

8th Annual Chemistry Research Symposium

Book of Abstracts

February 25, 2023

Watt Family Innovation Center | Clemson University



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Professor



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Associate professor



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Assistant professor



Jacob Alewine
Graduate Student representative

Venue



This year's symposium will take place at **The Watt Family Innovation Center**.

This is Clemson's most technology-enhanced academic building, featuring state-of-the-art information technology and special facilities. Established in 2016 with the support of more than \$25 million in corporate donations, the Watt Center's mission is to create an environment where collaboration among students, faculty, and leaders from industry and government agencies generates ideas and solves complex problems. The Watt Center is available for students and faculty in all disciplines as a flexible space for collaboration, innovation and project development.

Keynote Speaker



Measuring proteoforms to level up proteomics: applications of Ultra-High Performance Mass Spectrometry in top-down proteomics

Dr. Neil Kelleher, Professor, Department of Chemistry,
Weinberg College of Arts & Sciences, Northwestern University, 633 Clark Street,
Evanston, IL 60208

Abstract: Analysis of whole protein molecules provides the ability to examine protein sequences, mutations, and modifications in unprecedented detail. Proteoforms, or all of the different molecular forms in which a protein can be found, capture all sources of protein variability (i.e., isoforms, SNPs, post-translational modifications, etc.), and thus provide crucial insights into biological function of a protein by connecting primary sequence and post-translational modifications. This ‘top-down’ approach to proteomics has propelled rapid development of new instrumentation and technologies for ultra-high performance mass spectrometry and uncovered new insights on clinically relevant protein targets such as KRAS (Ntai et al., PNAS, 2018) and ApoA-1 (Seckler et al., J Proteome Res., 2018). The latest analytical technologies for scalable, streamlined and systematic discovery of proteoforms will be described in this seminar.

About the speaker: The Kelleher Group has been successful in driving both technology development and applications of high performance mass spectrometry at the interface of chemistry and biology. The group have generated over 250 publications, 50 Ph.D. students/postdoctoral trainees, and ProSight software via the web to over 650 labs worldwide. The core of the Kelleher Team is built around expertise in complex mixture analysis using Fourier-Transform Mass Spectrometry for targeted applications in proteomics and natural products research. They pursue the biosynthesis and discovery of polyketides and non-ribosomally produced peptides from soil bacteria and are leading the way to use intact proteins directly as the primary unit of measurement in proteomics to efficiently detect their post-translational modifications.

Abstracts

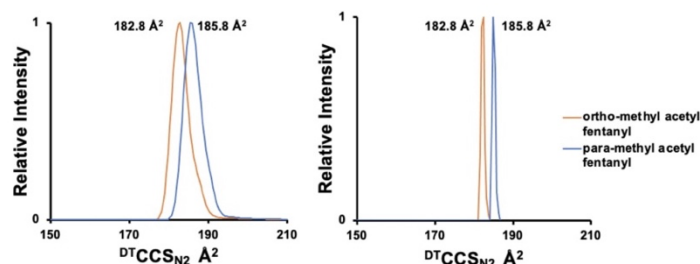
Poster #

1.

Detection and Improved Separation of Fentanyl Isomers using Liquid Chromatography-Ion Mobility-Mass Spectrometry (LC-IM-MS)

Ralph Aderorho (a) and Christopher D. Chouinard (a)

(a) Department of Chemistry, Clemson University



Fentanyl and its analogues are used as painkillers, sedatives, relaxants, and anaesthetics. However, due to extreme potency and rising rate of overdose globally, fentanyl constitutes a serious threat to public health. Fentanyl analogues include different structural isomers and can be difficult to separate. In this work, four groups of thirteen fentanyl isomers have been selected due to the challenging nature of their separations, with similar chromatographic retention times and indistinguishable MS/MS fragmentation patterns. However, ion mobility (IM) can better separate these isomers based on differences in their charge state, shape, and size and can thus improve the ability to identify unknown analogues in complex samples. Using an Agilent 6560 IM-QTOF, we measured the collision cross section (CCS) of the four groups of thirteen isomers, which ranged from 172.6-188.3 Å² for the [M+H]⁺ ion. Separation of isomer pairs was demonstrated, such as for *ortho*-methyl acetyl fentanyl (182.8 Å²) and *para*-methyl acetyl fentanyl (185.8 Å²), but the separations were further improved using the Agilent HRdm 2.0 high-resolution demultiplexing software which increased resolving power from ~50 to 200. The findings indicate that fentanyl and its analogues can be separated rapidly (<60 ms) with this technique.

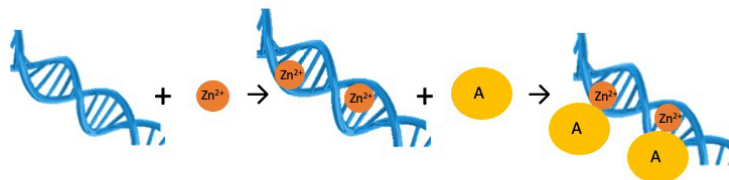
Poster #

2.

Metal Ions Control DNA-Antioxidant Interactions

Jacob Alewine (a), Craig Goodman (a) and Julia Brumaghim (a)

(a) Department of Chemistry, Clemson University



In the presence of hydrogen peroxide, DNA-bound Fe(II) generates hydroxyl radical that causes oxidative DNA damage. This damage is the underlying cause of neurodegenerative and cardiovascular diseases and cancer. Antioxidants can shield DNA from oxidative damage, but maximal protection requires targeting antioxidants to DNA. Naturally occurring glutathione and ergothioneine, the antithyroid drug methimazole, and related imidazole thiones and selones compounds prevent iron-mediated DNA damage, but their DNA interactions with antioxidants are not well understood. To investigate this, we used circular dichroism (CD) titrations to show that Fe(II) and Zn(II) similarly alter DNA secondary structure as a result of metal binding. Since Fe(II)- and Zn(II) show similar DNA interactions, Zn(II) was titrated into DNA using isothermal titration calorimetry (ITC) to avoid Fe(II) hydrolysis and precipitation. Zn(II) binding to DNA is spontaneous ($G = -6.9$ kcal/mol) with a maximum stoichiometry of 0.59 ± 0.02 Zn(II) ions per base and a K_d value of 9 ± 2 M. Linear dichroism (LD) studies indicate that Fe(II) and Zn(II) interact in the major groove of DNA. When no metal is present, glutathione binds DNA weakly in the minor groove. However, when glutathione is titrated into DNA pre-loaded with Zn(II), its association with DNA becomes significantly stronger and its association switches to the major groove where Zn(II) localizes. These effects of metals on antioxidant-DNA binding is also true for antioxidant-metal complexes: when Zn(dmit)₂Cl₂ (dmit = *N,N'*-dimethylimidazole thione) is titrated into DNA, an increase in the helicity band (245 nm) and a decrease in the base-stacking band (275 nm) are observed in CD spectra, and ITC data show that Zn(dmit)₂Cl₂ interacts more strongly with DNA than Zn(II) alone. These results indicate that metals can control small-molecule-DNA interactions and that antioxidant-metal-DNA interactions may be a novel mechanism by which they prevent metal-mediated oxidative DNA damage.

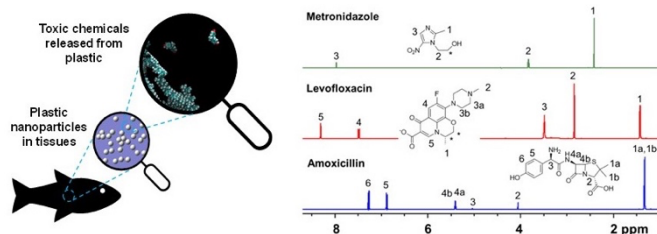
Poster #

3.

Multiphase NMR Studies of Small Molecules Binding to Nanoparticle Surfaces

Saduni Arachchi (1), Stephanie Palma (1), Charlotte Sanders* (1), Hui Xu (1),
Rajshree Ghosh Biswas (2), Ronald Soong (2), Andre Simpson (2) and Leah
Casabianca (1)

(1) Department of Chemistry, Clemson University, (2) Department of Chemistry, University of
Toronto Scarborough



Plastic pollution in world waterways is a growing concern. Over time, large plastic particles break down into smaller pieces, eventually forming micro- and nano-scale plastic particles. These particles pose a danger to wildlife as they can be mistaken for food, leading to malnutrition. Another concern is that plastic particles can concentrate other small molecules that are present in polluted waterways, such as carcinogenic polycyclic aromatic hydrocarbons, pharmaceuticals, and pesticides. Plastic has also been suggested as a medium for removal of toxic small molecules in remediation efforts, and understanding the interactions between small molecules and plastic surfaces is important for this application as well. Nuclear Magnetic Resonance (NMR) spectroscopy can provide unparalleled insight into the intermolecular interactions that are responsible for sorption of small molecules on the surface of nanoscale plastic particles. From a solution-state NMR perspective, saturation-transfer difference (STD) NMR has been a useful tool to identify small molecules that interact with a plastic nanoparticle surface. STD-NMR has been used to examine binding between plastic nanoparticles and a selection of antibiotics, which are also expected to be present in polluted waterways. However, solution-state NMR only gives half the picture, as it can only observe small molecules that are free in solution. Thus, we have used comprehensive multiphase NMR to examine the solid, liquid, and gel-like phases of the same sample containing polystyrene nanoparticles and amino acids.

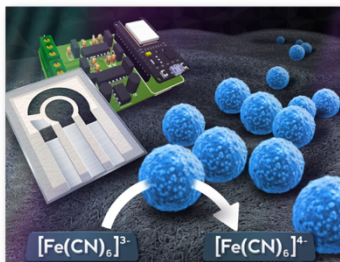
* Acknowledges the support from NSF CHE 2050042

Poster #

4.

A Paper-Derived Wearable Electrochemical Biosensor to Diagnose *Staphylococcus aureus* Skin Infections

Lucas B. Ayres (a), J. Brooks* (a), Kristi Whitehead (b) and Carlos D. Garcia (a)
(a) Department of Chemistry and (b) Department of Biological Sciences, , Clemson University



Aiming to address those limitations and leverage the state of the art of ePADs, we report the development of a wearable electrochemical sensor for the detection of skin infections. The sensor integrates a working electrode derived from pyrolyzed paper modified with chitosan (resulting in a flexible material) and that incorporates a thin layer of sputtered gold (that minimizes lateral resistivity and facilitates the connection with the potentiostat). These electrodes were controlled using a custom potentiostat and employed to detect the presence of *S. aureus* via the oxidation of the ferrocyanide produced by the bacteria, its respiration cycle. It is worth to mention that similar electroanalytical strategies have been reported to perform just-in-time antibiotic susceptibility tests for *E. coli*. However, the proposed approach represents the first report describing the possibility to detect *S. aureus* using a low-cost, wearable, electrochemical device.

* Acknowledges the support from NSF CHE 2050042

Reference:

1. Analytical Chemistry 94 (2022) 16847-16854

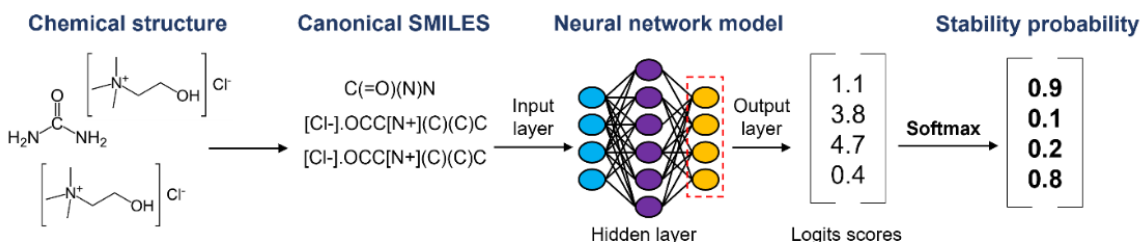
Poster #

5.

Predicting the Formation of NADES Using a Transformer-Based Model

Lucas B. Ayres (a), Federico J. V. Gomez (b), Maria Fernanda Silva (b), Jeb R. Linton (a,c) and Carlos D. Garcia (a)

(a)Department of Chemistry, Clemson University, Clemson SC 29634, USA (b) Instituto de Biología y Agronomía de Mendoza (IBAM-CONICET), Facultad de Ciencias Agrarias, Universidad Nacional de Cuyo, Mendoza, Argentina (c)IBM Cloud, Armonk, NY 10504, USA

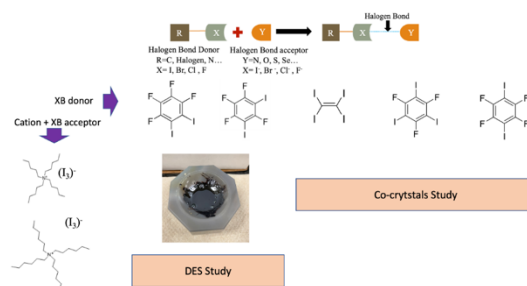


The application of natural deep eutectic solvents (NADES) in the pharmaceutical, agricultural, and food industries represents one of the fastest growing fields of green chemistry, as these mixtures can potentially replace traditional organic solvents. These advances are, however, limited by the development of new NADES which is today, almost exclusively empirically driven and often derivative from known mixtures. To overcome this limitation, we propose the use of a transformer-based machine learning approach. Here, the transformer-based neural network model was first pre-trained to recognize chemical patterns from SMILES representations (unlabeled general chemical data) and then fine-tuned to recognize the patterns in strings that lead to the formation of either stable NADES or simple mixtures of compounds not leading to the formation of stable NADES (binary classification). Because this strategy was adapted from language learning, it allows the use of relatively small datasets and relatively low computational resources. The resulting algorithm is capable of predicting the formation of multiple new stable eutectic mixtures (n=337) from a general database of natural compounds. More importantly, the system is also able to predict the components and molar ratios needed to render NADES with new molecules (not present in the training database), an aspect that was validated using previously reported NADES as well as by developing multiple novel solvents containing ibuprofen. We believe this strategy has the potential to transform the screening process for NADES as well as the pharmaceutical industry, streamlining the use of bioactive compounds as functional components of liquid formulations, rather than simple solutes.

Poster # **Halogen Bonding of Triiodide Anions with Organoiodine Molecules: Cocrystals or Deep Eutectics?**

6.

Madhushi Bandara, Arianna Ragusa*, Khadijatul Kobra, Hampton Warner, V. Critchley, Audrey Gasque, Colin D. McMillen and William T. Pennington (a)
 (a) Department of Chemistry, Clemson University



Halogen bonding has gained attention recently and it has been defined by the IUPAC in 2013. Halogen bonding is a noncovalent intermolecular interaction which arises between an electrophilic region of a halogen atom in a molecular entity and a nucleophilic region of another molecular entity. Anisotropic distribution of the electron density of the halogen atom causes this intermolecular attraction and the directional nature of the interaction. This could be seen commonly in iodine atoms. Directionality of the halogen bonding is the main difference when it compared with the hydrogen bonding. The donor-acceptor concept is the key feature of halogen bonding. The triiodide (I₃⁻) anion which has a nucleophilic nature, is a good example of a halogen bond acceptor with a highly directional attraction towards a halogen bond donor molecule like 1,2- diiodotetrafluorobenzene, 1,3-diiodotetrafluorobenzene, and tetraiodoethylene, which have iodine atoms with electrophilic nature. This has become a significant interaction in some applications: these interactions result in polymeric networks, crystal engineering, improve the lipophilicity of drugs, and enhance the penetration through lipid membranes. The intermolecular interaction between the triiodide anion and organoiodine molecules, could be seen in the salt-solvate cocrystals. Triiodide anions have a linear arrangement of iodine atoms. The organoiodine molecules which can be thought of as linkers, can connect the anions through halogen bonding into larger discrete units, chains, sheets, or frameworks. Different organoiodines with different number of iodine atoms and arrangement result in different cocrystals with a vast structural variety. Also, varying the stoichiometry of the halogen bond donor and acceptor molecules results in a variety of structurally and stoichiometrically different cocrystals which have promising applications in crystal engineering. Single-crystal X-ray crystallography is the key technique used to determine cocrystal structures. Differential Scanning Colorimetry (DSC) and Thermogravimetric Analysis (TGA) techniques are utilized to determine the melting points of the cocrystalline materials. The halogen bonding interactions between triiodide anions and organoiodine molecules do not always form crystalline materials. Deep Eutectic Solvents (DES) are solvents of a mixture of two or more components at ambient temperature with a lower melting/freezing temperature than of the components in it. So far, in the literature, DESs based on hydrogen bonding are widely reported. For an example the first reported DES (2003) is a mixture of choline chloride and urea. The depression of the melting point occurs due to the delocalization of charges over the

halide and the hydrogen bond donor. The first reported DES based on halogen bonding (2021) is a mixture of 1,3-dithiane (mole fraction 0.35 to 0.7) and 1,2-diiodo-3,4,5,6-tetrafluorobenzene with the eutectic point at 13.7°C. In addition to being the first example of a DES based on halogen bonding interactions, this system demonstrates that it is not necessary to have an ionic compound to make a DES. Here, the halogen-bonded DES study is continued with tetraalkylammonium triiodides (Tetrahexylammonium triiodide and tetrapentylammonium triiodide) and organoiodines (1,2 diiodotetrafluorobenzene and 1,3 diiodotetrafluorobenzene). These, and related systems are examined herein for their tendency to form DESs or cocrystals, and their intermolecular interactions characterized to better understand and predict their formation.

* Acknowledges the support from NSF CHE 1560300

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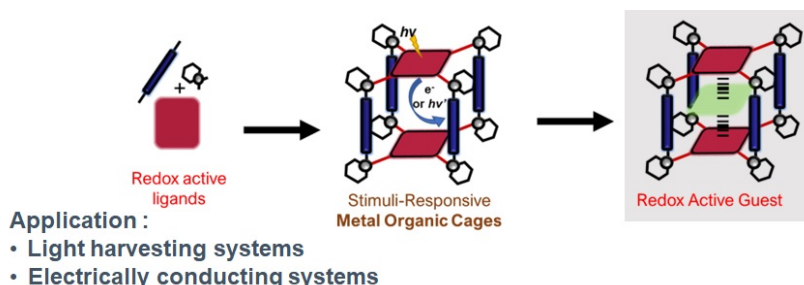
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Poster #

7.

Supramolecular π -Donor/Acceptor Arrays Based on Redox-Active Metal-Organic Coordination Assemblies.

Paola Andrea Benavides, Monica Andrea Gordillo, Shiyu Zhang, Ashok Yadav, Evan Thibodeaux and Sourav Saha
Department of Chemistry, Clemson University



The creation of 2D and 3D supramolecular coordination complexes has opened the door to the design of complex self-assembled structures whose properties and applications can be modulated by the choice of metal centers and organic ligands. In Dr. Saha's laboratory SCCs have been used to prepare complex systems that range from supramolecular metallo-squares to metal-organic frameworks with applications such as anion recognition, light harvesting devices and electrically conducting systems. Based on our previous experience, part of our research is currently focused on the preparation of SCCs capable of sustaining charge transfer events between the component of the self-assembly, which translates into enhanced electronic properties.

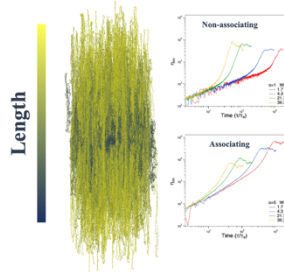
Recently, we reported the formation of 2D-bow ties complexes containing an electron-rich ZnTPP core which selectively formed a charge-transfer (CT) complex with highly electron deficient 1,4,5,8,9,12-hexaazatriphenylene-2,3,6,7,10,11-hexacarbonitrile (HATHCN) but not with another π -donor like pyrene, demonstrating their selective π -acid recognition capability. From these findings, in this work we present the preparation of a 3D-metal organic cage based on ZnTCPP, which are capable of selectively encapsulate π -acid guest molecules with association constant (K_a) ranging from 10^4 to 10^6 M^{-1} and how the donor-acceptor interaction between the host and guest systems sustains the formation of charge transfer interactions that further contribute to enhance the optical and electronic properties of the cage.

Poster #

8.

Uniaxial Elongational Flow of Ring-Polymer Melts with Associating Groups
John Bracewell (1), Supun Mohottalalage (1), Gary Grest (2), Thomas O'Connor (3) and Dvora Perahia (1)

(1) Department of Chemistry, Clemson University, (2) Sandia National Laboratories, (3) Material Science and Engineering, Carnegie Mellon University



Recent studies of effects of uniaxial extensional flows on linear polymers, driven by polymer processing challenges, have raised several fundamental questions regarding the impact of entanglements. Non-concatenated ring polymers, which have no free ends, do not entangle like linear polymers, thus serve as an excellent model for understanding flow response. Previous studies found that links formed spontaneously in the ring system under extensional flow, which led to the unexpected large increases in extensional viscosity observed experimentally. Associating groups were added to the bead-spring model to determine their effect on the formation of these topological links. The association strength was varied from 1-10k_{BT}. As for linear chains, the associating groups form clusters, which increase in size as the strength of the associating groups increase. These clusters are dynamic under flow, continuously breaking up and reforming. They govern the distribution of ring extensions which become heterogeneous for strongly interacting associating groups. Even for large interaction strength, some rings still form topological links, in which case the viscosity is due to a combination of these linked rings and the associating groups

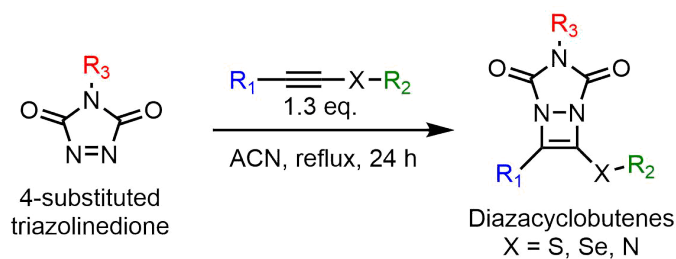
Poster #

9.

Structure-activity relationship study of the Diazacyclobutene (DCB) motif against the protozoan parasites *Trypanosoma brucei* and *Trichomonas vaginalis*

William T. Bridges, Monireh Noori, Brock A. Miller, James C. Morris and Daniel C. Whitehead

Department of Chemistry, Clemson University



70+ novel DCBs tested against BSF *T. Brucei*

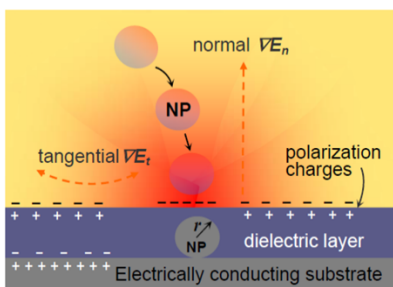
The eukaryotic protozoan parasite *Trypanosoma brucei* is responsible for causing the neglected tropical disease Human African trypanosomiasis (HAT) endemic to sub-Saharan Africa. This infection, which is transmitted via bite of the native tsetse fly as a vector, can be fatal if the infected individual does not receive treatment. The typical therapeutic treatments for this disease are hindered by tedious treatment regimens, toxicity, adverse side effects, and/or antibiotic resistance. Our lab has developed succinct synthetic routes to access Diazacyclobutenes (DCBs), a class of heterocycles which are a novel molecular scaffold with reference to their biological activity. Multiple DCB derivatives have exhibited low EC₅₀ values against blood-stream form *T. brucei brucei* and exhibit low-mammalian cytotoxicity. Utilizing the “parasite-hopping” paradigm, we have preliminary data that shows the DCB motif may also be biologically active towards the protozoan parasite *Trichomonas vaginalis*. This parasite is the cause of the most common non-viral sexually-transmitted disease in the world – Trichomoniasis. We plan to develop a sensitive, robust bioassay to test these DCB derivatives against *T. vaginalis*. This presentation will describe our preliminary biological results and our efforts to expand our library of DCB-based compounds for a thorough structure-activity relationship (SAR) against both parasite in order to identify the core pharmacophore responsible for anti-parasitic activity.

Poster #

10.

Fabrication of Nanostructured Dielectric Electrode for Production of Nonuniform Electric Field

Thomas Burgess, Cierra Harris, and George Chumanov
Department of Chemistry, Clemson University



Nanostructured dielectric electrodes (NSDE) were fabricated by immobilizing silver nanoparticles (Ag NPs) on a conductive substrate and completely embedding the NPs in a thin dielectric layer. The NSE functions as a dielectric electrode that produces an electrostatic field characterized by both normal and tangential field gradients. The NPs act as „sharp points,“ on the otherwise flat conductive surface, thus locally enhancing the electric field above the NPs and producing „hot-spots,“. The dielectric layer completely covers the NPs and fills the gaps between them and acts as an insulating layer so that no Faradaic processes take place at the surface of the NSE when potentials are applied. Multiple techniques were tested for the assembly of Ag NPs onto the conductive substrate. The thickness and uniformity of the dielectric layer were characterized using atomic force microscopy.

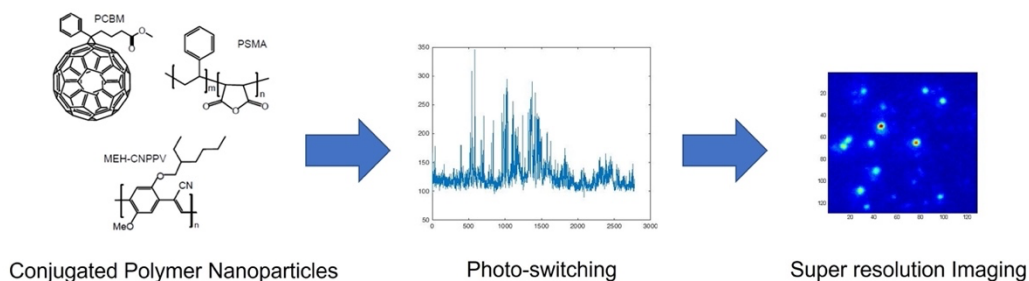
Poster #

11.

Understanding electron-transfer mediated photo-switching in conjugated polymer nanoparticles

Liaoran Cao and Jason McNeill

Department of Chemistry, Clemson University

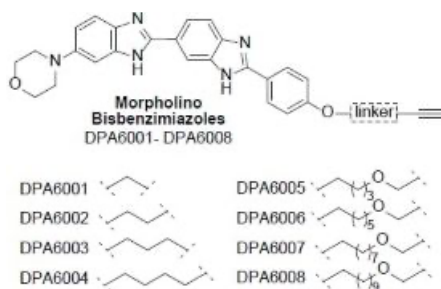


Previous publications from our lab demonstrated viable approaches to design a photo-switching nanoparticle with arguably superior brightness and photostability resulting in an improved resolution in localization-based microscopy, as compared to other photo-switching dyes or particles. As a follow-up, this research effort is focused on two major tasks: first, developing nanoparticles with better photo-switching properties for super-resolution imaging; second, trying to achieve a better physical picture of the mechanisms involved in photo-switching, including polaron dynamics, charge transfer, and energy transfer. A new class of photo-switchable nanoparticles was developed by blending the polymer MEH-CNPPV with PSMA and PCBM. Results show that MEH-CNPPV yields brighter particles than the previous polymer, F8BT, and blending with PSMA could improve the bulk fluorescence quantum yield of the nanoparticle and increase the on/off contrast in single-molecule experiments, which is critical for better localization accuracy. To understand how the dynamics of polaron in nanoparticle affects apparent photo-switching properties, single-molecule fluorescence spectra were collected from nanoparticles with different blending ratios and under various excitation laser intensities. Further modulation of the excitation laser intensity led to a transient fluorescent response consistent with previously published behavior of nanoparticles in bulk suspensions. The results of those experiments further help the development of a better physical model connecting polaron generation/recombination dynamics and photo-switching properties.

STRUCTURAL MODIFICATION IN BISBENZIMIDAZOLE ANALOGS FOR SELECTIVE INHIBITION OF *E. coli* TOPOISOMERASE I.

Andrea Conner (a) Geoff Chesser (a) and Dev P. Arya (a)

(a) Department of Chemistry, Clemson University



DNA topoisomerases are a class of enzymes that are involved in several cellular functions from removing supercoils to disentangling of intertwined DNA.¹⁻⁴ Within this class of enzymes we are primarily interested in targeting topoisomerase I in order to develop novel small molecules to combat the ongoing antibacterial resistance.⁵⁻⁷ One type of small molecule that has been well studied are Hoechst dyes, bisbenzimidazoles, that have been widely studied by our group and others because they are well known B-DNA binders and Topoisomerase I poison making for a great avenue for antibacterial drugs.⁸⁻¹⁰ Furthermore, the group has also explored the effect that linker length and composition have on the binding of Hoechst to the minor groove of B-DNA and the increase poisoning abilities. Looking at modifications of these Hoechst based compounds is a potential discovering novel therapeutics that possess properties including antibiotic, antifungal, and anticancer.

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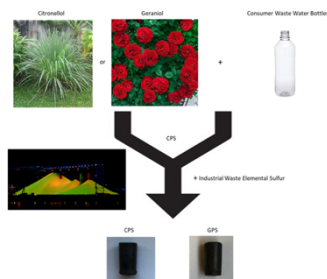
Poster #

13.

Transesterification-Vulcanization to Convert Post-Consumer Poly(ethylene terephthalate), Terpenoids, and Industrial Waste Sulfur to Durable Composites

Katelyn M. Derr (a), Rhett C. Smith (a) and Claudia V. Lopez (a), Charini P. Maladeniya (a), Andrew G. Tennyson (a, b)

a) Department of Chemistry b) Department of Materials Science and Engineering, Clemson University



Even with recent improvements in chemical recycling methods of consumer plastics, most plastic products are still deposited in landfills. The environmental contamination and pollution caused by un-recycled plastics is a growing concern and threat to human health and the environment. Herein we report a two-staged method for the chemical recycling of poly(ethylene terephthalate) (PET) using sustainable terpenoids and waste sulfur to yield a composite with mechanical properties competitive to commercially available building materials such as brick. In this method, terpenoids such as citronellol or geraniol are heated with PET in the presence of a catalysts in a transesterification reaction to form a new alkene monomer for inverse vulcanization with waste elemental sulfur to form a crosslinked terpenoid-PET-sulfur (CPS or GPS) network composite. The mechanical, thermal, composition, and morphological properties were characterized by nuclear magnetic resonance spectrometry, matrix assisted laser desorption/ionization (MALDI), infrared spectroscopy (FT-IR), compressive strength, dynamic mechanical analysis (DMA), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), toluene extraction, elemental analysis, and scanning electron microscopy. The composites CPS (compressive strength = 5.80 MPa, flexural strength = 3.10 MPa) and GPS (compressive strength = 5.20 MPa, flexural strength = 4.97 MPa) showed compressive strengths 67% and 60% of the requirements for brick standards, respectively. The composites also showed impressive resistance to acidic conditions and negligible water uptake. The approach delineated here represents a method to chemically recycle waste plastic with other waste material and green reagents to yield composites with properties comparable to existing building materials.

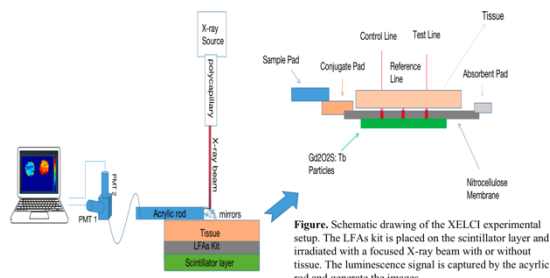
Poster #

14.

A Lateral Flow Assay Noninvasively Read Through Tissue Using X-ray Excited Luminescence Chemical Imaging

Yu Ding (1), Brad Kelly (1), Sriparna Bhattacharya (2), Tzuen-Rong J. Tzeng (3) and Jeffery Anker (1)

(1) Department of Chemistry (2) Department of Physics and Astronomy (3) Department of Biological Sciences, Clemson University



Lateral flow assays (LFAs) are simple point-of-care devices which can be exposed to a bodily fluid and rapidly generate a line if analyte is present. They are widely used in pregnancy tests and to detect infectious diseases; they are also used to detect C-reactive Protein which is a synovial fluid biomarker for prosthetic joint infection. Implanting a lateral flow assay (or smaller version) in a tissue of interest (e.g., joint to detect infection, or tumor to study progression) has not previously been tried likely because one would need to start the assay on command, and more importantly would need to read a small optically absorbing line through tissue. We address the first concern by sealing the LFA with wax, which only opens when activated with ultrasound. We address the second problem using X-ray Excited Luminescence chemical imaging (XELCI), which is a non-invasive technique and provides high spatial resolution images through thick tissue. We used a polycapillary lens to focus the ray from the x-ray source and let the beam penetrates the tissue without much scattering, then the beam will irradiate to the scintillator layer which is composed of scintillator particles. This scintillator layer could be excited by the x-ray and emit luminescence that could be absorbed more or less by the LFAs in different intensity. After the dilutions of the C-reactive protein and use LFA test kits to run different concentrations, the intensity of test lines could be obtained. The different intensity of the test lines will affect the how much light will be absorbed by the test lines. Then, the light will be collected by an in-house machined acrylic light guide and directed to a splitter which will transmit the light to two photomultiplier tubes (PMTs) that one will pass 620nm light and the other pass 700nm light. Finally, each PMT connects with a Data Acquisition (DAQ) board and a program called LabVIEW will record PMT counts and display an image on the computer screen during acquisition. We also use the XELCI to image the different intensity of the LFAs with 6 mm pork tissue. According to the obtained raw data from XELCI, the images could be analyzed by MATLAB and find the intensity of test line and control line.

Poster #

15.

Analysis of "Non-Toxic" Living on Tik-Tok, and Exploratory Study

Kelly Drummond (b) and Elliot Ennis (a)

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The rise of social media platforms, specifically TikTok, has allowed for the rapid and widespread misuse of scientific information to further an anti-science agenda. Additionally, scientific literacy of the general population has rapidly declined and has made them susceptible to false and misleading claims. As society has become more health conscious, people are becoming more intrigued by alternatives to the conventional way of life. The intrigue coupled with the plethora of information (factual or not) available 24/7 via smartphones is what allows scientific information to spread unchecked and allows charlatans to exploit public ignorance to make a profit. For this investigation, we began with the search term "Non-toxic Living" and selected the first 40 videos for analysis. Videos were analyzed for the types of claims made, the accuracy of the claims, the reputation of the claimant, the delivery of the video, and any misuse of scientific terms or concepts. The most common claims were further analyzed to reveal what the claimant had used incorrectly, taken out of context, or what information had been omitted. Common themes seen thus far include: the presence of toxins and forever chemicals like PFOS, PFOA and BPA in common household items. Chemicals in personal care products, kitchen utensils, household cleaners and in processed food. Results of the present investigation will be presented.

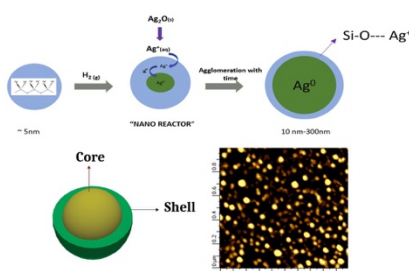
Poster #

16.

Metal Silicate Complexes as a Versatile Intermediate for the Synthesis of Metal Nanoparticles and Complex Nanostructures

Dimuthu Edirisinghe (a), T. Estrada-Mendoza (a) and George Chumanov (a)

Department of Chemistry, Clemson University



Metal nanoparticle (NP) synthesis, characterization, and applications have attracted a lot of attention due to their interesting and unique optical, magnetic, and electrical properties that are different from those in the bulk state. The size reduction to the nanometer range results in a large surface-to-volume ratio, thus leading to high surface energy, adsorption capacity, and chemical reactivity. High surface energy makes NPs thermodynamically unstable, driving the aggregation to minimize the overall surface energy. One of the significant drawbacks of the common NP synthesis process is the use of different surfactants, polymers, and ligands as stabilizing agents to stabilize the NPs against aggregation. The presence of stabilizing agents limits the applications of NPs by pre-determining their chemical properties. Therefore, developing NP synthesis methods capable of controlling their size, distribution, and morphology, at the same time using minimum stabilizing agents and harsh chemical conditions are important aspects of synthesis chemistry. Silver nanoparticles (AgNPs) exhibit plasmonic resonance, the collective oscillations of the conduction electrons upon the excitation with light. AgNPs interact with light more efficiently than any other chromophore, including other noble metal NPs. The AgNP synthesis method developed in our laboratory is based on the reduction of saturated silver oxide (Ag_2O) aqueous solution with hydrogen (H_2) gas. The method enables the easily scalable synthesis of NPs with fully controllable narrow size distribution, which are stable without adding stabilizing agents. It was determined later that the reduction reaction can proceed only in the presence of small amount of dissolved silica that also acts as a stabilizing agent against aggregation. Electron microscopy revealed that AgNPs are coated with a thin silica layer, most likely in the form of silver silicate. Even though the complete understanding of the silica role in the reduction process is not fully understood yet, a model is proposed based on different observations. In addition, the presence of silver silicate layer around AgNPs leads to a hypothesis that this layer can be explored as a nanoreactor for synthesizing core multi shell hybrid nanoparticles CMSH-NPs. The addition of multiple shells to the Ag core will result in a CMSH-NP. That will exhibit not only strong interactions with light but also plurality of other properties originating from the different materials of the shells.

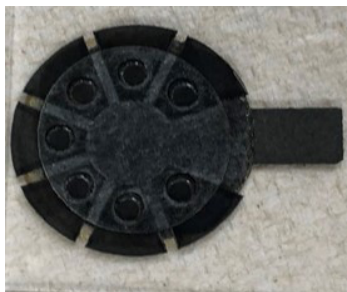
Poster #

17.

Electrochemiluminescent Microarray addressing the Rapid Electrochemical Antibiotic Susceptibility Testing

Nourhan E. Elashkar (a, d), Hala E. Zaazaa (b), Amr M. Mahmoud (b), Amira F. El-Yazbi (c) and Carlos D. Garcia (d)

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The challenge of antibiotic susceptibility has expedited the proposal of many studies to address this life-threatening issue. However, previous approaches showed multistep time-consuming methods that restrict the rapid selection of the appropriate antibiotic for each patient. Toward that goal, a smart novel electrochemiluminescence (ECL) biosensor was developed for a point of care antibiotic susceptibility testing. The sensor is based on a series of paper-derived carbon electrodes, patterned via laser engraver and assembled with double-sided tape. To increase the throughput of the analysis, arrays were designed containing 7 wells per array, that can be independently operated and interrogated using a smartphone. In order to select the most appropriate conditions for its preparation, the electrochemical behavior of the sensor was investigated by cyclic voltammetry. Based on these results, the ECL reaction was implemented requiring a sample of only 6 μL , including the reporter solution ($\text{Ru}(\text{bpy})_3^{2+}/\text{TPrA}$). The signal intensity was determined as a function of exposure time, voltage applied, and concentration of reactants. Under optimized conditions, a uniform ECL signal was obtained in less than 5 sec, opening the door to measure the metabolic activity of bacteria via the reduction of ferricyanide. We believe the obtained results with the developed sensor show its future applications in the clinical and pharmaceutical fields.

Poster #

18.

Neomycin Class Aminoglycosides Bind to 5'-G 4 C 4 -3' oligonucleotide with Salt and pH Dependence

Makala Fuller (a) and Dr. Dev P. Arya (a)
(a) Department of Chemistry, Clemson University



Aminoglycosides are known major groove binders of DNA. Using a specific sequence of oligonucleotide G 4 C 4 , the binding trends are studied thermodynamically and spectrophotometrically at varying aminoglycosides and buffer conditions. The aminoglycosides used were neomycin, paromomycin, and ribostamycin. Buffers contained the same concentration of sodium cacodylate and EDTA, while varying the concentration of sodium chloride. In addition, the pH of the buffers was adjusted using small additions of concentrated hydrochloric acid and sodium hydroxide. UV thermal denaturation studies were done to determine the thermal stability of G 4 C 4 , with and without the addition of aminoglycosides, which showed enhancement of the thermal stabilization of the oligonucleotide. The aminoglycosides studied for comparison each had a differing number of amine groups, which corresponds to the binding affinity hierarchy: neomycin (6), paromomycin (5), and ribostamycin (4). In addition, the thermal enhancement decreased with increasing salt concentration and pH of the buffer. This is consistent with the protonated amine groups contributing to the binding interaction electrostatically. Isothermal Titration Calorimetry was also used to study the thermodynamic profile of the binding interactions. The data was fit using the one set of binding sites model. These studies show that the aminoglycoside- G 4 C 4 binding is linked to the uptake of protons. The G 4 C 4 oligonucleotide is conformationally mixed between A-form and B-form. Circular Dichroism (CD) can be used to determine structural information about the conformation of DNA. CD studies showed that the aminoglycosides shifted the DNA conformation more towards A-form than B-form, while the complex remains mixed conformation. These thermodynamic and structural experiments add to the database of information dedicated to understanding the intermolecular forces involved in the aminoglycosides recognition of DNA.

Poster #

**Process Optimization for Nanoparticle/Polyurethane Coating on UHMWPE
Fibers**

19.

Aysiah Gibbs (1), Shuangyan Wu (2), Abhyuday Mandal (2) and Gajanan Bhat (2)

(1) Department of Chemistry (2) Department of Textiles, Merchandising, and Interiors

An essential part of combative careers are ballistic materials. These body armors are used by many personnel ranging from city police to active-duty military. Although they are useful for decreasing the number of fatal casualties from firearms and other weapons, they can not prevent serious injuries. The purpose of this research is to develop an improved ballistic material made from an Ultra High Molecular Weight Polyethylene (UHMWPE) fiber fabric that will decrease the number of injuries. We plan to achieve this by incorporating nanoparticles such as tungsten disulfide (WS₂) or graphene by coating them to create a lightweight material with increased energy dissipation capability. A total of 20 samples of WS₂ and 11 samples of graphene coated UHMWPE samples were produced using differing procedures. We performed wash durability and tensile tests to determine which coating conditions give the best results. After completing the tests, the optimum results for tungsten disulfide were determined to be: 10% PU, 2% WS₂, 5% stabilizer, 120 °C drying temperature, and 30 minutes drying time. These compositions represent weight percent in the original solution. Based on the results from tungsten disulfide, the optimization process for graphene is continuing.

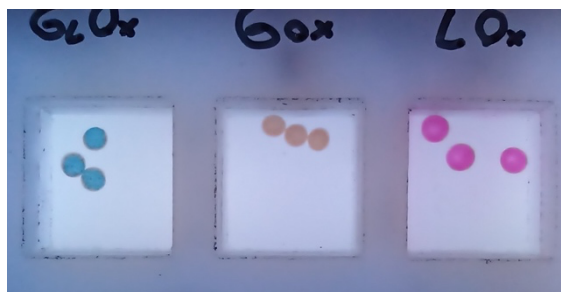
Poster #

20.

Lab-on-a-Bead: Polymeric Natural Deep Eutectic Solvents as a Versatile Platform for (Bio)sensor Design

Federico J. V. Gomez (a), Ezequiel Vidal (b), Maria Fernanda Silva (a) and Carlos D. Garcia (c)

(a) Instituto de Biología Agrícola de Mendoza, Facultad de Ciencias Agrarias, Universidad Nacional de Cuyo, (b) INQUISUR, Departamento de Química, Universidad Nacional del Sur, (c) Department of Chemistry, Clemson University



The last few decades have witnessed a significant push to replace synthetic polymers for biodegradable natural polymers. Natural polymers composed of polysaccharides offer not only low-cost, wide availability, biocompatibility, and biodegradability but also a rich chemical functionality towards custom modifications and new applications. Among those, and although cellulose and chitosan are probably the most used biopolymers towards the development of analytical applications, sodium alginate (ALG) offers a number of competitive advantages, including the ability to accommodate divalent ions (e.g., calcium, copper, strontium, barium, etc.), enabling the formation of hydrogel beads, with few mm in diameter and large internal pores. Thus, and considering the capacity of deep eutectic solvents (DES) to stabilize enzymes, the main objective of this work was to design and fabricate a new polymer-based DES using ALG as one of the components (ALG_{PODES}). This stable network would in turn, provide a new phase to preserve the activity of the biorecognition elements and retain other molecules of interest (chromogenic agents), thus supporting their use towards the development of colorimetric biosensors. The suitability of the ALG_{PODES} beads towards the development of colorimetric sensors for glucose, lactate and glutamate was also assessed and its applicability demonstrated with real food samples (soy and oyster sauces). We believe this platform, called lab-on-a-bead, provides a new analytical paradigm, where a handful of beads (sensors) can be added to a sample; instead of adding the sample to the sensor.

Reference

1. <https://doi.org/10.26434/chemrxiv-2023-cv3hv>

Poster #

21.

From cardboard to biosensors: Development of carbon electrodes modified with metallic nanoparticles using laser engraving

Juliana Gongoni (a), Lauro Pradela (a), Thiago Paixao (a) and Carlos Garcia (b)
(a) Department of Chemistry, University of Sao Paulo, (b) Department of Chemistry, Clemson University



Although a number of previous reports have described the possibility to use laser engraving to fabricate carbon electrodes via localized pyrolysis of paper,^{1,2} the material still features high electrical resistance and limited electron transfer kinetics. These factors have severely impaired the applicability of such electrodes towards real-life analytical problems. Aiming to address these shortcomings, the hypothesis of this project was that the engraving process, if done in the presence of metallic salts, would lead to the formation of carbon substrates containing metallic nanoparticles. Thus, carbon electrodes were developed containing various metallic salts and characterized in terms of electrical and electrochemical properties. The results showed that carbon electrodes fabricated in the presence of gold exhibit the highest electrocatalytical properties, followed by those fabricated in the presence of silver, copper, cobalt, zinc, and nickel. The resulting electrodes were applied towards the evaluation of the metabolic activity of various samples containing bacteria, via the reduction of ferricyanide. We believe this is a straightforward, highly versatile, and reproducible fabrication technique that allows the fabrication of electrodes of different sizes, shapes, and compositions.

References

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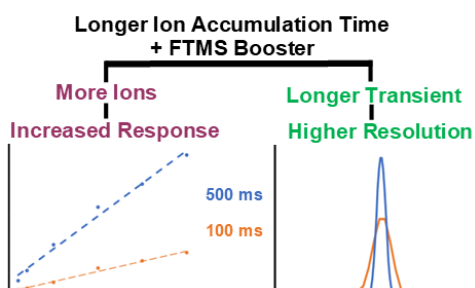
Poster #

22.

Uranium Responsivity Improvements with Varying injection Time with the LS-APGD / Orbitrap Coupling Using an FTMS Booster External Data Acquisition System

Joseph V. Goodwin (1), Benjamin T. Manard (2), Brian W. Ticknor (2), Paula Cable-Dunlap (3) and R. Kenneth Marcus (1)

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Determining uranium concentration and isotope ratios is essential in verifying member states' declarations to the International Atomic Energy Agency (IAEA). Traditional instrumentation for this challenging analysis includes multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS) and thermal ionization mass spectrometry (TIMS). While these instruments offer excellent performance, there are some drawbacks. Both are expensive, large-footprint instruments with high power and gas requirements that are not readily amenable to forward deployment and operation outside a controlled laboratory setting. In addition, complex sample preparation is required to remove potential interferences before analysis. The liquid sampling-atmospheric pressure glow discharge (LS-APGD) microplasma ionization source coupled with the high resolution Orbitrap Fourier transform mass spectrometer is a proven platform for uranium determinations. This coupling results in a smaller footprint instrumental platform with lower operational cost and utilizes the high resolution of the mass spectrometer to negate the need for complex sample preparation before analysis. As part of the ongoing efforts to optimize uranium measurements with the LS-APGD / Orbitrap coupling, varying ion accumulation times were investigated with an external data acquisition system (DAQ). The proprietary methods used to process data by the default Orbitrap software are not fully disclosed; however, FTMS transients can be collected and processed with an external data acquisition system (DAQ), such as with the Spectroswiss FTMS booster. This approach allows for simultaneous data collection by both the external DAQ and the manufacturer provided DAQ and permits a direct comparison between the data sets. With the Spectroswiss FTMS booster, changing the ion accumulation time from the traditionally used value of 100 ms to 500 ms resulted in a 3x gain in responsivity for ^{235}U and ^{238}U . In addition to the gains in responsivity, the resolution was also increased from $\sim 68\text{K}$ to $\sim 138\text{K}$ due to longer transient collection times.

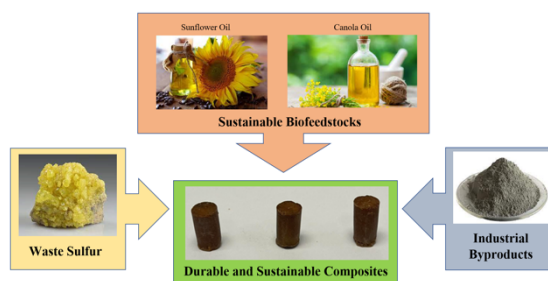
Poster #

23.

Influence of pozzolans on plant oil-sulfur polymer cements: More sustainable and chemically-resistant alternatives to Portland cement

Matthew J. Graham (a), Claudia V. Lopez (a), Charini P. Maladeniya, Andrew G. Tennyson (a) and Rhett C. Smith (a)

(a) Department of Chemistry and Center for Optical Materials Science and Engineering Technology



Ordinary Portland cement (OPC) has long since been the standard for residential and commercial-grade building materials. Characteristics such as low cost, ease of use, and rugged durability under load have made it the most used building material. However, OPC has many disadvantages that must be considered as the world becomes more environmentally conscious. The misuse of thermosets and thermoplastics is skyrocketing as demand for products increases. This leads to poor recycling practices and exposes a major issue in the field of sustainability.¹ OPC not only contributes to 8-10% of the total anthropogenic CO₂ emissions; it is also not capable of recycling.² To help shed light on issues like this, the 12 Principles of Green Chemistry were created.³ High Sulfur-Content Materials (HSCM) are one way to address these important issues in the area of sustainable building materials.⁴ HSCMs are synthesized in a greener fashion than OPC by using inverse vulcanization; a reaction coined by researchers at the University of Arizona.⁵ Inverse vulcanization utilizes waste sulfur and biofeedstocks, such as plant oils, in a solvent-free synthesis with much lower reaction temperatures ($T = 180^{\circ}\text{C}$) and is 100% atom economical. Plant oil-sulfur cement has shown to have many valuable properties that warrant further exploration.⁶ OPC is commonly mixed with sand or other minerals to add texture and structural support. However, this has adverse environmental implications. If plant oil-sulfur HSCMs are to replace OPC, further research needs to explore the use of sustainable sand surrogates as compatibilizers for HSCM. This led to the synthesis of plant oil-sulfur cements with industrial waste pozzolan compatibilizers of fly ash (FA), silica fume (SF), ground granulated blast furnace slag (GGBFS), and metakaolin (MK). Different pozzolans were mixed in 5 wt.% ratios with canola oil- and sunflower oil-sulfur cements and evaluated for mechanical strength, acid resistance, water uptake, and density parameters. The new pozzolan-HSCMs displayed <0.4% water uptake, comparable compressive strengths to OPC, and maintained 75%-100% of mechanical strength after acid exposure to 0.5 M H₂SO₄ for 24 h. These data support HSCMs to replace OPC as a sustainable building material.

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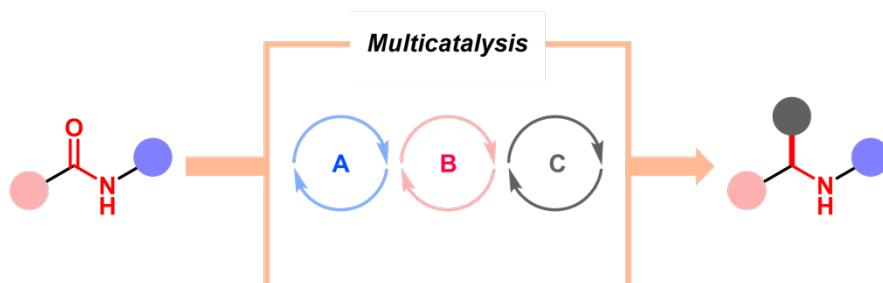
Poster #

24.

Multicatalysis: Accelerated Synthesis of Chiral Amines

Giovani Gutierrez, Jason Wilt, Megan Bishoff, Diego Rodriguez, Thomas Shealy
and Byoungmoo Kim

Department of Chemistry, Clemson University



Encouraged by the efficacy of enzymatic systems, the field of multicatalysis has developed as a powerful synthetic approach that enables access to unique transformations. Multicatalytic methods combine numerous catalytic reactions in a „one-pot,“ fashion, which decreases reaction time, chemical waste, and cost. We present our recent advances in the Kim Group, where we established a novel multicatalytic system that combines an amine and a carboxylic acid to furnish a chiral amine. Our multicatalytic system is based on a single, readily available titanium catalyst that can enable three catalytic transformations under mild conditions: 1) amidation between carboxylic acids and primary amines, 2) selective partial reduction of in-situ amides to imines, 3) enantioselective cyanation of imines to produce chiral amine products up to 90% ee. Further development of this methodology is underway to establish functional group tolerance and expansion of substrate scope. This strategy holds promise for streamline synthesis of pharmaceutical based chiral amine compounds and their derivatives.

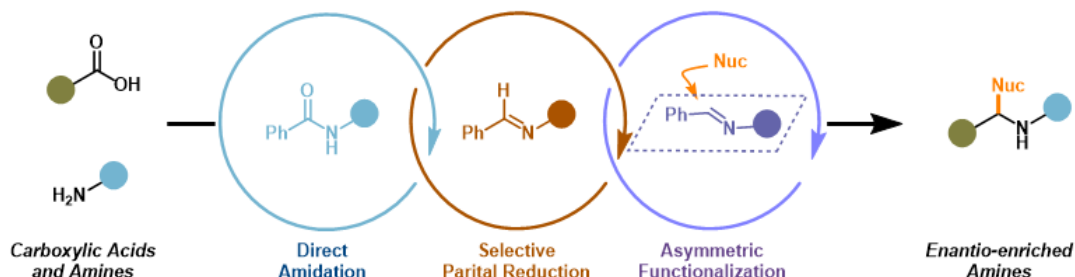
Poster #

25.

Enantioselective Reductive Strecker Reaction – Mild Amide Diversification to Access Enantio-Enriched Secondary Alpha-Aminonitriles

Giovani Gutierrez, Jason Wilt and Byoungmoo Kim

Department of Chemistry



Amides are one of the most important functionalities in biological systems and pharmaceuticals. However, often proteases are able to readily hydrolyze amide-containing drugs, rendering them worthless – hence to convert amides into bioisosteres has been an attractive method in the peptide drug discovery arena. Traditional means to modify amides require potent reagents, such as LAH. However, they are incompatible with many functional groups, which requires the use of protection/deprotection steps that reduce synthetic efficiency. Although recently milder catalytic methods have emerged, these employ precious metals and/or organocatalysts with narrow reactivity scopes that mainly target tertiary amides.⁴ In the Kim Group, we were able to develop a multi-catalytic approach using an inexpensive single titanium catalyst and electron-rich silane reductant to reduce secondary amides to imines, followed by enantioselective cyanation to yield secondary α -aminonitriles.^{5,6} Furthermore, we can even start from the corresponding carboxylic acid and amine to make the amide being reduced in situ, bypassing need for traditional peptide coupling reagents.⁷ This method is the first to achieve this with a titanium catalyst. Substrate scope is underway, with promising signs of chemoselectivity towards some reduction-sensitive functional groups. We plan to apply this methodology towards syntheses of pharmaceutical compounds and natural products such as Clopidogrel and Girgensohnine. Further goals are to investigate this methodology beyond just hydrocyanation reactions, given the common mode of Lewis acid activation of carbonyl derivatives across numerous nucleophilic addition reactions, as well as determine if the direct catalytic amidation step can also be applied to lactam syntheses to yield cyclic α -chiral amines.

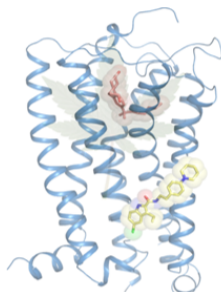
Poster #

26.

ZCZ011 Binding to the CB1 receptor and G Protein Stabilization

Antonio Hernandez (a), Fallon Goodman (a) and John Shim (a)

(a) Department of Chemistry, Dalton State College



Cannabis (Δ^9 -THC) and the endogenous lipid ligand N-arachidonylethanolamide (AEA) bind to the orthosteric site and activate the human brain cannabinoid (CB1) receptor, and the CB1 positive allosteric modulator (PAM) ZCZ011 enhances the CB1 receptor when activated by AEA (Figure 1). The therapeutic potential of ZCZ011 in the treatment of neuropathic pain requires a better understanding of the molecular mechanisms of ZCZ011. In the present study, with the aid of the recent X-ray crystal structures of the CB1 receptor, the binding poses of ZCZ011 in the CB1 receptor were explored by using advanced computational methods combining molecular docking with molecular dynamics (MD) simulations. We hypothesized that ZCZ011 binds to the cholesterol binding pocket on the CB1 receptor, a cryptic site that is formed in the intrahelical region of H2/H3/H4 within the lipid bilayer. To test the validity of the cholesterol binding pocket alternative to the extrahelical site for ZCZ011 binding, our ZCZ011 binding poses were compared with the X-ray determined ZCZ011 binding mode in the X-ray structure of the CB1 receptor (pdb code: 7WV9) published last year.

Poster #
27.

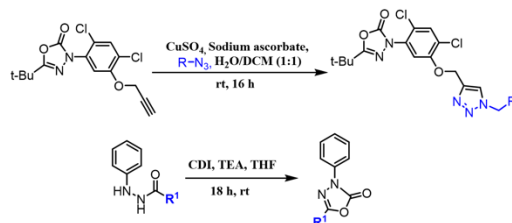
Investigating the structure-activity of Oxadiazon derivatives for developing an effective therapy for *Toxoplasma gondii* infections

Rajib Islam (a, c), Samuel Kwain (a, c), Vikky FNU (b, c), Md Al Amin (a, c),
Zhicheng Dou (b, c) and Daniel C. Whitehead (a, c)

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Toxoplasma gondii, a major species within the Apicomplexa phylum, is believed to infect approximately one-third of the human population worldwide. While *T. gondii* infections are generally asymptomatic and infrequently diagnosed in immunocompetent individuals, the parasite can cause severe and sometimes fatal diseases in people with impaired immune systems. Current treatments involve combinatorial therapy which can cause severe side effects in some patients. We previously reported that inhibition of the plant-like protoporphyrinogen oxidase (PPO) enzyme in the *de novo* heme biosynthesis pathway in *T. gondii* offers a potential druggable target to develop an effective therapy against this parasite. We showed that oxadiargyl, an analog of the herbicide, oxadiazon, that inhibits the PPO in the heme and chlorophyll biosynthesis in plants is capable of inhibiting the *T. gondii* PPO. Interestingly, structural modification of oxadiargyl with benzyl azides by means of an alkyne/azide click reaction resulted in new oxadiazon derivatives some of which showed potent inhibitory activity against the *T. gondii* PPO with IC₅₀ values below 2.5 μ M. Based on this interesting result, we have synthesized a library of 23 new oxadiazon derivatives based on the modification of oxadiargyl with a series of aliphatic azides containing other functional groups for a structure-activity relationship study. We believe that this study will further broaden our understanding of the structural effectiveness of oxadiazon derivatives and will help us develop an effective therapy against toxoplasma infections in humans and other animals.

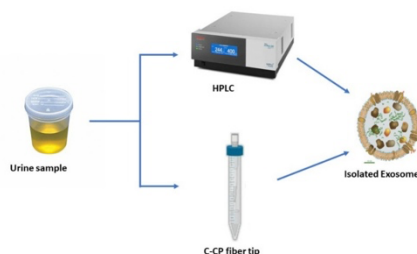
Poster #

28.

Isolation of Human Urinary Exosomes using Novel Tween Elution Solvent on Capillary-Channeled Polymer Fibers

Md Khalid Bin Islam and R. Kenneth Marcus

Department of Chemistry



Extracellular vesicles (EVs), released by all cells, carry genetic materials that are crucial elements of several biological processes. Exosomes, a subset of EVs, range in size from 50 to 200 nm, are a type of membrane-secreted vesicle essential for intercellular communication. There is a great deal of interest in developing methods to isolate and quantify exosomes for their use in intercellular processes and as therapeutic delivery systems. Current exosome isolation methods (i.e. ultracentrifugation, ultrafiltration etc.) are time- and cost-intensive and result in exosomes of low purity. This work uses a non-ionic detergent, Tween-20, to promote exosome elution from a cost-effective (~ \$5/column) polyester capillary channeled polymer fiber column using hydrophobic interaction chromatography. Previous methods by Marcus et al. have incorporated organic solvents (i.e glycerol and acetonitrile (ACN)) for the elution of exosomes in both chromatographic and spin-down tip formats. Tween-20 is a non-ionic detergent that is frequently used to dissolve membrane proteins and can be an efficient and mild elution solvent and storage of EVs, protecting their structural integrity and biological activity. Here we present, the performance of Tween-20 as an elution solvent compared to ACN and glycerol using high-performance liquid chromatography and micropipette spin down tip format. Future work will include the characterization of the Isolated EVs using transmission electron microscope (TEM), a Bradford protein purity assay and an enzyme-linked immunosorbent assay (ELISA) to evaluate presence and bioactivity of EVs. With the development of this method, it is believed that a wide range of new clinical and diagnostics applications will be possible.

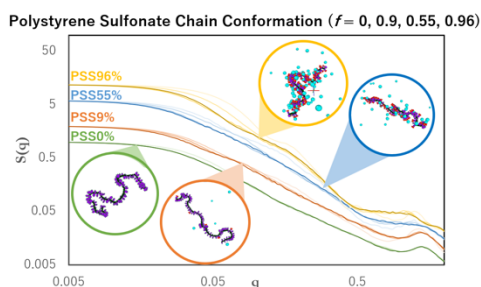
Poster #

29.

Behavior of Sulfonated Polystyrene in Dilute Solutions

Jailyn Johnson (1), Supun Mohottalalage (1), Gary S. Grest (2) and Dvora Perahia (1)

Clemson University Department of Chemistry (1), Sandia National Laboratories (2)

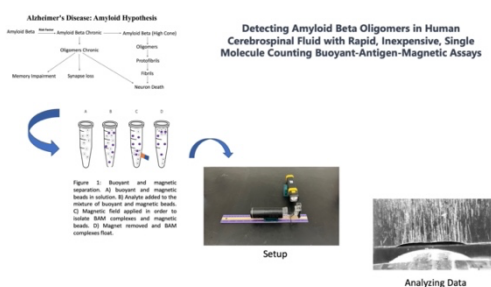


The current study explores the behavior of sulfonated polystyrene in dilute solutions. Ionizable polymers are often cast from solutions because of their high T_g induced by clustering of the ionic groups. Solution structure however often determines the structure of the polymer films and their properties. Here using molecular dynamics simulations, we probed the conformation of single polystyrene sulfonate at different sulfonation fractions. Sulfonation was varied from 0 to 95% across the transition from ionomer to poly electrolytes. Measurements were carried out in water ($\epsilon = 78$), THF ($\epsilon = 7.5$), toluene ($\epsilon = 2.8$), and cyclohexane ($\epsilon = 2.0$). The radius of gyration, the static structure factor of the polymer, and counterion condensation were calculated. In high dielectric solvents such as water, we observe a decrease of counterion and a faster rate of chain collapse than in the lower dielectric solvents such as toluene. In all solvents, the chain's structure is also affected by the sulfonation fraction, where we observe that low sulfonation are slower to collapse fully, if at all.

Poster #
30.

A new approach to identify amyloid beta oligomers in Human cerebrospinal fluid and plasma

Zahra Karimpourkalou(1), Chuanlei Wang(1), Kirsten L. Viola(2), William L. Klein(2), John Absher(3), Brandon McNaughton and Jeffrey Anker
Department of Chemistry, Clemson University(1). Department of Neurobiology, Northwestern University(2). School of Health research, Clemson University(3)



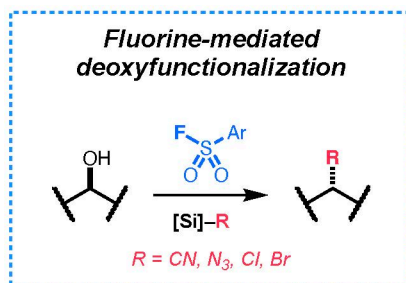
Alzheimer's Disease is a neurodegenerative disorder that lacks a definitive treatment and is known to progress slowly over time. Amyloid Beta Oligomers (ABOs) are known as one of the toxic biomarkers for Alzheimer's Disease. ABOs can affect the dysfunction of synapses before the clinical symptoms become noticeable. Our study aims to address the challenges in measuring ABOs due to their unique features and low concentration in biological samples. Detecting ABOs can aid in prognosis and identifying the effectiveness of treatments in reducing ABO concentrations and their effects on symptoms. A promising method to detect and quantify soluble amyloid beta oligomers (ABOs) in human cerebrospinal fluid has been developed using buoyant and magnetic beads that are functionalized with monoclonal antibodies specific to soluble ABOs. A complex is formed when buoyant and magnetic particles are in touch with amyloid beta oligomers (BAM). After formation of BAM complexes, they are initially collected using magnetic force and then allowed to rise by moving the magnet. The intense light scattering from buoyant particles provides a single-particle readout using a simple camera and flashlight. The recorded video of BAMs movement is analyzed to determine the number of BAMs rising, which is correlated to the concentration of ABOs in the sample. This assay's sensitivity toward oligomers and portable setup makes it easy to operate. Rapid mixing via buoyancy bead motion provides a higher capture efficiency. The orthogonal forces from magnetophoretic and buoyancy separation ensure complete separation. This method has demonstrated its capability to identify spiked synthetic ABOs in both cerebrospinal fluid and plasma samples obtained from three different groups, using only 20 microliters of samples, and requiring 40 minutes to complete. The assay's high sensitivity in detecting ABOs makes it an appealing solution for the isolation of ABOs from a mixture of components in a biological sample. This selective separation of ABOs creates an opportunity for subsequent in-depth analysis and investigation of these molecules.

Poster #

31.

Deoxy-diversification: A Functional Approach To Molecular Editing

Courtney Keeler* (a), Amaechi Odoh (b) and Byoungmoo Kim (b)
(a) University of Montevallo, (b) Department of Chemistry, Clemson University



Structurally diverse organic molecules have found vast application in both medicine and pharmaceuticals, owing to their ability to chemically interact with biological systems in a manner that elicit desirable therapeutic effects. But over the years, the exponential rise in cellular mutations has led to significant loss in drug potency. This is because existing drug molecules are not capable of effectively interacting with mutant pathogens. It is estimated that by the year 2050, more than 10 million deaths will occur as a result of multi-drug resistance and microbial mutations. The mechanism of drug action can be thought of as a lock and key relationship where a specific drug (*key*) effectively inhibits a disease by specifically binding to a molecular site on a causative pathogen (*lock*). Multi-drug resistance occurs when pathogenic cells mutate such that their receptor site (*“lock”*) can no longer effectively accommodate a drug guest (*“key,”*). Instead of creating new keys, which is tedious and capital intensive, we can tweak the shapes of existing keys using novel synthetic chemical toolbox. Such approach could potentially cut down the long years and high cost of drug development. Our Approach: This project aims to create a synthetic toolbox that can modify organic frameworks through their embedded functional groups. In the forward sense, functional modification causes a corresponding change in the shape, size, and conformation of the parent molecule. When applied to biomolecules, it could enable the creation of new derivatives of drug libraries with unprecedented therapeutic potential.

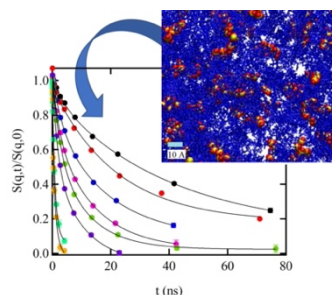
* Acknowledges the support from NSF CHE 2050042

Poster #

32.

Dynamics of Ionomers in Solution: Neutron Spin Echo and Simulations Insight

Chathurika Kosgallana,(a) Sidath Wijesinghe,(a) Manjula Senanayake,(a) Supun Mohottalalage,(a) Piotr Zolnierczuk,(b) Gary Grest (c) and Dvora Perahia (a)
(a) Department of Chemistry, Clemson University (b) Oak Ridge National Lab (c) Sandia National Laboratories



The association of ionic groups strongly affects the structure and dynamics of ionomers in melts and solutions. With the premise that cluster cohesion controls the path toward equilibrium, our study probes ionic clustering. Neutron spin echo and molecular dynamics simulations have been used to probe ionic clustering and follow the corresponding impact on the polymer dynamics. Solutions of 10 Wt% polystyrene sulfonate in toluene are studied as the ionic clusters are perturbed by the addition of ethanol as a polar solvent. Experimental and computational results for the dynamic structure factor $S(q,t)$, are in excellent agreement. The dynamic data are then correlated with characteristics of ionic clusters attained from the simulations. In toluene, where well-defined clusters are formed, the polymer motion is constrained. However, below the inter-cluster distance, motion persists. The solvent is macroscopically locked, even though a significant amount of solvent is in the system. Ethanol addition perturbs the clusters slightly but is sufficient to remove the constraints. These constraint releases without entirely breaking the clusters and impact the macroscopic dynamics leading to a shorter path toward equilibrium.

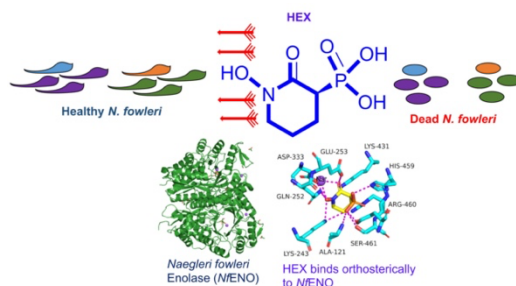
Poster #

33.

Synthesis and computational studies of Enolase inhibitors as therapeutic leads for *Naegleria fowleri* infection

Samuel Kwain (1), Kerrick C. Rees (1), Jillian E. Milanes (2), James C. Morris (2), Brian Dominy (1) and Daniel C. Whitehead (1)

(1) Department of Chemistry and (2) Department of Genetics and Biochemistry



The pathogenic free-living amoebae *N. fowleri* can cause severe and sometimes fatal illness in infected individuals. Currently, there is a paucity of treatment options for the infections caused by this parasite in humans. A recent investigation of the human enolase 2 (ENO2) phosphonate inhibitors revealed that (1-hydroxy-2-oxopiperidin-3-yl)phosphonic acid (HEX) and its structural analogs in particular (1,5-dihydroxy-2-oxopyrrolidin-3-yl) phosphonic acid (SF2312) elicit potent inhibitory activity against *N. fowleri* ENO (NfENO) with the former being more potent inhibitor (IC₅₀ value of $0.14 \pm 0.04 \mu\text{M}$). To gain insight into how these compounds bind and inhibit the (NfENO) enzyme, we performed a molecular docking simulation of the compounds with the X-ray crystal structure of NfENO (PDB 7UGH) using Autodock Vina. The docking model revealed that Hex and SF2312 bind strongly to the active site of NfENO with binding affinities of -8.6 and -8.5 kcal/mol respectively. Detailed analysis of the binding poses of the NfENO-HEX and NfENO-SF2312 complexes show that the hydroxamate moiety present in these compounds chelates the sodium metal ion and also interacts through hydrogen bonding with other important catalytic residues at the active site of the NfENO enzyme. This result suggests that Hex and SF2312 have the desired structural and electrostatic complementarity to fit and interact effectively at the active site of NfENO. The main functional groups present in HEX and its analogs are the hydroxamate and the phosphonate moieties. In the current effort, we hope to replace the phosphonate group with sulfonate and other functional groups and probe their binding properties and inhibition efficacy with the NfENO parasite using the docking model and experimental bioassay. This would help us develop a potent small molecule inhibitor against the *N. fowleri* parasite.

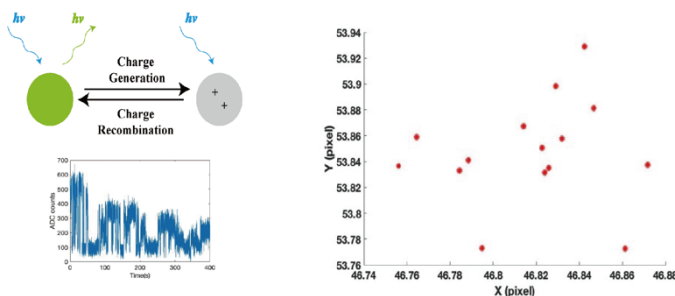
Poster #

Improved Superresolution Imaging Using Single-chain Organic Semiconductor Nanoparticles

34.

Ming Lei(a), Liaoran Cao(b) and Jason D. McNeill(a)

(a) Department of Chemistry



Several powerful and advanced fluorescence tools have developed rapidly in recent years and have attracted the attention of chemical, physical and biological researchers. In the previous research, the nanoparticle fluorescence rarely exhibits single-step switching or displays low on/off contrast owing to insufficient quenching. 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 abrupt switching fluorescence of organic semiconductor nanoparticles because the charge acts as highly efficient fluorescence quenchers. Nanoparticles of the conjugated polymer PFBT blended with PSMA, rapidly establish a fluctuating steady-state population 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. The fluctuations in the number of charges lead to occasional bursts of fluorescence. Our novel nanoparticles exhibit promising properties and helpful to enhance localization precision of $\sim 3\text{nm}$ which is several times better than the results of conventional dye molecules.

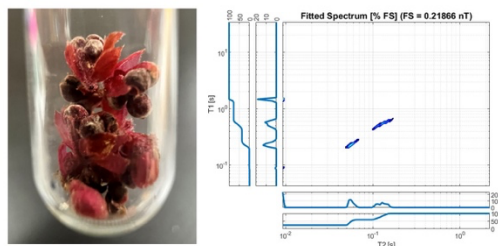
Poster #

35.

Towards MRI Characterization of Cherokee Pottery

Vi Vi Lin (a) and Leah Casabianca (a)

(a) Department of Chemistry, Clemson University



Unlike other analytical methods in archaeology, magnetic resonance imaging (MRI) is a technique that does not require the destructive preparation of samples. MRI relies on a stationary but powerful magnet that forces the alignment of protons in a sample, but the magnetic field can be temporarily disrupted by a source of radiofrequency (RF) light. MRI analysis is primarily based on two parameters: longitudinal (T_1) and transverse (T_2) relaxation times. T_1 is associated with the energy transfer between atoms, while T_2 is associated with entropy, but both T_1 and T_2 measure the time for the protons to shift from their altered state back to their original alignment with the magnet. In this study, our main objective was to calibrate our benchtop MRI machine. We sampled various items, including water, a russet potato, and twigs from a flowering plant. Through T_1 - T_2 maps, we were able to distinguish between pure water and a sample with confining pores. Additionally, we were able to get signal from a sample, low in water content. Based on our results, we think that there is potential to use MRI for the characterization of ceramics. Our end goal is to apply the noninvasive techniques of MRI to differentiate and potentially identify pieces of pottery, predating 1840 CE, that were excavated from Clemson's local archeological site.

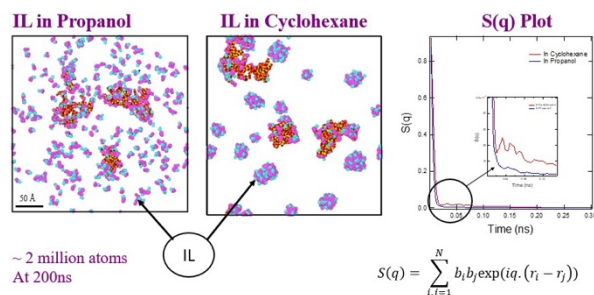
Poster #

36.

Effect of Ionic Liquids on the Conformation of Penta block Ionizable Polymers in Cyclohexane and Propanol.

Amod Madurapperumage (1), Shalika Meedin (1), Manjula Senanayake (3), Gary S. Grest (2) and Dvora Perahia (1)

(1) Department of Chemistry - Clemson University, (2) Sandia National Laboratories, NM, (3) Oakridge National Laboratories, TN



Ionizable polymers have been incorporated successfully into light weight energy applications. However, the mobility of ions, critical to the function of these polymers is rather low. To overcome this issue, highly mobile salts have been added, among them are ionic liquids (ILs). Though salts enhance mobility, they interact with the polymers, affecting their structure and dynamics. Here we probe the effects of a model ionic liquid family, 1-ethyl-3-methylimidazolium methyl sulfate (EMIM-ETSO₄) on the conformation of polystyrene sulfonate (PSS) in the ionomers and the polyelectrolyte regimes, using molecular dynamics simulations. Results for the interactions of IL with polymer, static and dynamic structure factors $S(q)$ and $S(q,t)$ of all components, the of the ions by the polymers will be discussed.

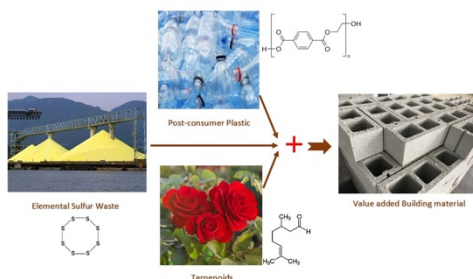
Poster #

37.

Post-consumer plastic, terpene derivatives and elemental sulfur towards sustainable building materials

Charini P. Maladeniya (a) and Rhett C. Smith (a)

(a) Department of Chemistry, Clemson University



The search for a sustainable approach to utilize post-consumer plastic (PET) has emerged to create recyclable building materials with the aid of elemental sulfur and natural terpenoids. Elemental sulfur is a waste by-product of petrochemical refining, separated by desulfurization process. Thermally treated sulfur depolymerizes to di-sulfur radicals and form covalent bonds with olefinic units in organic components via the atom economical inverse vulcanization process. At higher temperatures, PET degrades to olefinic fragments and react with sulfur radicals forming a crosslinked network. In this research, PET, di-unsaturated geraniol and elemental sulfur reacts at different temperatures and, the thermal and mechanical properties of the synthesized polymers are evaluated. These polymers were characterized by elemental analysis, thermogravimetric analysis, differential scanning calorimetry, compressive strength and dynamic mechanical analysis (DMA). The synthesized materials showed high compressive and flexural strength when compared to other traditional building materials such as Ordinary Portland Cement. This initial investigation suggests that the polymers hold stable thermal and mechanical properties and demonstrate a potential application to recyclable and produce sustainable building materials via inverse vulcanization process.

Poster #

38.

Toward greener world: A Review of Natural Deep Eutectic Solvents and Therapeutic Deep Eutectic Solvents Properties and Applications

Mays Alhoubani, Lucas Ayres, and Carlos D Garcia

Department of Chemistry, Clemson University



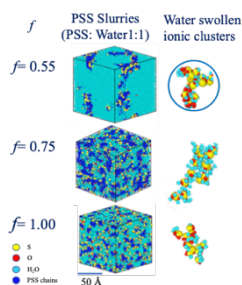
Deep Eutectic Solvent (DES) is a novel class of solvents that has gained increasing attention in recent years due to its unique physiochemical properties and sustainability. Compared to Ionic Liquid (IL), DES is a more cost-effective, less toxic, and biodegradable option due to the nature of its components. Regarding its composition, DES consists of two or more components that form a eutectic mixture with a lower melting point than each component. DES has proved its role in many applications, such as extraction, purification, and biocatalysis. Among DES, Natural Deep Eutectic Solvent (NADES) is a subclass composed of natural compounds such as amino acids, sugars, organic acids, and polyols. Additionally, Therapeutic Deep eutectic Solvent (THEDES) is another subclass composed of at least one active pharmaceutical ingredient. Despite the growing interest in these solvents, a comprehensive review of these solvents' properties, applications in many fields specifically the pharmaceutical industry, challenges, and future perspective is still lacking. In this sense, our review paper aims to address this gap by providing a critical assessment of NADES and THEDES. This will include the historical perspective, physiochemical properties, and potential applications of NADES and THEDES. A particular focus will be given to their application in the pharmaceutical industry, where they have shown great promise in improving drug solubility and bioavailability, a main issue for many drugs. Moreover, the fine-tuning of their physiochemical properties leverages the possibility of designing formulations to meet specific drug delivery requirements. While the potential of NADES and THEDES in various applications is high, their usage comes with its own set of challenges. This poster will explore these challenges and provide possible solutions with a future perspective of these solvents, aiming to provide a comprehensive and up-to-date summary of NADES and THEDES, and bridging the gap to benefit researchers, scientists, and industries interested in this novel class of solvents.

Poster #

39.

Water Swollen Sulfonated Polystyrene Polyelectrolyte Slurries: Far from the Equilibrium

Shalika Meedin (a), B. A. Thurston (b), Gary S. Grest (c) and Dvora Perahia (d)
(a) Clemson University, Clemson, SC, (b) Sandia National Laboratories, Albuquerque, NM, (c) Clemson University, Clemson, SC, (d) Sandia National Laboratories, Albuquerque, NM



The presence of ionic aggregates in ionizable polymers is known to affect the mechanical and transport properties of the polymer. Hence, the behavior of these polymers through electrostatic interactions is crucial to understand the polymer characteristics at the equilibrium and their response to external stimuli. With the complex nature of ionizable polymers, any electrostatic perturbation drives the system out of equilibrium. Here, using atomistic molecular dynamics simulations we follow water-sulfonated polystyrene (PSS) complexes to capture structure and dynamics. Water swollen PSS in the polyelectrolyte regime at sulfonation levels $f=0.55-1.00$ are followed as a function of time. PSS at $f=0.55$ shows a phase segregation. With increasing f , nano-phase segregation dominates between ionic and nonionic domains. Water penetrates clusters for all f and with the addition of more water, the large ionic clusters break and concurrently enhances polymer mobility. $g(r)$ shows that the S-S distance increases with the time indicative of slow water penetration. With increasing f , for all water concentration, the mobility of the polymers increases, though all components are dynamic and remain far from equilibrium.

*DOE funding DE - SC0019284

Poster #

40.

Polymer Hyaluronic Acid Mimetic for Targeting Glioblastoma Multiforme

Lindy Morgan (1) and Dr. Nicole Snyder (1)

Davidson College Department of Chemistry, Heinrich Heine Universität Department of Chemistry

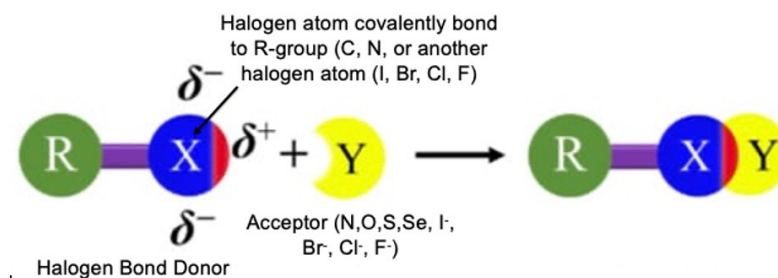
Glioblastoma Multiforme (GBM) is an aggressive form of brain cancer with the average survival time ranging from 12 to 18 months following its diagnosis. As such, GBM is considered one of the deadliest forms of cancer. Today, there are several treatment options for GBM which include surgery, chemotherapy, and radiation to slow tumor growth, but no cure. The research that I perform explores the therapeutic potential of two biomolecules: a complex, specialized sugar called hyaluronic acid (HA) and a cell surface receptor called CD44 which is located on GBM cells. The goal of this research is to create compounds that mimic HA to target CD44 and deliver specialized light activated therapeutics to GBM cells. Once inside the cells, the drug can be activated with light to kill the cells via hyperthermia in a highly selective fashion. To mimic HA, a highly complex biomolecule, we use smaller sugar molecules that will be presented on a special, biocompatible scaffold, like pendants on a chain. These sugar molecules will deliver the therapeutic, which is attached to one end of the scaffold. One of the project goals will be to explore how this presentation impacts the therapeutic potential of the drug.

Poster #

41.

Expanding Deep Eutectic Solvents from Hydrogen Bonding to Halogen Bonding

Maryelle Nyeck (a), Dr. Collin McMillen (a) and Dr. William Pennington (a)
(a) Department of Chemistry, Clemson University



Deep eutectic solvents, also known as DESs are a modern class of solvents that have gained attention for their versatility and unique properties in different applications in fields such as green chemistry, biotechnology, and material science. Hydrogen-bonded DESs are defined as a class of ionic liquids that are formed due to the mixture of two or more hydrogen bond donor (HBD) and hydrogen bond acceptor (HBA) components in specific stoichiometric ratios which result in a homogeneous liquid with a low melting point, high solubility, and unique chemical and physical properties. The interaction between the HBD and the HBA disrupts the lattice structure of the individual components, consequently lowering the melting point and creating a homogeneous liquid from the hydrogen bond interactions. Identification of these liquids as „deep“ eutectics is made when the observed melting point of the liquid is lower than the predicted melting point of the mixture, as calculated using enthalpic data of the individual components. Because of their low melting points and high solubility, DESs can be more attractive than other solvents such as organic solvents and water for specific chemical reactions or applications. The design of new DESs, and DESs that may exhibit different solvating properties in an area of significant interest. One approach that our group as used is to leverage the similarity of halogen bonding to hydrogen bonding to form new DESs where halogen bonding interactions are prevalent. Halogen bonding is defined as a non-covalent interaction between an electronegative halogen atom and the center of a positive charge or electron deficiency which is found in the neighboring molecule or ion. Halogen bonding can occur between halogen atoms (fluorine, chlorine, bromine, and iodine) and electron-rich atoms or functional groups (other halogens, nitrogen, oxygen, and sulfur atoms). This can be viewed as similar to a hydrogen bond donor such as amines or carboxylic acids interacting with a hydrogen bond acceptor to form a homogeneous liquid. The presence of halogen bonding in DESs has the capability of increasing the stability and improving the solubility of DESs, particularly towards hydrophobic systems. The current study aims to test combinations of molecules and salts that have various capabilities towards hydrogen and halogen bonding for the formation of eutectic versus cocrystalline products. These products will then be characterized by appropriate techniques (thermal analysis, single crystal X-ray diffraction, Raman spectroscopy, etc.), depending on their form of matter, to identify the specific intermolecular interactions involved in their formation. A longer-term goal seeks to develop a

library of eutectic- and crystal forming combinations that can form the basis of predictive models using machine learning approaches.

References:

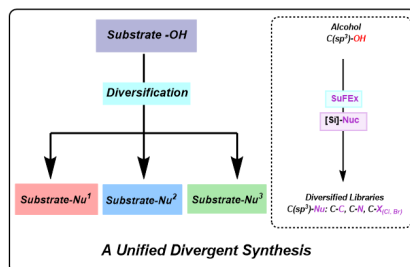
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Poster #

42.

A Robust Diversification of Biomolecules via SuFEx Activation of Hydroxy Motifs

Amaechi Odoh, Courtney Keeler* and Byoungmoo Kim
Department of Chemistry, Clemson University



Natural products (compounds from biological sources) are valuable templates for drug discovery because they are structurally configured to interact with biological targets in a manner that elicits distinctive physiological and therapeutic effects. However, the scope and extent of their biological potential highly depend on the functional constitution of their molecular scaffold. Consequently, new properties can readily emerge from the peripheral modification of their embedded functional motifs using chemical methods. There are only a few available routes for chemically modifying natural products, and these routes generally suffer from the drawback of low efficiencies and narrow scope. Hence, devising robust chemical methods for diversifying natural products is a highly sought endeavor in the chemical and pharmaceutical science. From a molecular standpoint, hydroxy motifs (alcohols) are prevalent in natural products. Thus, we sought to develop a unified protocol for transforming hydroxy motifs into a diverse range of pharmaceutically relevant functional handles. By subjecting alcohols to a rapid Sulfonate-Fluoride Exchange (SuFEx) in the presence of silicon-bound nucleophiles, we were able to diversify several hydroxy-embedded natural products into new classes of derivatives with highly sought bond connections (C-C, C-N, and C-X: X = Cl, Br) and chemical handles such as azides (-N₃) and nitriles (-CN). Gratifyingly, this protocol is run under mild conditions that enable broad compatibility and good product yield.

* Acknowledges the support from NSF CHE 2050042

Poster #

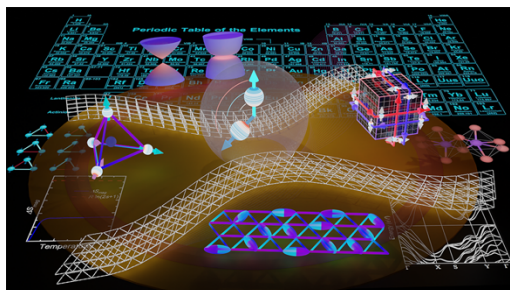
43.

Adventures in Materials Design and Development

Zoe Ohlstein, Collin Swanson, Annie Zemp, Keegan Hommerding, Uchenna V. Chinaegbomkpa, Dasuni Rathnaweera, Xudong Huai, Ebube E. Oyeka and Thao

T. Tran

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Any new technological innovation can be traced back to a specific material development. Steel advanced steam engines and silicon powered semiconductor-based technologies. Consequently, future advances in technologies will depend on the design and creation of new multifunctional and quantum materials. Compounds exhibiting unconventional magnetic, electronic, and optical properties provide avenues for developing electronic devices that can have uses in quantum computing, memory storage, laser technology, sensors, etc.^{1,2} While materials research has shown substantial progress, many difficulties remain, especially in engineering targeted properties and understanding the underlying chemistry behind the emerging physical phenomena. To address this challenge, our research team designs, creates, and develops new materials that display desired quantum behaviors and multifunctional properties by combining fundamental chemistry concepts, appropriate synthetic techniques, advanced physical property characterizations, and electronic band structure calculations.^{1,2} Examples include new $\text{Ln}_2(\text{SeO}_3)_2(\text{SO}_4)(\text{H}_2\text{O})_2$ ($\text{Ln} = \text{Sm}, \text{Eu}, \text{Dy}, \text{Yb}$) and CaMnTeO_6 materials that exhibit simultaneously magnetic and optical properties, those often do not coexist.^{3,4} We will discuss the design consideration, synthesis, characterization (e.g., single-crystal, synchrotron X-ray, and neutron diffraction), physical property measurements (e.g., magnetization, heat capacity, second harmonic generation, photoluminescence, etc.), and electronic structures of these systems.^{3,4} Our results connect the fundamentals to new physical phenomena, enabling a worthwhile pathway for navigating the journey of materials design and development.^{3,4}

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3. Oyeka, E. E.; Winiarski, M. J.; Swiatek, H.; Wyatt, B.; McMillen, C. D.; Liang, M.; Sorolla II, M.; Tran, T. T., $\text{Ln}_2(\text{SeO}_3)_2(\text{SO}_4)(\text{H}_2\text{O})_2$ ($\text{Ln} = \text{Sm}, \text{Dy}, \text{Yb}$): A mixed-anion pathway to new lanthanide(III) multifunctional

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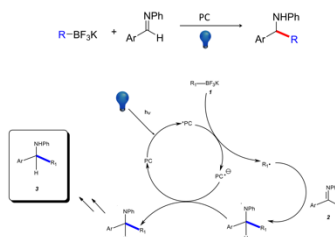
Poster #

44.

Photoredox Mediated Alkylation of Imines with Potassium Organotrifluoroborates

Molly Quetel (a) and Dr. James M. Hanna Jr. (a)

(a) Winthrop University-Department of Chemistry, Physics, and Geology



During the last 10-12 years, visible-light photoredox catalysis (VLPC) has been developed into a practical method to achieve a wide variety of synthetic transformations. The approach often involves a transition metal complex of ruthenium or iridium, which, upon absorption of visible light, can participate in a series of single-electron-transfer (SET) events with organic substrates, leading to productive chemistry. However, these transition metal catalysts can be quite expensive, which led our group to investigate the use of less expensive organic photocatalysts in our studies of the alkylation of aryl imines with potassium organotrifluoroborates. Using an organic photocatalyst, substituted potassium organotrifluoroborates and aryl imines were employed in visible light promoted organic synthesis. This protocol is applicable to broad range of substituted imines, including electron donating and electron withdrawing substituted groups. The resulting products, -aryl amines, are important pharmaceutical substructures and useful in numerous applications. In this presentation, the application of a widely used organic photocatalyst, 9-mesityl-10-methylacridinium tetrafluoroborate (**Mes-Acr-Me**), will be explored; data from optimization experiments, along with those from the scope and limitations studies including both imines and organotrifluoroborates, will be surveyed. In addition, results from Stern-Volmer quenching studies — carried out to verify the initial electron transfer event of the proposed mechanism — will be discussed.

Support was provided by the Donors of the American Chemical Society Petroleum Research Fund (58270-UR1). Additional support was provided by an SC-INBRE grant from the National Institute for General Medical Sciences (8 P20 GM103499).

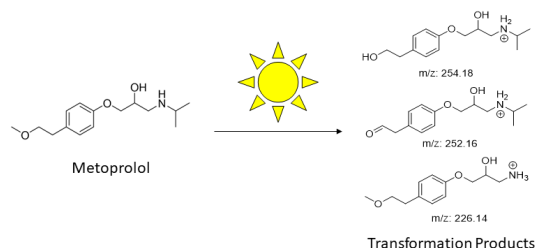
Poster #

45.

Solar Photodegradation of Metoprolol in Simulated Natural Water Samples

Heidi Sabatini (a) and Wendy Cory (a)

(a) College of Charleston Department of Chemistry and Biochemistry



As pharmaceutical contamination in our waterways increases, there is an urgent need to understand the behavior of pharmaceutically active compounds (PhACs) and their solar photodegradation products in the aquatic environment. Determining the rate of solar photodegradation and any potential transformation products in natural water samples is an important step in assessing the risk that pharmaceuticals pose to human and environmental health. In this research, metoprolol (MTP), a common blood pressure medicine, was investigated as a potential pharmaceutical pollutant. In order to study its solar photodegradation, samples were prepared in a dilute aqueous buffer solution (pH=7.0) to mimic realistic environmental conditions. Dissolved organic matter known as humic acid (HA) was added to investigate the possibility of indirect photodegradation. The solutions were photoexposed using a solar simulator to mimic natural sunlight and then analyzed using High Performance Liquid Chromatography (HPLC) to determine the rate of solar photodegradation. Results indicate that increasing concentration of HA caused an increase in the rate of degradation of MTP. Transformation products were observed using a Liquid Chromatography - Mass Spectrometer (LC-MS) and tandem MS was used to propose structures for these products.

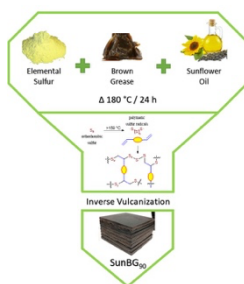
Poster #

46.

Thermal and Mechanical Properties of Recyclable Composites Prepared from Bio-olefins and Industrial Waste

Perla Y. Saucedo-Olono (a), Ana C. Borbon-Almada (b), Martin A. Gaxiola-Ruiz (b) and Rhett C. Smith (a)

(a) Department of Chemistry, Clemson University, Clemson, South Carolina, 29634, United States. (b) Departamento de Ingenieria Civil y Minas, Universidad de Sonora, Hermosillo, Sonora, 83000, Mexico.



Portland cement, also known as OPC, is a type of hydraulic cement widely used in construction due to its strength and durability. While OPC has many benefits and is a significant building material for construction, there are some drawbacks associated with its use. The production of OPC is a significant source of greenhouse gas emissions, with the manufacturing process accounting for about 8% of global CO₂ emissions. Concrete made with OPC can be prone to cracking, especially if exposed to freeze-thaw cycles or other environmental stresses. These drawbacks highlight the need for continued research and development of alternative, more sustainable building materials. Efforts to produce materials derived from plant oils, low-cost waste vegetable oils, grease, or animal fat, have increased in recent years due to the many resources available. Sulfur, the third most abundant constituent in fossil fuels, is a waste byproduct obtained from the desulfurization of fossil fuels, generating millions of tons of waste, making it a low-cost, abundant product and raw material easily accessible for its recovery. We recently reported preliminary data on high-strength compounds prepared by a reaction of sulfur, sunflower oil, and brown grease, which, without the need for aggregates, exhibited remarkable mechanical properties in ranges comparable to some compounds made from sulfur biomass, and exceeding the properties presented by OPC. The scalability of kilogram-scale batches and the fabrication of high sulfur-content materials (HSMs) into tiles and bricks of commercial relevance is demonstrated in the current research. Several fundamental physical properties from ASTM and ISO testing were obtained, revealing mechanical and thermal properties that overcome commercial cement and can potentially be used as construction materials.

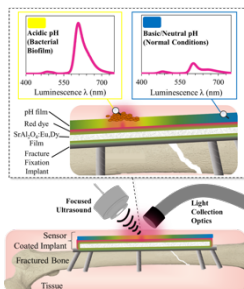
Poster #

47.

Early detection of implant associated infection by monitoring pH using ULCI (Ultrasound Luminescence Chemical Imaging) scanner

Gretchen B. Schober, Unaiza Uzair, Morgan Reel, Herbert Behlow, Vigna Abbaraju (Presenting author), Apparao M. Rao, Sriparna Bhattacharya and Jeffrey N. Anker

(a) Department of Chemistry, (b) Center for Optical Materials Science Engineering Technology, (c) Department of Physics & Astronomy, Clemson Nanomaterials Institute, (d) Department of Bioengineering, Clemson University

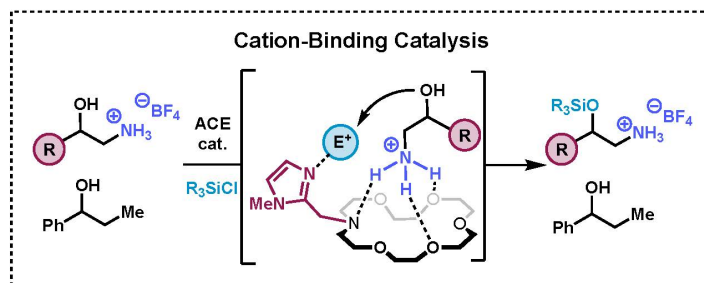


Orthopedic implants and other medical devices are susceptible to infection by bacterial biofilms which are resistant to antibiotics and the host's immune system. Early detection of infection would avoid painful surgical treatment thereby reducing the risk of re-infection. Rapidly changing pH and oxygen in the bacterial micro-environments serve as early indicators of infection. Therefore, we developed a chemical imaging technique to monitor pH changes on the implant surface using a pH sensor and focused ultrasound pulses. The sensor consists of a mechanoluminescent and a pH indicating dye film (each of them embedded in a biocompatible polymer matrix). Upon initial UV excitation, the mechanoluminescent film emitted green luminescence with a afterglow at 520 nm, and when an ultrasound beam is irradiated it showed brighter luminescence only in the focal region. This luminescence is modulated by turning the ultrasound ON and OFF and can be distinguished from the afterglow. Since red light scatters less in tissue, the green emission of the mechanoluminescent film was red shifted using a green excited/red emitting fluorescent dyes (initially with KrylonTM fluorescent spray paint, and then Nile red fluorescent dye). This emission overlapped with the absorption spectrum of the pH indicator dye, bromothymol blue, reducing the luminescence at alkaline pH. This principle was applied to image monitor biologically relevant pH environments (pH 6.0 -8.0) through a light scattering media. By moving the sample on a stage, the ultrasound was scanned across it, and the pH dependent emission intensity was collected with a liquid light guide and detected using a photomultiplier tube (PMT). The time dependent intensity was converted into an image given the stage position using custom MATLAB scripts. Our results demonstrated spatial resolution of ~3 mm through optically scattering phantoms, limited by the focused ultrasound spot size. This novel technique may permit elucidation of implant infection at the implant surface and can be further developed for the measurement of other relevant chemical species in the future.

Poster #

48.

Selective Hydroxyl Functionalization via Bifunctional Macrocyclic Catalysts
Austin Seilkop, Amaechi Odoh, Nick Coradi, Jacob Wright and Byoungmoo Kim
Department of Chemistry



Selective derivatization of natural products is a significant challenge that organic chemists seek to overcome. Direct modifications of complex molecules with multiple hydroxyl and amino groups are challenging due to chemo- and site-selectivity issues. In addition, utilizing orthogonal protecting group strategies requires multiple steps, and transition-metal catalysts can be inhibited[†] by binding strongly to the Lewis basic hydroxyl and amino groups. To address this challenge, we designed an alternative strategy by combining ammonium-recognition of crown ethers and multiple weak non-covalent interactions for selective catalysis that promotes direct functionalization of complex molecules. Herein, we have developed a bifunctional crown ether-based organocatalyst for silylation of hydroxyl groups via ammonium-binding recognition-driven selectivity. Mechanistic studies based on substrate competition experiments shows catalytic silylation of ammonium-alcohols over their aliphatic alcohol counterparts up to >20:1 selectivity. In the future, we hope to use this strategy for peptides as well as complex aminoglycoside antibiotics.

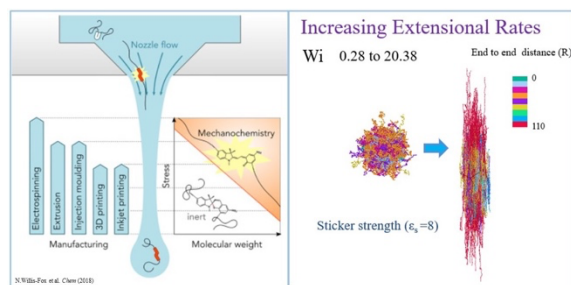
Poster #

49.

Uniaxial elongational flow of entangled, associating linear polymer melts

Rosita Sivaraj (a), Supun S. Mohottalalage (a), Thomas C. O'Connor (b), Gary S. Grest (c) and Dvora Perahia (a)

(a) Department of Chemistry, Clemson University (b) Carnegie Mellon University (c) Sandia National Laboratories



The response of polymers to uniaxial elongational flow affects the structure of polymers which is critical for their processing. The more structured the polymer, the more complex their response becomes. Here we probe the effects of uniaxial elongational flow on entangled, linear polymer melts. The polymers are depicted by a bead spring model with 5% randomly incorporated interacting associating beads, as the interaction strengths varying from 1kBT to 10kBT, using molecular dynamics simulations. Chains of length 100 to 800 beads/chain are studied, covering the range from weakly to highly entangled chains. We find that cluster size increases with increasing interaction between the associating beads. Under flow, these clusters continuously break and reform as the chains stretch. As the sticker strength increases, distribution of end-to-end distances becomes heterogeneous. Surprisingly, for polymers bearing strong associating group even at high extension rates, the clusters do not fully break up and only a fraction of chains is fully stretched. Results from constant pressure and constant volume simulations are compared.

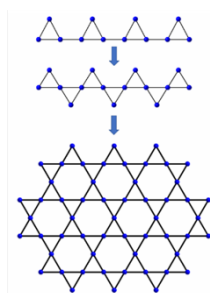
Poster #

50.

Geometrically Frustrated Molybdates and Vanadates

Megan Smart (1), Tiffany Pellizzerri (2), Duminda Sanjeewa (3), Colin D. McMillen (1) and Joseph W. Kolis (1)

(1) Clemson University, Department of Chemistry (2) Eastern Illinois University, Department of Chemistry and Biochemistry (3) University of Missouri, Department of Chemistry



Transition metal inorganic oxides have many desirable properties studied for potential applications in chemistry and material science. Tetrahedral molybdate and vanadate oxyanions (MoO_4^{2-} and VO_4^{3-}) provide a rich basis as a building block to enforce threefold symmetry that leads to geometric frustration. Additionally, they are d^0 systems, with no unpaired electrons that could couple with magnetically active ions of interest. Geometrically frustrated systems with open-shell transition metals can lead to magnetic frustration, complex magnetic behavior, and the development of quantum materials (spin-liquids, spin-ice, etc.) Some of these desirable metals are those with a $S = 1/2$ state, naturally occurring for Cu(II) and induced in low-temperature Co(II) materials due to the formation of a Kramer's doublet. Several different geometric motifs can produce frustrated systems, both 1-dimensional (half-delta and full-delta chains) and 2-dimensional (Kagome and honeycomb lattices.) Using hydrothermal synthesis with supercritical hydroxide mineralizers allows access to these new frustrated crystal geometries containing magnetically silent molybdate and vanadate oxyanions and desired first-row transition metals. Several crystal systems, as well as the most current magnetic data and neutron diffraction studies, are presented.

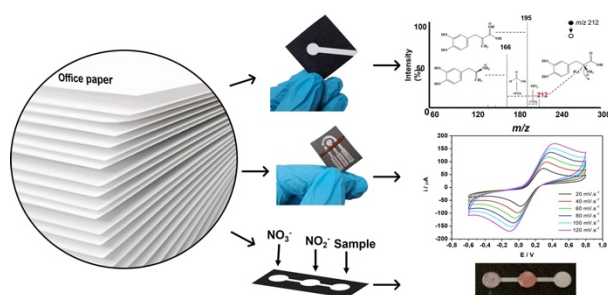
Poster #

51.

Office paper: a versatile and globally affordable platform for the development of analytical devices

Lucas Sousa(a), Barbara Guinati(a), Thaisa Baldo(a), Lanaia Maciel(a), Ronaldo C. Faria(b), Boniek G. Vaz(a), Thiago R. L. C. Paixao(c) and Wendell K. T. Coltro(a)

(a) Federal University of Goias, (b) Federal University of Sao Carlos, (c) University of Sao Paulo



Microfluidic paper-based devices ($\sim\mu\text{PADs}$) have gained attention in recent years due to their many advantages, such as low cost, portability, simplicity, as well as low consumption of reagents and samples. Many studies have demonstrated that these devices have great potential for point-of-care analysis. Despite the advantages mentioned, these papers have higher price compared to office paper, and office paper is much more available. Thus, this work describes the use of office paper for the development of paper-based analytical devices for different applications using different detection methods. In this way, office paper was explored for the development of colorimetric, electrochemical, and paper spray ionization devices. First, the influence of paper grammage in assays response was evaluated for all devices. Grammage of 90 g m^{-2} showed better performance compared to 50 , 75 , 140 , 200 , and 240 g m^{-2} , thus, it was chosen to be used for paper devices fabrication. For colorimetric detection four types of devices were constructed, spot, distance, and two different microfluidic devices, all devices were delimited by tonner barriers. Spot test was evaluated for paracetamol determination in pharmaceutical pills, the distance-based device was used for iron detection and microfluidic devices were used for iron, copper, nitrite, and nitrate colorimetric determination in environmental samples. All assays were performed in the chromatographic paper for comparison purposes. Electrochemical sensors were also fabricated by pencil drawing and electrodes areas were delimited by 3D pen polymer. The operational and assembly simplicity makes the ePAD drawn on office paper platform a powerful and promising analytical tool for clinical applications. Therefore, an electrochemical immunosensor was proposed to detect prostate-specific antigen (PSA) biomarker for prostate cancer screening test, providing an early diagnosis. Afterward, office paper was also used as a platform for the development of paper spray ionization devices. These devices were used to determine methyldopa which is an anti-hypertensive drug.

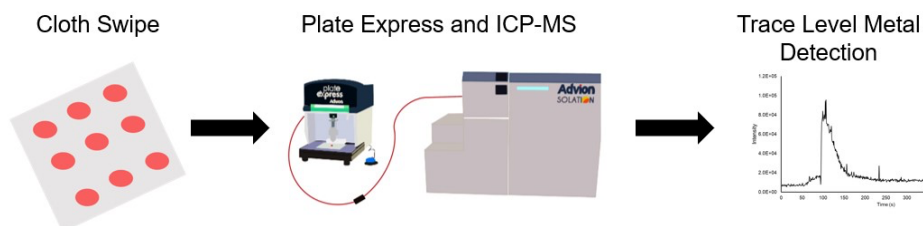
Poster #

52.

Simultaneous Detection of Swipe Particulate Metal Concentrations using Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

Cameron Stouffer (a) and Dr. R. Kenneth Marcus (a)

(a) Clemson University, Chemistry Department



Cloth swipes are a fairly ubiquitous sampling modality, having relevance across a wide variety of environmental exposure, forensics, and risk assessment applications. One of the biggest attractions of swipes is the ease of use and transportation, where just a swipe of a surface is required to collect particulate and solution-phase species and they are ready for transport to laboratory facilities. Swipe surfaces can be probed directly by optical methods or collected species readily. Swipe sampling and analysis is a very common approach in the world of nuclear forensics/non-proliferation. In a typical analysis, whole swipes are ashed and the remnant elemental species are resuspended and subjected to isotopic analysis by a multi-collector inductively coupled plasma mass spectrometer (ICP-MS). In many instances, chemical separations are necessary prior to the MS analysis. As an alternative, this laboratory demonstrated the use of the Advion Plate Express as a means of solution-elution off of the fabric substrate with analytes transported to a liquid sampling atmospheric glow discharge (LS-APGD) microplasma coupled to an Orbitrap MS for uranium isotopic analysis. Subsequent efforts of swipe elution involved coupling the Plate Express to ICP-MS systems at the Oak Ridge National Laboratory. In this sampling method, a $\sim 2 \times 4$ mm region of the swipe is exposed to a flow of 2% HNO_3 , with adsorbed species removed quantitatively in 1 min, and carried to the ICP nebulizer. Here we describe the coupling of the Advion Plate Express for extraction to the quadrupole-based Advion SOLUTION ICP-MS, providing a method for rapid, high sensitivity, multielement detection of solutions deposited on swipe substrates. The use of aqueous standards is projected to allow a common quantification approach for microextraction of swipe particulate matter and solution residues with applications in environmental, nuclear, and clinical analyses.

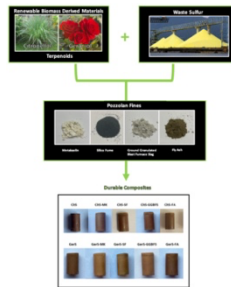
Poster #

53.

Sustainable Composites from Waste Sulfur, Terpenoids, and Pozzolan Cements

Katelyn A. Tisdale (a) and Rhett C. Smith (a), Charini P. Maladeniya (a), Claudia V. Lopez (a) and Andrew G. Tennyson (a, b)

(a) Department of Chemistry and Center for Optical Materials Science and Engineering Technology and (b) Department Materials Science and Engineering

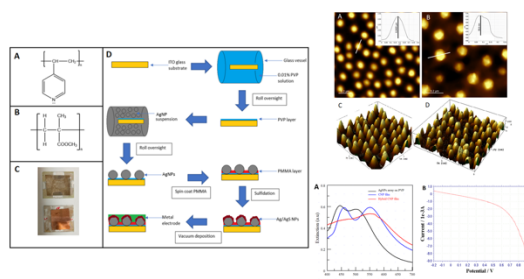


Human civilization's modern infrastructure, such as bridges, roads, and houses, is mostly built from cement and petrochemical products. However, the manufacturing of cement takes a large ecological toll. Therefore, there is a demanding need for the development of alternative structural goods able to be synthesized or recycled more sustainably while also taking advantage of renewably sourced products or waste products. The materials assessed in the current research have the potential to serve as alternatives for commercial building materials such as Ordinary Portland Cement (OPC). These materials include terpenoids and terpenes-olefins that are produced by various plants, algae, and bacteria. These materials show great potential for replacing petrochemical olefins to work towards a greener economy. In structural materials, terpenoids have found use in sulfur cements/composite materials. The sulfur employed in sulfur cements is a byproduct of fossil fuel refining. It is produced every year in megatons of unutilized material for valorization. When sulfur is heated above 159 °C with the olefins, it undergoes a reaction known as inverse vulcanization in which the sulfur forms crosslinks with the olefins in a 100% atom-economical process. Pozzolanic fines including fly ash (FA), silica fume (SF), ground granulated blast furnace slag (GGBFS), and abundant clay resources like metakaolin (MK) were incorporated in the terpenoid-sulfur composites to assess the possible changes in properties upon addition. Ten composites were prepared by combining sulfur, terpenoids and the pozzolans. Composites showed favorable densities (1,800–1,900 kg/m³), water uptake (< 0.7 wt%) compressive strengths (11.7–23.2 MPa) and retention of compressional strength after exposure to acid (80%–100% strength retained). Notably, composite compressional strengths were competitive with that of mineral cements used for residential building foundations (17 MPa).

Development of Ag/Ag₂S nanoparticle-based photosensitive and light-harvesting devices

Madhuka Vithaksha and George Chumanov

Department of Chemistry, Clemson University



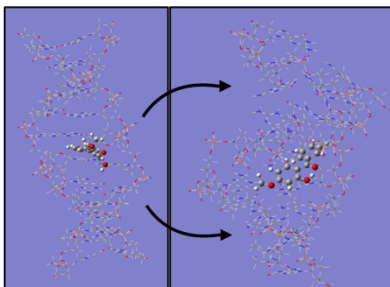
Silver nanoparticles (AgNPs) exhibit highly efficient interaction with light across visible and near IR spectral range due to the excitation of plasmon resonance that is the collective oscillation of the free electrons. It has been demonstrated that the resulted extinction spectra of large AgNPs consist of low absorbance and high scattering components. Absorbance can be increased at the expense of decreasing the light scattering by chemically transforming AgNPs into hybrid Ag/Ag₂S nanostructure. Further studies indicate that the absorbed light energy is trapped in the Ag₂S layer of the hybrid nanostructure. Ag₂S is a semiconductor and when it is in electrical contact with another metal it can form a Schottky barrier which can harvest the trapped light energy in the nanostructure. In this study, AgNPs were uniformly deposited as a thin film on a conductive ITO glass substrate using PVP (Poly(4-vinyl pyridine)) as a binding polymer. PMMA (Polymethyl methacrylate) was spin-coated on the substrate to render films stable in the air. PMMA layer fills the gaps between particles leaving the tops of particles exposed. Sulfidation was carried out on the exposed surface of the nanoparticles producing Ag/Ag₂S hybrid nanostructures. The resultant film demonstrates strong light absorbance in the visible spectral region. The Schottky structure was engineered by vacuum depositing another metal (Au or Al) on to Ag₂S layer, and the resulted I-V curves measure and provide evidence of the formation of a Schottky barrier thus opening a possibility for designing photosensitive and light-harvesting devices.

Poster #

55.

Exploring the Interactions Between Double-Stranded DNA and Sunscreen Ingredients Using Quantum Mechanical Methods

Kyle Volk (a) and Leah Casabianca (a)
(a) Department of Chemistry, Clemson University



Organic compounds homosalate and oxybenzone are popular sunscreen agents. Quantum mechanical methods were used to observe the interactions between these organic compounds with double-stranded DNA and individual nucleotide bases. Using a 2-layered (high and low) ONIOM calculation, interactions between sunscreen ingredients and Watson-Crick-Franklin double-stranded DNA were studied through double-insertion and minor groove binding. Calculations were conducted using density functional B3LYP with a 6-31G(d,p) basis set for the high-layered sunscreen ingredient and universal force field (UFF) molecular mechanics method for the low-layered double-stranded DNA. The geometry-optimized structures indicate homosalate and oxybenzone are capable of disrupting hydrogen bonding between nucleotide bases, inducing a geometrical rearrangement of the double-stranded DNA. Furthermore, the binding energies between sunscreen ingredients and individual nucleotide bases in a pi-stacked and hydrogen-bonded configuration were calculated using MP2/6-31+G(d) level of theory. The results were found to be similar to the binding energy of adenine-thymine and cytosine-guanine base pairing. These findings indicate the possible toxic effects of common sunscreen ingredients on human DNA.

Poster #

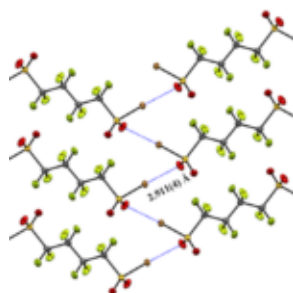
56.

Cooperative Intermolecular S—Br···O, O···F, and F···F Interactions in the Crystal Packing of α , ω -Di(sulfonyl bromide) Perfluoroalkanes: A New Motif in Halogen Bonding

Max Wacha,[a, b] David L. Helm,[b, c] Megan M. Smart,[c] Colin D. McMillen,[c] Leah B. Casabianca,*[c] Rakesh Sachdeva,[c] Catherine R. Urick,[b, c] London P.

Wilson,[b, c] Andreas Terfort,[a] and Joseph S. Thrasher[b, c]

[a] Institut für Anorganische und Analytische Chemie, Goethe-Universität Frankfurt, Max-von-Laue-Str. 7, 60438 Frankfurt am Main, GERMANY, [b] Department of Chemistry, Clemson University, Advanced Materials Research Laboratory, 91Technology Drive, Anderson, South Carolina 29625, USA, [c] Department of Chemistry, Clemson University, Hunter Laboratory, 211 S. Palmetto Blvd., Clemson, South Carolina 29634, USA



The first examples of S—Cl···O halogen bonding complemented by short F···F interactions between neighboring chains resulting in stabilized crystals of ClSO₂(CF₂)₄SO₂Cl and ClSO₂(CF₂)₆SO₂Cl were recently reported by us. Since then, other researchers suggested through Independent Gradient Model (IGM) studies of our crystallographic data that more noncovalent interactions between fluorine atoms on neighboring chains in addition to Cl···Cl, Cl···S, O···F, and O···S attractive associations can be found if one would look beyond the IUPAC's proposed 'less than the sum of the Van Der Waals radii' criterion. With this, we are reporting samples of the related BrSO₂(CF₂)_nSO₂Br derivatives (n = 4, 6, 8, and others) which display stronger S—Br···O halogen bonding interactions that are complemented slightly by O···F as well as F···F intermolecular interactions observed by X-Ray crystallography in addition to computational methods via IGM isosurface plots. Additional characterization (multinuclear NMR, FT-IR, and MS) of the disulfonyl bromide derivatives BrSO₂(CF₂)_nSO₂Br (n = 4, 6, 8) was also obtained in addition to preliminary spectroscopic evidence for BrSO₂(CF₂)₂SO₂Br and BrSO₂CF₂O(CF₂)₂OCF₂SO₂Br.

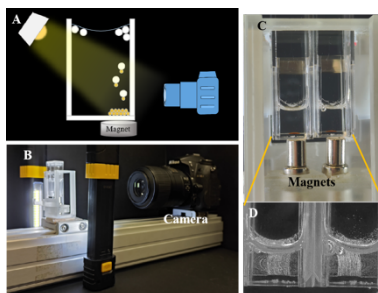
Poster #

57.

Buoyant and Magnetic Microbeads for COVID-19 Rapid Detection

Chuanlei Wang, Stuart Taylor, and Delphine Dean and Jeffrey Anker

(a) Department of Chemistry (b) Department of Bioengineering



Purpose Statement: Covid-19 is a world-wide pandemic which has killed an estimated 6.5 million people to date and caused massive economic and social disruption. Moreover, it is likely similar pandemics will emerge in future. Widespread testing is key to controlling disease spread, and remains critical for disease management. While saliva PCR provides accurate results, it uses expensive equipment, specialized training, and has longer results turnaround time. Alternatively, lateral flow assays (LFA) provide rapid inexpensive detection, and are easily delivered and used, but are subject to false negatives due to low sensitivity. Thus we are developing an assay with the high sensitivity associated with PCR, but at lower cost, and more rapid and portable.

Methods: We are developing an immunology-based, rapid on-site test that detects the presence and the concentration of SARS-CoV-2 in a patient's saliva using buoyant and magnetic microbeads. This test can be finished in 40 minutes. The buoyant and magnetic microbeads are functionalized with monoclonal antibodies that specifically target and bind to different epitopes on SARS-CoV-2 nucleocapsid protein (NC). Both types of beads are mixed with the saliva and an incubation buffer; any NC in the saliva binds to both types of microspheres forming buoyant-and-magnetic (BAM) complexes. A magnet is placed to collect unlabeled magnetic particles and BAM complexes at the bottom of the container and removing the magnet releases the BAM complexes, where they can be observed from their intense scattering and counted as they rise.

Results: In the test with 10% simulated saliva, under negative conditions, 0-2 non-specific bound BAM complexes appeared in the background. In saliva mimic fluid, the BAM test has 99% capture efficiency and a non-specific bound BAM complex background of 1-2 complexes. But we expect more non-specific binding in real saliva test. With the effort that optimizes antibody concentration and PEG modification on the surface of buoyant beads and magnetic beads to reduce the non-specific binding in real saliva, the capture rate in spiked sample (concentration of NC ranges from 0.5fg/mL to 12fg/mL) is 84%.

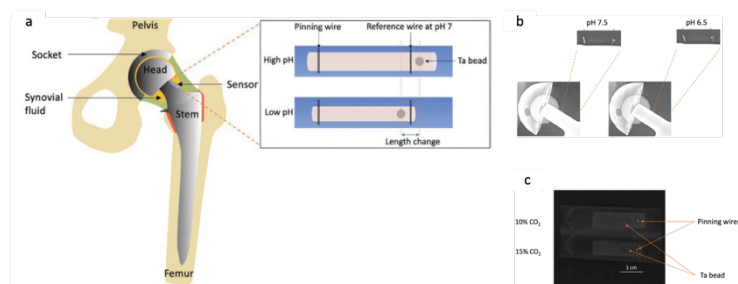
Conclusion: The BAM test's provides a remarkable simple and sensitive approach using inexpensive and portable equipment and rapid protocol. Nonetheless, we plan further increasing the specificity of our tests by verifying our results with RT-PCR, the most specific COVID test to-date. This two-step approach will allow us and many others to detect COVID-19 more efficiently and effectively.

Poster #
58.

Development of an X-Ray Visualized Hydrogel Biosensor for Early Detection of Hip Infections

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(a) Department of Chemistry, Clemson University (b) Department of Biological Sciences, Clemson University



Implant-related infection is a devastating complication that occurs in approximately 0.5% to 2% of total hip arthroplasties cases. If detected early, these infections can be promptly treated with antibiotics and surgical debridement. However, if left untreated, biofilms can develop and mature on implants, typically necessitating implant removal to address the infection. This process can result in revision surgery with associated risks of morbidity, mortality, and substantial expenses. Therefore, detecting and monitoring early deflection during the healing process would be crucial in reducing the need for expensive revision surgeries. Synovial infection markers, such as glucose, pH, lactate concentrations, C-reactive protein, alpha defensin, interleukins etc. may be helpful in detecting early infections. Based on the recent studies, an increase in partial pressure of carbon dioxide (P_{CO_2}) and a decrease in pH of synovial fluid can be indicative of hip infections. As a result, we have developed the first X-ray visualized sensor for early detection of prosthetic joint infection based on a pH responsive poly (acrylic acid-co-octyl acrylate) hydrogel. Hydrogels are a class of cross-linked hydrophilic polymers that can absorb a large amount of water and respond to various stimuli, such as pH, temperature, ion concentration, etc. Poly (acrylic acid) (PAA)-based hydrogels have been extensively used in the biomedical field including drug delivery, biosensors, membrane and separation devices due to their high biocompatibility, tunable biodegradability, suitable mechanical strength and extended lifespan. This sensor allows for the measurement of the hydrogel sensor's length changes through plain radiography. To observe the hydrogel sensor's response to pH changes under X-rays, a radio-dense tantalum bead and a metal wire were embedded at the two ends of the hydrogel. This PAA-based pH sensor has an effective acid dissociation constant (pK_a) of 5.6 and exhibits a sensitivity of 3 mm/pH unit between pH 4 and 8. And the sensor demonstrates reversibility and a linear response in the physiologically relevant pH range of 6.5 to 7.5, as observed in both buffer and bovine synovial fluid solutions. The response time constant is estimated to be 30 minutes. In addition, a carbon dioxide (CO_2) sensor was developed by sealing the pH responsive hydrogel inside a carbonate buffer solution with a carbon dioxide permeable membrane. This sensor exhibits good responsiveness in the medical relevant range of 15 to 115 mm Hg CO_2 levels, with a 4.26 mm Hg precision at 15 mm Hg CO_2 level and 6-hour response time. And the hydrophobic CO_2 -permeable membrane makes the sensor selective to

CO₂ and it did not respond to the pH of external liquid, which could be measured with a separate X-ray visualized pH sensor. This sensor can be attached to a prosthetic hip and provide non-invasive measurements in synovial fluid via plain X-ray.

Poster #
59.

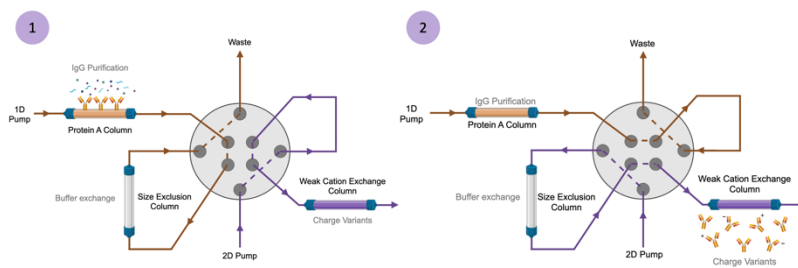
Characterizing Immunoglobulin G Charge Variants from Chinese Hamster Ovarian Cell Lines using Two-Dimensional Liquid Chromatography

Sarah K. Wyszor 1, Benjamin F. Synoground 2, Sarah W. Harcum 2 and R.

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Cell lines are commonly employed for producing monoclonal antibodies, specifically Chinese Hamster Ovary (CHO) Cell lines, for their high titers of immunoglobulin G (IgG). Due to its use in biopharmaceuticals, IgG is the desired end product of cell lines, meaning there is a constant drive to improve the development of IgG using faster and more cost-effective processes. However, this can lead to post-translational modifications or degradation, creating new profiles of IgG charge variants. The charge variants of IgG can influence immunogenicity and efficacy in the development of monoclonal antibody drugs, making the characterization and monitoring of IgG charge variants essential. Current methods for charge variant characterization are offline, where IgG is isolated and purified using protein A (ProA) chromatography at a pH \sim 2.5, followed by sample dilution for pH adjustment. Then the charge variants are determined using weak cation exchange (WCX) chromatography, which is not ideal for extensive sample monitoring. Here we report the fully automated isolation and charge variant determination of IgG using two-dimensional liquid chromatography (2DLC). For the 2DLC coupling, ProA chromatography was implemented in the first dimension, followed by WCX in the second dimension. Initially, the coupling proved incompatible as the ProA separation's eluate was at a pH \sim 2.5, while the WCX separation was at a pH of 7. To solve this, a size exclusion column was placed in the switch valve loop of the 2DLC instrumentation, where it could act as a means of solvent exchange, not for chromatographic performance. \rightarrow Using this coupling, the successful isolation and charge variant determination of a NIST IgG standard was completed with 16.5%, 73.3%, and 10.2% for the acidic, main, and basic species, respectively. Additionally, the charge variants of IgG from CHO cell supernatant were successfully isolated, exhibiting the online monitoring capability for monitoring the charge variants of a cell line over time.

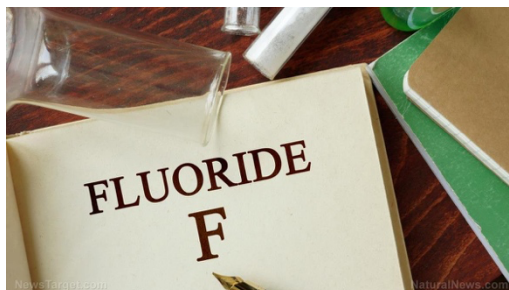
Poster #

60.

Analysis of Fluoride on Tik-Tok, an Exploratory Study

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(a) Department of Chemistry, (b) Department of Biological Sciences



The rise of social media platforms, specifically TikTok, has allowed for the rapid and widespread misuse of scientific information to further an anti-science agenda. Additionally, scientific literacy of the general population has rapidly declined and has made them susceptible to false and misleading claims. For this investigation, we began with the search term fluoride and selected the first 25 videos for analysis. Videos were analyzed for the types of claims made, the accuracy of the claims, the reputation of the claimant, the delivery of the video, and any misuse of scientific terms or concepts. The most common claims were further analyzed to reveal what the claimant had used incorrectly, taken out of context, or what information had been omitted. Common themes seen thus far include demonization of fluoride use in dentistry, that fluoride is poison, and that fluoride causes calcification of the pineal gland. Additionally, conspiracies related to the government and higher spiritual awakening have been observed. Results of the present investigation will be presented.

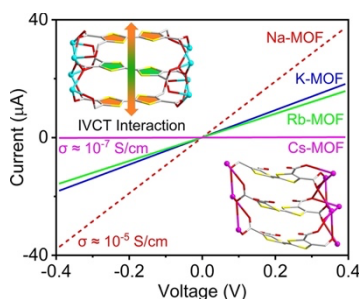
Poster #

61.

Effects of intervalence charge transfer interaction between π -stacked mixed valent tetrathiafulvalene ligands on the electrical conductivity of 3D metal-organic frameworks

Shiyu Zhang,^a Dillip K. Panda,^a Ashok Yadav,^a Wei Zhou,^b and Sourav Saha

a. Department of Chemistry, b. NIST Center for Neutron Research, National Institute of Standards and Technology



Metal-organic frameworks (MOF), as the name suggests, are self-assembled from metal ions or clusters as nodes and organic ligands as linkages through coordination bonds. Electrically conducting MOFs have become one of the most promising electronic materials due to their diverse potential applications in charge and energy storage, chemiresistive sensing, electrocatalysis, light-harvesting systems, etc. However, compared to conductive 2D-MOFs, which usually contain highly effective through-bond charge movement pathways and display high intrinsic electrical conductivity, it is much more challenging to develop electrically conducting 3D-MOFs and requires deep understanding of their structure-property relationships.^{8,9} Electrical conductivity is a product of two parameters: (1) charge carrier concentration and (2) charge mobility. While redox-active ligands, metal ions, and/or guest molecules supply charge carriers,¹⁰⁻¹² charge mobility depends on the efficacy of charge transport pathways, which can be classified into following categories: (1) through-bond: via metal-ligand covalent coordination bonds and conjugated π -bonds, and (2) through-space: π -stacked ligands and redox hopping. These pathways are inherently present in intrinsically conducting MOFs while appropriate guest molecules can also create them.

In this project, I have constructed four novel alkali-metal-based (Na, K, Rb, and Cs) 3D-MOFs with continuous π -stacks using an electron-rich tetrathiafulvalene tetracarboxylate (TTFTC) ligand and demonstrated how the structures and components of MOFs affect their electrical properties, including electrical conductivity, electronic and optical band-gaps. These MOFs also contained different amounts of aerobically oxidized TTFTC $\bullet+$ radical cations that were quantified by electron spin resonance (ESR) spectroscopy. Density functional theory calculations and diffuse reflectance spectroscopy demonstrated that depending on the π - π interaction and TTFTC $\bullet+$ population, these MOFs enjoyed varying degrees of TTFTC/TTFTC $\bullet+$ intervalence charge transfer (IVCT) interactions, which commensurately affected their electronic and optical band gaps and electrical conductivity. Having the shortest $d\pi$ - π (3.39 Å) and the largest initial TTFTC $\bullet+$ population (~23%), the oxidized Na-MOF 1-ox displayed the narrowest band gap (1.33 eV) and the highest room temperature electrical conductivity (3.6×10^{-5} S/cm), whereas owing to its longest $d\pi$ - π (3.68 Å) and a negligible TTFTC $\bullet+$ population,

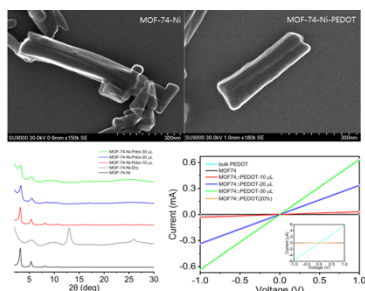
neutral Cs-MOF 4 exhibited the widest band gap (2.15 eV) and the lowest electrical conductivity (1.8×10^{-7} S/cm). The freshly prepared but not optimally oxidized K-MOF 2 and Rb-MOF 3 initially displayed intermediate band gaps and conductivity, however, upon prolonged aerobic oxidation, which raised the TTFTC \bullet + population to saturation levels (~25 and 10 %, respectively), the resulting 2-ox and 3-ox displayed much narrower band gaps (~1.35 eV) and higher electrical conductivity (6.6×10^{-5} and 4.7×10^{-5} S/cm, respectively). The computational studies indicated that charge movement in these MOFs occurred predominantly through the π -stacked ligands, while the experimental results displayed the combined effects of π - π -interactions, TTFTC \bullet + population, and TTFTC/TTFTC \bullet + IVCT interaction on their electronic and optical properties, demonstrating that IVCT interactions between the mixed-valent ligands could be exploited as an effective design strategy to develop electrically conducting MOFs.

Poster #

62.

Doping Conducting Polymer to Metal-Organic Framework to Enhance its Electrical and Structural Properties

Shiyu Zhang (a), Weikang Zhang (a), Ashok Yadav (a) and Sourva Saha (a)
(a)Department of Chemistry



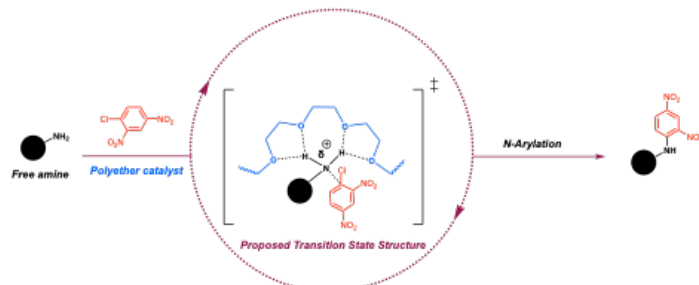
Metal-organic frameworks (MOFs) are a class of porous compounds that use the concept of reticular chemistry. MOFs consist of metal ions or clusters coordinated to organic ligands to form coordination network which could be extended in two or three dimensions through repeating coordination entities. The porosity of MOFs allows its various applications in gas storage, gas separation, and catalysis. However, for some MOFs, large pore structure brings challenge to structural stability during removing the guest molecules. MOF-74 type framework is known for its remarkable structure, high density of open metal sites, hexagonal channels along c-axis, and high porosity¹. Due to the large pore size of MOF-74, combining MOF-74 with other components to gain additional functionality becomes possible. Herein we present a method of doping conducting polymer PEDOT, Poly(3,4-ethylenedioxythiophene), to MOF-74-Ni. The electrical conductivity of MOF-74-Ni got greatly enhanced with the aiding of conducting polymer. In addition, the polymer inside MOFs provided mechanical support to the mesopore structure, which significantly increased the structural stability of MOFs.

Poster #

63.

Amine Activation

Andrew Storer, Amaechi Odoh, Austin Seilkop and Byoungmoo Kim
Department of Chemistry



Polyether catalyzed amine activation was inspired by site-selective functionalization of polyamines and thread formation using rotaxanes in macromolecular chemistry. The group started this project by investigating the best polyether catalyst for a $\text{S}_{\text{N}}\text{Ar}$ reaction at the nitrogen of a free amine nucleophile using an aryl halide electrophile. The best polyether catalyst was judged off a variety of parameters, such as polyethylene chain length and rigidity. Furthermore, the amine nucleophile scope was examined once the best polyether catalyst was determined. Electron-deficient free amines were found to be the best nucleophiles for the polyether catalyzed $\text{S}_{\text{N}}\text{Ar}$ reaction. In the future, the group aims to expand polyether catalyzed N-diversification as well as explore other more complex polyether catalyst and site-selective N-diversification of polyamines.

