approach, our team established that bimetallic contact between Cu ball-bonds and Al bond pads is the key driver for the aggressive Al pad corrosion, induced by chloride ion penetration, that often leads to device failure. With this improved mechanistic understanding, we developed a corrosion prevention treatment specifically targeted to Cu/Al bimetallic contact and showed the new strategy can achieve highly effective Al pad corrosion inhibition. Since the wirebond interface is a complex stack and interconnection of Cu, different Cu-Al IMC phases, and Al, we further sought a deeper understanding of the role of IMCs in wirebond liftoff corrosion, and characterized their corrosion behavior utilizing fundamental electrochemical experiments. We found, utilizing zero resistance ammetry technique, that the rate of corrosion between the galvanic pairs is as follows: Cu-Al > $CuAl_2$-Al > Cu_9Al_4- $CuAl_2$ > Cu-Cu_9Al_4, with the higher Cu-containing metals behaving as the cathodes within the pairs. We investigated the hypothesis that the cathodic hydrogen evolution originating from Cu surfaces, for both Cu bonding wire and the Cu within the IMCs, could be the key cathodic reaction enabling the aggressive anodic corrosion observed

on Al bond pads and Al-containing IMCs. We also explored the effects of the Cu-selective passivation treatment on suppressing the galvanic corrosion Cu-Al IMCs when electrically connected to Cu wire or Cu rich IMCs. Preliminary data shows that the same compound used to inhibit the bimetallic-induced corrosion of Al, by blocking the cathodic half-reactions on Cu surface, is also able to provide protection to the IMCs by a similar mechanism.

Vanadium oxide/nitride embedded in carbon fibers for supercapacitor electrode

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In hybrid supercapacitors, both EDLC (electrochemical double-layer capacitors) and TMeX (transition metal oxides, nitrides, sulfides, and carbides) are combined to achieve high energy and power density. Nanoscale vanadium oxide (V2O3)/nitrides (VN) were in-situ dispersed in carbon fibers via the electrospinning method, followed by high-temperature carbonization, where polyacrylonitrile (PAN) acts as the carbon source, V2O5 as a metal compound precursor, and poly(methyl methacrylate) (PMMA) as a porogen /chelating agent. VN and V2O3 are combined to take advantage of VN's high conductivity and V2O3's redox activity. Furthermore, having the vanadium species contained within the carbon can benefit in the electrode's stability. Coin cells were fabricated and demonstrated a high specific capacitance of 216 F·g-1 at 5 mV/s using 1 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in polycarbonate as electrolyte. The use of a polymer blend with functional groups to increase the uniformity and accessibility of metal oxide/nitrides in carbon fibers is demonstrated in this study as a new strategy for creating hybrid supercapacitor electrode materials.

Bimetallic ZIF-8 for Improved Metal-Organic Framework-Based Vaccines

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The tunability and large cargo capacity of metal-organic frameworks, MOFs, has led to their increasing interest in a biomedical application. One of the target applications for MOFs is use in vaccines because of their ability to stabilize and preserve biomolecules from thermal degradation. Beyond thermal stability, MOF encapsulation has been shown to enhance the immune response to encapsulated material through improved antigen delivery and prolonged presentation. Currently, one of the most used and promising MOF candidates for in-vivo applications is zeolitic imidazolate framework 8 (ZIF-8). This framework is well known for its high surface area, biofriendly synthesis conditions, and its relative biocompatibility. However, there are some toxicity concerns particularly with nano sized ZIF-8. The framework itself does not contribute to immunogenicity which is a negative in uses for vaccines. To decreases toxicity and increase immunogenicity of ZIF-8, partially substituting manganese into the framework is being investigated. Recently, manganese (II) ions have been shown to act as an immune adjuvant with the ability to activate bone marrow dendritic cells (BMDCs) even at very low concentration of 10 μg / ml. BMDC activation is the first step to a robust immune response and is imperative to creating the next generation of vaccines. MOFs doped with immune adjuvating metals could actively contribute to immune response increasing the effectiveness of MOF based vaccines. Further, by doping the crystal with a different metal, the amount of one metal is reduced, which could lead to lower cytotoxicity. In this project, a water-based synthesis of bimetallic manganese zinc ZIF-8 (Mn-ZIF-8) was developed with size control and a 10 weight precent manganese concentration in mind. Manganese doped ZIF-8 was previously reported by organic solvent-based synthesis, but water allows for encapsulation of biologic materials and was necessary for future

applications. Mn-ZIF-8 was first shown to improve cytotoxicity through LDH assays where it was compared to pure zinc ZIF-8 of the same size at equal concentration. Significant improvement in cytotoxicity was observed at 300 nm size above concentration of 150 µg/ml. With confirmation of improved cytotoxicity, in vitro BMDC activation studies are being conducted in which Mn-ZIF-8 is being compared against equivalent ZIF-8 and Mn2+ salts to see if a MOF with manganese can illicit the same response as plain Mn2+ salt is reported to. Future application of this project will be to apply Mn-ZIF-8 in a vaccine using either encapsulated bacteria or protein and studying if the immune response is improved versus a ZIF-8 based vaccine.

Metal-Organic Frameworks (MOFs) based on a Texas-sized Tri-carboxylate Linker and Their Applications on Small Hydrocarbon Separation

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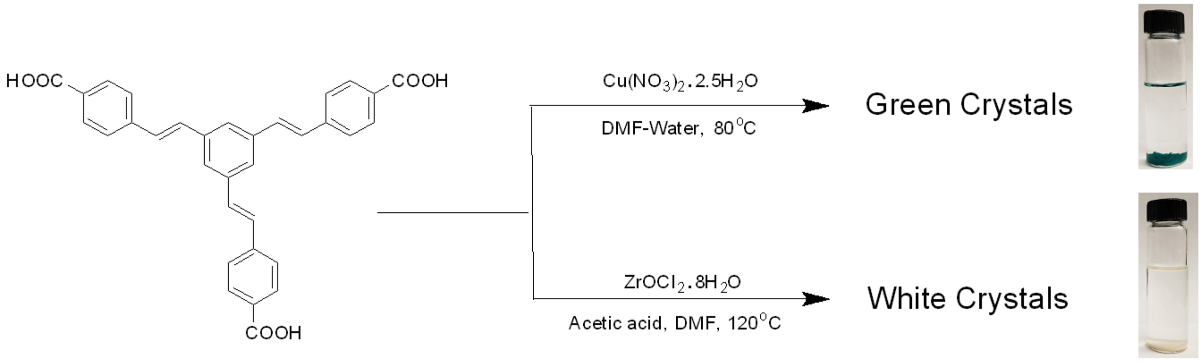
Among many others, two factors are particularly important in advancing the chemistry of MOFs, the size of the organic linker (higher surface area usually requires longer/larger organic linkers, barring interpenetration and other complications that could counteract the expected greater porosity) and the identity of the metal ion (controls geometry, covalent radius, electronic configuration, etc. that can modify the structure, properties beyond porosity including electrical conductivity, magnetic, and/or optical properties). In this report, the synthesis of two new MOFs (one Cu(II)-MOF, and one Zr(IV)-MOF) is presented based on a larger tri-carboxylate linker (H3L) named 4,4',4''-((1E,1'E,1''E)-benzene-1,3,5-triyltris(ethene-2,1-diyl))tribenzoic acid. This linker is symmetrical and larger in size than the closest literature analogue, BTC (1,3,5-benzenetricarboxylic acid). Solvothermal reactions of H3L with Cu(II) and Zr(IV) afforded crystals of Cu-MOF and Zr-MOF respectively. The MOFs were characterized using PXRD, TGA, and FTIR. The porosity was established by the N2 adsorption measurements at 77 K revealing higher surface areas. Single component adsorption isotherms were measured for CH4, C2H2, C2H4 and C2H6 up to 1 atm at 273 and 298 K, respectively. The measurements indicate these MOFs could be promising materials for adsorptive separation of C2 hydrocarbons from C1 methane at 273 K and room temperature.



Bacteria-sensing Magnetic Resonance Imaging (MRI) Probe

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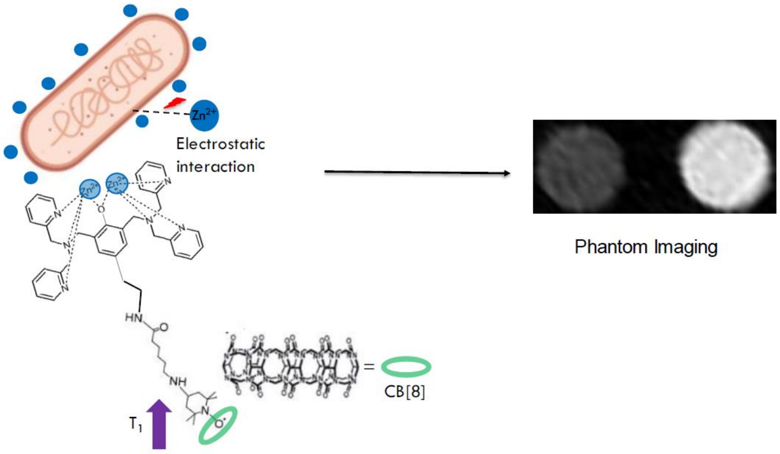
Even though there has been a significant advancement in imaging technology, rapid, precise, and accurate diagnosis of bacterial infection is still a challenge. Selectively recognizing bacterial cells is one of the important characteristics of a bacterial imaging agent and drug candidates. Bacterial have anionic cell membrane whereas the charge on healthy mammalian cell membranes is close to neutral. Zinc dipicolylamine (Zn-DPA) — a positively charged Zn-based ligand — is a widely used agent for targeting cellular death (since dead cells have anionic surface charge) and bacterial infections. Bacteria-sensing Magnetic Resonance Imaging (MRI) probes can be made by attaching an organic radical contrast agent (ORCA) to Zn – DPA. These complexes have a strong affinity towards bacteria because of their anionic surface charge and can selectively tightly bind to bacterial cells while remaining inert to any interaction with mammalian cells.



Mimicking enzymatic noncovalent interactions with functionalized covalent organic frameworks

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Tuning catalytic centers in heterogeneous catalyst, both in a chemical and a spatial manner, is a powerful approach to improve the stability and the efficiency of catalysts. While the chemical aspects are largely understood, the spatial interactions around active sites, comprised of noncovalent interactions, are difficult to maintain and challenging to study. Herein, we utilized the unique properties of covalent organic frameworks (COFs) to establish an ideal reaction environment for the hydrolysis of cellobiose and other common disaccharides in mild, metal-free, neutral aqueous conditions. The chosen COF, HCl-PSA-IM-COF-OMe, was modified to be ultra-stable in aqueous conditions and possessed sulfonic acid groups for general acid catalysis and intraporous chloride anions for enhanced hydrogen bonding with reactants and oxocarbenium intermediate stabilization. In addition, the system also relies on the differences in adsorptive binding behavior, Kads, of the reactants and the products to the functionalized framework and benefits from a separate physical, kinetic process to boost the catalytic cycle.

Uniform sub-five-nanometer diamond particles via geochemistry-inspired synthesis

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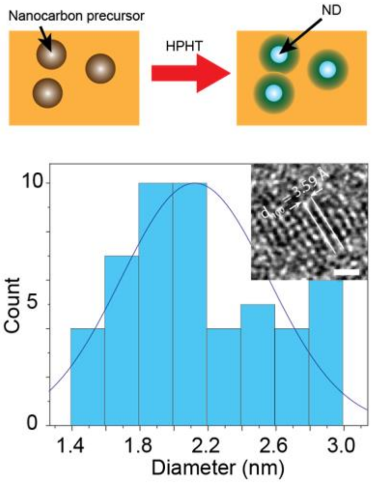

Diamond nanoparticles in the sub-five-nanometer size regime are crucial for several emerging technologies including subcellular imaging, quantum information processing, and drug delivery. State-of-the-art methods to produce nanodiamonds include mechanical grinding of bulk crystals, decomposition of hydrocarbon molecules, and detonation of explosives. However, no existing technique is capable of precise size control in the sub-five-nanometer regime. Here we describe a method for controlled synthesis of nanodiamonds with 2-5 nm diameter. The key innovation lies in the utilization of metal carbide nanoparticles as carbon sources. The reaction between these metal carbides with metal oxides under high-pressure-high-temperature conditions yields diamond nanoparticles with <5 nm diameter, uniform size, and high crystallinity. The size of the nanodiamond is precisely tuned by the nanostructured carbon precursor. Chemical doping of the precursor allows controlled incorporation of functional defects, enabling these nanodiamonds for key applications as bio-compatible high-resolution fluorescent markers, storage bits for quantum information processing, photon, and electron sources, as well as vehicles for targeted drug delivery.

Enhanced nanobubble formation: Gold Nanoparticle conjugation to Qβ virus-like-particles

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Plasmonic gold nanostructures are a prevalent tool in modern hypersensitive analytical techniques such as photoablation, bioimaging, and biosensing. In fact, recent studies have shown gold nanostructures generate transient nanobubbles through localized heating. Notably, these nanobubbles produce shear forces that can temporarily or permanently alter vasculature. However, the current method of plasmonic nanoparticle cavitation has several disadvantages. For one, these methods use large metal nanostructures (≥30 nm) which lack size control, tunability, and tissue localization. Additionally, these nanobubbles use high-speed pulse (ns, ps) and high-energy lasers resulting in tissue damage. This research investigates a method to immobilize either 3.5 or 5 nm AuNPs onto a chemically modified thiol-rich surface of Qβ virus-like particles (VLPs). The findings demonstrated the multivalent display of sub-10 nm gold nanoparticles causes a profound increase in photo-cavitation by upwards of two or three orders of magnitude when compared to traditional 30 nm gold nanoparticles. Lastly, computational modeling showed the cooling time of QβAuNP scaffolds is significantly longer than that of individual AuNPs, proving greater control of laser fluency and nanobubble generation. Ultimately, these findings showed how QβAuNP composites are effective at nanobubble generation than current methods of plasmonic nanoparticle captivation.

Development of a New Passivation Coating on Copper Interconnects to Eliminate Electrochemical Migration Failure Defects

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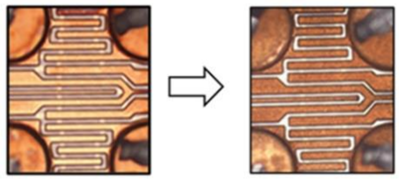

Bare Cu RDL Device

Inhibitor coated Cu RDL surface

Copper (Cu) is the metal of choice for metallic interconnects, or redistribution layer (RDL), to facilitate fast I/O communication in an integrated circuit (IC). This Cu film can electrochemically migrates (ECM) resulting in short circuit formation between adjacent metallization stripes under DC bias. ECM is fundamentally an ionic process that requires an electrolyte, moisture, and electrical bias The epoxy molding compounds used for packaging devices can release ion impurities. When the moisture from the atmosphere seeps into the package an electrochemical cell is set up. At the anode, copper dissolves forming Cun+ ions(n=1,2). Cun+ ions then combine with OH- to Cu(OH)n which decomposes to CunO & H2O. As the anodic dissolution continues, the copper ion concentration increases within the electrolyte. These ions are deposited on the cathode leading to dendrite formation. The electric field is deformed at an initial deposition site and the growing speed increases at the edges; thus, dendrites are deposited. To achieve the near zero ppb defectivity goal, elimination of (ECM) defects in packaged devices is critical. In this talk, we will discuss development of a novel Cu-selective passivation. Our aim is to selectively passivate Cu surface by a coating chemistry designed to have a minimal moisture retention and induces a negligible stress for enhanced reliability of wafer level packaging. Fig.1 shows Cu interconnects coated by dry processes. The new Cu-selective passivation coating is thermally stable, strongly adheres to Cu (passed thermal stress test), corrosion resistant, low cost and shows good potential to prevent ECM defects. The coated packaged devices were tested by a PEG drop test (PDT). PDT testing analyzes the ionic migration between the interdigitated Cu electrodes within an applied potential window using a potentiostat. SEM/EDS analysis was used for elucidating the ECM whiskers growth morphology. The coated interconnects devices were studied to explore its ECM prevention capabilities. FTIR and Potentiodynamic polarization were utilized to characterize the coating.

Development of a New Passivation Coating on Copper Interconnects to Eliminate Electrochemical Migration Failure Defects

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The +5 oxidation state of antimony induces push-pull style intramolecular charge transfer in an elegantly designed axial dimethoxyantimony(V) porphyrin series: SbP(OMe)2.PF6, SbMP(OMe)2.PF6, SbDMP(OMe)2.PF6, SbTMP(OMe)2.PF6 with phenyl (P), 4-methoxyphenyl (MP), 3, 5-dimethoxyphenyl (DMP), and 3,4,5-trimethoxyphenyl (TMP) units, respectively, in its meso positions. The Sb(+5) makes the porphyrin ring electron-poor, whereas the methoxy groups on the phenyl unit produced electron-rich sites within the molecule. The presence of electron-poor and electron-rich parts in the same molecule resulted in a push-pull type intramolecular charge transfer (ICT). However, the ICT is strongly dependent on the position of the methoxy groups on the phenyl ring. The charge transfer character is more pronounced in meta-methoxy substituted antimony(V) derivatives (SbDMP(OMe)2.PF6, SbTMP(OMe)2.PF6) than the para-methoxy or no-methoxy substituted antimony(V) derivatives (SbP(OMe)2.PF6, SbMP(OMe)2.PF6). Steady-state and transient spectroscopic techniques, as well as solvatochromism techniques, were employed to establish the tunable ICT. Additionally, timedependant density functional theory (TD-DFT) calculations were used to complement the experimental results. The systematic study of antimony(V) porphyrins, especially tunable push-pull nature could play an important role in instigating high yield charge-separated states in multi-modular donor-acceptor systems for solar energy conversion and molecular electronic and photonic applications.

Encapsulation of superparamagnetic iron oxide nanoparticles in hollow wrinkled mesoporous silica

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Wrinkled mesoporous silica has gained attention as drug delivery vehicles for cancer therapy owing to the potential high loading capacity of anticancer drugs. A convenient method for the encapsulation of superparamagnetic iron oxide nanoparticles (SPIONs) in hollow core of wrinkled mesoporous silica will be reported. Superparamagnetic Fe3O4 and Co:Fe3O4 nanoparticles have been synthesized by a reduction–precipitation method. SPIONs have been encapsulated in hollow wrinkled mesoporous silica during synthesis using a surfactant template method. The SPIONs and encapsulated wrinkled mesoporous silica particles have been characterized by TEM, SEM, UV-Vis, PPMS, and XRD. Encapsulation of SPIONs in wrinkled mesoporous silica prevents oxidation of SPIONs surface and improves the dispersibility and colloidal stability. Additionally, it provides a surface for the conjugation of drug molecules and targeting ligands. Encapsulated wrinkled mesoporous silica (Fe3O4@WMS and Co:Fe3O4@WMS) combines the advantages of mesoporosity with the properties of superparamagnetic iron oxide nanoparticles.

Reduced physical aging in CMSMs derived from polyimide precursor incorporating cardo moiety and MOP-18

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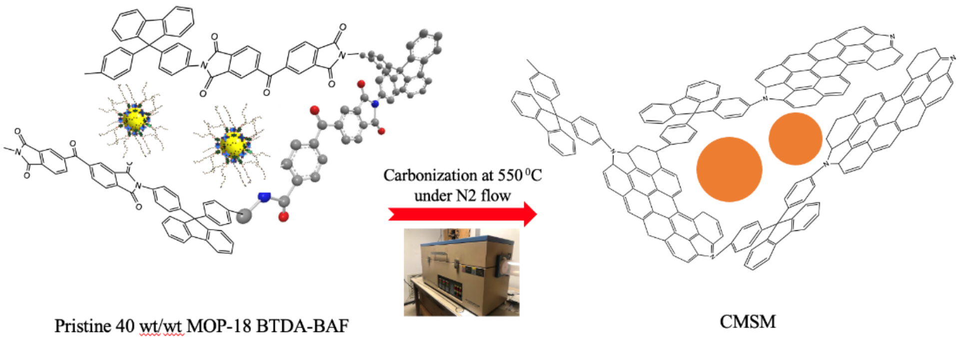
Carbon molecular sieve membranes (CMSM) were prepared by incorporating of bis(phenyl)fluorene-based cardo moiety as contorted diamine in the polyimides structure. The bulky group of cardo diamine in polyimides precursor prevents tight packing of the structure. Also, the rigidity in backbone restricts the ring rotation which will enhance the gas permeability. However, the design of the polymer precursor will affect the performance of resulted CMSM at the end. By introducing the cardo moiety in the polymer structure, the permeability has been increased in BTDA-BAF compared to Matrimid. On the other hand, CMSM are suffering from physical aging which is the densification of membranes. It means that the pore collapses over the time will decrease the permeability of membranes. Given that the aging of CMSM are exceeding through time, the strategy of using the copper metal particle in the membrane has been shown effectiveness on membrane permselectivities. Incorporation of metal organic polyhedra-18 (MOP-18) as a pillar agent into the polymer precursor of BTDA-BAF will prevent collapsing of the large unconnected graphene domains.



Detection and Remediation of Pharmaceuticals in Wastewater Using Gum Based Biopolymers

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Due to the improper dosage and disposal of pharmaceuticals, pharmaceutical wastes build up in the water at detectable levels. Drug Pollution, or the contamination of water sources due to pharmaceuticals or their metabolites, affects the growing concerns of water scarcity in modern civilization. These pharmaceuticals pose a persistent threat to the aquatic environment and have historically resulted in fish and bird kills. Biopolymers were chosen as the remediation agent due to the minimal to nonexistent toxicity to the aquatic environment and the ability to utilize locally sourced food grade produce. Simulated water samples spiked with standard were flocculated using four different biopolymers. These samples were extracted using solid phase extraction (SPE) and analyzed utilizing reverse phase high pressure liquid chromatography (HPLC). All polymers saw a minimal of 30% reduction of pharmaceuticals. Flaxseed polymers saw the highest removal rates of 70% to complete non-detection on all eight analytes. This test is currently being repeated under both neutral and acidic pH levels. It is the goal of this research to see a live water application of this trial providing the proof of concept for the applications of biopolymers in the remediation of drug pollution.

Understanding the Thermally Activated Dynamics of Silver-Gold Nanocages via in-situ Scanning Transmission Electron Microscopy

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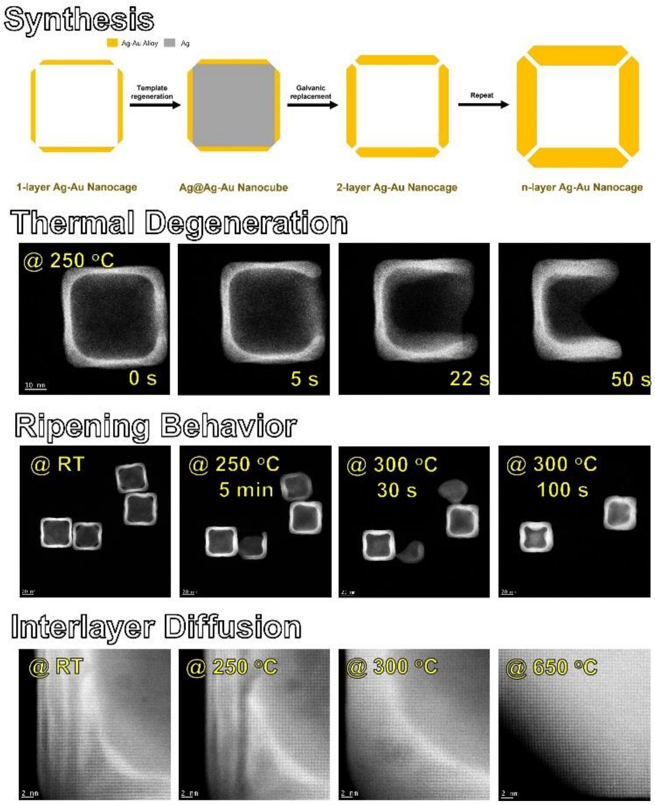
The real-time thermally induced evolution behavior of nanocages is of great research value in both fundamental studies and practical applications. In this work, by focusing on silver-gold (Ag-Au) alloyed nanocages as a model system, the thermal stability of nanocages is systematically evaluated by in-situ scanning transmission electron microscopy (STEM) from RT to 650 C^{o}. The results showed that nanocages with thicker walls displayed better stabilities. At sufficiently high temperatures, the nanocages were deformed to thermodynamically more stable nanostructures, which is surface-free energy derived. The deformation processes were found to be different for nanocages with various wall thicknesses, which were carefully monitored and analyzed by electron microscopy imaging. Further, the interlayer diffusion between Au-Ag and Ostwald ripening behavior is investigated at nanoscale with time-resolved serial STEM images. The insights from this study may serve as a solid foundation to inspire future fundamental and applied research on nanocage materials.



MOP-18/Matrimid based composite electrode for high energy hybrid supercapacitor electrodes

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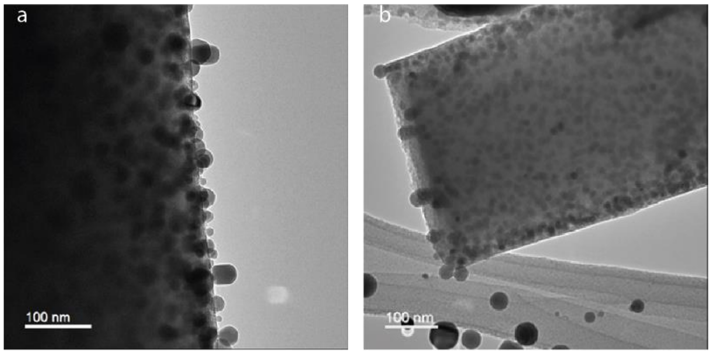

Fundamental development in electrical energy storage systems is required to meet the requirement caused by extensive grid implementation of renewable energy sources and the widespread adoption of electric vehicles. Supercapacitors, with their high-power density and long cycle life compared to other energy storage systems, hold promise to meet these toughening expectations. In this study, an in situ dispersion of metal-organic polyhedra (MOP)-18 in Matrimid is utilized to fabricate a hybrid supercapacitor electrode with superior redox activity and enhanced electrical conductivity resulting in impressive energy density. A homogenous solution of Matrimid and MOP-18 was electrospun and carbonized to obtain Cu/Cu2O decorated carbon fiber electrode materials. Exceptional solubility of MOP-18 was utilized to ensure uniform dispersion of Cu/Cu2O nanoparticles, resulting in significant pseudocapacitance in 6 M KOH electrolyte solution. N- containing carbon fiber from Matrimid precursor afforded excellent EDLC performance and sufficient electrical conductivity to support pseudocapacitance. Synthesized composite material achieved a maximum capacitance of 253 F g-1 at 1 A g-1 and an energy density of 25.4 Wh kg-1 at 1 A g-1. As demonstrated in the study, using soluble metal-organic structures to deliver redox-active materials in highly conducting carbon can be utilized to achieve composite electrode materials with synergistic properties.

Organic Section

SCI 2.215—Organic Chemistry

Entry	Time	Activity
Greetings	**9:40 am – 9:45 am**	***Greetings***
01	9:45 am – 10:00 am	Niyati Arora
02	10:00 am – 10:15 am	Jacob Randall Arvidson
03	10:15 am – 10:30 am	Sam Boardman
04	10:30 am – 10:45 am	Courtney Cooper
Break	**10:45 am – 11:00 am**	***Intermission***
05	11:00 am – 11:15 am	Ting Han
06	11:15 am – 11:30 am	Kara Kassees
07	11:30 am – 11:45 am	Cristina Cu Castillo
08	11:45 am – 12:00 pm	Milinda Chathuranga Senarathna
09	12:00 pm – 12:15 pm	
Break	**12:15 pm – 1:45 pm**	***Lunch Break***
10	1:45 pm – 2:00 pm	Sumon Sarkar
11	2:00 pm – 2:15 pm	Ziyuan Ma
12	2:15 pm – 2:30 pm	Spenser Lloyd Washburn
13	2:30 pm – 2:45 pm	
Break	**2:45 pm – 3:00 pm**	***Intermission***
14	3:00 pm – 3:15 pm	
15	3:15 pm – 3:30 pm	
16	3:30 pm – 3:45 pm	
17	3:45 pm – 4:00 pm	
Break	**4:00 pm – 4:30 pm**	***Break***
Awards Ceremony	**4:30 pm – 5:00 pm**	***Awards Ceremony (SCI 1.220)***

For questions about scheduling for Organic Section, e-mail:
Phillip Arche pea190001@utdallas.edu

2D-Covalent Organic Frameworks with inter layer Hydrogen Bonding for improved strength at small and large scale

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2D Covalent organic frameworks (COFs) are a class of crystalline porous polymers that are synthesized under thermodynamic control. This research describes the synthesis and characterization of a class of COFs called COFamides whose stacked sheets adhere together by hydrogen bonding interactions. To achieve this, we have designed monomers that use a sterically crowded design that forces the amide side groups out of the plane to direct the hydrogen bonds between the COF sheets. Hydrogen bonds can add significant structural strength to the COFamides when compared to conventional COFs that are held together by other kinds of non-covalent interactions. We have characterized COFamides for their surface area, crystallinity and pore size. The processability challenges of the COFs makes characterizing hydrogen bonding through conventional techniques such as 1H NMR challenging. We aim to use both spectroscopic and chemical modifications to the COF structure to help elucidate structure-function effects on COFamide polymerization related to hydrogen bonding. Advanced infrared spectroscopy methods such as variable temperature, and H/D exchange, will be employed to enable direct measurements of hydrogen bonding interactions.

Polycyclic Aromatic Hydrocarbon-Fused π-Extended β-Functionalized Porphyrins

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β, β'-functionalized and π-extended porphyrins represent large aromatic systems which give rise to unique photophysical and optoelectronic properties. These properties can be tuned by increasing the size and type of aromatic systems fused through the β, β'positions of the porphyrin. Pentacenes and higher acenes are notoriously unstable and previous research in our group has revealed that dramatic increases in stability arise when a pentacene moiety is fused to the β-positions of Ni(II) porphyrin. This research is focused on extending and tuning the aromaticity of the porphyrin through fusion of groups such as acenaphthene to the β, β' positions. This presentation covers the synthesis, characterization, and spectral analysis of a series of acenaphthene-fused porphyrins.

Interlayer Hydrogen Bonding Containing 2D-Covalent Organic Frameworks

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Covalent Organic Frameworks (COFs) are a class of crystalline porous polymers that are assembled in two-dimensional sheets to form covalently linked architectures. Through the design of sterically crowded aromatic systems containing hydrogen bonding sidechains, out-of-plane torsions break coplanarity and promote interlayer hydrogen bonding between COF sheets. A series of urethane, hydroxyl, and amide-containing monomers have been synthesized and subsequently used for the synthesis of COFs to study the effect interlayer hydrogen bonding imparts on COF crystallinity, porosity, and surface area.

Synthesis of Dimer and Trimer β, β’-naphtho-fused dithiophenyl-porphyrins with diethynylbenzene linkers via Sonogashira Coupling

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Porphyrin arrays have been around since the early 1980s and have been widely used in furthering the field's understanding of inter-porphyrin electronic interactions in terms of energy and electron transfer. Palladium-catalyzed cross-coupling reactions have been the primary mode of synthesizing these porphyrin arrays(1,2); however, carbon coupling on porphyrins with the reactions like Suzuki, Heck, and Sonogashira coupling is predominantly through coupling at the meso-positions between two or more porphyrin; carbon-coupling through the β-positions has not been widely studied or reported. Those that have been, by groups such as Van Lier (3) and Osuka (4,5), used metal-inserted β-haloporphyrins to generate their ethynylated products in yields ranging from 20-78% yields. Our group has extended the β, β’-positions in our naptho-fused-dithiophenyl-porphyrins initially through a cascade-heck-6π-cyclization reaction followed by a Scholl reaction and mono- and di-bromination of the 5-position of the thiophene moieties in yields of 74-87% yield(6). From these compounds, our group has successfully performed Sonogashira coupling with a few ethynylbenzene derivatives on freebase porphyrins in high yields (87-100%). In this report, the synthesis and characterization of these porphyrins and their subsequent use to synthesize novel β, β’-extended freebase porphyrin dimers, and trimers via Sonogashira coupling will be detailed.

Design and Synthesis of Polyimide Covalent Organic Frameworks based on the β-Functionalized Porphyrin

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Since the seminal work of Yaghi and co-workers made the first COFs in 2005, the rapid development in this research area has attracted intensive interest from researchers with diverse expertise.1 There is a growing interest in tetrapyrrolic

macrocycle-based COFs in which naturally occurring porphyrin and the synthetic analogs of porphyrin are employed as building blocks. Due to the intriguing properties of porphyrin units, the resulting COFs have found applications in different areas such as gas absorption, storage of energy, optoelectronics, and catalysis.2 All the porphyrin-based COFs have utilized meso-functionalized porphyrins.3-4 In contrast, β-functionalized porphyrins of the type shown below have remained unknown. In this project, the synthesis and characterization of the first examples of β-functionalized porphyrin polyimide covalent organic frameworks will be presented

Development of an Estrogen Receptor Alpha Inhibitor and the Structure-Activity Relationship

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After the development of novel estrogen receptor alpha inhibitor (ERα) ERX-11, alterations to the design to increase affinity and potency were extensively explored (eLife, 2017). Upon the discovery of ERX-41, which included an addition of a C-terminal trans-4-methylcyclohexane moiety greatly improved both binding affinity and potency at the ERα receptors in ER+ breast cancer (JMC, submitted). Additions to this moiety eventually revealed a new analogue, ERX-208, that showed activity at both breast and ovarian cancer ERα receptors (Ahn et al, unpublished). Attempts to elucidate the structure-activity relationship between this compound and the ERα receptor led to the discovery of the novel compound KK1. In vitro assays showed significant activity on ovarian cancer cell lines SKOV3 and A2780, with increased potency in 4 separate breast cancer cell lines, most notably the triple-negative cell lines, Sum159 and MDB-MB-231. This finding suggests a potential secondary target previously unidentified for the mechanism of action for KK1, which is currently still being explored. KK1 also offers improved solubility as compared to previous analogues. Solubility has previously been a hurdle to diagnostic and clinical applications due to the highly hydrophobic nature of the tris-benzamide scaffold. The development of the structure-activity relationship between KK1 and ERα is ongoing in research which will be discussed in this work.

Photo-responsive materials for Organic Field-Effect Transistors (OFETs)

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Organic Field-Electronic Transistors (OFETs) are devices that possess unique advantages due to ease of preparation in large-area flexible plastic films, significant charge mobility, and synthetic control over electronic properties. Some OFETs have been constructed with photochromic-switching moieties in the past decade which exhibit photo-responsive electronic properties. Photochromic molecules undergo isomerization between two stable states upon irradiation. The unique photo-switching performance provides an essential role in photo-responsive OFETs devices. An irradiation light trigger can reversibly tune the output signal of a photochromic OFET by introducing photochromic units into the electronic materials system, resulting in a stimuli-responsive device with potential applications. This abstract provides a brief information relevant development of photochromic switching moieties incorporating organic electronic materials in OFETs, based on different photochromic classes such as diarylethenes, spiropyrans, and azobenzenes. Lastly, a brief perspective of photo-switchable OFETs materials based on bicyclic-aziridine is shown.

Understanding the bulk mechanical properties of solution processable hydrazone linked covalent organic framework films

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Covalent organic frameworks (COFs), known as a promising class of materials for various types of applications. However low solution processability limits their utility in many areas. Specially with hydrazone linked COFs, due to their high chemical stability processing is difficult. Here we report side chain engineering method to improve processability of hydrazone COFs (COF-PEO-3) and to develop COF films. Understanding the mechanical properties of these films is important to actual applications of COF films and it is challenging to understand the behavior of bulk materials using localized and non-direct techniques. Straightforward Instron technique is more valuable in large scale applications. Here we synthesized free-standing films with micrometer range thickness and mechanical testing conducted directly in Instron. Crystalline, flexible COF-PEO-3 films were synthesized with Ultimate tensile strength 14.81±2.19 MPa and Young modulus of 391.77±118.67 MPa.

Photoinduced metal-free radical α-C(sp3)–H borylation of amines

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We have developed a mild, photoinduced, transition metal-free α-C(sp3)–H borylation of amines. This general, selective, and operationally simple method features: (a) visible light-induced diboron reagent mediated aryl radical generation; (b) employment of commercially available and easily installable/removable reactive amide-based tether leading to the remote C–H activation; (c) a 1,5- hydrogen atom transfer (HAT) process for the generation of key α-amino radical intermediate; and (d) efficient radical addition to diboron reagents leading to borylation product. The generality of this method is demonstrated by the employment of a wide range of acyclic and cyclic amines, including complex and pharmaceutically relevant molecules. Complementarity with the existing approaches, as well as mechanistic studies and synthetic utilities of this new method will be discussed.

Investigation of Chalcogenopheno[3,2-b]pyrrole Containing D-A-D Small Molecules for Organic Field-Effect Transistors

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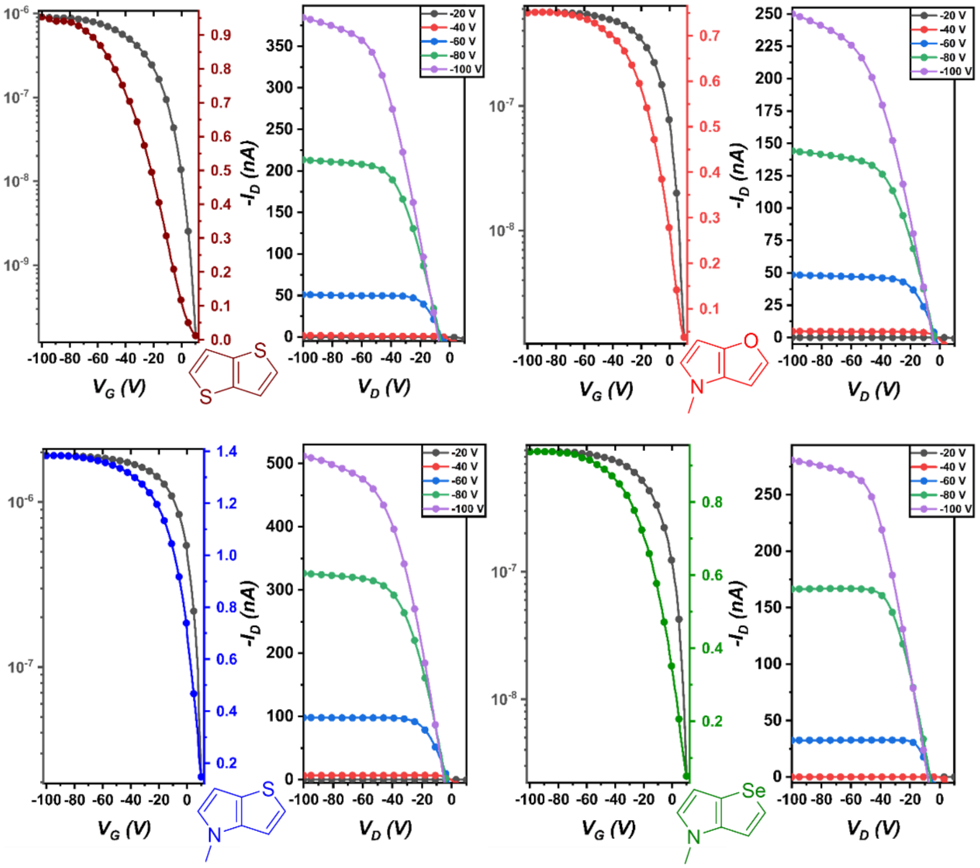
Chalcogenopheno[3,2-b]pyrrole, including thieno[3,2-b]pyrrole (TP), furo[3,2-b]pyrrole (FP), and selenopheno[3,2-b]pyrrole (SeP), has been studied as donor moieties coupled with benzo[c][1,2,5]thiadiazole (BT) based acceptor in small molecules and applied on organic field-effect transistors (OFETs). However, a systematic investigation of the performance of chalcogenopheno[3,2-b]pyrrole containing molecules is limited. In this study, we systematically designed, synthesized, and characterized four new donor-acceptor-donor (DAD) small molecules which contain three chalcogenopheno[3,2-b]pyrroles and thieno[3,2-b]thiophene (TT) as donor and diketopyrrolopyrrole (DPP) as acceptor.

TT containing molecule was designed as a reference due to the similar bicyclic aromatic structure compared to chalcogenopheno[3,2-b]pyrrole and its utilization in organic semiconductors. Optoelectronic properties, thermal analysis, and OFETs application of four molecules were investigated. All molecules showed OFETs activity with maximum hole mobility at lower annealing temperatures. All three chalcogenopheno[3,2-b]pyrrole containing molecules showed better performance in OFETs compared to TT containing molecule, and FP containing molecule showed the highest mobility among these molecules. The result of this work instills confidence for further studies to replace thieno[3,2-b]thiophene with chalcogenopheno[3,2-b]pyrrole in conjugated polymers.



Synthesis of β, β’-fused polycyclic hydrocarbon porphyrins

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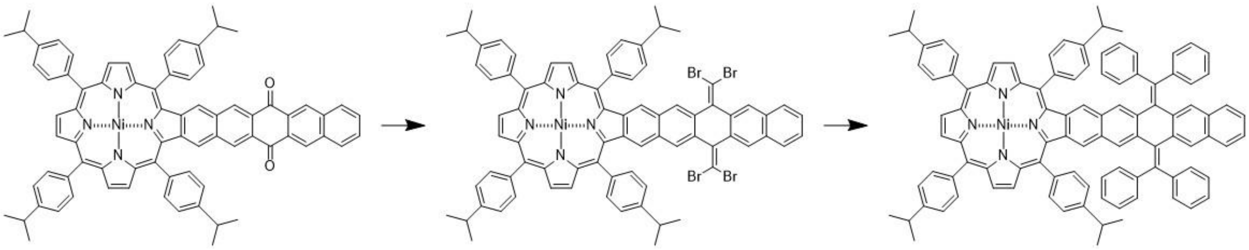
Cross-conjugation, where two separate conjugated branches are linked to the same carbon atom that participates in conjugation with each branch independently, for neutral molecules it was seen unfavorably due to its impedance of linear conjugation. However, the advancement of molecular electronics quickly changed those perceptions. Chemically synthesized circuits where the desired electronic function is controlled through careful consideration of the substituents, has pushed cross-conjugation to the forefront. Where linear conjugation will act as the “wires” for the electronics, cross-conjugation can step into the roles of switches, logic gates, or even memory elements. Combining cross-conjugation with polycyclic aromatic systems may provide the best of both worlds into one compound. In this talk, the synthesis and characterization of a novel class of cross-conjugated π-extended systems incorporating both porphyrin and polycyclic aromatic hydrocarbons (PAHs) will be presented. With the intention of uniting PAHs and cross-conjugation, our group began with a β, β’-fused pentacene quinone porphyrin. Functionalization of the quinone would maintain the cross conjugation but would also allow us to expand the π conjugation into larger PAHs. Through a modified Ramirez reaction, the ketone groups of the quinones were transformed into halogenated methine groups. There are several advantages to this reaction, the first being that the halogenated methines are prime candidates for carbon-coupling reactions. Another advantage being it allowed for the symmetrical addition to the methine bridges, while maintaining the cross conjugation to the pentacene moiety. The Suzuki-Miyaura coupling reaction was utilized to attach benzyl groups to the methine bridges. Characterization methods for these compounds were studied using UV-Vis, NMR, and XRD.



Physical/Computational Section

SCI 1.210—Physical/Computational section

Entry	Time	Activity
Greetings	**9:40 am – 9:45 am**	***Greetings***
01	9:45 am – 10:00 am	Ayesh Kalapuwage
02	10:00 am – 10:15 am	Yazdan Maghsoud
03	10:15 am – 10:30 am	Madison Berger
04	10:30 am – 10:45 am	Kevin Alberto
Break	**10:45 am – 11:00 am**	***Intermission***
05	11:00 am – 11:15 am	Sicheng Wang
06	11:15 am – 11:30 am	Zhou Lu
07	11:30 am – 11:45 am	Shubham Chatterjee
08	11:45 am – 12:00 pm	Juliana Josephine Antonio
09	12:00 pm – 12:15 pm	Bárbara Maria Teixeira Costa Peluzo
Break	**12:15 pm – 1:45 pm**	***Lunch Break***
10	1:45 pm – 2:00 pm	Kira Mills
11	2:00 pm – 2:15 pm	Arkanil Roy
12	2:15 pm – 2:30 pm	Mauricio Martil de la Garza
13	2:30 pm – 2:45 pm	Dineli Ranathunga
Break	**2:45 pm – 3:00 pm**	***Intermission***
14	3:00 pm – 3:15 pm	Tao James Chen
15	3:15 pm – 3:30 pm	Jacob Koehler Lynd
16	3:30 pm – 3:45 pm	Margaret McCutcheon
17	3:45 pm – 4:00 pm	Mateus Macedo Quintano
Break	**4:00 pm – 4:30 pm**	***Break***
Awards Ceremony	**4:30 pm – 5:00 pm**	***Awards Ceremony (SCI 1.220)***

For questions about scheduling for Physical/Computational Section, e-mail:
Kira Mills Kira.Mills@utdallas.edu

Analyzing Hydrogen-Bond Patterns from Protein-Drug Compex via Machine Learning Approach

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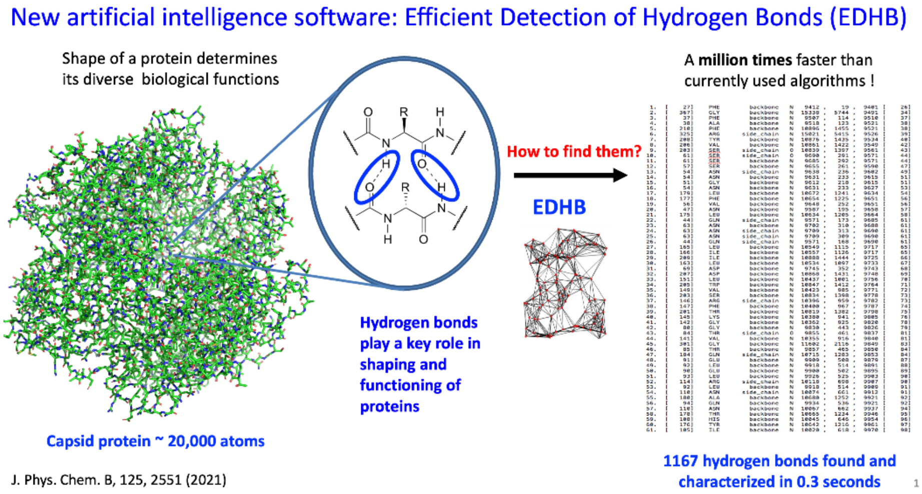
Interaction between protein and small molecules with a high specificity and affinity to form a specific complex, designs the fundamental basis for contemporary structure-based drug design research. Mainly hydrogen bonds (HB) are the elementary interaction and special geometric requirements of HBs constitute the selectivity in protein-drug complexes. Therefore HB patterns appropriate a detailed analysis. Efficient Detection of Hydrogen Bonds (EDHB) is a software that systematically identifies HB geometries based on the nearest neighbors algorithm. Nearly 7200 proteins with their specific ligands were utilized for the analysis and 21928 HBs detect.



New artificial intelligence software: Efficient Detection of Hydrogen Bonds (EDHB)

Shape of a protein determines its diverse biological functions

A **million times** faster than currently used algorithms !

How to find them?

EDHB

Hydrogen bonds play a key role in shaping and functioning of proteins

Capsid protein ~ 20,000 atoms

J. Phys. Chem. B, 125, 2551 (2021)

1167 hydrogen bonds found and characterized in 0.3 seconds

1

Glycine, Aspartic acid and Threonine amino acid show the best donor properties while Proline was the least. On the other hand, Glycine, Glutamic acid and leucine exhibit the most favorable acceptor properties. HB length, angle, type and network are the main factors calculating the HB strength. The HB length is majorly distributed around 1.5 Å- 2.4 Å and HB angle around 110°-180°. Shorter bonds are not always stronger bonds as a result of strength variation according to the environment. Electrostatic energies largely deviate due to variations of electronegativity in N and O atoms. N-H...O HB type depicts nearly 70% and O-H...O and N-H...N show 14% and 13% respectively. Two or more HBs share the same acceptors called HB networking. More than half of the interactions were 0-0-0(No network) and HB networking is also possible. Quantitative measure of intrinsic HB strength is needed for further analysis.

QM/MM Studies on the Reaction Mechanism of the Cas9 HNH Domain

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The clustered regularly interspaced short palindromic repeats (CRISPR) technology is an RNA-guided targeted genome-editing tool using the Cas family proteins. Two magnesium-dependent nuclease domains of this enzyme termed HNH and RuvC are responsible for the cleavage of the t-DNA and nt-DNA, respectively. It is believed that the HNH domain determines the DNA cleavage activity of both nuclease domains and is sensitive to the complimentary of the RNA-DNA. Thus, investigation of the structure and dynamics of the catalytic state of Cas9 with either matched or mismatched t-DNA is critical for improving its specificity. Hybrid quantum mechanics/molecular mechanics (QM/MM) studies have been done by either metal-bound water or a second coordination shell water to propose detailed mechanisms for the cleavage reaction by the HNH domain. However, these efforts were based on an inactive structure, which shows the necessity of more investigations into the mechanistic details and structures of the t-DNA cleavage mechanism in this domain. In the current study, by using a recent catalytic-active structure of the Cas9 and employing the classical molecular dynamics (MD) and hybrid QM/MM, we have studied the mechanism of t-DNA cleavage reaction at the HNH domain. Moreover, by designing a mismatched t-DNA structure called MM5 (C to G in the fifth position of the PAM region), the impact of sg-RNA and t-DNA complementarity on the catalysis process was also investigated.

Comparison of Two Polarization Coupling Approximations in Polarizable QM/MM

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Quantum mechanics/molecular mechanics (QM/MM) methods are a useful tool to help bridge the gap between using pure QM or MM on particularly large systems. Greater accuracy can be achieved by using polarizable force fields to better explain some of the many-body effects a system can experience such as polarization or charge transfer. The layered interacting chemical models (LICHEM) program enables QM/MM calculations with polarizable force fields such as AMOEBA. The current design of LICHEM has full polarization of both regions but not of the two coupled together. Our newest implementation improves upon this by using the induced dipoles from an initial MM calculation and incorporating them into the calculation of the new effective Hamiltonian. This new addition was tested on a variety of water systems as well as a small solvated diaspartate reaction.

Controlled Payload Release of Photoswitchable Liposomes for Drug Delivery: A Molecular Dynamics Approach

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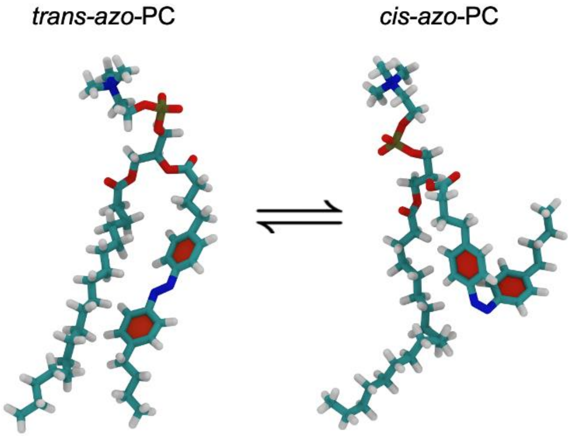
The need for increased drug treatment efficacy has led to the rise of stimuli-responsive nanocarriers for drug delivery. This talk explores the use of novel liposomes as one such nanocarrier. Specifically, we explore liposomes containing azo-PC, a phospholipid functionalized with an azobenzene moiety in one of its tails which allows it to undergo a light-induced conformational change. When irradiated with 365-405 nm light, structural changes in the membrane induced by the transition from trans-azo-PC to cis-azo-PC allow the contents of the liposome to be released. Conversely, irradiation with 455 nm light, which causes photoisomerization from cis-azo-PC to trans-azo-PC, arrests the release. We employ molecular dynamics simulations to characterize the structural features of azo-PC membranes to help identify the nature of permeation.



Two-Dimensional Conjugated Covalent Organic Frameworks under High-Pressure

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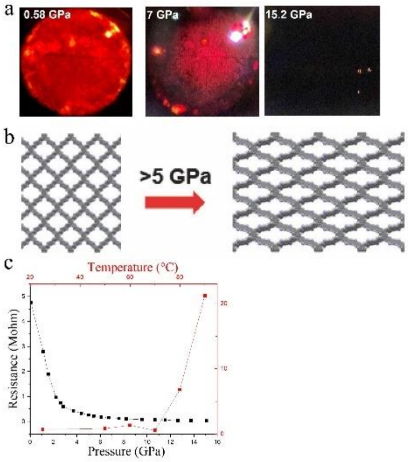

Covalent organic frameworks (COFs) possess high stability due to the covalent backbones and are promising platforms for electrocatalyst, sensors, energy storage as well as quantum information systems1-5. These mechanically robust COFs provide exciting opportunities to probe the electronic states of porous materials under high pressure. In this work, we investigate a two-dimensional conjugated COF known as sp2-c-COF6. Raman spectroscopy and X-ray diffraction show that the 2D COF is stable up to 15 GPa. Interestingly, in situ electrical transport reveals an insulator-to-metal transition in tetracyanoquinodimethane (TCNQ)-doped sp2-c-COF at 9 GPa, representing the first porous crystalline material with true metallic transport. Density-functional tight binding (DFTB) modeling show pressure-induced coplanarity as the main structural driving force for the evolution of electron states. These results pave the way for further investigation of COFs as a new class of electronic materials under extreme conditions.

Modulating the Extent of Cuprophilicity Under High Pressure

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Metallophilicity (i.e. closed-shell metal–metal interaction) has been widely adopted in inorganic chemistry as a significant supramolecular interaction. The studies of metallopholicity have well developed since the 1970s through the combination of X-ray crystallography, spectroscopy, and theoretical calculations. However, the origin and extent of metallophilicity remain controversial over the past decades, especially on the attractive or repulsive nature and the role of spd hybridization of the metal atoms. Herein, we report the anomalous anisotropic changes in crystallography, Raman vibrations, and interaction energies in a multinuclear Cu(I) pyrazolate complex upon mechanical compression to probe the nature of cuprophilicity. The high-pressure powder X-ray diffraction (PXRD) and density-functional theory (DFT) results indicate the contraction of the inter-molecular Cu–Cu distances below the sum of their van der Waals radii at 10 GPa, signaling the onset of cuprophilicity under pressure. In contrast, the intra-molecular Cu–Cu distances increase, directly opposing the general trend of shrinking interatomic distance under pressure. In-situ high-pressure Raman spectroscopy revealed opposite shift trend for the intra- and inter-molecular Cu-Cu stretching modes, highlighting the anomalous weakening of the intramolecular cuprophilicity upon compression. Energy decomposition analysis (EDA) indicates the net dispersion attraction between the dimers at ambient pressure is overwhelmed by electrostatic and Pauli exclusion interactions at higher pressure. DFT further reveals that compression pushes electron from filled N 2p orbitals to empty Cu 4p orbitals, thereby favoring 4p-3d hybridization to enhance intermolecular cuprophilicity and blue-shift of vinter. Overall, our work highlights the anisotropy of metallophilicity which has been largely omitted in previous research, and reveals the repulsive nature of cuprophilicity arising from Pauli repulsion in lack of the inner-shell d-orbitals and spontaneous induced (n+1)p/nd hybridizations.

Possible Reaction Mechanisms for Direct C-H Arylation using Density Functional Theory Calculations

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Arylated five-membered (hetero)aromatic compounds are used in various electronics like transistors, solar cells, and light-emitting diodes due to their electron-withdrawing nature. Negishi, Suzuki, or Stille cross-coupling method are conventional synthesis methods for these compounds, which are not as atom economic as some recent methods like direct C-H arylation. A novel iminopyridine-based α-diimine nickel (II) complex has been synthesized that can catalyze a direct C-H bond (hetero)arylation. This is the first study that uses a nickel-based catalyst for such synthesis and thus presents a challenge to guess the possible mechanism involved. Here, we have used density functional theory (DFT) to investigate the possible reaction profiles for the catalytic mechanism of the Ni-based catalyst. All calculations have been done at the PBE0/def2-TZVP level as implemented in Gaussian16 in the gas phase and implicit solvent using the Solvation Model Based on Density (SMD). The transition states were tested for connecting the desired reactant and product using Internal Reductant Coordinate (IRC) calculations. Calculated results provide insights into the preferred oxidation state and possible products.

DFT Investigation of Para-Substitution Effects on the C-CN Bond Activation of Benzonitrile by a Zerovalent Nickel Complex

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C—C bond activation has been an active area of research due to its extensive range of applications in in industry and synthesis. Despite its significance, the cleavage of a C—C bond has been challenging due to the thermodynamic stability and steric hindrance of the C—C bond. In this study, density functional theory (DFT) calculations on the C—CN bond activation of para-substituted benzonitriles, p-XC_6H_4CN, where X= NH_2, OCH_3, CH_3, H, F, CO_2CH_3, CF_3 and CN, with the [Ni(dmpe)] fragment as a model for [Ni(dippe)] fragment will be reported. A comparison of the computational results with the previously reported experimental will also be presented.

Uranium Complexes: Beyond Nuclear Fission

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Uranium is widely known for being used as nuclear fuel in energy generation purposes. Moreover, U containing molecules, in particular, coordination compounds, present potential applications in many fields; catalysis, for example. Due to its complex electronic structure, a direct result of relativistic effects, a broader range of oxidation states is observed and, by consequence, a higher number of compounds. Even though, for a long time, it was believed that U(III)

was the lowest stable oxidation state, until the first U(II) molecule was experimentally observed. Since then, U(II) compounds have received considerable attention. Recently, a bi-coordinated U(II) complex, in the shape of a “sandwich”, was synthesized by Layfield and collaborators. A key aspect of this molecule lies in its geometry: uranium and ligands are in a perfectly linear arrangement.

This study aims to investigate a series of U(II) sandwich molecules, derived from Layfield complex. We focusing in addressing U-ligand bond strength and character. Moreover, we also discuss about the possibility of observing a bent molecule, and in establishing an explanation for the molecular geometry, with respect to ligand-U-ligand angle. In order to do so, the electronic structure was investigated through Density Functional Theory with the relativistic Hamiltonian NESCau, a two-component exact Dirac method, developed in our group. U-ligand bond strength was addressed through our Local Vibrational Mode Analysis, that allows one to decouple the molecule’s vibrational spectra and look directly at a specific fragment, rather than the entire system. The bonds covalent character were investigated through energy density analysis, using the Cremer-Kraka criterion for covalent bonds. Finally, valence orbitals occupancy were evaluated.

Molecular Dynamics Study of Proton-Coupled Fluoride Transport in the CLC^F Antiporter

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Fluoride (F^-) is well-known to act as a natural antibiotic, inhibiting the enolase and phosphoryl-transfer enzymes necessary for bacterial survival, at concentrations as low as 10-100 μM. It’s unsurprising, then, that researchers recently discovered a riboswitch which, upon F^- binding, turns on transcription for two phylogenetically unrelated bacterial fluoride exporters: the CLC^F F^-/H^+ antiporter, belonging to the CLC superfamily of anion-transport proteins; and Fluc, a fluoride-specific ion channel. Since their discovery in 2012, there have been few studies examining these proteins, leaving many questions unanswered. As such, my research involves the use of computational models to specifically study the bacterial CLC^F antiporter and discover details about its structure and mechanism of transport. Through extensive MD simulations of a double bilayer system, I have been able to uncover new details of the transport pathway utilized by CLC^F, and the combination of this information with umbrella sampling simulations has provided additional knowledge on the mechanism of transport and the key residues involved.

Computational Study of Mitochondrial DNA Polymerase

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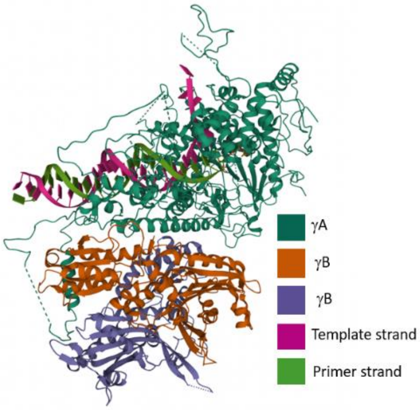
Classification: Graduate



DNA polymerases are a class of enzymes that catalyze the process of DNA replication during cell division. They are essential in ensuring that each daughter cell gets an identical copy of DNA and are involved in the process of DNA repair. One such polymerase is the mitochondrial DNA polymerase, pol gamma. Pol gamma is the only polymerase in the eukaryotic mitochondria and is essential for the replication of the mitochondrial DNA and the process of oxidative phosphorylation that provides the body with ATP. Mutations in the polymerase cause certain disorders and are known to cause certain types of cancer, namely breast, prostate and melanoma. This study deals with the computational study of the structural and thermodynamic properties of cancer causing variants of pol gamma using molecular dynamics methods, and comparing the results with those of the wild type. This will help in development of diagnostic and clinical tools. Structural and dynamical results of wild type pol gamma with the two different ions, as well as cancer variants will be presented.

Computational Characterization of Cancer-Associated Mutations on POT1

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Mutations caused by single nucleotide polymorphisms (SNPs) have been associated with the development of cancerous cells. For example, mutations on the protection of telomeres 1 (POT1) have been shown to increase the length of telomeres and facilitate the development of melanoma. POT1 plays an important role in the shelterin complex for the binding to the telomere and signals the end of the chromosomes, this is an example of how mutations produced by SNPs can affect the structure and function of a protein. Three particular mutations have been experimentally shown to affect POT1. Here, we have used classical molecular dynamics (MD) simulations to investigate how these mutations change the structural and/or dynamic behavior of the three POT1 variants compared to the wild type protein. Our results provide insights on the particular effects that each of these melanoma-associated mutations play on the function of POT1.

Histone Tail Dynamics Regulate the Ubiquitylation Machinery

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The BRCA1 (breast cancer susceptibility protein type 1) gene, which belongs to the family of tumor suppressor genes, is well known for its ability to protect cells from turning into cancer. It plays a vital role in genomic stability and control of cell division by participating in DNA double-strand break (DSB) repair. BRCA1 is a RING domain protein that contains the largest class of recognized ubiquitin (Ub) ligases and promotes the Ub transfer reaction. The formation of BRCA1/BARD1 heterodimeric complex is important for their mutual stability, as well as for the correct nuclear localization and maximum activity of Ub ligase (E3). Recently, nucleosome histone H2A was discovered to act as a substrate for BRCA1/BARD1-dependent E3 ligase activity. BRCA1/BARD1-dependent H2A ubiquitination is essential for its function as a tumor suppressor, and to promote DNA DSB repair through homologous recombination and serve as a marker of transcriptional repression. The mechanism of nucleosome ubiquitination by the BRCA1/BARD1 heterodimer has not yet been fully understood. Here, we use molecular dynamics simulations to provide molecular-level insights into the dynamics of nucleosomal histone tails and BRCA1/BARD1/BRCA1-Ub conjugating enzyme (E2) on the nucleosome surface. The interaction between histones and the BRCA1/BARD1/E2 complex is also studied primarily focusing on the lysine residues in the less studied, flexible, and disordered H2A tail region. Substrate residues that stand close to the E2~Ub active site and their approach mechanism to E2 were further investigated. Since BRCA1/BARD1 mutations predispose cells to chromosomal instability and greatly increase the possibility of cancer development, the effect of mutations on Ub-ligase activity is been carefully studied. The findings of this research help to explain the interactions between the BRCA1/BARD1 complex and nucleosome histones at the molecular level to understand its role as a tumor suppressor.

An Investigation of Singlet Fission with the Presence of Correlated Vibrational Motion for the Electronic States

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Singlet fission refers to a photophysical process which converts a singlet excited state into two triplet excited states, potentially enabling solar cells that exceed the Shockley-Queisser limit. In this talk, I will first demonstrate that the hierarchy of pure states (HOPS) method can reproduce previously reported singlet fission dynamics. The process of singlet fission is often mediated by the presence of charge transfer states. In previous models, independent vibrational environments have often been assumed for the singlet, charge transfer, and triplet pair states. Here, I will explore how singlet fission dynamics could be modified by the presence of correlated vibrational motion for the electronic states localized on the same molecules.

Simulating Organic Photovoltaic Charge Separation with a Size-Invariant Formally-Exact Method

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The process of charge separation in organic photovoltaic (OPV) materials can be described using an open quantum system formalism in which a relatively small system of electronic degrees of freedom is coupled to a macroscopic thermal environment of vibrational modes. Because exact solutions to open quantum system dynamics scale catastrophically with the number of molecules, investigations into the role of dimensionality in the mechanism of charge separation have previously been limited. Furthermore, because the timescales of the bath vibrational modes vary greatly, accurate simulations require fine time steps, making calculations inconvenient even when they are tractable. In this talk, I will present a solution to both issues: the adaptive Hierarchy of Pure States (adHOPS) with a low-temperature correction. adHOPS is a formally-exact method of solving open quantum systems that exhibits size-invariant scaling in large systems via adaptive basis set truncation, making simulations of 2- and 3-dimensional OPV complexes tractable. A low-temperature correction to the adHOPS equation of motion will allow the contribution of ultrafast bath modes to be treated independently of simulation time step, significantly increasing the time step at which dynamics are accurate and thereby speeding up simulations. By using this low-temperature-corrected adHOPS, I will, for the first time, survey the combined roles that dimensionality and vibrational relaxation timescales play in charge separation with a formally-exact method.

Nitrile Photo-Dissociating Ruthenium Drug Candidates – A Local Vibrational Mode Study

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Classification: Graduate

In this work, we investigated the local properties of 15 Ru(II) complexes of the type $[Ru(tpy)(L)\text{-}(CH_3CN)]n^+$, where tpy = 2,2':6',2''—terpyridine and L indicates the unique ligand for each compound. These complexes have been found to dissociate CH_3CN when allowed to interact with wavelengths of light that induce Singlet-to-Triplet transition. Therefore, they are good candidates for modeling the release of nitrile containing drugs. Such targeted therapy is of great interest in the medical field, especially oncology. To explain overall experimental outcomes of these compounds, we investigate local properties using local force constants as a quantitative measure of Ruthenium-Nitrile (Ru-NC) and Ruthenium-ancillary ligand (Ru-L) bond strength. This was complemented by analyzing the energy density of these bonds, the bond orbitals, Singlet-Triplet splitting energies, and the reaction energetics. 12 compounds, originally synthesized by an experimental group, were investigated. We have identified properties of the changing ligand which correlate to increased release of nitrile, thus modeling increased release of drugs. Based upon the conclusions we draw herein; we propose three new compounds. These results form a valuable basis for future design and fine tuning of nitrile releasing Ruthenium compounds, as well as for the understanding of how local properties affect overall experimental outcomes.

The Salt-cocrystal Continuum Seen Through the Eyes of Vibrational Spectroscopy

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Prior to crystallization in a specially prepared mixture, the prediction of cocrystal or salt formation is given based on the relative tendencies for its constituent species, namely, the protonated form of the base (BH^+) and the acid (HA), to undergo dissociation in solution. While salt is characterized by the complete proton transfer from the acid (HA) to the base (B), a two-component cocrystal that is maintained by hydrogen bonding can be pictured as the neutral A−−H−−B structure, where the proton is “frozen in time” halfway through. So far, salt/cocrystal assessment is mostly based on an empirical rule, the so-called pK_a rule, using differences in the acid dissociation constant (ΔpK_a) as guidance. If $\Delta pK_a = pK_a(BH^+) - pK_a(HA)$, is negative, the acid-base complex is considered a cocrystal. If ΔpK_a is positive and larger than 3, the acid-base complex is considered a salt. In a range of $0 < \Delta pK_a < 3$, both cocrystal and salt formation are possible. We have developed a new protocol for the identification of salts/cocrystals based on hydrogen bonding assessed with local vibrational mode theory.

Polymer Section (Morning)/ Undergraduate Section II (Afternoon)

SCI 2.230—Polymer chemistry in the morning/ Undergraduate section II in the afternoon

Entry	Time	Activity
Greetings	**9:40 am – 9:45 am**	***Greetings***
01	9:45 am – 10:00 am	Sachini D Perera
02	10:00 am – 10:15 am	Dr. Jing Ge
03	10:15 am – 10:30 am	Rebecca M Johnson
04	10:30 am – 10:45 am	Hanghang Wang
Break	**10:45 am – 11:00 am**	***Intermission***
05	11:00 am – 11:15 am	Ashele Kiwana Remy
06	11:15 am – 11:30 am	Abhi Bhadran
07	11:30 am – 11:45 am	Karen Paola Cortes-Guzman
08	11:45 am – 12:00 pm	
09	12:00 pm – 12:15 pm	
Break	**12:15 pm – 1:45 pm**	***Lunch Break***
10	1:45 pm – 2:00 pm	Rebecca Walker
11	2:00 pm – 2:15 pm	Joanna Ngoc-Truc Vo
12	2:15 pm – 2:30 pm	Andrew Duy Vu
13	2:30 pm – 2:45 pm	Taryn Michelle Gibbs
Break	**2:45 pm – 3:00 pm**	***Intermission***
14	3:00 pm – 3:15 pm	Sneha Sinha
15	3:15 pm – 3:30 pm	Emily Marie Alonzo
16	3:30 pm – 3:45 pm	Arun Raja
17	3:45 pm – 4:00 pm	Nikolas Rune Rasmussen
Break	**4:00 pm – 4:30 pm**	***Break***
Awards Ceremony	**4:30 pm – 5:00 pm**	***Awards Ceremony (SCI 1.220)***

For questions about scheduling for Polymer Section, e-mail:
Tejas Shah (Tejas.Shah@UTDallas.edu)

For questions about scheduling for Undergraduate Section, e-mail:
Laurel Hagge (laurel.hagge@utdallas.edu)

Polymer Section (Morning)

3D Printing of Aramid Nanofiber Composites by Stereolithography

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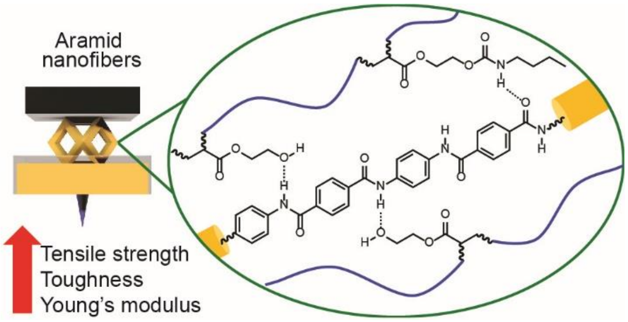
Classification: Graduate

Vat photopolymerization is a versatile 3D-printing method that produces parts using polymeric materials with uniform mechanical properties, high-quality surface finish, and high-resolution features. However, it is challenging to make composite materials with vat photopolymerization mainly because of the imperfect filler dispersion in the photoresin. Herein, we describe a methodology to incorporate aramid nanofibers (ANFs) into a 3D-printable photoresin as a dispersion, followed by a solvent-exchange process that limits anisotropic shrinkage and cracking of the printed polymer. By incorporating 0.60 wt % ANFs, both the tensile strength and toughness increased by 264% and 219%, respectively, while Young's modulus had a 406% increase compared to the control photoresin.



All-Conjugated Poly(3-alkylthiophene) diBlock Copolymers: Synthesis, Microphase Separation, Crystallization, and Performances

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Classification: Postdoctorate

All-conjugated poly(3-alkylthiopene) diblock copolymers (P3AT diBCPs) with different side-chain lengths, narrow polydispersity indices (PDIs), and well-controlled block ratios were synthesized via quasi-living Grignard metathesis (GRIM) polymerization method with designed monomers. P3AT diBCPs could show both cocrystallization and microphase-separated crystallization behaviors depending on the length difference between the side chains, revealed by the DSC and WAXD results. Control over the block ratios of P3AT diBCPs was conducted to precisely tune the molecular organization and nanoscale morphology in P3AT diBCPs-based solar cells, and the optimized power conversion efficiency (PCE) of 4.02% was achieved with the tailored block ratio of 2:1. The microphase separation and crystallization behaviors of P3AT diBCPs were systematically investigated via temperature-resolved wide-angle X-ray diffraction (WAXD), Fourier transform infrared (FTIR), and synchrotron small-angle X-ray scattering (SAXS), which revealed that during the cooling process, the crystallization of P3AT blocks with shorter alkyl side-chains happened first and led to the formation of microphase separated lamellar structure consisting of crystalline domains and amorphous domains, followed by a rapid crystallization of P3AT blocks with longer side-chains in the amorphous domains between the prior crystalline domains. Based on these, a "two-step" thermal annealing treatment method was designed to produce attractively high crystallinity, 3-fold enhancement over those of its homopolymer counterparts. And the P3AT diBCPs with the highest crystallinity also showed the highest carrier mobility, which is 5-fold enhancement over those of its homopolymer counterparts.

Biobased Lignin Resins with Dynamic Transesterification Repairability for Reprocessable Thermosets in Stereolithography 3D Printing

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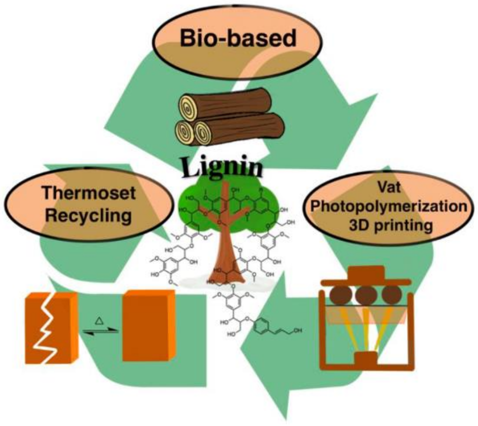

To improve the sustainability of plastics, renewable, reprocessable and bio-based materials must be incorporated to lessen the negative environmental effects. Most plastics used today are made from non-renewable resources, such as petroleum. Some types of bio-based materials include lignin, which is obtained from trees and grassy plants. Lignin is an abundant waste material from the paper industry making it sustainable. Additionally, many plastics known as thermoset materials cannot be recycled. Thermosets can be improved by incorporating dynamic covalent linkages, such as ester bonds, which can undergo transesterification. The covalent bonds can undergo dynamic exchange through external stimuli such as heat. Various thiol-ene resins were synthesized using bio-based materials such as lignin, vanillin, and soybean oil with photoactive methacrylate and acrylate groups. These resins are compatible with photo printing methods of 3D printing, such as digital light projection (DLP). The reprocessability was tested through scratch tests and hot press recycling. These materials can replace non-sustainable 3D printable resins, providing a longer lifetime through reprocessability by the incorporation of dynamic transesterification.

Self-assembly behavior of functional polycaprolactones

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Amphiphilic homo polycaprolactones (PCLs) having di-, tri-, tetra(ethylene glycol) (ME2, ME3, ME4) mono functional groups and a tri(ethylene glycol)/dodecyl (ME3DD) di functional group were synthesized by ring opening polymerization (ROP) of the corresponding γ-functionalized ε-caprolactone (CL) monomers. All the homopolymers formed spherical micelles in aqueous media with variable sizes between 73.2 nm-152.0 nm. The critical micelle concentration (CMC) for PME2CL, PME3CL, PME4CL, and PME3DDCL were 2.2 × 10−1, 2.4 × 10−1, 3.7 × 10−1 gL−1, and 1.8 × 10−2 gL−1, respectively. With the increasing of hydrophilic oligo(ethylene glyco) chain length, the polymeric micelles became less stable and their cloud point tempeature increased from 58.6 oC–85.8 oC. PME3DDCL micelles were more stable due to the increased hydrophobicity from the additonal dodecyl functional group and had the highest loading capacity of 4.8%. However, it significantly affected the cloud point tempeature (Tcp) of PME3DDCL which was not detected even lowing temperature to 4 oC. Compared with homopolymers, amphiphilic blcok copolymers tend to have higher thermodynamic stability. Therefore, a new amphiphilic diblcok copolymer polycaprolatone-block-poly(triethylene glyco/propyl-di-substituted caprolacotne) (PCL44-b-P(ME3PyCL)56) with a mocelular weight of 5,300 g/mol and a PDI of 1.69 was prepararred by sequential polymerization. The self-assembly was achieved in aqueous media and the CMC was 2.41 × 10−3 gL−1. It is comparable to that (1.54 × 10−3 gL−1) of polycaprolactone-block-poly(triethylene glycol) (PCL48-b-P(ME3)52) diblock copolymer with a molecular weight of 6,000 g/mol and a PDI of 1.38.

Tunable, Photodegradable Polymers for Cargo Delivery in Cosmetics

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The creation of drug delivery systems has posed a unique challenge within the biomedical field. Biocompatible materials have been modified to respond to various stimuli such as heat, light, and pH. Light responsive molecules have gained recent interest due its spot targeted approach which is desired in treatment of certain diseases such as cancer. By incorporating the well-studied o-nitrobenzyl group into a hydrogel, we were able to create a photodegradable and biodegradable carrier for its application in skin care products. In this study, we utilize the thiol Michael click chemistry to create a microsphere polymer capable of drug release upon the illumination of light. We synthesized hyaluronic acid acrylate and o-nitrobenzyl dithiol to create the polymeric foundation of a photodegradable hydrogel.

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

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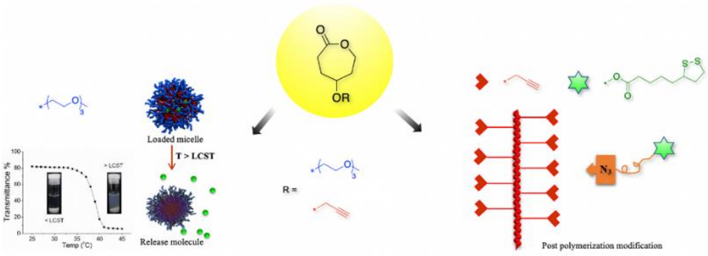
Poly(ε-caprolactone)s (PCL)s are among the most important classes of aliphatic polyesters for biomedical application due to their biodegradability, biocompatibility and synthetic versatility. The properties of this synthetic polymer can be easily tuned by introducing different functionalities. However, 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.



Vanillin-Jeffamine® derived resin formulations for 3D printing with self-healing and reprocessability based on transimination reactions

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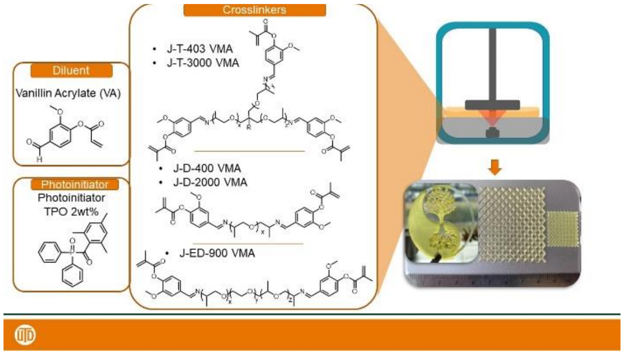
Transimination reactions are one of the best dynamic covalent reactions to pursue when providing reprocessability to thermosets, as they can undergo exchange without the need for catalysts, by exposing the materials to stimuli like heat. In this work a series of five biobased vanillin derived resin formulations consisting of vanillin acrylate with vanillin methacrylate functionalized Jeffamines® were synthesized, and 3D printed using digital light projection (DLP). The resulting thermosets can be produced with a range of mechanical properties (Young's modulus 0.26 – 332 MPa) which allows for an array of possible applications. The materials we obtained have self-healing abilities which were characterized by scratch healing tests. Additionally, dynamic transimination reactions enable these thermosets to be reprocessed when thermally treated above their glass transition temperatures under high pressures using a hot-press. Due to the simple synthetic procedures and the readily availability of commercial Jeffamines®, these series of resins provide a promising alternative to commonly used 3D printable resins, in order to shift to materials with predominantly biobased content and help drift away from polymers made from non-renewable resources.



Undergraduate Section II (Afternoon)

The Effects of Humidity on the Thermal Decomposition of Acetylsalicylic Acid

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Tarrant County College Distric

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Classification: Undergraduate

Acetylsalicylic Acid, better known as Aspirin, works as an analgesic, antipyretic, and anti-inflammatory drug. As a platelet aggregation inhibitor, Aspirin is also commonly prescribed for daily use to reduce the risk of blood clots, stroke, and heart attack. Acetylsalicylic acid is known to decompose into salicylic acid and acetic acid in the presence of water. Heat is also a contributing factor to decomposition. The thermal decomposition of acetylsalicylic acid in both dry and humid environments was studied at various temperatures. Proton nuclear magnetic resonance and infrared spectroscopy were used to analyze the products. It has been proposed that intermediate decomposition products of ASA consist of cyclic oligomers and/or dimers. Salsalate, a dimer, was analyzed as a potential comparison to these intermediate products. Thermal decomposition of acetylsalicylic acid was shown to be more efficient under humid conditions and intermediate aromatic products were formed. Effectiveness of drugs can decrease with decomposition and there is the possibility that harmful products will form. Results of this experiment could be applied to storage indications for over-the-counter Aspirin in unfavorable environments or formal assessment of pharmaceuticals.

The transformation of new copper complexes into 3-D frameworks

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Metal-organic frameworks (MOFs) are crystalline coordination polymers with permanent porosity created through a rigid framework system. MOFs have a vast range of applications, including sensing, catalysis, gas separation, and gas storage. This project utilizes metalloligands to synthesize the MOFs. These are ligands that contain metal centers, allowing for controlled manipulation and placement of the ligands, increased structural stability, and rigidity. The metalloligand used in this research is identified as Cu-4-(2-pyridyl) benzoic acid, or Cu-4-2-pbz (Figure 1a), which is a newly synthesized coordination complex. Cu-4-2-pbz has 4 coordinated 4-2-pbz molecules and 2 coordinated DMF molecules. The coordinated DMF was replaced by 4,4’-bypyridine and the 4-2-pbz was replaced by acetic acid to form a new 1D dimer copper polymer as shown in figure 1b. New structures were synthesized using the 1D copper polymer as a metalloligand and adding different linkers such as terephthalic acid (BDC), 4-biphenyl carboxylic acid, 2,2’-bipyridine-5,5’-dicarboxylic acid, and 2,2’-bipyridine-4,4’-dicarboxylic acid. The formation of new complexes and their chemical structures and properties is determined through powder X-ray diffraction (PXRD), single-crystal XRD, and thermogravimetric analysis (TGA).

Europium Oxide-Catalyzed Formation of Redox-Active, Electrically Conductive Carbon for Supercapacitors

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Supercapacitors are known for their rapid ability to charge and discharge with long cycle lifetimes. Supercapacitors could be the future of energy storage because they balance power density and energy density. The goal of this project is to create redox-active, electrically conductive carbon as a supercapacitor that has an energy density comparable to batteries and a power density comparable to conventional capacitors. Europium oxide (Eu2O3) will be used to create a special type of capacitor called a pseudocapacitor because europium is known to be redox active. Europium can cycle between the +3 and +2 oxidation states, which allows for the storage of additional charge. The incorporation of redox-active europium will provide a solution to the drawbacks of current supercapacitors. The redox-active, electrically conductive carbon was created and had a nanorod morphology that was confirmed by Transmission Electron Microscopy as can be seen in Figure 1. Electrochemical characterization yielded promising results. The resultant material showed that there was pseudocapacitance present, allowing for additional charge to be stored.

Measurement of 1-Octanol/Water Partition Coefficients and Abraham Hydrogen Bonding Acidities (A) for the Catechol Flavones

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Classification: Undergraduate

The flavones are a class of natural products, present in fruits and vegetables, that have demonstrated anti-cancer, anti-atherosclerosis and neuroprotective activities. The structures of many dietary flavones, such as quercetin and fisetin, include a catechol (ortho-dihydroxy) group on the flavone ring system. Very recently, catechol-flavones (CFs) have been demonstrated to have efficacy in pre-clinical models of several neurological diseases. For dietary flavones to function as therapeutic agents, they must be absorbed in the small intestine and transported by the bloodstream to target organs. For the treatment of brain disorders, CFs must cross the blood-brain barrier to achieve therapeutic levels in specific regions of the human brain. The logarithm of the 1-octanol/water partition coefficient (LogPoct) is the most used physical descriptor for predicting absorption, distribution, metabolism and excretion (ADME) properties of drugs. For a compound to be absorbed by the small intestine, a LogPoct value between 1.38 and 1.80 is considered ideal. For a compound to cross the blood-brain barrier, a LogPoct value of 2.00 (or slightly greater) is considered ideal. Each of the five synthetic CFs and 3,2'-dihydroxyflavone (3,2'-DHF) were assayed for LogPoct with the aqueous phases at pH=3.0 and at pH=1.5. For each compound, the measured LogPoct values at both pH values had overlapping 95% confidence intervals. The values of the Abraham summation hydrogen bonding acidity (A) were measured by 1H-NMR spectroscopy and used in the AGSE to calculate LogPoct values. There was good agreement between measured LogPoct values and those calculated by the AGSE.

Using Abraham Model Multidimensional Regression Analysis on Hippuric Acid to Unlock Drug Targeting and Effluent Discharge Impact of Organic Waste

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Classification: Undergraduate

With burgeoning interest in targeted drug delivery, more-cost effective effluent discharge of organic waste, and automated compound predictability models, further research on relevant pharmaceutical compounds, like Hippuric Acid, can provide direction for new developments. The utilization of the Abraham solvation parameter model to predict aqueous solubility, and subsequent biological responses, allows for an accurate way of analyzing absorption, distribution, and toxicological properties of compounds like Hippuric Acid. Encompassing all data on Hippuric Acid collected through experimentation as well as from published literature, there were 42 mathematical equations used in deriving the six solute descriptors (E, S, A, B, V and L) through the Abraham model. The results shown have an overall standard error of SE = 0.101 log units indicating an accurate prediction of solubility interactions with various organic solvents. The data was applied to various equations to predict toxicity levels in aquatic organisms as well as tissue absorption in the body. Further, Hippuric Acid is unique in that it is a solute, and the first carboxylic acid containing an amide group to be added to the database. Increasing structural diversity of known compounds aids in developing automated machine learning models in order to accurately predict solubilities of unknown compounds. Determining experimental-based equation coefficients for other molecules, both solutes and solvents inclusive, will provide more data to base predictions of solubility capability of unknown compounds and create avenues for integration of advanced technology to the Abraham Model, for targeted drug delivery systems, and for efficient, ethical disposal of organic waste.

Fluorescence Emissions Enhancement of Tetraphenylethylene by Limiting Intramolecular Rotation

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Classification: Undergraduate

Tetraphenylethylene (TPE) is a commercial product commonly used in medical equipment, construction, and lighting. In a dilute solution of TPE, the four phenyl groups rotate freely, therefore quenching the fluorescence intensity close to zero. However, if the intramolecular rotation of the phenyl bond is restricted, they possess a strong fluorescence intensity. TPE is loaded onto wrinkled mesoporous silica (WMS) and biphenyl-modified WMS (BPWMS) to restrict the intramolecular rotation to enhance fluorescence emission. WMS has a 3-D conical-shape pore structure with Si-OH and Si-O-Si bonds. BPWMS contain Si-OH, Si-O-Si, and phenyl groups. These phenyl groups can have π - π stacking with the phenyl group of TPE, further restricting the intramolecular rotation of TPE when loaded, producing a stronger fluorescence intensity than WMS. The loaded product is analyzed and characterized via UV-Vis, Fluorometer, and Transmission Electron Microscopy (TEM). The fluorescence intensity of TPE loaded onto both WMS and BPWMS results higher than TPE alone. Higher fluorescence intensities in TPE loaded BPWMS than TPE loaded WMS are observed as well. TPE loaded WMS and BPWMS increases colloidal dispersibility of TPE while enhancing the fluorescence emission intensity.

Use of Zeolitic Imidazolate Frameworks for Mechanical Protection of Liposomes

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Liposomes have been proven to be advantageous for vaccine delivery as they are biofriendly, can carry hydrophobic, hydrophilic as well as lipophilic drugs and antigens and have an inherent immunogenicity due to their shape and size. However, a few key issues exist with liposomal based vaccines. Liposomes themselves are prone to aggregation, changes in size and lamellarity, and must be stored at a specific temperature from when they are first produced to when they are injected, a system known as the “cold chain.” In order to combat these issues, we encapsulated various liposomes in ZIF to test whether ZIF can protect the liposomes from stressors such as heat while also providing enough structural support against aggregation and size changes. We also wanted to demonstrate that this method of protection is very versatile, and the protective crystal can grow around biomaterials irrespective of surface charge of the liposomes. In order to validate the proof of concept of the project, a variety of liposomes were prepared (neutral, PEGylated, anionic, cationic). Then the liposomes were encapsulated in ZIF with varying ligand-to-metal ratios (32,16, 8, 4). The encapsulation efficiency was found to be highest in ratios 32 and 16. To ensure that the ZIF coating is not toxic, the liposomes were removed using a chelating agent and characterized using TEM and DLS. It was found that the ZIF coating did in fact protect the size and lamellarity of the liposomes irrespective of surface charge and lipid composition. All in all, this project aims to apply this protective formulation to current liposomal vaccines as well as some other vaccine platforms in the future. These vaccines can be packed and shipped across the world without any worry about temperature or antigen degradation.

Innovative and Cost-Effective Methods of Detection and Using Plant Derived Polymers for Treatment of Microplastics in Aquatic Environments

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Tarleton State University

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Classification: Undergraduate

Microplastics are a new, emerging contaminant that has been detrimental to aquatic environments globally. The contamination is due to the high demand for plastic production and lack of disposal management practices. The purpose of the research was to identify plant derived polymers that are equally as effective in removing microplastics from aquatic environments as polyacrylamide. Polyacrylamides are linked to several health concerns. Alternatively, plant derived polymers are non-toxic, biocompatible, biodegradable, polyfunctional, and cost effective. Previous research in our laboratory has demonstrated successful removal of various pollutants in different water sources using the plant derived polymers: Fenugreek (Trigonella foenum-graecum), Cactus (Opuntia ficus-indica), Aloe Vera (Aloe barbadensis miller), Okra (Hibiscus esculentus), Taro (Cocalasia Esculentus) and Psyllium (Plantago psyllium). The plant derived polymers contain chemical and biological properties that aid in the removal of contaminants through flocculation. The present research studies plant derived polymer efficiency in removing microplastics in groundwater. The research was accomplished by testing individual and combinations of the following four plant derived polymers: Fenugreek (Trigonella foenum-graecum), Okra (Hibiscus esculentus), and Tamarind (Tamarindus indica). All polymers were tested at the concentration of 1 g/L with samples collected at intervals of 0, 15, 30, and 60 minutes. All polymer combinations used were at 1:1 ratio. It was determined that the plant derived polymers were competitive with polyacrylamide in flocculating microplastics in groundwater.

Undergraduate Section I

Entry	Time	Activity
Greetings	**9:40 am – 9:45 am**	***Greetings***
01	9:45 am – 10:00 am	Amanda Maceda
02	10:00 am – 10:15 am	Advika Varadharajan
03	10:15 am – 10:30 am	Sindhoora Ponnam
04	10:30 am – 10:45 am	Victoria Alicia Chavez
Break	**10:45 am – 11:00 am**	***Intermission***
05	11:00 am – 11:15 am	Alyssa Kohler
06	11:15 am – 11:30 am	Haley Sachse
07	11:30 am – 11:45 am	Abhinay Varma Adlooru
08	11:45 am – 12:00 pm	Matthew D'Souza
09	12:00 pm – 12:15 pm	Caroline Jordan Crocker
Break	**12:15 pm – 1:45 pm**	***Lunch Break***
10	1:45 pm – 2:00 pm	Abi Adailalamkathal Veerappan
11	2:00 pm – 2:15 pm	Harrison Chiu
12	2:15 pm – 2:30 pm	Shea Garland
13	2:30 pm – 2:45 pm	Amanda Marie Darling
Break	**2:45 pm – 3:00 pm**	***Intermission***
14	3:00 pm – 3:15 pm	
15	3:15 pm – 3:30 pm	
16	3:30 pm – 3:45 pm	
17	3:45 pm – 4:00 pm	
Break	**4:00 pm – 4:30 pm**	***Break***
Awards Ceremony	**4:30 pm – 5:00 pm**	***Awards Ceremony (SCI 1.220)***

For questions about scheduling for Undergraduate Section, e-mail:
Laurel Hagge (laurel.hagge@utdallas.edu)

Synthesis & Post-Modification of Copper-Based Metal-Organic Polyhedrons into Metal-Organic

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The drastic increase in carbon dioxide emissions can no longer be controlled by natural geochemical processes, and thus new technologies are needed to prevent severe global warming by mid-century. One hopeful initiative for these ambitions is carbon dioxide capture and storage technologies. Traditional approaches include activated carbon, in-situ carbonate mineralization, and zeolites. Metal Organic Frameworks (MOFs) are microporous crystalline solids formed through the connection of metallic nodes with organic ligands. When assembled and activated, these materials provide a high surface area through housing large cavities and various openings in structure. Metal-organic polyhedrons (MOPs) are hybrid materials which suffer in ability due to the tendency of individual units to collapse upon activation. We proposed that MOPs can serve as supramolecular building blocks in MOF formation. By combining 2,2'-bipyridine and copper MOP-1, a new MOF (UTD-100) was synthesized. UTD-100 has a pore dimension of 9.5 x 6.5 Å and has a potential in gas separation & storage of carbon dioxide.

Using Abraham Model Multidimensional Regression Analysis on Hippuric Acid to Unlock Drug Targeting and Effluent Discharge Impact of Organic Waste

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With burgeoning interest in targeted drug delivery, more-cost effective effluent discharge of organic waste, and automated compound predictability models, further research on relevant pharmaceutical compounds, like Hippuric Acid, can provide direction for new developments. The utilization of the Abraham solvation parameter model to predict aqueous solubility, and subsequent biological responses, allows for an accurate way of analyzing absorption, distribution, and toxicological properties of compounds like Hippuric Acid. Encompassing all data on Hippuric Acid collected through experimentation as well as from published literature, there were 42 mathematical equations used in deriving the six solute descriptors (E, S, A, B, V and L) through the Abraham model. The results shown have an overall standard error of SE = 0.101 log units indicating an accurate prediction of solubility interactions with various organic solvents. The data was applied to various equations to predict toxicity levels in aquatic organisms as well as tissue absorption in the body. Further, Hippuric Acid is unique in that it is a solute, and the first carboxylic acid containing an amide group to be added to the database. Increasing structural diversity of known compounds aids in developing automated machine learning models in order to accurately predict solubilities of unknown compounds. Determining experimental-based equation coefficients for other molecules, both solutes and solvents inclusive, will provide more data to base predictions of solubility capability of unknown compounds and create avenues for integration of advanced technology to the Abraham Model, for targeted drug delivery systems, and for efficient, ethical disposal of organic waste.

Exchanging Coronal Proteins on Photothermal Virus-Like Particles

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Cancer is a primary cause of mortality globally. A potentially viable cancer therapeutic that is being researched is photothermal therapy or PTT. Cancer therapeutics development is one of the most serious issues confronting the healthcare sector today. Chemotherapy, radiation, and surgery are frequently used as the initial line of defense against cancer. However, therapeutic effectiveness, refractory, and post-treatment adverse effects are significant obstacles that must be solved in the field of oncology. To address the aforementioned difficulties, photothermal therapy is being investigated as a possible cancer therapeutic. Photothermal therapy is a minimally invasive therapeutic approach that utilizes near-infrared (or NIR) light lasers (700-1100 nm) to produce heat in the tumor microenvironment. The laser's NIR light is absorbed by the NIR absorbent and converted to heat. When sufficient heat is created in the tumor microenvironment and the temperature of that environment rises over a particular point, cancer cells can undergo apoptosis or programmed cell death. The Gassensmith laboratory recently demonstrated that photothermal therapy is beneficial in the treatment of breast cancer by intratumorally injecting a proteinaceous virus-like particle (VLP), Qß, coupled to a stable photothermal agent, croconium dye. Croconium dye is a good photothermal agent due to its high near-infrared extinction coefficient, low fluorescence quantum yield, and strong photostability, which means it can endure a large number of photothermal heating cycles. Qß is a Virus-Like Particle that is a biocompatible, biodegradable, and thermally stable platform for site-specific functionalization and immunization. In fact, Qß contains 720 potential sites for labeling with croconium dye. To further the research aforementioned, we are researching the exchange of coronal proteins on photothermal VLPs. When nanoparticles enter the body, particularly the circulation, they interact with blood proteins, forming a protein corona by adhering to VLPs. Three phases comprise the protein corona: the inner hard corona, the outer hard corona, and the soft corona. Coronal protein exchange on VLPs should occur as a result of 808 nm laser irradiation inducing tumor cell apoptosis, immunogenic cell death, and the release of tumor-associated proteins. Now, we are studying serum interactions with VLPs in order to determine whether heating at the tumor site can be utilized to remove tightly bound coronal proteins and exchange them for tumor-associated antigens, thereby forming a new corona and creating an in situ cancer vaccine.

The Effects of Reagents on the Formation of the Diels-Alder Products with Maleimide Dienophiles

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Recent research has shown that Lewis acids can modify the regiochemistry of the Diels-Alder adduct of dienophiles with anthracene from 9,10 adduct to 1,4 adduct. This project investigates the reaction of anthracene with maleimide and (S)-(-)-N-(1-Phenylethyl)maleimide with and without aluminum chloride in chloroform or xylene solvents. Preliminary analysis of products with NMR and IR spectroscopy indicate that aluminum chloride facilitates the reaction. Furthermore, the reaction seems to be accelerated by xylene rather than chloroform. No evidence of 1,4-adduct was observed for either solvent system with or without Lewis acid. The results open discussion on how to examine ranges that make the Diels-Alder reaction favorable, ranging from longer reflux periods to utilizing solvents with different boiling points.

Efficacy of Using Oral Insulin with a Plant-Based Drug Delivery System in a Pig Model

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Diabetes Mellitus is a life-changing condition that roughly 34.2 million Americans suffer from and is the seventh leading cause of death in the United States. The development of a form of insulin that can be taken by mouth would not only significantly reduce the amount of pain diabetics endure from continuous injections, but would also limit the number of needles used, thus providing benefits to the environment as well. Currently, an oral insulin medication is not available, since insulin is digestible and is degraded in the stomach before it can reach the blood stream. However, it is hypothesized that with the right drug delivery system, insulin can be taken orally and be protected from premature degradation by the digestive system. This research study utilized fenugreek, a plant-derived polymer with natural abilities to lower blood sugar, as a non-toxic drug delivery system for insulin that is taken orally. The study was performed on pigs who were induced with diabetes, then treated with either insulin and fenugreek, insulin, fenugreek, or fenugreek equivalent to the amount of insulin and fenugreek treatment. Initial analysis of the data from the experiment showed promising results. It was discovered that the insulin with fenugreek treatment was more effective at lowering blood sugar levels in males than it was in females. This is likely due to hormonal differences, and future trials of this experiment may involve monitoring hormone levels to identify a correlation between blood glucose levels and specific hormones.

Glucose and fructose metabolism in cultured SfXL glioblastoma cells over long incubation time periods probed by 13C NMR

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Glioblastoma, the cancer of the cerebral glial cells, is an aggressive type of tumor that is known to be addicted to sugars and exhibit Warburg effect. In this study, we have investigated via carbon-13 (13C) NMR spectroscopy the long-term metabolism of glucose and fructose in cultured SfXL glioblastoma cells over a four-day period of incubation times. To achieve this, eight flasks of glioblastoma cells were cultured, four were doped with 10mM uniformly labeled 13C glucose and four were doped with 10mM unlabeled glucose. The flasks were then left to incubate for a set time period. One 13C glucose vial and one unlabeled glucose vial were then harvested at 24-hours, another pair at 48-hours, another at 72-hours, and the final pair at 96-hours. This process was then repeated with fructose instead of glucose. Both media and cell extracts of each flask were then processed for 13C NMR analyses. The NMR data for glucose showed that lactic acid increased significantly throughout the 96-hour period, and secondary metabolites such as acetate and alanine also increased. The details of the 13C NMR results for glucose metabolism as well as those of fructose will be presented here.

Carrier Gas Triggered Biolistic Delivery of DNA with Metal-Organic Frameworks

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Genetic engineering and modification has improved nutritional quality and yields by promoting plant resistance to herbicides, pesticides, insects, diseases, and drought. One method used for plant genetic engineering is biolistic delivery, which uses “gene guns” to physically deliver DNA into plant cells and can be used for large scale crop production. While this technique is quite useful, it has several drawbacks. Gene guns are very expensive, with most commercial guns ranging between $10,000 and $30,000. Furthermore, the materials needed for sample preparation (metal microparticles like gold or tungsten) add even more to the cost of this approach and are non-biodegradable, meaning that they will persist in the plants indefinitely. In addition, intratumoral injections in cancer therapy, while promising, also have drawbacks such as poor diffusion of the drug, limited accessibility of tumours, and leakage at the injection site. To overcome these shortcomings of gene guns and cancer therapy, our lab has developed a novel “MOF-gun” delivery system. MOFs (metal-organic frameworks) are porous materials made from interconnected metal nodes and organic linkers. Zeolitic Imidazolate Framework-8 (ZIF-8), a particular type of MOF, is composed of the organic ligand methylimidazole and zinc metal nodes. Our lab has shown that ZIF-8 nucleates on the surface of biomacromolecules and fully encapsulates them. The rigidity of the ZIF-8 structure enhances the thermal stability of the encapsulated biomaterial and prevents it from being degraded. ZIF-8 also biodegrades slowly, allowing it to release the encapsulated biomaterial into the tissues over the course of many days. Due to ZIF-8’s thermal stability, biodegradability, and low toxicity, we have chosen it as the MOF for our MOF-gun system. Our delivery system involves shooting a DNA plasmid encapsulated within ZIF-8 into cells along with pressurized CO2 gas. Using CO2 as a carrier gas enhances the dissolution of the ZIF-8 shell once inside the cell and increases gene expression of the encapsulated DNA plasmid. We have obtained preliminary results showing that ZIF-8 particles labeled with the fluorescent dye Cy-5 effectively penetrate agarose gels (which emulate soft tissues in the body) and do not damage the gel surface. Moreover, when tested on onion cells, the MOF-gun has also shown more gene expression when used with CO2 than with air.

Expression of Virus-like Particle Qβ as a Nanocarrier in Drug Delivery

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Virus-like particles (VLPs) are engineered protein structures that imitate the structure of viruses. However unlike a virus, VLPs do not carry any infectious genome. An important characteristic of VLPs is their ability to work as a nanocarrier through bioconjugation. This characteristic allows VLPs to be applied in vaccinations, drug delivery, and imaging. This project focuses on the production of a specific VLP known as Qβ. Qβ is a 28-d.nm icosahedron composed of 32 disulfide lined pores along with 180 identical coat proteins. It is derived from bacteriophages and has 720 solvent exposed amino groups on its surface. The Qβ is synthesized through a process that begins with a nutrient-rich media that is inoculated with IPTG to express the protein Qβ. After a series of centrifugation and purification processes, the Qβ is characterized to determine its concentration and quality. Ultimately, this method is conducive to the production of Qβ which can serve as a nanocarrier in many biomedical applications.

13C NMR Probe of L-Aspartate Metabolism in Lymphoblastic Leukemia Cells

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Leukemia is the most common childhood cancer, and while survival rates are steadily improving, there is currently no cure. In order to better understand leukemia, it is crucial to investigate the nutrients that feed through its rapid cellular proliferation. In order to elucidate this, 13C-aspartic acid, which feeds through the crucial tricarboxylic acid (TCA) cycle, was added to the media in separate flasks containing cultured SUP-T1 lymphoblastic T-cells and then harvested at intervals of 1 hour and 48 hours. The cells were processed by perchloric acid extraction method, lyophilized, and then resuspended in deuterium oxide for carbon-13 NMR analyses. Both cell and media extracts were analyzed to investigate the intracellular and extracellular metabolite production from aspartate, respectively. Our preliminary results indicate the detection of the TCA cycle metabolites malate and isocitrate. These preliminary NMR data and other relevant results will be presented in this talk.

The Enhancement of T1 Agents with Supramolecular Pyrene Derivatives

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In clinical medicine, biological research, and preclinical research, magnetic resonance imaging (MRI) is a widely used diagnostic tool. Within magnetic resonance imaging, contrast agents are incorporated to provide scientists with a broader understanding of the fluids and structures regarding the internal organs. Gadolinium (Gd(III)) complexes are the most prevalently used contrast agents (CAs) due to their strong paramagnetic ions, which allow the element to reduce the T1 relaxivity rate of cellular material. Gadolinium was known to be safe until recent observations stated that minuscule amounts of Gd injected can be retained within tissues and lead to nephrogenic systemic fibrosis (NSF) in patients suffering from renal issues. This is widely known to be associated with poor chelation of the metal ion within a chelating ligand. Chelation is a necessary process for GBCAs as it enhances biocompatibility allowing for safe passage through the body while maintaining the strong MRI capabilities. Chelating ligands also provide a scaffold for more specific targeting of metabolites, ions, and enzymes.5 GBCAs are classified into two types based on their chemical structures: linear & macrocyclic. Linear agents are in a snake-like pattern, chelation ions coil around gadolinium ions. On the contrary, in macrocyclic agents,2,3 Gadolinium is completely encapsulated by the ions like a cage. To reduce the amount of free gadolinium released, macrocyclic Gd(III) complexes are preferred over linear Gd(III) complexes based on thermodynamic and kinetic stability. The anticipated outcome is an increase in relaxivity, allowing for the use of lower doses. Over the years, much research has been done to determine which structural and dynamic factors influence the relaxivity of Gd-containing agents. If the exchange rate of the coordinated water molecule is in the proper range, slowing molecular motion in the magnetic fields of clinical scanners has been shown to be a useful way to improve relaxivity. In order to enhance the relaxivity, four types of gadolinium complexes were combined with varying concentrations of pyrene derivative, HPTS. HPTS (8-hydroxypyrene-1,3,6-trisulfonic acid) was chosen as the pyrene derivative because it is the most well-known among biologists and is frequently used as a pH-sensitive fluorescent dye in cellular studies. The outer rims of the pyrene derivatives used are incorporated with hydrogen and sulfur trioxide, giving them good water stability. The four gadolinium complexes used exhibit hydrophobic systems with no specific ability to bind to endogenous molecules that can affect their relaxivity in a significant way. Hydrophobic interactions between the two macrocyclic complexes and substituted pyrene derivatives have been observed. The molar ratio of 1:3 (GBCA : HPTS) allows for up to a 50 percent increase in relaxation due to the strong binding affinities. They are potential sites for attracting second sphere water molecules, which could help improve the relaxivity observed. Through

the use of 1 H-relaxometry at varying concentrations, the interaction between HPTS & gadolinium macrocyclic complexes are investigated.

Design and synthesis of novel pH- responsive MRI Contrast Agents

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Cancer and various ischemic diseases are associated with a decrease in pH in the extracellular environment. Therefore, an imaging method to provide a direct measure of pH in the extracellular environment could be useful for early detection of disease conditions and to monitor the treatment efficacy. Many spectroscopic methods have been used in the past, but MRI is ideal for mapping the pH of tissues since it can detect water protons directly and shows more detailed anatomical images with unlimited tissue depth, which can be used to monitor the progression of diseases to determine the type of therapy that is used. Gd-DOTA-4AMP, one of the first successful pH-responsive T1 contrast agents reported by our group, is a cyclen-based macrocycle with four amide pendant arms with phosphonate groups. It has been found that the four phosphonate groups are important in catalyzing proton exchange between a Gd-bound water molecule and bulk water. However, a more recent study of a similar complex containing only one phosphonate group, Gd-DOTA-1AMP, surprisingly showed a relaxivity versus pH profile that appears to be even more favorable than Gd-DOTA-4AMP. Thus, the goal of my project was to design other complexes with slightly different pendant arms on the DOTA ring to further test the mechanism. One initial target compound, GdL1, (structure shown in the Figure) has four amide arm substituents but only one phosphonate arm. It has a structure very similar to Gd-DOTA-1AMP but the four tetraamide groups will ensure that water exchange is slower in this compound. This will allow us to evaluate the role of water exchange in this process.

Carbazole – Porphyrin Hybrid: A Synthetic Host for Anion Recognition Applications

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The purpose of this project was to synthesize a carbazole-capped porphyrin hybrid and evaluate its anion recognition properties. The host was prepared from a monoamino tetraphenyl porphyrin and 1,8-diamino carbazole. The carbazole projects over the porphyrin surface to create a pocket for guest binding. The binding pocket has multiple available interaction sites for an anion guest: a zinc metal center, two urea N-H, an amide N-H, and two amino N-H functionalities. UV-Vis titration studies have been performed, with some anion guests interacting with the host in a way that resulted in erratic spectra. However, some anions gave a 1:1 host:guest complex with isosbestic points and these K values are reported. 1H-NMR spectroscopic titration studies will need to be utilized to assess the selectivity of the host for an assortment of anions with varying geometries (spherical, trigonal planar, and tetrahedral) and will help clarify how the hydrogens of the host interact with the guest. This project contributes to a goal of developing receptors for anions that could aid in the treatment of diseases, monitoring of contamination sites in the environment or in environmental remediation efforts.

Modern overview of CBD in the Academic & Public Arenas with an Updated Analysis of Labeling Accuracy

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Recently a wide variety of cannabinoid products have flooded the consumer market. Claims of safety and efficacy for various conditions have been made, but variable laws from state to state and cannabis's status as a schedule one drug have created barriers for medical application. The 2018 Farmers Bill Act opened more opportunity for the academic study and analysis of cannabinoids but also created a largely unregulated and unmanageable market flow. This work examines the market, social, and legal state of cannabinoids and related compounds, with a specific focus on CBD products sold as dietary supplements. Furthermore, isolated cannabidiol was analyzed and used to create a calibration curve for evaluation of commercial cannabidiol products using benchtop NMR.