Fourth Annual Chemistry Research Symposium

Saturday March 9, 2019
8:30 - 11:00 A.M. - Life Science Building
11:30 - 12:30 P.M. - Hunter 100
Dear Faculty, Staff, Students and Honored Guests,

Welcome to the 2019 Chemistry Research Symposium, which highlights research performed at Clemson by our students and at other institutions by our honored guests. All of these students have worked very hard to highlight the variety and importance of research being done in chemistry. Interact with the poster authors and experience the enthusiasm and dedication they have for their work. Enthusiasm is contagious, and we hope that you will be inspired by your conversations with them to want to know more. Science isn’t hard work for the curious, but it does provide education and training for a wide variety of careers and vocations, and chemistry, as the central science, provides a jumping off point to a world full of opportunities.

We hope you enjoy your time with us!

Bill Pennington,
Chair
Keynote Lecture

Nanotechnology: Graphene, Devices and Medicine

Dr. James Tour, T.T. and W.F. Chao Professor of Chemistry, Professor of Computer Science, Professor of Materials Science and NanoEngineering, Rice University NanoCarbon Center, Houston, TX, 77005

New routes to the formation of graphene will be discussed including laser-induced graphene which is made in the air and without furnaces. A series of devices including supercapacitors, gas sensors, triboelectric generators, electrocatalysis beds for water splitting and the oxygen reduction reaction, air filters and water purifiers have been made from this flexible platform. The use of graphene nanoribbons and graphene quantum dots in medicine will be discussed. And the spinoff of many of these technologies into standalone companies will be presented.
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1. Developing an Injectable Hydrogel Biosensor

Sachindra D. Kiridena*, Uthpala N. Wijayaratna, Md. Arifuzzaman, Jeffrey N. Anker

Department of Chemistry, Clemson University

Hydrogels are a group of three-dimensional, crosslinked polymeric materials that are capable of adsorbing large amounts of water or biological fluids without dissolution. Hydrogels have been extensively used in the biomedical fields due to their unique characteristics of flexibility, softness and biocompatibility. A pH responsive hydrogel composed of acrylic acid, n-octyl acrylate, poly(ethylene glycol) diacrylate was photopolymerized by UV light with 2-oxoglutaric acid as the photoinitiator. The hydrogel, together with a tantalum (Ta) bead, was incorporated in a needle, which can be injected using a breast cancer biopsy marker. The pH response of the hydrogel can be determined using X-ray radiography and the developed injectable hydrogel could be used as a potential x-ray imaging functional chemical sensor. As a preliminary study, a moisture sensor was developed as part of a mechanized system for sensing, integrity, drug release, and evaluation of responses. The sensor could be incorporated in a sliding hip screw (SHS), which is a type of orthopedic implant used to stabilize fractures of the hip. The developed moisture sensor would be helpful to determine any breach to the integrity of the screw, due to large pieces falling in. The moisture sensor was prepared using a scale of cesium iodide, enclosed in a laminating sheet, with alternating regions of laminated and non-laminated regions. Cesium iodide was used in this preliminary study due to its radiopaque properties. The cesium iodide scales were viewed radiographically.

Paul W Millhouse MD, MBA*; Md. Arifuzzaman PhD; Apeksha C Rajamanthrilage BS; Nathan T Carrington BS; Caleb Behrend MD; John D DesJardins PhD; Jeffrey N. Anker PhD

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Pseudarthrosis or nonunion of the cervical spine is the result of failed attempted fusion and is a leading cause of postoperative axial pain or radiculopathy. Failed cervical fusions range 4.4 - 50% and pseudarthrosis accounts for 45 – 56% of revision surgeries. Nonunion is difficult to detect clinically and diagnosis is based on symptomatology and imaging. Using interspinous motion analysis, sufficient bone growth (fusion) occurs when the distance between the tips of adjacent cervical spinous processes differs by less than 1-2mm on dynamic films. Intervertebral motion can be more accurately detected using a simple passive implantable device that responds to the vertebral body movement between the flexed and extended positions of the cervical spine. A cervical interbody spacer with integrated fluidic pressure sensor was developed and prototyped. The working principal involves a fluid reservoir and indicator channel. The spacer was placed between Sawbones® vertebral phantoms and loads applied to simulate dynamic spinal positions. Radiographs were taken of a device loaded with cesium acetate and channel diameter of 0.5mm. Simulations demonstrated the device would fit well in the cervical spine. Prototypes placed under load suggest the indication would be apparent clinically. Previous work showed that fluid displacement into the indicator was in the appropriate scale (0 – 6.9 mm) under applied loads in the range experienced clinically (0 – 110 N). The resolution of the device loaded with a radiocontrast agent was also suitable. Finite element analysis (FEA) simulations indicated that polycarbonate urethane (PCU) of a specified stiffness could be used as the implant material. An implantable fluidic sensor is potentially a viable option for assessing fusion status in the cervical spine.
3. Non-invasive Monitoring of Tibial Plate Bending with an Implantable Fluidic Sensor, Read via Plain Radiography

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Tibial fractures are the most common type of long-bone fracture encountered by orthopedic surgeons. This is also the most common site of bony nonunion. Thus, precise and practical methods are required to determine when it is safe to resume weight-bearing. For this, they routinely acquire plain radiographs to visualize the hardware and fracture callus as a method of diagnosis and evaluation. However, these images are incapable of assessing the mechanical properties of the fracture callus. We describe a sensor to non-invasively measure orthopedic tibial plate bending, read using plain radiography. Bending of the tibial plate under load presses an integrated lever upon a sensor bulb which pushes a radiopaque fluid through a channel. The degree of plate bending is directly related to the change in fluid level within the channel. The fluidic sensor was tested under various loading conditions using a Sawbones® tibia phantom and a human cadaver tibia with unstable fractures. In each occasion the fluid displacement (mm) vs the applied force (N) was monitored. Experimental results showed a fluid displacement of 1 mm for applied load of 100 N. Reproducibility of the sensor was examined by executing five loading/unloading cycles while monitoring the fluid level using radiography. The hydraulic action amplifies the signal from the plate bending motion and the radiopaque fluid level is easily observed using plain radiography. This approach provides bio-mechanical information by plain radiography. In addition, analyte-specific gel swelling can be coupled with hydro-mechanical amplification for non-invasive in vivo chemical measurements using plain radiography.
4. Synthesis and Characterization of Bright Eu and Tb doped NaGdF$_4$ Nanoparticles

Meenakshi Ranasinghe* and Jeffrey N. Anker

Department of Chemistry, Clemson University

Rare earth doped phosphors have interesting optical properties depending on their size, crystal structure and type of dopant. They are used in bio imaging, chemical sensing and radiology imaging screens. We are interested in synthesizing X-ray excited nanoparticles for a non-invasive, in vivo optogenetic neuron simulation method. However, it is challenging to synthesize monodisperse nano-size particles that emit bright visible light photons when irradiated with X-ray. We are synthesizing Eu- and Tb-doped NaGdF$_4$ nanoparticles using a citrate method which involves lanthanides-citrate complex formation followed by nucleation and growth upon addition of NaF. Then, the nanoparticles are annealed at high temperature to increase the emission intensity by removing defect sites that can quench luminescence. The synthesized NaGdF$_4$: Eu and Tb are characterized using powder X-ray diffraction, transmission electron microscopy and X-ray luminescence spectroscopy. The TEM images confirm that the size of the nanoparticles is around 100 nm. Eu and Tb doped NaGdF$_4$ nanoparticles are synthesized by varying the amount of dopant (Gd: 0.1, 1, 15, 20, 100mol% Eu and Tb). According to the X-ray luminescence spectroscopy measurements, at low and high dopant levels, they show low emission intensity, likely due to lack of luminescent centers and self-quenching, respectively. After annealing, the intensity of most samples increased by factor of 2-2.5; another factor of 5 is gained by sintering the particles at high temperature, though this causes them to fuse, negating their bio-application. In future, we plan to optimize the synthesis, annealing, and surface passivation protocols to obtain bright monodisperse nanophosphors. We will also functionalize them and test their application as in situ light sources for sensing and actuating in vivo.
5. Measuring Local Drug Concentrations via Radioluminescence

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The goal of this project is to develop a non-invasive method to measure radiolabeled pharmaceutical accumulation and release in vivo. To monitor accumulation and release of radiolabeled drugs, we will use radioluminescent phosphor micro- and nanoparticles as light emitting indicators. This will be useful for biomedical implants, such as orthopedic fracture fixation implants, which are susceptible to colonization by bacterial biofilms. Bacterial biofilm infections require aggressive antibiotic therapy for eradication, which has led to the development of antibiotic eluting implants for prevention and treatment. There is currently no method for evaluating drug release from these implants non-invasively. Similarly, there has been an explosion of nanotechnologies developed for drug delivery applications. However, there is currently no method for evaluating drug release from nanoparticle surfaces in vivo. The method described herein permits surface specific quantification of drug release and accumulation, non-invasively, in vivo.
6. Detecting Implant Associated Infection on the Surface of Orthopedic Implants Using a pH Sensitive Coating

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Implant-associated infection is a leading cause of fixation failures and is often challenging to detect due to lack of symptoms and specific tests to detect localized infection. Low pH is believed to be associated with infection as bacteria and inflammatory responses cause a pH drop in the affected area. We have developed a pH sensitive coating to detect changes in pH on the implant surface using X-ray excited luminescence chemical imaging (XELCI). The surface of the orthopedic implant is coated with a layer of scintillator particles (GOS:Eu) followed by a pH doped hydrogel. The scintillators act as an in situ x-ray excited light source emitting red light and the biocompatible hydrogel contains a pH dye that differentially absorbs the scintillator emission depending on the pH, therefore modulating the signal and providing surface specific pH value of the region. pH changes were studied during formation of biofilm on the pH coating in vitro and a significant change in pH was observed. XELCI imaging was conducted for a series of pHs through different thicknesses of chicken tissue and in human cadaveric tissue. The pH coated implant was fixed in a rabbit and pH was imaged in the live rabbit. Even though, we did see a pH change in the in vivo study, we didn’t see a significant pH drop as observed in the in vitro study. Further studies are planned to image pH changes on device surface during infection and antibiotic treatment in animal models.
Biosensing of Breast Cancer Biomarkers Using a Hydrogel

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Breast cancer is a disease in which there is uncontrollable growth of cells in the breast. A biopsy involves the removal of small amount of tissue for laboratory analysis. Biopsy clip markers maybe placed at the site after a biopsy, which facilitates tumor localization and tracking in patients undergoing chemotherapy for breast cancer. Even though radiography is the preferred imaging technique, it is not able to provide information on local biomarker concentrations, which would assist in the diagnosis and treatment of breast cancer. A previously developed hydrogel pH sensor was used to measure local pH near the biopsy clip. As a preliminary study, the hydrogel pH sensor was attached to a vascular clip together with a radiodense tantalum (Ta) bead. The experiment was repeated with a biopsy marker clip and viewed radiographically. The pH response of the hydrogel with the incorporated clip and Ta bead could be developed as a potential x-ray imaging functional chemical sensor. The hydrogel pH sensor was extended to detect glucose by incorporating glucose oxidase and catalase into the hydrogel. The preliminary results of the prepared hydrogel demonstrate that the hydrogel responds to glucose and can be developed as a sensor to measure glucose at the site. In future, different molecular recognition elements specific to a particular biomarker can be incorporated to the pH sensitive hydrogel for the detection, treatment and progress of breast cancer.
DNA topoisomerases are a class of enzymes that facilitate the replication of DNA in both humans and bacteria. These topoisomerases maintain the DNA topology during replication by relaxing supercoils and disentangle intertwined DNA strands. Consequently, topoisomerases are an effective target for antibacterial and anti-cancer drug development. Several small molecules have been discovered that inhibit DNA topoisomerase. Bisbenzimidazoles derived from Hoechst 33258 have been known for their topoisomerase I inhibition, recent reports have identified that some of these exhibits' selectivity toward the bacterial DNA topoisomerase I over mammalian inhibition. One such drug is Linezolid, an antibiotic that is metabolized in the liver by oxidation of its morpholine ring apart from the cytochrome P450 enzyme system. The P450 system is responsible for the metabolism of a vast majority of drugs and avoiding it is highly desirable since disruption can lead to adverse drug effects. Therefore, we intend to continue developing Hoechst 33258 derivatives, focusing on variations with morpholino substituted for methylpiperazine in hopes of selectively inhibiting bacterial DNA topoisomerase I. Finally, experiments to determine the change in therapeutic index and how auxophores effect inhibition are currently under way.

Docking

(a) Docked pose of Hoechst 33258 (red) and compound 3 (magenta) at the active site of *E. coli* topoisomerase I covalent complex showing differences in the bisbenzimidazole unit orientation of the two compounds. (b) A closer view compound 3 (magenta) bound at the active site showing the amino acid residues that are involved in the ternary interaction.
An Exploration of DNA:RNA Hybrids as Potential Sites for Gene Regulation

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At the terminal end of the Central Dogma, proteins have long been main targets for drug inhibition. However, the little-researched DNA:RNA hybrid acts as an important intermediate in the transfer of genetic information and is also an enticing target for small molecule inhibition. DNA:RNA hybrids are involved in numerous biological processes including transcription and reverse transcription, telomerase activity, and maintenance of genome integrity. The wide scope of actions involving these stable structures makes them a valuable therapeutic interest for novel binding ligands that could serve as antiretrovirals, telomerase inhibitors, and gene silencing technologies. Here, we discuss the pathways in which these structures are involved and the potential applications for DNA:RNA hybrid binding.
Brumaghim group research focuses on exploring the coordination chemistry of d- and f-block metals with sulfur- and selenium-containing ligands and other antioxidants. Metal-mediated DNA damage is the primary cause of cell death under oxidative stress conditions, and this damage can cause neurodegenerative and cardiovascular diseases, diabetes, cancer, and aging. Antioxidants have great potential to prevent these diseases, and studies of antioxidant activity typically focus on scavenging damaging reactive oxygen species. In contrast, we have quantified and compared the abilities of widely-studied sulfur, selenium, and polyphenol antioxidants to inhibit metal-mediated DNA damage and found that metal binding, not radical scavenging, is the primary mechanism for their DNA damage prevention activity. All three classes of antioxidants prevent DNA damage by coordinating the iron and copper ions responsible for hydroxyl radical generation. From these studies, we have developed the first predictive models for polyphenol DNA damage and cell death prevention based on iron binding. This innovative and general antioxidant mechanism highlights the critical role of metal coordination in the development of antioxidant supplements and therapies. In collaboration with Drs. Modi Wetzler and Brian Powell as well as researchers at Idaho National Laboratory, we are also designing, synthesizing, and testing sulfur-containing, chelating ligands for f-element coordination. These novel sulfur-containing ligands explore differences in covalency of actinide and lanthanide binding, a fundamental question with implications for nuclear waste separations. Our expertise in understanding the reactivity of sulfur-containing antioxidants with radical species will enable us to tune ligand radiolytic stability to improve actinide/lanthanide separations.
11. Determination of the Metal-Binding Properties of Glutathione Through Strategic Glutathione Mimics

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Glutathione (GSH) is the most abundant antioxidant produced by cells, and is present in mammalian cells in concentrations up to 15 mM. GSH is vital for catalytic hydrogen peroxide decomposition by glutathione peroxidase enzymes. It also has the ability to bind iron and copper, preventing them from forming hydroxyl radical. Oxidative damage by hydroxyl radical leads to biological damage, including oxidative DNA damage. By reducing H2O2 levels and by binding to metals to prevent hydroxyl radical formation, GSH can prevent DNA damage and cellular oxidative stress. The coordination chemistry of GSH to metals, however, is poorly understood. The goal of this project is to compare the metal binding and DNA damage prevention properties of GSH to those of synthetic GSH analogs that have strategic structural changes. Synthesis has begun on GSH mimic 2 (see figure). This mimic was chosen because it changes a metal-binding carboxylic acid to an amide group that will not bind metal ions. After synthesis, 2 will be tested using plasmid DNA damage assays to determine whether or not this carboxylate group is necessary for GSH antioxidant activity. In future work, the metal-binding properties of GSH and selected GSH mimics will also be examined by potentiometric titration and crystal structure determination. The overall goal of this project is to create a derivative of GSH that maintains the antioxidant properties but is able to be orally administered to a patient without being broken down immediately by enzymes and is able to permeate cell membranes, unlike GSH.
With the rapid development of nanotechnology, various kinds of nanoparticles have been synthesized and applied into biological systems with applications in diagnostics and therapeutics, such as drug delivery, biosensors and imaging contrast agents.1-3 Therefore, a detailed mechanistic understanding of nanoparticles-proteins interaction is crucial for the development of biomedicine. However, direct observation of atomic-scale surface morphology is impossible up to now. In recent years, ligand-detected techniques such as saturation transfer difference (STD) NMR have been used to study the effect of nanoparticles (NPs) on biological systems. Based on our group previous work, it revealed that there were 8 amino acids (AA) showing STD signal, which means that they bind to the surface of carboxylate modified polystyrene nanoparticles.4 However, we can’t determine their binding affinity due to the concentration limit. In this work, we use competition STD NMR to determine relative ligand binding affinity of amino acids on the polystyrene nanoparticles surface.5 We choose Trp as the reference and determine the relative binding affinity of each amino acid to NPs by comparing the STD effect of Trp before and after adding competing amino acid. The STD effect of Trp will decrease more when adding a strong-binding AA than a weak-binding AA. In addition, we also vary the concentration of the competing amino acids to see how their concentration affects the STD effect of Trp. We found the STD effect of Trp decreases with increasing concentration of competing amino acid.
13. Simple Formation of Metal Sulfide Nanocrystals

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Metal sulfide nanocrystals (MSN) have potential for many semiconductor applications. Nanocrystals can be engineered to exhibit various enhanced optical properties. This study describes a simple method based on ion-exchange in aqueous media for synthesizing mono- and bi-metallic sulfide nanocrystals. The reactions were carried out in silica matrix where metal ions were first entrapped and further sulfidized resulting in stabilized nanocrystals. UV-Vis Spectroscopy, Transmission Electron Microscopy (TEM) and Atomic Force Microscopy (AFM) were used to monitor the formation.

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The characteristic dynamics of an enzyme have been proposed to be critical for its catalytic efficiency. Correspondingly, it has also been proposed that mutations that disrupt these dynamical features will adversely affect its catalytic efficiency. Considering allosteric mechanisms in the effect of deleterious mutations, the present study examines the role of correlated dynamics as a constraint on the evolution of HIV-1 Protease (PDB id: 1hxw). HIV-1 Protease is a key target for AIDS therapy, and therefore, identification and characterization of constraints on its evolution is necessary for predicting drug resistant mutations. The role of “dynamics” as a constraint on the evolution of HIV-1 Protease is addressed by comparing correlated dynamics profiles obtained through molecular dynamics simulations of multiple HIV-1 Protease single point mutants with catalytic activity profiles of these same mutants obtained experimentally.
15. Thermal Degradation of Chemical Warfare Agents Utilizing Pyrolyzed Cotton Balls

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Since the Chemical Warfare Convention (CWC) Treaty was established in 1997, it has been prohibited for countries to stockpile, produce, or use chemical warfare agents (CWAs). However, it can be assumed that not every country or group is in accordance with these regulations, and therefore a method to deactivate and destroy these agents is necessary for international security. Current methods for destroying chemical warfare agents have predominantly relied upon hydrolysis, high pressure peroxides, or oxidation reactions utilizing bleaching agents. While these methods are effective, they require a large quantity of decontamination agents relative to the amount of CWA present and can produce secondary hazardous byproducts. By utilizing pyrolyzed cotton balls as a vessel for igniting the agents with napalm, it is possible to quickly and effectively destroy a wide variety of chemical warfare agents with limited residue or byproducts. This presents a simple, low cost, and effective method to rapidly decompose large quantities of CWAs with limited waste or cross contamination.

Figure 1: Infrared image of CEES burning after ignition with pyrolyzed cotton balls embedded with napalm
16. Analytical System Based on Magnetohydrodynamics for Analyte Deliver on Fluidic Chips with RGB Detection

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When an electrolyte fluid is in the presence of a magnetic field and an electric potential is applied against two electrodes a flow is observed and known as magnetohydrodynamics (MHD). Devices that use such mechanisms are known as nonmechanical pumps and offer many advantages over traditional lab-on-a-chip (LOC) devices based on electrophoresis. In this work we propose a MHD-based system capable of fluid handling and coupled to RGB detection. The MHD pumps were first characterized as a function of channel width, potential applied, and electrolyte type and concentration. Our results indicate that the proposed system can handle flow rates of 0.07 mm s⁻¹ up to 12.77 mm s⁻¹. Bubbles and pH variations can occur in the proposed system, due the electrolysis, but these limitations were addressed by increasing the buffer capacity of the system and incorporating and bubble-release channels. The resulting system features 3 pumps in a T configuration automated by an Arduino board and relays. When operated using 15V, phosphate buffer (pH 4.3) and a cellphone camera with a 60x Zoom as detector, the system can perform 13 consecutive injections of a model dye (methylene blue) with a RSD of 4.6%. Results linked to an additional network developed to investigate enzyme kinetics will be also discussed.
Protein adsorption occurs spontaneously when a protein adheres to a solid surface. The amount adsorbed and rate of adsorption depends on the protein’s size and charge, the surface’s energy and charge, and the solution in which the adsorption is occurring. Hydrophobic and electrostatic forces mostly dictate how the proteins interact with the surface. As the protein relaxes on the surface, it spreads out to cover more surface area and to allow more layers to be added. This project focuses on measuring the thickness of adsorbed bovine serum albumin (BSA) to a silica wafer. The thickness is expected to be about 2-3 nm which is measured using spectroscopic ellipsometry. Spectroscopic ellipsometry is an optical technique that measures the phase difference and the changes in reflectance between the perpendicular and parallel components of a beam of polarized light that is reflected off a surface. Since the ratio of these two values are measured from the same signal, this technique is very accurate and sensitive to protein thickness on the surface. Overall, protein adsorption is useful to study for immobilized enzyme and antibody assays. As such, this project will measure the thickness of BSA adsorbed to a silica wafer in a dynamic scan ellipsometric mode. The dynamic mode allows calculation of thickness at various time intervals to determine amount of adsorption versus desorption. Eventually a voltage will be applied to the wafer to determine how it affects protein adsorption or desorption.
18. Electrochemical Paper-Based Microfluidic Device with Prussian Blue Modified Pyrolyzed Electrodes to Detect Amino Acid Chirality in the Search for Extraterrestrial Life

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For over four decades Mars has remained an exciting astrobiology target due to intense interest in the possibility of past or present extraterrestrial life. Amino acids, which are the building blocks of proteins and necessary components of nucleotide synthesis, are a key indicator of life. Despite unimaginable possibilities of amino acids available, terrestrial life only utilizes 20 amino acids, almost exclusively in the L-enantiomeric form. Thus, it is reasonable to consider that this pattern of homochirality will be present in extraterrestrial life as well. Although there are multiple technologies that can be used to detect amino acid chirality, most of them integrate a separation step to determine enantiomeric distributions and often utilize detection methods that require derivatization steps. These detection methods are also quite bulky and/or need additional pretreatments steps to reach the required sensitivity and selectivity for extraterrestrial exploration. Considering the complexity and size of all of these instruments, an electrochemical paper based analytical device was designed for the quick and sensitive detection of amino acid chirality for space exploration in a small and simple package. The device is complementary to other approaches and could be used as a screening tool for potential signs of life before more complex analyses take place. The device was shown capable of nM limits of detection and was unaffected by various salinity conditions.
19. Development of a Paper-Based Electric Nose Sensor

Makenzie Reynolds* and Dr. Carlos D. Garcia

Department of Chemistry, Clemson University

Paper-based analytical devices have been suggested for many electrochemical applications due to their ease-of-use, quick and simple operation, and low fabrication cost. Paper is a highly diverse medium with physical and chemical properties that can be useful in many applications such as the forensic, environmental, food, and pharmaceutical field. There are many methods for producing paper-based sensing devices like drop casting and inkjet printing but most of them are expensive and lack reproducibility. As an alternative, laser-induced local pyrolysis of materials have also been used for electrochemical devices but most of these approaches have been applied towards the development of electrochemical sensors, most of which show significant kinetic limitations (slow electron transfer). Taking advantage of the possibility to perform direct laser scribing of paperboard, we propose the fabrication of a paper-based electric nose sensor. The poster will describe the initial findings related to the electrical characterization of the material.
Carbon is one of the most versatile materials to develop electrochemical and optoelectrochemical systems. Although a number of carbon-based substrates are currently available in the market, only a few of those offer an adequate balance between cost, homogeneity, transparency, and conductivity. These are critical requirements to couple these substrates with optoelectrochemical systems, and a number of groups have developed substrates using photoresist. Unfortunately, processing this material is time consuming and requires specific instrumentation. Aiming to develop an alternative route to coat substrates with homogeneous layers of optically-transparent carbon, we propose the use of hydrothermal carbonization. This method is simple to use and has proven to be a successful one-step process for fluorescent carbon nanoparticles. Here, we describe the properties of films formed by hydrothermal treatment of fructose in the presence of hydrophobic surfaces. The goal is to obtain uniformly thin carbon layers compatible with ellipsometric measurements.
Salt-inclusion solids feature a composite structure consisting of an integrated lattice of ionic salt and metal-oxide covalent framework in a host-guest relationship. An intriguing geometry highlighted by Cs$^+$ ions was observed in a previously reported polyoxovanadate salt, where the extended lattice of Cs$^+$ cations exhibit a half sodalite (SOD) $\beta$-cage unit. In the structure of Cs$_5$V$_{14}$As$_8$O$_{42}$Cl, two different lattice geometries, the sodalite geometry of the Cs$^+$ cations and the pseudo-S4 geometry of the anionic clusters (POV14), contribute to the overall structure of the crystal. How is this possible during “crystal assembly”? Using classical Lennard-Jones and Coulombic interactions, we model the crystal assembly for this complex salt. We are able to use classical electrostatic interactions to map how the ions position during crystal growth. As assembly progresses, the high degree of symmetry within the electrostatic fields is broken due to interactions amongst clusters, resulting in higher energy barriers and localized ions. This resulted in the Cs$^+$ ion probes mimicking the half-$\beta$ cage geometry in the final product.
Traditionally, crystal growth of complex oxides containing polyoxometalate (POM) clusters relies on evaporative or hydrothermal techniques. These techniques can be time consuming or destructive to the POM structure, thus there is need for a new, less destructive and time-efficient technique. Our lab has developed a bench-top technique employing electrochemical driving force to allow a convenient synthesis of POM-based crystals at room temperature. The new technique taking the advantage of electrochemical energy allows the reduction of POM-containing clusters in situ during the crystal growth in aqueous solution. Compared to conventional synthesis under hydrothermal conditions, the e-chem method offers an attraction especially to the synthesis of POMs that are otherwise subject to thermal decomposition. Further, using electrochemical methods for crystal growth facilitates a means for the selective synthesis of compounds with desired frameworks for electrical conductivity. We have had some initial successes in electrochemical crystal growth where newly discovered compounds exhibit fascinating structures of one-dimensional (1D), alternating POM anion and transition metal (M) cations, as well as two-dimensional (2D) frameworks featuring tethered POM clusters on metal-oxide chains and three-dimensional (3D) M-POM porous network. In addition to using X-ray diffraction methods to investigate crystal structures, we have employed thermogravimetric analysis/Differential Scanning Calorimetry (TGA/DSC) methods to examine the thermal behaviors, XPS (X-ray photoelectron spectroscopy) for the oxidation states of transition metal ions, etc. Because of the structural openness of the resulting compounds, we also plan to carry out lithium ion insertion reaction to chemically modify the framework structure to show its feasibility for materials application as capacitors.
Optogenetics can be used to modulate targeted neurons in vivo using visible light. Currently the visible light sources are surgically implanted into the brain tissue, but this harmful and invasive technique may be avoided if suitable scintillating nanoparticles can be inserted via injection. The particles could then be externally activated to provide the energy necessary to stimulate neuronal activity. We began a synthesis program to prepare suitable cerium doped gadolinium silicate nanoparticles using a modified core-shell technique. This produced several phases including Ce:Gd$_{4.67}$(SiO$_4$)$_3$O (Ce:GSAP), Ce:Gd$_2$SiO$_5$ (Ce:GSO), and Ce:Gd$_2$Si$_2$O$_7$ (Ce:GPS) nanoscintillators. The silica core serves as both a template to ensure uniformity in size and shape, and can be manipulated to elicit different silicate phases. The chemistry leading to the various phases will be outlined. Photoluminescence and radioluminescence properties of the gadolinium silicate phases were studied to determine their potential for optogenetic application. The addition of lutetium into the gadolinium silicate nanoparticles was also investigated. The mixed gadolinium/lutetium materials could also be engineered to produce different silicate phases and showed enhanced light output under X-ray stimulation. This work led to a number of gadolinium silicate nanospheres that are attractive candidates for a less-invasive optogenetics. Initial exploration on other gadolinium containing nanoscintillators such as NaGdF$_4$ and Gd$_2$O$_2$S will also be discussed.

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A wide variety of synthetic techniques are available to chemists for materials discovery, where typically the preparation of each new composition is ultimately achieved by utilizing a unique set of optimized reaction conditions. One method for materials synthesis is the hydrothermal method, which is a way to synthesize high quality single-crystals of new solid-state compounds. In this study, we are investigating the hydrothermal synthesis of iron molybdate compounds. These compounds have a potential for many physical properties including interesting optical, ferroic, and magnetic behavior. This study has yielded crystals of three new iron molybdate compounds, namely Fe(MoO$_4$)(OH), NaFe(MoO$_4$)$_2$(H$_2$O), and Na$_{0.375}$Fe$_2$Mo$_3$O$_{12}$(H$_2$O), which were synthesized hydrothermally in Teflon-lined autoclaves at 200 °C. Herein, the synthesis and structural characterization of these new compounds will be discussed.
25. Hydrothermal Synthesis of Rare-Earth Pyrochlore (A$_2$B$_2$O$_7$) Stannates and Fluorite-type Actinide Oxide Single Crystals

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Crystals possessing the pyrochlore A$_2$B$_2$O$_7$ structure type (space group Fd-3m) have garnered interest as of late due to their unique tetrahedral arrangement of trivalent “A”-site cations in the lattice. This arrangement allows for the possibility of magnetically interesting systems with potential applications for study as quantum spin liquids and other magnetically frustrated systems. Careful choice of size and spin state of tetravalent “B”-site cations can allow for all rare-earth (Ln and Y) pyrochlores to be synthesized with their magnetic properties based solely on the spin state of the rare-earth cation. Tetravalent tin is the only known “B”-site cation that is closed-shell and adequate size to form the pyrochlore structure type with all rare-earth cations. Unlike solid-state and flux-melt crystal growth methods, hydrothermal synthesis methods provide a means for controlled, ordered growth of high-quality single crystals. This technique has yielded all rare-earth pyrochlores for use in magnetic and spin-oriented neutron studies. Additionally, the controlled growth and unique conditions of hydrothermal methods allowed for the synthesis of highly refractive actinide oxide crystals (AO$_2$, where A = Th, U, Np) for studying long-term etching and erosion of these radioactive species in various environmental settings.
Inorganic oxides, especially those of transition metals, have wide application in chemistry and material science. Silicate oxyanions are common tetrahedral building blocks in inorganic oxide materials and can be useful to produce great structural variety by forming complex polysilicates from polymerized tetrahedra. Alternatively, germanate oxyanions are perhaps an even more versatile building block as they readily adopt 4-, 5-, and 6- coordinate geometries. This flexibility allows for the synthesis of otherwise inaccessible compounds and novel structures not found amongst the silicates. Our group synthesizes these materials with high temperature (>500 °C), high pressure (~ 2 kbar) hydrothermal techniques which mimic common mineral-forming conditions. Several transition metal germanates are presented and compared to structurally or synthetically analogous silicates, revealing new oxyanion structural chemistry. This includes unusually large unit cells, uncommon space group symmetry, potentially frustrated triangular systems, and complex chemical formulas.
Nanoparticles have seen an increased presence in commercial markets in recent years due to their useful properties for cosmetics, sporting equipment, food packaging, and more. Due to increased consumer and governmental monitoring, precise quantification of these nanoparticles is becoming an increasingly relevant field of research. Current methods in the literature are poorly described and seldom reproduced by other groups, making reproducing methods difficult. While methods are ill-defined, the vast majority of published nanoparticle quantification schemes involves inductively coupled plasma optical emission spectroscopy or mass spectrometry (ICP-OES/MS). While very effective, ICP instruments have a large base cost and are expensive to use and maintain. To address this, the liquid sampling – atmospheric pressure glow discharge (LS-APGD) microplasma was used for quantification of silver nanoparticles. The LS-APGD can be used as an excitation source for OES or an ionization source for MS. Additionally, the operational requirements are far less than that of an ICP, consuming less power (<100 W), gas (<1 L min⁻¹), and sample (<1 mL). This work focuses on the advancements made towards using the LS-APGD-OES system for nanoparticle quantification and compares achieved analytical performance to that of a commercial ICP-OES instrument.
28. Isolation and Quantification of Human Urinary Exosomes by HIC on a Polyester Capillary-Channeled Polymer Fiber Phase

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Exosomes are membranous vesicles ranging from 30-150 nm in diameter, which are secreted by virtually all cell types and found in most bodily fluids, including blood, urine, and saliva, under both healthy and morbid conditions. Exosomes carry diverse cellular constituents from their parent cells including proteins, messenger RNAs (mRNAs), microRNAs (miRNAs), and DNA. As such, they are important in intracellular communication, and play key roles in many intercellular functions, including immunomodulation, differentiation, antigen presentation, and cancer progression. Furthermore, mounting evidence suggests that tumor cells secrete more exosomes than normal cells. These features have prompted extensive research to isolate and quantify exosomes for prognosis as well as to serve as biomarkers for disease and cancers. Current exosome isolation methods are time-consuming, have low purity yields, and cause exosome aggregation and none of them effectively excludes remnant proteins of the initial sample matrix from the targeted exosome population. Besides, current quantification methods face equivalent challenges as methods for isolation in terms of trade-offs between sensitivity, selectivity, and throughput. However, while these methods enable one to isolate or quantify exosomes, very little research combines isolation and quantification into a singular operation scheme. A missing tool in the realm of exosome diagnostics and processing is a high throughput, generic method of isolation and quantification. This study developed an efficient, low-cost, high recovery and mild online human uranyl exosome isolation and quantification method by using poly(ethylene terephthalate) (PET) capillary-channeled polymer (C-CP) fibers in a hydrophobic interaction chromatography (HIC) method.
29. Isolation and Characterization of Tumor-Derived Exosomes for Ovarian Cancer Biomarker Detection

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Because early stage ovarian cancers show little to no symptoms, or present symptoms that could easily be credited to other ailments, a main challenge is presented in diagnoses in the emergence of the disease. This causes patients to remain undiagnosed until the malignancy has reached the stage of fatality as 4/5 of diagnoses made are in cases of stage III or IV cancers. With the many invasive cancer detection treatments of today, this research project aims to create a noninvasive approach to early cancer detection using exosome-rich samples. Exosomes are cell-derived vesicles that are ejected from the cell and are essential in cell-to-cell communication, disease progression, and are suggested in applications of drug delivery. Because exosomes contain many molecular constituents of their host cells including DNA and biomarker proteins, they have been suggested in applications as a “liquid biopsy” for disease detection. In this project, exosomes are isolated using specialized capillary channeled polymer fiber micropipette tips during solid phase extractions or hydrophobic interaction chromatography. The characterization of exosomes is done by using a primary antibody specific to ovarian cancer (anti-CA125) and visualized with a fluorescent or nanoparticle labeled secondary antibody in junction with Confocal Fluorescent Microscopy or Scanning Electron Microscopy with Energy Dispersive X-Ray Spectroscopy, as well as with various immunoassays. The long-term goal of this research is to create a means of synchronized isolation and characterization of biomarkers from exosome-rich samples derived from ovarian cancer tumors that can be applied directly to early cancer diagnosis and detection.
An Ambient Desorption-Liquid Sampling – Atmospheric Pressure Glow Discharge (AD-LS-APGD) plasma has been demonstrated in this study to simultaneously obtain both molecular and atomic information from an analyte. Building upon previous works that demonstrated the capability of the AD-LS-APGD for the detection of organic molecules via mass spectrometry (MS) and atomic species via optical emission spectrometry (OES), here the analytical portfolio of AD-LS-APGD is further extended to atomic mass spectrometry. Moreover, the geometry of the AD-LS-APGD-MS is transformed to the optical emission variant. This change provided multiple benefits: it allowed for simultaneous detection by both MS and OES and also appeared to greatly increase the sensitivity of atomic detection by mass spectrometry. Meanwhile the capacity for molecular mass spectrometry is still maintained. To demonstrate applicability, over-the-counter medications were adulterated with lead and copper salt and tested with the AD-LS-APGD. Detection was attempted by both optical emission and mass spectrometry. It was demonstrated that the inclusion of organic molecules appears to reduce the response of metal adulterant. Fortunately, elemental response for optical emission does not appeared to be diminished. This demonstrates, to our knowledge, the first time in which both molecular and atomic information is detected simultaneously from a single ionization source.
The liquid sampling-atmospheric pressure glow discharge (LS-APGD) microplasma has shown great promise in recent years in the fields of optical emission spectroscopy and mass spectrometry. To this point, it has allowed traditional organic mass spectrometers, including high resolution Orbitrap instruments, to be used for inorganic applications, including high precision isotope ratio measurements. The LS-APGD-Orbitrap system is a particularly attractive alternative to traditional elemental MS systems (such as inductively-coupled plasma and thermal ionization multi-collector instruments) due to its ability to investigate numerous analytes in a multielement solutions simultaneously, as well as having the ability to perform ultra-high-resolution mass analysis eliminating isobaric interferences which normally require extensive chemical separation prior to analysis. While previous work has included a detailed optimization of the LS-APGD for both analyte response and isotope ratio analysis, there has been no investigation of the applying different powering modes to the plasma. The LS-APGD is unique in its ability to operate using four different powering modes; solution grounded cathode (SGC), solution grounded anode (SGA), solution powered cathode (SPC), and solution powered anode (SPA) modes. In order to investigate the utility of each powering mode, the pertinent operating parameters (operating current, liquid flow rate, gas flow rate, and inter-electrode displacement) were monitored for analytical response and isotope ratio measurements in each powering mode of the LS-APGD.
32. Employing Polypropylene Capillary-Channeled Polymer Fiber Column as the Second Dimension in a Comprehensive Two-dimensional System for Analysis of Complex Protein Mixture and E. coli Cell Lysis

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While the advent of sub-2-micron particle sizes and high temperatures have enhanced the ability to separate complex mixture, a single chromatographic dimension is inherently a limiting factor. Therefore, it was of interest to explore the use of two-dimensional liquid chromatography (2D-LC) to improve the resolving capability while using the flexibility of UHPLC, providing a greater separation power (peak capacity). Online, comprehensive 2D-LC has become an attractive option for the analysis of complex nonvolatile samples found in various fields (e.g. environmental studies, food, life, and polymer sciences). The research presented here leverages the developments of C-CP fiber stationary phases directed at high throughput protein and rapid separations as 2D materials in comprehensive 2D-LC. The ability to operate C-CP fiber columns at high linear velocities (>75 mm sec\(^{-1}\) at < 1000 psi) without sacrifice in protein resolution is first step toward 2D implementation. What must be realized are fast elution gradients and rapid re-equilibration to minimize cycling times (modulation periods). Thus, different flow rate and gradient program have been tested to assess the potential benefits of C-CP fiber comparing to commercial columns. Here, high shear rates and shorter column residence times allow elution in shorter gradient windows. Very importantly, at the shortest possible gradient recycling time on this instrument, 30s, there should has no significant degradation in peak capacity. Finally, a comparison of separation efficiency, recovery and reproducibility between five commercial RP columns and the PP fiber column is presented for a standard, eleven protein mixture and a E. coli cell lysis solution, using optimal operating conditions for each column type.
Inductively coupled plasma – mass spectrometry (ICP-MS) has long been the standard for elemental analysis. One of the major challenges of these instruments is their upfront costs and enormous consumable use. ICP-MS instruments typically require a large power consumption to operate and use approximately 17 L min⁻¹ of Ar to operate. Despite these limitations, the ICP-MS remains dominant in its field due to its incredible sensitivity, however the need for lower cost, transportable instrumentation remains. The liquid sampling – atmospheric pressure glow discharge (LS-APGD) microplasma, developed as a versatile ionization source, makes for an attractive alternative. The LS-APGD maintains a high-power density plasma (~10 W mm⁻³), while utilizing low gas flow rates (0.5 L min⁻¹). In addition, the LS-APGD operates in a total consumption mode, requiring significantly less material for analysis than that of an ICP-MS. To this point, the LS-APGD has been interfaced with a variety of mass spectrometers, showing exceptional capabilities in the analysis of elemental, small organic, and proteomic samples. Unfortunately, the majority of these instruments are still large, laboratory scale instruments, with high upfront costs and high power consumption requirements. To further improve the portability of the source, the LS-APGD has been interfaced with an Advion ExpressionL compact mass spectrometer (CMS). This inexpensive instrument operates on significantly lower power requirements, and at only 70 lbs, has great potential for field deployment. Coupling this instrument with the LS-APGD presents a notable step towards the miniaturization of atomic mass spectrometry instrumentation. Presented here will be the preliminary figures of merit and benchmarking comparisons for the analysis of diverse analyte types. While the studies performed here are in a benchtop configuration, the CMS has previously been travel-hardened. Ultimately, it is believed that this instrumental platform holds great promise by virtue of its analytical flexibility both inside, and outside, of the analytical laboratory.
A unique technique was developed to map the energy landscape of conjugated polymer nanoparticles based on simultaneous correlated charge carrier tracking and single-molecule fluorescence spectroscopy. With this technique, a two-dominant-chain conformation was observed on the conjugated polymer nanoparticle of poly[9,9 dioctylfluorenyl-2,7-diyl]-co-1,4-benzo-{2,1′-3}-{thiadiazole}] (PFBT). The conformation consists of a red-emitting phase and a blue-emitting phase. Polaronbs were found to be mostly trapped in the red-emitting phase and can only escape to the blue-emitting phase occasionally. Hopping between red-emitting polaron traps were observed within a time scale from tens of milliseconds to several seconds. This work provides unprecedented details for the charge transport in conjugated nanoparticles.
Improved Superresolution Imaging Using Photoswitching in Conjugated Polymer Nanoparticles

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Small semiconductor structures often exhibit "telegraph noise". If the number of charge carriers is small, then spontaneous changes in the number of carriers can lead to abrupt switching between two or more discrete levels, leading to burst noise or popcorn noise in transistors. We have observed similar behavior in the fluorescence of organic semiconductor nanoparticles, where typical carrier populations are often less than ~10 carriers per nanoparticle. Spontaneous changes in the number of charges results in abrupt switching between 2 or more fluorescence intensity levels, since the charges act as highly efficient fluorescence quenchers. The equilibrium number of charges is determined by competition between a photodriven ionization process and spontaneous recombination. Doping with redox-active molecules also affects the balance. Nanoparticles of the conjugated polymer PFBT doped with the fullerene derivative PCBM, rapidly establish a fluctuating steady-state population of tens of hole polaron charge carriers, sufficient to nearly completely suppress nanoparticle fluorescence. However, fluctuations in the number of charges lead to occasional bursts of fluorescence. This spontaneous photoswitching phenomenon can be exploited for superresolution imaging. The repeated, spontaneous generation of short and intense bursts of fluorescence photons results in a localization precision of ~0.6 nm, about 4 times better than typical resolution obtained with dye molecules.
36. X-Panding Around tppz [2,3,5,6-tetra(2’-pyridyl) pyrazine] via Halogen Bonding

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The compound tppz [2,3,5,6-tetra(2’-pyridyl) pyrazine] is a useful molecule for supramolecular synthesis in the study of crystal engineering and study structure-property relationships. Because of its conjugated aromatic rings, tppz exhibits fascinating electrochemical, photophysical and photochemical properties. [1] It is a versatile electron donor that has a multitude of binding modes by adopting different conformers and supporting varying degrees of protonation to act as a cationic species. When these tppz-based cations are coupled with polyiodide anions via halogen bonding, an enormous structural diversity is realized. [2] Addition of organoiodine molecules, such as tetraiodoethylene (TIE), 1,2-diiodotetrafluorobenzene (o-F4DIB), or 1,4-diiodotetrafluorobenzene (p-F4DIB) to these systems can also lead to cocrystals with additional halogen bonding interactions, which we have labeled as “X-panded polyiodides”. The resulting extensive halogen-bonded networks can prove useful in developing crystal engineering principles, and we are interested in understanding the dimensionality and controlling factors involved in these supramolecular structures. This study examines the structural variety in tppz triiodide and pentaiodide salts, along with a family of cocrystals, [H2TPPZ] I3 ·o-F4DIB and [H2TPPZ] 2I3 ·p- F4DIB, including the cationic behavior and conformation of tppz. The resulting halogen bonding networks between the organoiodine molecules and the polyiodide anions are also studied in detail.


37. Solvent Effects on the Structure of Sulfonated Polystyrene

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At low ionic content, ionomers form dynamic sparse networks in solutions. Here we investigate the factors that affect structure of slightly sulfonated polystyrene (PSS) using small angle neutron scattering (SANS). Measurements were done in toluene/ethanol solutions in 0.25-10Wt% in range of temperatures 25-55°C. In toluene, an upturn characteristic to networks was observed at low q. The SANS patterns consist of a broad signature at intermediate q, attributed here to an average network mesh size, which was determined by the distance between ionic physical crosslinks. As concentration increases, the characteristic dimensions decrease due to increasing numbers and cluster size. The dimensions were calculated from R of a Gaussian chain. The long-range correlations were captured using the Beaucage model. The PS chains assume an overall Gaussian configuration around the ionic clusters. The long-range correlations diminish with addition of ethanol. PS chains assume a more constrained chain configuration while ionic clusters become less defined.
Ionomer networks are formed in solutions at extremely low concentrations. Tuning these networks offers a means to control the structures that remain trapped as the solvents evaporate to form membranes. Here, we probe the diffusion of the polymers and the solvents in networks formed by polystyrene sulfonate (PSS) by pulse field gradient NMR. The diffusion of the polymer reflects the properties of the network and that of the solvent. Specifically, PSS networks with sulfonation levels of 0, 3 and 9 mole % were studied in toluene and cyclohexane neat and mixed with ethanol. Toluene is a good solvent for polystyrene and cyclohexane is a theta solvent at room temperature. We find that with increasing sulfonation levels, both the polymer and the solvent motions decrease in both solvents. Regardless of sulfonation level, the diffusion of PSS is almost same in cyclohexane and toluene at room temperature. With increasing temperature, the diffusion of all components increases in both solvents however it is more pronounced in cyclohexane. The solvents diffuse faster than the polymers but follow similar trends. While perturbing the ionic clusters affect the overall network dynamics, the polar solvent also affects the hydrophobic network rigidity.
Owing to their unique ability to assemble and organize redox- and photoactive building blocks and guest molecules in a highly ordered fashion, crystalline porous metal–organic frameworks (MOFs) can perform myriad complex functions, including charge conduction and light to electrical energy conversion. Taking full advantage of the light-harvesting capacity of chromophoric MOFs in photovoltaic devices requires robust, uniform, precisely oriented MOF films directly attached to suitable electrodes that can promote charge separation, diffusion, and injection upon photosensitization. Herein, we demonstrate spontaneous solvothermal growth of predominantly [100]-oriented, robust, uniform pillared porphyrin framework-11. When introduced as photoanodes in liquid-junction solar cells, the [100]-oriented PPF-11 films display excellent photovoltaic response (JSC: 4.65 mA/cm², VOC: 470 mV, photocurrent efficiency (PCE): 0.86%) and relatively small photoanode/electrolyte interfacial charge-transfer resistance (259 Ohm) under 1-sun illumination, easily outperforming control devices (PCE ≤ 0.2%) and all intrinsically light-harvesting 3D porous MOFs reported to date by quite wide margins. The non-catenated porous PPF-11 was also able to accommodate electron deficient large C60 guests, filling nearly half of its cavities upon saturation. Despite experiencing significant ZnTCPP/C60 charge transfer interaction, the C60-doped PPF-11 films displayed much weaker photovoltaic response to undoped PPF-11 films, possibly due to exclusion of I⁻/I³⁻ electrolytes from the C60-occupied cavities and the inability of isolated C60 guests to support long-range charge movement.
40. Energy Transfer in a Novel Light-harvesting Luminescent Metal-Organic Framework

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Metal-organic frameworks (MOFs)- hybrid porous materials made of organic ligands linked by metal ions or metal clusters nodes which are well known for their chemical and structural tunability. Recently, MOFs have attracted considerable attention as potential light-harvesting systems. The long-range ordering of chromophore and fluorophores in crystalline MOFs offer directional energy transfer (ET) within the frameworks in a predesigned pathway. This possible energy transfer (ET) opens a door for considering MOF materials as a potential light-harvester for solar cells, photocatalysis, sensors and light-emitting diodes. Among all possible energy transfer pathways in MOFs, herein we present a new PPW-MOF featuring two fluorophoric ligands with overlapping emission and absorption spectra for ligand-to-ligand energy transfer, which allowed us to excite the donor ligand and observe emission from the acceptor ligand. Our studies on this new PPW-MOF suggest promising application of this MOF as an efficient light-harvesting system.
Metal-organic frameworks (MOFs) have been gaining momentum in the fields of energy storage, energy transfer, and even light harvesting. Because of their unique electron deficient properties and pi-interaction potential, naphthalenediimide (NDI) ligands have been incorporated into an array of energy-related MOFs. This group has constructed a redox-active BMOF composed of N,N'-bis(4-pyridyl)-2,6-dipyrrolidyl naphthalenediimide (BPDPNDI) pillars and 1,2,4,5-tetrakis-(4-carboxyphenyl)benzene (TCPB) struts. Stable, uniform films of the BMOF were grown on ZnO substrates. With the addition of a methyl viologen (MV$^{2+}$) guest, the BMOF showed electrical conductivity of $2.3 \times 10^{-3}$ S/m. Furthermore, a honeycomb-shaped, MOF (based on MOF-74) was constructed with a salicylic acid-functionalized NDI Ligand and an electron-rich planar tetrathiafulvalene (TTF) guests. With the addition of the TTF guest, the electronic bandgap of the original material was lowered by about 1 eV. The most recent NDI-based MOF to come from this group was a water-stable 2D sheet-like neutral Cu(I)-Sulfonate MOF. Upon infiltration of LiClO$_4$ and pellet formation, the MOF’s ionic conductivity was raised by a factor of a million to $2.3 \times 10^{-4}$ S/m and the activation energy for charge carrier transport dropped to a mere 0.167 eV. This MOF showed a rare, if not first example of a neutral, practically solvent-free, not post-synthetically modified MOF and offers a new strategy to develop ion-conducting sulfonate for potential battery application.
Lignin is the most abundant polyaromatic biopolymer and is responsible for the mechanical strength of plants and timber-built structures. The complex chemical structure and the difficulty in fractionation, characterization and modification are significant barriers to wide-spread commercial application of lignin. Another abundant industrial waste is elemental sulfur produced as a by-product in petroleum refineries. The major drawback of using sulfur as an individual composite material is its low mechanical strength. Sulfur does, however, have numerous attractive non-mechanical properties including hydrophobicity, antimicrobial properties, high electrical resistivity, and low thermal conductivity. It was thus hypothesized that durable, recyclable biocomposites can be obtained through chemically modified lignin crosslinking with sulfur. Different strategies on chemical modification of lignin and the characterization techniques including $^1$H NMR spectrometry, differential scanning calorimetry IR spectroscopic techniques and an approach to quantifying the degree of substitution reliably with $^{31}$P NMR spectrometry are discussed. According to the synergistic analysis via dynamic mechanical analysis, thermogravimetric analysis, and differential scanning calorimetry, these were found to be less brittle, mechanical strength improved composite materials compared to pure sulfur based structural materials. Further analysis is ongoing to increase the mechanical properties via alternative crosslinking with lignocellulose biomass and sulfur.
Comparison of Surface Characteristics of Perfluoroalkoxy Alkane (PFA) Copolymers with Bulkier Perfluorinated Substituent Groups

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The Thrasher research group undertook a program dedicated towards the development of a library of fluorinated materials that focused on the synthesis and characterization of perfluoroalkoxy (PFA) copolymers of tetrafluoroethylene (TFE) and perfluoroalkyl trifluorovinylethers. One aim of the project was to improve upon the mechanical strength and wearability of commercial PFA resins by incorporating bulkier perfluoroalkoxy trifluorovinylether monomers into these copolymers. We have prepared copolymers of trifluorovinylethers containing either a bulky perfluoroneopentyl group or a bulky pentafluorosulfanyl-(SF5)-substituent with TFE. Our desire is for the bulkier pendant groups to orient towards the surface, thus improving the surface properties of these synthesized materials when compared with similarly synthesized benchmark PFA copolymers. In addition to the preparation and characterization of the new monomers and their copolymers with TFE by both aqueous emulsion and solution techniques, we will report on the surface properties of the copolymers via contact angle, AFM, and XPS measurements.

\[
\begin{align*}
\text{RO} - \text{F} & \quad \text{F} - \text{F} \\
\text{F} & \quad \text{F} \\
\end{align*}
\]

\[
\begin{align*}
\text{R} &= -\text{CF}_3, -\text{C}_2\text{F}_5, -n\text{-C}_3\text{F}_7, -\text{CF}_2\text{C(CF}_3)_3, -\text{C}_2\text{F}_4\text{SF}_5
\end{align*}
\]
44. Efficient Synthesis of 3:1 Desymmetrized Cyclen via Richman-Atkins Cyclization and Investigation of the Thorpe-Ingold Effect

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Cyclen (1,4,7,10-tetraazacyclododecane), a useful ligand for a variety of metals and the backbone of the cyclic gadolinium-based MRI contrast agents, is traditionally synthesized via Richman-Atkins cyclization. However, many ensuing applications seek to desymmetrize cyclen in order to add additional functionality. Currently such processes add several additional synthetic steps, primarily by juggling protecting groups which incurs atom-inefficiency and require difficult or low-yielding purifications. Presented herein is an efficient synthetic pathway towards 3:1 desymmetrized cyclen whereby desymmetrization occurs via selective choice of protecting groups before cyclization. Also provided is the first structural evidence for the steric Thorpe-Ingold effect, which has long been proposed to direct the Richman-Atkins cyclization, as well as data which calls into question the role of the Thorpe-Ingold effect in this process. Present desymmetrization methodology is broadly applicable to the wide variety of azamacrocycle ligands.
Wetzler group research utilizes related synthetic approaches in two broad areas of applications: ligand development and therapeutic development. In ligand development we are developing more efficient approaches to existing azamacrocycle ligands, enabling their facile desymmetrization, and studying their underlying mechanisms, all with the ultimate goal of building new capacities for lanthanide and actinide coordination chemistry and separations (collaborators: Brian Powell in Environmental Engineering and Earth Science and Julia Brumaghim in Chemistry). In therapeutics we are developing analogs of creatine for the treatment of the intellectual disability creatine transporter deficiency, as well as peptides for use in muscle and nerve regenerative medicine applications (collaborators: Susan Chapman in Biological Sciences, Dan Simionescu in Bioengineering, and Jeff Twiss at the University of South Carolina).
Herein, we investigated strategies for the synthesis of a new class of porous and nonporous biodegradable microparticles (MPs) based on poly(D,L-lactic acid)-poly(ethylene glycol)-COOH (PDLLA-PEG-COOH) or poly(D,L-lactide-co-glycolide) (PLGA) copolymers. Further, these materials were coated with polyethylenimine (PEI) in order to compare the performance of the naked and PEI-capped MPs for the gas phase capture of model aldehyde VOCs, hexanal and octanal. The removal efficiencies of the various MP formulations ranged from 50% reduction to 97% reduction of VOC vapors. By coupling the intrinsic gas adsorption properties of the parent, naked MPs with the potential for covalent capture by means of PEI-surface coating, we have generated new materials exhibiting a dual modality for VOC capture. These materials represent a new scaffold for the remediation of VOCs based on renewable polymers.
The identification and assignment of the absolute stereochemical structure of organic molecules is essential and vital to multiple disciplines of chemistry. Current methods typically use circular dichromism (CD) because of its inherent sensitivity to asymmetric compounds. However, this approach involves the use of specialized analytical equipment (CD) which is not universally available and is often complicated due to the need for extensive derivatizations to the sample. The presented strategy involves sulfation of a nucleophilic functional group on the substrate of interest, followed by crystallization of the sulfated product with guanidinium, and subsequent structure determination via X-ray crystallography. A guanidinium-sulfate network has been proven to be a sound strategy for material design due to the highly directing hydrogen-bonding and ionic character of the guanidinium-sulfate network. The established two-step guanidinium sulfation process takes advantage of this flexible hydrogen bonding network allowing for the crystallization and identification of chiral substrates that otherwise would prove to be recalcitrant.
Hypervalent iodine (HI) reagents have become attractive alternatives to transition metals due to their mild reactivity, high selectivity, and commercial availability as oxidants and electrophiles. Recently, iodine (III) species have been utilized in a variety of organic transformations. In particular, chiral iodine(III) reagents have the potential to be useful in the development of efficient asymmetric catalytic systems. Chiral information can be transferred from the HI reagent to the substrate by employing catalysts that have the active iodoarene site attached to chiral information, such as small peptides. Peptides have the ability to induce high enantioselectivities into organic molecules due to the immense chiral space they provide and can thereby create a chiral environment for selective substrate recognition. Their modularity and facile preparation following standard Fmoc-Solid-Phase Peptide Synthesis techniques facilitates the synthesis and evaluation of numerous catalyst structures in a timely manner. The overall goal of this research is to merge the fields of hypervalent iodine chemistry with peptide-mediated asymmetric catalysis to generate chiral HI peptides that effectively act as enantioselective catalysts for a range of important synthetic reactions.
Heterocyclic molecules that contain nitrogens and consist of four, five and six membered rings such as azetidinones (eg: β-lactams), azoles, triazoles, oxadiazines and oxadiazinones have shown significant usage in pharmaceutical fields. Particularly, the vicinal diamine skeleton has been seen in numerous drug directing candidates such as penicillin, cephalosporins, oseltamivir (Tamiflu). Historically, there has been minimal effort toward synthesizing a broad scope of vicinal diamines, which is in stark contrast to related processes, such as dihydroxylations and aminohydroxylations. Furthermore, accessing the vicinal diamine motif in few synthetic steps with a broad substrate scope has remained challenging. In this work, we accessed the vicinal diamine skeleton through the reactivity of various azodicarboxylates (as the main nitrogen source) with various electron-rich alkynes. These investigations lead us to develop a novel method to generate a class of vicinal diamine motif containing products, such as diazacyclobutene (four-membered heterocyclic ring) and 2-imidoimide derivatives (acyclic vicinal imino compounds) in good yields.
50. Development of Small Molecules for the Selective Inhibition of the Polysaccharide Metabolism in Human Gut Microbes

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Research into the cause of human autoimmune diseases has shifted focus from single host events to complications arising from the vast microbiological community living within our bodies. This research has found that large shifts within our microbiome can cause dramatic effects that impact our overall health. Therefore, it is of the utmost interest to develop methods that control and maintain these systems as a preventative means to protect our health. Our previous research has established that using the FDA approved drug acarbose, we are able to inhibit the growth in a non-microbicidal manner of Bacteroides, a genus of bacteria which are believed to play a causal role in the development of type 1 diabetes. The goal of this research is to expand upon our knowledge by testing known α-glucosidase inhibitors within our system in the hopes that they behave in a similar manner as acarbose by inhibiting the growth of Bacteroides while having little effect on other gut microbes. These efforts include the synthesis of various triazole sugar derivatives as well as a unique synthetic route towards a variety of natural products from the Salacia family of α-glucosidase inhibitors such as salaeinol and salprinol. With these new, structurally unique compounds we hope to further expand upon our success with acarbose and develop more potent non-microbicidal growth inhibitors as a potential preventive treatment option from the development of type 1 diabetes and other similar autoimmune diseases.
51. Non-Lethal Inhibition of Bacteroides dorei strains, a Clinically Relevant Species Associated with Type 1 Diabetes, using the α-Amylase Inhibitor Acarbose

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Changes in the human gut microbiota (HGM) have been linked to various diseases and health complications. Therapies that selectively modulate community members via a non-microbicidal mechanism offer a tantalizing avenue for treatment of such disorders. Studies presented here show the inhibition of the starch utilization mechanism belonging to the clinically relevant species Bacteroides dorei using the α-amylase inhibitor acarbose. A bloom in this HGM constituent has been linked to the onset of type 1 diabetes in children predisposed to the disease, and other bacteria belonging to the same phylum have been connected to various autoimmune conditions. Disrupting B. dorei’s ability to utilize these carbohydrates inhibits growth in numerous ways, rendering it unfit for survival in the highly competitive environment that is the human gut.
52. Functional Peptides for Enantioselective Hypervalent Iodine(III)-Mediated Chemistry

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Hypervalent iodine reagents (HIR) have been known since the late 19th century. Recently, interest in this area has intensified due to their mild reactivity, high selectivity, and commercial availability. In particular, the emergence of catalytic and enantioselective processes with iodine(III) species is starting to make these compounds competitive with metal catalysis. While there are many successful catalytic and enantioselective hypervalent iodine mediated processes, they represent only one approach to catalyst design, requiring multi-step synthetic and purification protocols. An alternative way to impart enantiocontrol, without these synthetically demanding processes, is to attach the active iodoarene site to chiral information, such as a short peptide sequence consisting of 5 to 6 amino acids. The modularity and facile preparation of peptides facilitates the synthesis and evaluation of numerous catalyst structures in a timely manner. The goal of this research is to merge the fields of hypervalent iodine chemistry with peptide-mediated asymmetric catalysis to facilitate the implementation of hypervalent aryl-iodo peptides for the catalytic diacetoxylation of alkenes and the oxidative cyclization of a keto-acid to a ketolactone.
Polyketides are structurally complex compounds with potent biological activities that are biosynthesized through sequential condensation reactions. Polyketides have a broad range of uses, particularly in the antibiotic (e.g. erythromycin) and anti-cancer (e.g. doxorubicin) areas. Many polyketides are produced by modular polyketide synthases that utilize malonyl-derived CoA thioesters, particularly malonyl-CoA and methylmalonyl-CoA, as substrates. Each ‘extender unit’ is incorporated by an individual module in the biosynthetic pathway. This allows for use of varied natural and non-natural malonyl-CoAs to formulate new compounds with improved biological and commercial properties. The biosynthesis of many different malonyl-CoA derivatives in vivo is necessary to achieve maximum production via microbial fermentation. To achieve high levels of substrate availability, we propose to use a genetically-encoded biosensor as a tool for directed evolution. We have modified a malonyl-CoA sensing transcription factor for use as a biosensor to screen libraries of enzymes and pathways that synthesize non-natural extender units. The ability to quantify and analyze varying natural and non-natural malonyl-CoAs at different concentrations will allow for further research and development of non-natural polyketides.
Thin films of copper-doped CdS were prepared on conductive oxide substrates (FTO) by application of a cathodic current in an electrolyte bath of Cd$^{2+}$, Cu$^{2+}$, complexing agents and S0 in DMSO at elevated temperature with a duty cycle of 20%. The thickness of the films was controlled via the number of pulses. Profiler analysis later confirmed the thickness. P-type conductivity was confirmed by open circuit and Mott–Schottky analyses. Furthermore, the photoactivity of the films was assessed in neutral media using a three-electrode setup. By depositing this material onto the surface of a p-type oxygen evolving catalyst (OEC) with suitable band structure, a z-scheme photocatalytic device can be produced and employed for water splitting.
Carbon dioxide is a greenhouse gas. Too much carbon dioxide in the atmosphere can trap too much heat and cause climate change. The combustion of fossil fuels creates carbon dioxide. This experiment looks at different types of fuels used in automobiles. Do different types of automobile fuels create different amounts of carbon dioxide? Diesel, premium and regular grade gasoline were tested for carbon dioxide content. The exhaust from vehicles using the different fuels were collected in 2-liter plastic bottles. The indicator bromothymol blue (BTB) was added to each emissions sample. The color change in the samples was compared to a BTB pH chart. The more carbon dioxide created, the lower the pH would be, which would mean a lighter shade of yellow. The diesel produced the darkest shade of yellow and the premium grade gasoline changed to the lightest shade of yellow. All of the fuel types showed the presence of carbon dioxide and contribute to climate change. Diesel created the least carbon dioxide and premium created the most carbon dioxide. Some solids were seen in the diesel sample which may have given the appearance of a darker solution than it really was.
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