2014 Southeast Undergraduate Research Conference
Knoxville Tennessee
46th Annual Conference
Jan. 30th - 31st

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Southeast Undergraduate Research Conference

46th Annual Conference


Hosted by the Department of Chemistry
The University of Tennessee Knoxville
Buehler Hall 552, 1420 Circle Dr., Knoxville, TN 37996-1600
Department Head: Dr. Charles Feigerle

2014 SURC Organizing Committee:

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Program

Thursday, Jan. 30, 2014
- 5:00 - 6:00 Registration (University Center, 213, Ballroom)
- 6:00 - 7:00 Welcome Reception & Recruiting Booth Set Up (University Center, 213, Ballroom)

Friday, Jan. 31, 2014
- 7:00 - 8:00 Breakfast & Registration & Morning Poster and Recruiting Booth Set Up (University Center, 213, Ballroom)
- 8:00 - 2:30 Graduate School Fair (University Center, 213, Ballroom)
- 8:00 - 09:30 Oral Presentations (Analytical, Inorganic, Physical) (University Center, 241, Auditorium)
- 9:30 - 10:00 Break, Poster Set Up (University Center, 213, Ballroom)
- 10:00 - 11:30 Morning Poster Presentations (Analytical, Inorganic, Physical) (University Center, 213, Ballroom)
- 11:30 - 1:00 Lunch, Afternoon Poster Set Up (NOT included in registration)
- 1:00 - 2:30 Afternoon Poster Presentations (Biochemistry, Organic, Polymer) (University Center, 213, Ballroom)
- 2:30 - 4:00 Oral presentations (Biochemistry, Organic, Polymer) (University Center, 241, Auditorium)
- 4:30 - 5:30 Department Tours (Meet outside of UC Ballroom. Students will be split into roughly equal sized groups selected from analyt+inorg+pchem as well as from org+polymer+biochem. The tours will be led by chemistry faculty members)
- 6:00 - 8:00 Awards Banquet & Keynote Speaker: Dr. Jimmy Mays, Professor and ORNL Distinguished Scientist (University Center, 213, Ballroom)
  - Certificate and Monetary Awards will be given to the best presentations in each division of chemistry (Students must be present at Banquet to receive an award).
Keynote Speaker

Dr. Jimmy Mays
Professor and
ORNL Distinguished Scientist
Fellow of American Chemical Society
Founding Fellow, ACS Division of Polymer Chemistry
Herman Mark Senior Scholar
2012 Fellow of ACS PMSE Division
2012 Fellow of AAAS

Professor Jimmy Mays received the B.S. degree in Polymer Science from the University of Southern Mississippi in 1979 and a Ph.D. in Polymer Science from the University of Akron in 1984 under the direction of Professor Lewis Fetters. After graduation he worked for several years at Hercules Research Center, prior to joining the faculty at the University of Alabama at Birmingham. In 2002 he moved to his current position as UT/ORNL Distinguished Scientist at the University of Tennessee, Knoxville, and Oak Ridge National Laboratory. Professor Mays’ research is centered on polymer synthesis, especially synthesis of polymers having controlled architectures. He has published about 350 peer reviewed papers on polymer synthesis, characterization, and properties. He is a Fellow of the American Chemical Society, Fellow of ACS POLY and PMSE Divisions, and Fellow of the American Association for the Advancement of Science. He and his wife, Trish, enjoy reading, traveling, walking, drinking great wine, and playing with their three dogs: Bits, Precious, and Taz.
BY STUDYING THE LOCAL STRUCTURES IN AMORPHOUS MATERIALS WE MAY ATTEMPT TO UNDERSTAND HOW MICROSCOPIC PROPERTIES CONTROL BULK PROPERTIES. PHOSPHATE GLASSES ARE USED IN A VARIETY OF APPLICATIONS SIMILAR TO SILICATE GLASSES INCLUDING BIOCOMPATIBLE MATERIALS AND RADIOACTIVE WASTE CONFINEMENT. USING THE NEWLY INVENTED TWO-DIMENSIONAL PHASE INCREMENTED ECHO TRAIN ACQUISITION (PIETA) NUCLEAR MAGNETIC RESONANCE EXPERIMENT UNDER FAST MAGIC-ANGLE SPINNING (MAS) CONDITIONS, WE MEASURED THE HOMONUCLEAR $^{31}$P TWO-BOND J-COUPINGS IN VARIOUS PHOSPHATE GLASSES MODIFIED BY ZINC, BARIUM, AND LEAD (SEE FIG. 1 BELOW). THESE PIETA MEASURED J-COUPLING DISTRIBUTIONS WERE COMPARED WITH THE TRADITIONAL HAHN-ECHO AND CARR-PURCELL-MEIBOOM-GILL (CPMG) METHODS. IT WAS SEEN THAT PIETA IS EQUAL IN SPEED AND SENSITIVITY TO CPMG BUT WITHOUT THE ZERO-FREQUENCY ARTIFACT THAT OBSCURES THE J-COUPINGS UNDER CPMG CONDITIONS.

THE PIETA METHOD IS FULLY EQUIVALENT TO THE TRADITIONALLY USED HAHN-ECHO METHOD BUT MUCH FASTER FOR THE SAME SENSITIVITY. OUR OBSERVATIONS SUGGEST THAT THE MODIFIER CATION HAS A SIGNIFICANT IMPACT ON THE MEASURED RANGE OF J-COUPINGS ACROSS THE P–O–P BONDS AND WE ARE INVESTIGATING HOW TO MAP THIS DISTRIBUTION OF J-COUPINGS INTO A DISTRIBUTION OF BOND-ANGLES IN THESE GLASSES, ACTING AS A DIRECT MEASURE OF MEDIUM RANGE ORDER IN THESE SAMPLES. ALSO BY USING A TWO-DIMENSIONAL APPROACH WE ARE ABLE TO SEPARATE OVERLAPPING SITES IN A GLASS USING THE J-RESOLVED DIMENSION (SUCH AS DISTINGUISHING BETWEEN CLOSED-RING AND OPEN-CHAIN STRUCTURES THAT OVERLAP IN A STANDARD MAS EXPERIMENT). THERE ARE NO OTHER TECHNIQUES ABLE TO GIVE THIS LEVEL OF DETAILED LOCAL STRUCTURAL DISTRIBUTION INFORMATION IN THESE KINDS OF SYSTEMS.

**Fig. 1:** Pulse sequence (top) and $^{31}$P two-dimensional NMR spectrum (bottom) for Zn$_2$P$_2$O$_7$ glass. A clear doublet is seen in the −18 ppm region for pyrophosphate units and a singlet near 0 ppm for the orthophosphate.
MICROWAVE SPECTRUM AND AB INITIO CALCULATIONS OF 2-CHLORO-3-FLOUROPYRIDINE

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Hartsville, SC 29550

The rotational spectrum of 2-chloro-3-flouropyridine has been measured by chirped-pulse Fourier transform microwave (CP-FTMW) spectroscopy from 8-18.5 GHz. The spectrum has been analyzed to determine the rotational constants and quadrupole coupling constants of the 2-chloro-3-flouropyridine molecules. The rotational constants for both the \(^{35}\text{Cl}\) and the \(^{37}\text{Cl}\) isotopologues have been determined and compared to the ab-initio calculations performed using the Gaussian 03W software package. The figure below shows the experimental spectrum. The spectrum in Figure 1 is the result of 10,000 signal averages (approximately 40 hours measurement time). For this experiment the backing pressure was set to 50 psi and the nozzle was at 60° C.

Fig. 1:
3 UTILIZATION OF METATHESIS TO ACHIEVE WATER SOLUBILITY OF NANOPARTICLES

Laura Mast, Dr. Janet E. Macdonald, Michael J. Turo
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Nashville, TN 37235

One fundamental challenge facing current nanochemistry research is achieving water solubility of particles that are prepared in organic solvents for biological and photocatalytic applications. Many syntheses of nanoparticles are conducted in the presence of organic solvents and surfactants to yield monodisperse nanoparticles, but leave nanoparticles with coronas of long hydrophobic alkyl chains, thus rendering them insoluble in water. Current methods for improving water solubility, such as ligand exchange, only work for a few nanoparticle systems. A unique opportunity lies in the exploitation and manipulation of the chemistry of common surfactant molecules, especially the unsaturation in oleic acid and oleylamine. Here we show that after nanoparticle synthesis, using the Grubbs’ metathesis reaction, the outer portion of the ligand can be replaced with a chain containing a polar functional group. The reaction allows for precise control of the resultant structure of the ligand and thus the chemical functionality and water solubility of the nanoparticles.

4 BIS (BIPHENYL) PHOSPHINE COMPLEXES OF GOLD: NEW VARIANTS IN LIGAND STRUCTURE

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Winston-Salem, NC 27109

Homogeneous gold(I) catalysts activate unsaturated hydrocarbons (p-systems) toward nucleophilic addition and involvement in skeletal rearrangements, and the products are basic to materials and pharmaceutical syntheses. They offer a mild and non-toxic alternative to other transition metals. A commonly used catalyst in synthetic gold chemistry is “JohnPhos” or chloro[(1,1-biphenyl-2-yl)di-tert-butylphosphine]gold(I). Many possible catalysts can be created by modifying the JohnPhos scaffold. In this work we chose to modify the scaffold by introducing a second biphenyl substituent. This modification was chosen because one biphenyl substituent is known to stabilize gold complexes, but the literature does not report catalysts with bis(biphenyl)phosphines, that is, phosphines with two biphenyl substituent. Two new catalysts were synthesized and characterized in solution and in solid state: chloro[di(1,1’-biphenyl-2-yl)(phenoxy)phosphine]gold(I) and chloro[di(1,1’-biphenyl-2-yl)(tert-butyl)phosphine]gold(I). With the new complexes comparisons to other known catalysts can be made. Preliminary reactivity studies are also discussed.
5 Ion Chromatographic Study of Aerosol Samples Collected From Jonesboro, AR

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Aerosols affect Earth’s ecosystem by changing the global reflectance properties of the atmosphere. This reflective property depends on their chemical composition. They may also cause adverse health effects when their concentrations increase due to increase in activities such as urban traffic congestion and/or enhanced farming practices like foliage burning. All these activities result in an increase in aerosol concentration, and consequently an increase in pollution. This study was performed to try and characterize the chemical composition of aerosols found in an urban town, Jonesboro AR, which is also surrounded by farming areas. Aerosol samples were collected in using a mini-particle collector and analyzed using ion chromatography. It was found that the majority of the aerosols contained chloride, nitrate, and sulfate components at different concentration levels. Further studies are being conducted to determine the origin of the collected aerosols and their distribution around Jonesboro AR.

6 Automated Data Fusion for Chromatographic Calibration and Prediction

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   Salisbury, MD 21801

Stacking (or fusing) parallel regression results has recently be shown to reduce the error associated with multivariate calibration models when applied to spectral data. Stacking makes use of all available data and weights the sections of the data that correlate strongly with the target property more heavily than the sections that are less correlated. In this study, we combine the technique of stacking with principal component regression (PCR) and partial least squares (PLS) for the quantitative analysis of biochemical chromatographic data. A set of simulated data is also examined for proof-of-principle. A two-way optimization is used to determine the ideal number of intervals to split the data into for analysis and the optimum number of principal components (PCR) or latent variables (PLS) needed to accurately model future unknown data. We observe a significant decrease in calibration and prediction errors when compared to results obtained from traditional chemometric analyses.
NONCOVALENT INTERACTIONS IN NETWORKS OF TRIMETHYLAMINE-\textit{N}-OXIDE, UREA, AND WATER

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Trimethylamine-\textit{N}-oxide (TMAO) belongs to a small class of organic molecules called osmolytes, which have been studied extensively because they play an important role in a biological functionality. TMAO promotes the folding of biopolymers, such as proteins and nucleic acids, and also counteracts the denaturing effects of urea on the same biopolymers. Even though TMAO demonstrates a substantial degree of hydrophobic character, it has been found to be highly soluble in water. In fact, it has been suggested that these osmolytes are effective because of their noncovalent interactions with solvated water molecules in biological media. Previous spectroscopic studies involving TMAO, therefore, have concentrated on perturbations on the vibrational spectra of solvated water molecules using infrared spectroscopy. In a recent study of Munroe, Magers, and Hammer, the effects of hydration on the normal modes of TMAO were investigated using Raman spectroscopy and electronic structure computations. Good agreement between experiment and theory in that study suggests that the oxygen atom in TMAO accepts on average at least three hydrogen bonds from neighboring water molecules. TMAO’s effectiveness as an osmolyte is likely a direct result of this restructuring of the water network in its immediate vicinity. To begin to try to understand how TMAO can also counteract the denaturing effects of urea, optimum geometries and the corresponding vibrational frequencies of networks of TMAO, urea, and water have been computed using density functional theory. The DFT functional employed is the M06-2X high nonlocality hybrid functional from Thulør and Zhao. Two correlation-consistent basis sets with diffuse functions are employed: aug-cc-pVDZ and aug-cc-pVTZ. Initial results indicate that the most stable configurations are those in which urea and TMAO each form hydrogen bonds with each other and with water. We gratefully acknowledge support from the NSF (EPS-0903787) and the W.M. Keck Foundation.
Photovoltaic cells are being used as alternative sources of energy due to our heavy dependence on fossil fuels. These cells convert sunlight into useable electric energy. Copper nanoparticles have great potential to be used as photovoltaic cells. In this study, copper nanoparticles are electrodeposited onto single-walled carbon nanotube (SWNT) networks on a glass slide forming a gradient of different sized nanoparticles. The size gradient is useful because the different sized nanoparticles absorb different wavelengths of light, leading to a more efficient cell. The SWNT’s are held to the glass surface with two different silanes, 3-aminopropyltriethoxysilane (3APTES) and phenyltriethoxysilane, which give different properties to the nanotube networks. The 3APTES silane has an amino group that contributes charge to the surface, while the phenylsilane has an aromatic group that can conjugate with the nanotube’s π electrons. The nanoparticles were then analyzed with Raman Spectroscopy, UV-Vis, and Energy-dispersive x-ray spectroscopy to confirm the identity of copper species. Images from atomic force microscopy and scanning electron microscopy showed that the nanoparticles form differently on the different silanes. The nanoparticles grown on the phenylsilane/SWNT network had longer and thinner branches, while the nanoparticles grown on 3APTES/SWNT network had short, fat branches. UV-Vis and Raman spectra showed different copper species (Cu, Cu₂O) in various locations on the sample. Additionally, these nanoparticles showed some surface-enhanced Raman scattering (SERS) properties, but the samples were not optimized for this effect.
3. **CALORIMETRIC DETERMINATION OF ENERGY CONTENT OF BIODIESEL FUELS FROM PLANT CROPS**

Loubna Pagnotti, William Mayberry, Haider Khan, Haniff Baccas, Monte Wolf, and Md. Humayun Kabir

Department of Chemistry, Oglethorpe University
Atlanta, GA 30319

Energy demand is the single most critical challenge facing humanity today— not just the U.S., but also worldwide. Combustion of fuels provides the energy that sustains our modern way of life. The increasing importance of sustainability in energy production has led to a global commitment to the use of fuels derived from renewable biological sources, such as biodiesel produced from plant crops. We report results of the energy content of biodiesels from soy, sunflower, palm, and olive from calorimetric measurements.

4. **MODULATING MICELLE FLUIDITY FOR MEMBRANE PROTEIN STRUCTURAL STUDIES**

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Membrane protein studies rely heavily on detergent micelles as in vitro mimics of cell membranes. However, a lack of understanding about the micelle physical properties and requirements for stabilizing a membrane protein fold and function significantly hinders these investigations. Currently, detergents are empirically screened and usually not chosen on a rational basis. One physical property of interest we aim to investigate further is micelle fluidity: how the dynamics of the micelles affect membrane protein fold and activity. To quantify micelle dynamics, spin labeled lipids were doped into various detergent micelles at a ratio of one label per roughly ten micelles (to limit populations of micelles with multiple spin labels) and the dynamics were quantified using Electron Paramagnetic Resonance (EPR) Spectroscopy. In addition, the fluidities of micelles with additives like cholic-acid derivatives were also investigated. The results suggest that, in addition to modulating micelle shapes and sizes, fluidity can be manipulated with binary mixtures of detergents increasing the number of controllable physical properties of micelles for membrane protein investigations.
**5 IMPACT OF ARYL RING LOCATION IN BENZOBISAXOZOLE POSSESSING CRUCIFORMS**

Kiley Morgan, Aimee Tomlinson  

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  Dahlonega, Ga 30597

An alternative form of energy is photovoltaic cells, which are long, conjugated polymers. A series of molecules possessing benzobisaxozole cores and various aryl ring substituents (i.e. phenyl and thiophenyl) were examined using TD-DFT B3LYP/6-31G*. The HOMO, LUMO, and optical band gaps were generated and compared. In addition, the electrostatic potential maps and the frontier orbitals were examined. The results of these studies are presented here.

**6 THE CONVENTIONAL STRAIN ENERGIES OF BICYCLOALKANES AND THEIR METHYL DERIVATIVES**

KAITLYN V. KISS, David H. Magers  

Department of Chemistry & Biochemistry, Mississippi College  
  Clinton, MS 39058

The conventional strain energies for bicyclo[1.1.1]pentane, bicyclo[2.1.1]hexane, bicyclo[2.2.1]heptane, bicyclo[3.1.1]heptane, and bicyclo[2.2.2]octane are determined within the isodesmic, homodesmotic, and hyperhomodesmotic models. In addition, the conventional strain energies for the methyl derivatives of these systems are also computed. For example, the four methyl derivatives for bicyclo[2.1.1]hexane (1-methyl-bicyclo[2.1.1]hexane, 2-methyl-bicyclo[2.1.1]hexane, endo-5-methyl-bicyclo[2.1.1]hexane, and exo-5-methyl-bicyclo[2.1.1]hexane) are investigated. Optimum equilibrium geometries, harmonic vibrational frequencies, and corresponding electronic energies are computed for all pertinent molecular systems using SCF theory, second-order perturbation theory, and density functional theory. The DFT functionals employed are Becke’s three-parameter hybrid functional using the LYP correlation functional and the M06-2X high nonlocality hybrid functional from Thular and Zhao. Two correlation-consistent basis sets are employed: cc-pVDZ and cc-pVTZ. In addition, single-point CCSD(T) results are computed at the MP2/cc-pVTZ optimum geometries using both the cc-pVTZ and the cc-pVQZ basis set. Results are compared to the conventional strain energies of other cyclic hydrocarbons. We gratefully acknowledge support from the NSF (EPS-0903787) and the W.M. Keck Foundation.
**7 BASICITIES OF PESTICIDES FOR DETERMINING SUPPRESSION EFFECTS IN DART MASS SPECTROMETRY**

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Knoxville TN 37996

Modern mass spectrometry uses atmospheric pressure ionization techniques like DART to allow direct introduction of a sample without pre-purification. Because ionization of the sample in DART is usually by protonation to form [M+H]^+ ions, it has been observed that a more basic analyte can steal the proton from a less basic one, thus suppressing its signal. In order to identify which analytes are likely to be suppressed, the gas phase basicities of a wide range of pesticides (often sampled directly from water or urine in DART) have been determined, by computational methods at the B3LYP/6-311+G(d,p)//B3LYP/6-31G* level. This reproduces experimental basicities of small molecules accurately, and the computations can be done far quicker than experiments on the large pesticides.

**8 UNDERGRADUATE RESEARCH PARTNERSHIP BETWEEN GEORGIA COLLEGE AND SASCO, CHEMICAL GROUP, INC**

Benjamin Gibson, Catrena H. Lisse, PhD.  
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Georgia College is partnering with SASCO Chemical Group, INC through an undergraduate internship program that provides students with industrial experience. This presentation highlights the research conducted by an undergraduate chemistry major focused around the compound Master Blend L, a product created by SASCO.  Currently, two MBL formulations are sold by SASCO: MBL-479 and MBL-436.  The product is sold to customers in the rubber industry as an anti-tack coating for use in processing rubber. Calcium stearate is a major component of SASCO’s MBL formulation contributing 45-55% of the formula on a dry weight basis.  In an effort to reduce formula cost, this experiment seeks to replace the current calcium stearate with a more cost effective alternative.  The formula revision relies heavily on viscosity to ensure colloidal suspension and pumpability.  In this experiment, laser diffraction particle size analysis is used to determine particle size distribution of several pallets of calcium stearate and a Brookfield viscometer is used to determine the viscosity as a function of time.  This data is compared to the control formula of MBL and is used to determine the effectiveness of the lower cost, potential raw material replacement calcium stearate.  The experimental design and preliminary results are summarized in the presentation.
VOLUMETRIC PROPERTIES OF CYCLIC ETHERS IN AQUEOUS SOLUTIONS AT VARIOUS TEMPERATURES

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Volumetric properties, particularly the apparent molar volumes and compressibilities provide information about hydration (solute-solvent) and solute-solute interactions. These interactions are important in understanding solution behavior and for that reason they have been studied extensively over the years in both electrolytes and non-electrolyte solutions. In recent years, with the realization that these interactions are important in determining the conformation of biological macromolecules, the study of volumetric properties has gained a new impetus. In this presentation we report the apparent molar volumes and compressibilities of aqueous solutions of cyclic ethers at various temperatures. Special attention is paid to the role of group contributions to the volumetric properties as the compounds studied differ from each other by the systematic addition of specific chemical groups.

AN STM INVESTIGATION OF COADSORPTION OF CARBOXYLIC ACIDS ON GRAPHITE

Jeff Davidson, Leanna Giancarlo
Department of Chemistry, University of Mary Washington
Fredericksburg, VA

Scanning Tunneling Microscopy (STM) has been used to examine the surface of bare graphite surface and two carboxylic acids physisorbed on graphite. Solutions of octadecanoic acid (OA) and tetracosanoic acid (TA) were deposited on graphite, and the resulting self-assemblies were characterized via STM: collected images of each acid reveal lamellae containing the molecules with dark regions attributed to the hydrogen bonding COOH groups. The molecular length differences between OA and TA (2.3 and 3.7nm, respectively) suggest that OA and TA molecules can be distinguished from one another. Research has shown that when OA and TA are mixed in solution and physisorbed on to graphite, preferential adsorption occurs with TA dominating the surface coverage even at low solution concentration. This phenomenon is due to the fact that the heat of adsorption for carboxylic acid molecules increases by 2kJ/mol for every methylene group, resulting in a 12 kJ/mol higher heat of adsorption for TA relative to OA.

Reference:
CHARACTERIZATION AND INVESTIGATION OF THE PROPERTIES OF SILK FIBROIN

Chris Crain, Sean Barton and J. Z. Larese
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Natural products have been the focus of renewed scientific activity lately because they offer new pathways for developing novel biomimetic materials with specific physical properties. The mechanical properties of many such biological materials are a direct reflection of an abundance of non-covalent (i.e. weak) interacting ions, which play a critical role in the assembly and performance of bio-structures like F-actin in muscles, tubulin in the cytoskeleton, viral capsids, and silk [McGrath K]. Recently, many researchers in fiber and biomedical fields have been interested in natural silk fibers because of their outstanding mechanical properties [Asakura]. The silk filaments produced by orb-weaving spiders and silkworms are among nature’s most highly engineered structural materials [Rousseau]. Among silkworms, the one of interest here is the domesticated Bombyx mori which has been of interest for at least 5000 years due to its excellent characters as textile fiber.

Two major factors are responsible for the diverse range of silk’s mechanical properties. The first is the nanoscale semi crystalline folding structure, which gives high strength and toughness. The second is the degree of hydration of the disordered fraction which acts to modify these properties. The control of these two factors is believed to be the key to adjusting the functionality of protein elastomers and renders silk an ideal model protein for biomimetic material design. Its microstructure contains two significant phases: a highly crystalline fibroin phase (which is our focus) and sericin which is the amorphous binding protein for the overall structure. Much of the uncertainty in the physical properties of fibroin involves an imperfect determination of water-solvent content, a method using a quartz microbalance was used as an accurate gauge of the relationship between the amount of water-solvent and the changes in the internal properties of the native and hydrated fibroin protein. A discussion of the purification process and the characterization of the protein structure using x-ray and neutron scattering techniques will be presented. Finally a description of the electro spinning process, wherein a high electric potential is applied to a droplet of a silk solution at the tip of syringe and directed at a surface that is grounded will be included.


12 EXPERIMENTAL DETERMINATION OF ENERGY CONTENT OF ALTERNATIVE FUELS

Haniff Baccas, Loubna Pagnotti, Haider Khan, William Mayberry, Monte Wolf, and Md. Humayun Kabir
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Energy demand is the single most critical challenge facing humanity today. Combustion of fuels provides the energy that sustains our modern way of life. Because of dwindling petroleum reserves and climate change caused by combustion of conventional fuels motivated people all over the world to search for renewable alternative fuels in the recent decades. We report results of energy content for a wide range of alternative fuels such as methanol, ethanol, ether, and biodiesel from bomb calorimetric measurements.

13 STRUCTURAL DIVERSITY IN THE REACTIONS OF MIXED- DONOR LIGANDS WITH BROMINE AND IODINE

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Abstract: This presentation describes the reactivity of several new mixed-donor ligands containing pyridine and wither thione or selone donor groups towards halogens. More specifically, the reactions of the (mercaptoimidazolyl)picoline (mpicMe) and (mercaptoimidazolyl)ethylpyridine (mepyMe) ligands towards elemental bromine and iodine will be discussed. Similarly, the corresponding reactions of the selenium analogues (sepicMe and seepyMe) will be presented. These reactions proceed in three distinct pathways: charge-transfer, oxidative addition or heterolytic cleavage of the halogen-halogen bond, as corroborated by X-ray crystallography.
Conjugated materials have become an attractive area of research due to their optoelectrical properties and wide scope of applicability in solar cells and other organic electronic devices. Most widely used conjugated materials are electron-rich; electron-deficient conjugated systems are less common. Due to its empty p-orbital, the insertion of tri-coordinate boron into a conjugated polymer is an attractive technique to create electron-deficient materials. We are currently developing boron congeners of fluorenes and will report on their synthesis and characterization.
FUNCTIONALIZATION OF SILICA SURFACE USING N-ARYLATION
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The reaction of arylation of amines is a convenient method of synthesis of N-aryl compounds. In this project, N-arylation was used for functionalization of silica surface (Fig. 1) by various functional groups, i.e., alkyl, methoxy, methylthio, carbonyl, haloids and vinyl (Fig. 2). Attempts were made to also functionalize silica surface by non-aromatic and heterocyclic compounds. The first step of the project included determining the optimal conditions for catalytic N-arylation, with copper being chosen as the most active catalyst and dimethylformamide/chloroform mixture being chosen as the most appropriate solvent. These conditions were then used for preparation of various functionalized materials. The reactivity of the surface functional groups were tested in characteristic reactions, and the products were studied using elemental analysis, FT-IR spectroscopy and porosimetry.

Figure 1. Reaction of Boronic Acid with Silica Surface

Figure 2. Compounds Used in Silica Gel Functionalization
DEVELOPMENT AND PRODUCTION OF NUCLEAR DEBRIS SURROGATES FOR FORENSIC METHODS DEVELOPMENT WITHIN THE ACADEMIC COMMUNITY

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The essential goal of this research project is to establish a capability for producing and characterizing nuclear debris surrogates in a laboratory at the University of Tennessee. The debris surrogates will be essential for the development and validation of nuclear forensic analysis techniques. Cold samples will contain many of the chemical and morphological signatures associated with nuclear melt glass and will be analyzed using ICP-MS, XRD, XRF, SEM and other techniques in order to characterize the composition and microstructure of the samples. Hot samples (activated via neutron irradiation) will also contain radioactive signatures similar to nuclear debris and will be characterized using Alpha, Beta and Gamma Spectrometry, as well as ICP-MS. This work will also have applications for solid waste storage of nuclear material.
ORGANIC CHEMISTRY OF BELOUSOV-ZHABOTINSKY OSCILLATING REACTIONS. STEREOCHEMISTRY OF MALONIC ACIDS AND THERMOCHEMISTRY OF KETOMALONIC ACID FORMATION

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Belousov-Zhabotinsky (BZ) reactions generally involve the metal-catalyzed oxidation of a carboxylic acid by an acidic bromate solution. While BZ reactions have become the quintessential model of non-equilibrium thermodynamics, many mechanistic details remain elusive about the inorganic, organic and organometallic reaction steps. We have been studying the kinetics of the ferroin/ferrin catalyzed BZ reaction of malonic acid (Fig. 1). Starting with the red ferroin complex, one observes a color change to the blue ferrin complex as Fe²⁺ is oxidized to Fe³⁺, and the concentrations of the iron ions and of bromide oscillate for up to an hour with oscillation periods ranging from 10 to 60 seconds depending on conditions (i.e., pH, pM).

Here, we report on the thermodynamics of the reactions of Scheme 1 for the formation of ketomalonic acid (KMA) from malonic acid (MA) at the MP2(full)/6-311G* level. The stereochemistries of hydroxy-, dihydroxy, and hydroxybromo derivatives of malonic acid are discussed in detail and with consideration of all possible cis-cis, cis-trans and trans-trans diacids. Interestingly, trans-trans diacid structures may compete or even dominate because of intramolecular H-bonding. We considered the reactions of MA and its derivatives both with HOBr and also with H₂O₂ and all are highly exergonic. While the equilibrium reaction DHMA ⇌ KMA + H₂O lies on the left as expected, the equilibrium reaction HBMA ⇌ KMA + HBr essentially is thermoneutral.

# Fellow, MU Arts and Science Undergraduate Research Mentorship Program.
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TRIPODAL PYRIDINE-BASED LIGANDS FOR GADOLINIUM(III) COMPLEXATION: IMPLICATIONS FOR THE DESIGN OF HIGH-RELAXIVITY MRI CONTRAST AGENTS

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The unique magnetic and luminescence properties of the lanthanide metals enable a variety of applications including medical imaging and biosensor development. For example, coordination complexes of the Gd(III) ion are often used in magnetic resonance imaging (MRI) due to the ability of such complexes to enhance the images produced from a scanner. When injected into the body, such agents are bound by \textit{in vivo} water molecules causing an increase in the relaxation rate of water protons, and improving image contrast between healthy and diseased tissue. The effectiveness of such contrast agents relates to the number of bound water molecules \((q)\) that coordinate the metal. Additionally, metal complexes utilizing Eu(III) often exhibit unique photophysical properties that can be used for sensing anions that bind to the metal ion causing an increase in luminescence intensity. Luminescence decay lifetimes of Eu(III) complexes can also be used to determine the number of bound solvent molecules, and thus provide valuable insight into the effectiveness of either application.

In this study, tripodal pyridine/Schiff base ligands for lanthanide complexation were synthesized and the potential of one particular Gd(III) complex as an MRI contrast agent was explored. This complex was made from the so-called TRIPy ligand which effectively binds Gd(III) in a hexadentate manner, leaving space for additional water molecules in solution to attach. Luminescence decay lifetimes of the Eu(III) analog were used to determine the number of bound waters, and these results agree with relaxometric characterization performed for the Gd(III) derivative. The TRIPy complex exhibited the binding of \(2.3 \pm 0.5\) water molecules, however, solution thermodynamic studies suggest instability of the complex at high pH. These findings have led to the synthesis of more stable derivatives employing amide linkages as alternatives to the imine groups of TRIPy which will be discussed.
SYNTHESIS OF A CATALYTIC METAL OXIDE SURFACE THROUGH THE USE OF CLICK CHEMISTRY

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By attaching an azide-terminated compound to a metal oxide surface through a phosphonic acid head-group, a surface bound molecule with the ability to participate in click chemistry is generated. Through a copper-catalyzed azide-alkyne cycloaddition (CuAAC) click reaction, a transition metal catalyst can be attached to the metal oxide, provided one of the ligands has a terminal alkyne. Two compounds, diethyl 2-bromoethylphosphonate and 11-hydroxyundecylphosphonic acid, were used to modify a metal oxide surface and, subsequently, perform CuAAC with the azide-terminus to form a triazole.

The ethoxy groups of diethyl 2-bromoethylphosphonate were removed via a deprotection reaction, converting the phosphonate moiety to a phosphonic acid (99% yield). Tethering By Aggregation and Growth (TBAG) deposition was used to covalently bind this compound to a copper oxide surface through the phosphonic acid head-group before being used in an in-situ CuAAC reaction, which both attaches an azide and forms a triazole. 11-hydroxyundecylphosphonic acid was attached to a copper surface through the same deposition method. The hydroxyl group was then converted into either a bromo or mesyl intermediate, and successively reacted in an in-situ CuAAC reaction. Surface reflectance infrared (IR) spectroscopy was used to verify surface modifications.
SYNTHESIS AND STRUCTURES OF BIS (PYRIDYL) SELONE COMPLEXES

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The synthesis and reactivity of a new mixed-donor ligand containing a N-heterocyclic selone flanked by two pyridine donor groups, namely the bis(pyridyl)selone (2-py)$_2$se, will be described in this presentation (Figure 1). A series of group 12 metal complexes \([(2-py)_2se]MX_2\) (\(M = Zn, Cd, Hg; X = Cl, Br, I\)) and \([(2-py)_2se]_2MX_2\) (\(M = Cd, X = I; M = Hg, X = Cl, Br, I\)) have been prepared and fully characterized and their structures illustrate the different coordination modes and versatility of this N$_2$Se donor ligand. In addition, a series of related complexes of copper(I), silver(I), indium(III), tin(IV), lead(II), antimony(III) and bismuth(III) have been synthesized and will be compared with the corresponding bis(pyridyl)thione analogues that have been previously isolated.

Fig. 1: The (2-py)$_2$e Ligands (e = m, se)
A BAYESIAN APPROACH TO BROAD-AREA NUCLEAR/RADIOLOGICAL OPERATIONS

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The conventional approaches to nuclear/radiological detection rely exclusively on the output of a detector’s response function and associated counting statistics. Current methods are not equipped to account for radiation transport phenomena, and therefore do not provide the necessary geo-positional data. This research effort seeks to advance the current technologies with respect to nuclear/radiological search operations with the development of the Broad-Area Search Bayesian Processor (BASBP). The first objective of this research seeks to develop an adaptive Bayesian data processing algorithm that cycles data from multiple sensors through a predict-sense-update process in order to arrive at a set of maximum-likelihood indicators that suggests the location(s), strength, and identification of nuclear/radiological sources. The second essential component of this research project addresses the means to fuse the probability-space stemming from detector data with probability-space from disparate data sources to effectively reduce the size of the search space. In summary, this will allow the user to increase the range at which detection/localization/identification decisions are made and maximize the allocation of resources.

Figure 1: Conceptual approach to implementing the Bayesian data processing scheme.
INVESTIGATING LEAD REMOVAL FROM SOILS BY VARIOUS PLANTS AND VEGETABLES

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Heavy metal contamination is a serious environmental problem faced in most mining towns of Zambia. Lead contamination of soils, water bodies and plants has been the major problem, especially in Kabwe. Earlier studies have reported total soil lead concentrations of over 25,000 mg/kg in various parts of the town, and high levels of lead in plants, such as Tithonia diversifolia, which dominate the local vegetation. Our current study investigates the extent and changes over time of lead contamination in Kabwe using previous records, reporting the spatial and temporal distribution of lead over the last decade. We also investigate the effectiveness of various plants and vegetables to remove lead from contaminated soils under laboratory conditions. Chinese cabbage, mustard and sunflower plants were grown in the laboratory and total tissue lead concentrations were analyzed using handheld probes, HACH colorimeters and Flame Atomic Absorption Spectrometry. Results from this study have the potential for use in the development of combinations of best management practices (BMPs) for the reclamation of lead contaminated soil and water bodies in Kabwe.

REACTIVITY PROFILE AND MECHANISTIC INSIGHT TO NI-CATALYZED SUZUKI-MIYAURO CROSS-COUPLING REACTIONS

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From 2001 to 2010, the Suzuki-Miyaura (S-M) Cross-Coupling reaction was the most cited metal-catalyzed cross-coupling reaction, which resulted in a Nobel Prize in 2010. Typically, the reaction is performed with palladium but because of its cost, abundance, oral exposure limits, and carbon footprint, there is an increasing push to replace palladium with nickel in Pd-catalyzed cross-coupling reactions in industry. Although research has been done with Ni-catalyzed S-M cross-coupling reactions, the level of understanding with nickel is not as complete as the understanding we have with palladium. We investigated three main aspects of the Ni-catalyzed S-M reaction: 1. Ni’s selectivity between chlorine and bromine; 2. Which Ni/phosphine combinations work best with different substrates; 3. The mechanism of the Ni-catalyzed S-M reaction. Selectivity between chlorine and bromine was seen in select circumstances, but results gave insight to the effects of initial arylation on the rest of the phenyl system. A class of phosphines was found that, when S-M reactions need to be run for a wide range of substrates, can be used in initially screening systems. Finally, by running multiple rate studies, it was found that there is strong evidence that anionic exchange is the rate-determining step in the S-M reaction, which differs from its palladium counterpart.
CONTROLLED FORMATION OF SILICATE MONOLAYERS ON SILICON WAFERS

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1 – 2 nm monolayers of the cubic silicate building block, Si₈O₂₀ are covalently bonded to the surface of clean silicon wafers via CVD of the tin silicate cube (Si₈O₂₀(SnMe₃)₈) followed by UV (254 nm) irradiation. Exposure of this layer to volatile metal or silicon chloride reagents results in the replacement of tin with metals or tethered functional groups. The synthesis and XPS characterization of several examples will be described.
Access to potable water remains one of the most significant public health challenges of the 21st century, with an estimated 4,000 children dying daily worldwide from waterborne diseases. One approach to mitigating this problem, which has received a great deal of attention in recent years, is Household Water Treatment and Storage (HTWS). In this approach, communities without access to potable water are provided with a simple filtration device that can be used to purify water in the home. Over the last 10 years, HTWS filters have been distributed in “Las Canas”, a rural community in the Dominican Republic (DR). During the last two years, students from Rollins College have traveled to the DR to perform chemical and microbiological testing on the water produced by the filters. In this presentation, we discuss the work we have done to assess the quality of the water treated with the HTWS systems. We begin with a description of the filter unit and the process of distribution, followed by a description of the testing protocols used. The results of the chemical and microbiological measurements performed during the summers of 2012 and 2013 will be presented. We conclude with comments regarding what we have come to learn about the filters and what makes for a successful HTWS project.

A platform for the electrochemical reduction of carbon dioxide can be formed by attaching an inorganic catalyst to a metal oxide surface. The catalyst-coated plate functions as a reusable electrode, allowing for the valuable formation of new carbon-carbon bonds. Bipyridine functions to coordinate a ruthenium catalyst, and when substituted with alkyl chains terminated in phosphonic acids, the molecule also has the potential to be covalently bound to an electrode surface. In an effort to synthesize the necessary organometallic catalyst, modification of 4,4'-dimethyl-2,2'-bipyridine was attempted via two routes: a haloalkylation and a radical bromination of the methyl substituents.

The addition of an alkyl chain to 4,4'-dimethyl-2,2'-bipyridine is facilitated by the use of an extremely strong organic base, lithium disopropylamide (LDA). A methyl proton is removed, creating a highly reactive carbanion. Subsequent introduction of alkyl chains functionalized by primary halogens yields a product that can then be converted to the intended phosphonic acid. Alternatively, a reflux in the presence of a radical initiator (azobisisobutyronitrile, AIBN) and a source of bromine (N-bromosuccinimide, NBS) radically brominates the methyl substituents of the bipyridine starting material. The two synthetic approaches will be discussed mechanistically, as well as in terms of yield, purification, and subsequent reaction success.
THE ROLE OF SPECTRAL FLUORESCENCE IN THE TAXONOMIC CLASSIFICATION OF MARINE PHYTOPLANKTON USING MULTIVARIATE OPTICAL COMPUTING

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Abstract:
Phytoplankton play a vital role in global carbon cycling through carbon fixation. The mechanism by which individual species of phytoplankton perform photosynthesis varies with photosynthetic pigment composition, which is determined by taxonomy. Spectral fluorescence is a popular method used to detect changes in phytoplankton community structure\textsuperscript{3} and to classify phytoplankton taxonomically\textsuperscript{1}. Our lab collects fluorescence excitation spectra of phytoplankton which we use as variables in Linear Discriminate Analysis (LDA)\textsuperscript{4}. The outputs of these analyses are used to create Multivariate Optical Elements (MOEs)\textsuperscript{4}. These MOEs are used as optical filters in a specialized fluorescence imaging photometer\textsuperscript{5} that has been shown to successfully discriminate and classify phytoplankton into broad classes\textsuperscript{2}.

References:
GC-MS METHOD DEVELOPMENT FOR $\alpha$-PINENE IN JUNIPER LEAVES

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Juniper leaves were harvested from the grounds of Kennesaw State University. These were analyzed for percent loss on drying and for analysis of $\alpha$-pinene by GC-MS. The percent loss on drying was 59 ± 4. Extraction methods and method development will be described. The internal standard used for the GC-MS analysis was o-xylene. The $\alpha$-pinene was quantified by both the external calibration method and the standard addition method.

ATR-FTIR STUDY OF THE ADSORPTION OF SODIUM ARSENATE ON THE SURFACE OF IRON OXIDES.

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The rise in global temperatures due to climate change has resulted in low rain fall around the world. This decrease has put pressure on the remaining freshwater resources like rivers, lakes and underground aquifers, to support the population growth and its need for freshwater. Furthermore, the increase in the use of pesticides to increase crop yield, has resulted in the incomplete removal of contaminants from waste water and their subsequent re-introduction into the environment. As the most common ingredient of pesticides, arsenic derivatives have been detected in aquatic environment and have been found to be bio-accumulative and persistent in these environments.

Since adsorption of organic compounds onto the surface of minerals limits their volatilization, the adsorption of sodium arsenate onto the surface of iron minerals as an alternate remedial method will be studied here. Different iron minerals (Goethite, Hematite) will be investigated under different environmental conditions (pH, ionic strength, contaminant concentration) using Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) spectroscopy. Prominent peaks from adsorbed sodium arsenate on the surface of iron minerals will be used to investigate adsorption characteristics in the hope of testing the feasibility of using iron minerals to naturally degrade these organic contaminants. Results will be important in enhancing our knowledge of degradation mechanisms and pathways, so we can improve the degradation capabilities of waste water treatment plants, with the long term goal of conserving/reusing the available freshwater resources.
INVESTIGATION OF PHARMACEUTICAL POLLUTION OF SURFACE WATER IN GEORGIA

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A collaborative group of chemistry and environmental science undergraduate students at Georgia College and State University is investigating the presence of pharmaceuticals in local water. Xenoestrogens are synthetic compounds that mimic the hormone estrogen when introduced to the human body. These compounds can be present in human waste after the consumption of pharmaceuticals, which leads to the contamination of sewage. Although the sewage is treated by a sewage treatment plant there is little to no treatments for xenoestrogens leaving the compounds nearly untouched. Once the sewage treatment water is released the xenoestrogens may contaminate surface water areas such as lakes and rivers. This project focuses on testing various surface water areas in middle Georgia for xenoestrogens due to human waste and comparing the results with EPA standards. The presentation summarizes the experimental design and preliminary results of the collaborative group findings.

WATER QUALITY COMPARISON BETWEEN THE OCMULGEE RIVER AND OCONEE RIVER

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Abstract

The Ocmulgee and Oconee Rivers are tributaries to the Altamaha River, which is the primary drainage to the Piedmont and Coastal Plains in central Georgia. The Ocmulgee and Oconee River Basins are monitored by an undergraduate research group from Georgia College. The water quality is monitored based on EPA guidelines. The parameters analyzed include nutrients levels, temperature, pH, conductivity, dissolved oxygen, and turbidity using HACH on-site probe kits. Testing locations are mapped using Global Positioning Systems technology to ensure reproducibility. Water quality trends between the rivers of interest will be highlighted in the presentation.
IONIZATION AND STRUCTURAL QUANTIFICATION OF CHONDROITIN SULFATE A AND DERMATAN SULFATE THROUGH ESI AND CID MASS SPECTROMETRY

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Our research involves the implementation of several techniques to assist in the structural analysis and molecular identification of glycosaminoglycans (GAGs). Finer structural details of GAGs have been identified. Analysis of GAGs is challenging due to decomposition of sulfo-modifications during fragmentation. Two important members of the GAGs that are being analyzed are chondroitin sulfate A (CSA) and chondroitin sulfate B (CSB), more commonly referred to as dermatan sulfate. These two molecules differ only by the C-5 epimerization of uronic acid, which results in diastereomers that cannot be separated by a mass analyzer. The structural differences of CSA and CSB significantly influence biological functions. ESI is a novel ionization technique used to produce ions of GAGs. MS yields the molecular weight and composition of an oligomer. Components are further examined by MS/MS. Isolated precursor ions are fragmented through collisional-induced dissociation (CID). The mass spectrum of the resulting product ions, obtained from the Fourier transform of the transient signal, allows structural quantification and epimer differentiation. Specific product ions formed during the fragmentation of precursor ions appear to distinguish between glucuronic and iduronic acid within the residue chain. The $^{2,4}$A$_n$ product ion is particularly diagnostic of glucuronic acid.

Figure 1: A comparison of the mass spectra of the product ions of CSB (top) and CSA (bottom). The $^{2,4}$A$_3$ product ion appears at a much higher intensity in CSA relative to CSB.
LIQUID MICROJUNCTION SURFACE SAMPLING – HPLC – MS/MS PROFILING OF ACETAMINOPHEN, TERFENADINE, AND THEIR METABOLITES IN WHOLE-BODY RAT THIN TISSUE SECTIONS

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Tissue distribution and metabolism studies are essential for optimizing drug quality, safety, and efficacy – and such studies depend on being able to visualize, in tissues, the spatial distributions of drugs and their metabolites. Limited ability to detect and differentiate parent compounds from their associated metabolites has hindered advances in pharmacokinetic and pharmacodynamic analyses. To resolve this visualization limitation, a new paradigm has emerged by the use of a fully automated liquid-extraction based surface sampling system. In this study, we adapted a commercially available autosampler coupled with high performance liquid chromatography-tandem mass spectrometry (HPLC-MS/MS) to analyze distinct positions on whole-body thin tissue sections of rats that had been dosed with acetaminophen and terfenadine (two commonly used over-the-counter drugs). By co-registering the sampling spots with HPLC-MS/MS data, we created 2-mm resolution heatmaps of the parent drug and their metabolites, using in-house software. The HPLC-MS/MS results compared well with the spatial distributions of acetaminophen and terfenadine in rat tissues obtained previously using other methods. The ability to make synchronized measurements of drug and drug metabolite distributions, both qualitatively and quantitatively, using a highly integrated, automatic surface sampling system, overcomes existing limitations imposed by other currently available methods, and thus is a major advance.

A FORENSIC ANALYSIS OF NAIL POLISH PERFORMED WITH DART MASS SPECTROMETRY

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The analysis of nail polish can be useful to gain information about a suspect, victim at a crime scene, or help link individuals to other locations. While current techniques have been employed for this analysis, a study to complement and enhance these techniques has been performed on a variety of nail polishes using Direct Analysis in Real Time (DART) with mass spectrometry. The unique ambient ionization DART source allows little to no sample preparation and analysis of the polish can occur directly from different substrates. Initial analysis was performed with twelve different polish samples applied to individual glass slides that were inserted directly into the DART source. Multiple scans were performed for each sample to monitor desorbed ions in both positive and negative mode. The mass spectral data collected from the DART-MS will be presented to show common and unique ions between the types of polish analyzed. Comparisons will be made to determine if differentiation between the brand of nail polish or different types of nail polish in the same brand is possible. Analysis of this type is relatively non-destructive for evidence, which is a highly sought after quality in forensic analyses. This type of analysis will then be compared to a known type of forensic analysis, Pyrolysis Gas Chromatography (PGC) with mass spectrometry for the twelve samples. PGC is a destructive analysis with no chance of recovery of the original sample. Finding an alternate method (DART-MS) to analyze such samples has the potential for time and cost savings with respect to trace evidence for forensic laboratories.
IMPACTS OF NUTRIENT COMPETITION ON MICROALGAE BIOMASS PRODUCTION

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Knoxville, 10/2013

The atmospheric level of CO₂ is largely determined by the global balance of biological CO₂ fixation and release. Over the last two centuries, industrialization has accelerated the release of anthropogenic CO₂ into the atmosphere. The ocean helps compensate for some of the anthropogenic CO₂ flux by dissolving atmospheric CO₂, which can then be converted to biomass by marine phototrophs.

The contribution of ocean ecosystems to carbon flux is difficult to measure largely because of the complex metabolism occurring in communities of marine phototrophs. Modeling the influence of interdependent species-species metabolisms and competition factors may improve our understanding of carbon flux compensation. Here, we investigate the impact of the biological environment on CO₂ sequestration by marine microalgae species.

The experimental studies are based on two marine microalgal species, namely *Nannochloropsis oculata* and *Dunaliella parva*. Growth behavior is described by semi-empirical models for (i.) a species’ growth rate and (ii.) the amount of biomass produced. By comparing species growth behavior in cultures containing both species to that of pure cultures of the individual species grown under otherwise identical conditions, namely nutrient concentration, conclusions regarding the impact of nutrient competition were drawn. The growth rates of each species in the mixed culture were found to decrease by 50-200% compared to those of the corresponding pure cultures. Even larger changes were observed in the maximum cell concentration, a measure for the amount of biomass produced. We conclude that competition in marine ecosystems, particularly among marine microalgae species, impacts inorganic carbon uptake as well as the amount of biomass produced.
GAS-PHASE THERMOCHROMATOGRAPHIC SEPARATIONS OF FISSION AND ACTIVATION PRODUCTS

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Solution phase separations are a fundamental and traditional process for performing radiochemical analysis. However, these methods are generally cumbersome and slow, so it is a prerogative to find more rapid separation techniques. This work involves the manipulation of gas-phase chemistry for the isolation of fission and activation products in the immediate aftermath of a nuclear explosion. Gas-phase separations are much faster for separations. However, little work has been done in researching gas-phase separations for radiochemical analysis due to the difficult experimental setups, the technological needs for handling the elements, and obtaining the elements themselves. In this work, the synthesis of the rare earth element (REEs) complexes with 1,1,1,5,5,5-hexafluoroacetyl-acetonate will be presented. 1,1,1,5,5,5-hexafluoroacetyl-acetonate has the volatility necessary to put the REE’s into the gas phase at higher temperatures. Furthermore, this series of compounds will be classified and detailed. Characterization of these products with FT-IR, P-XRD, ICP-TOF-MS, and melting point analysis will be discussed. In addition, this work will support a number of applications. First, it will support the growing need for rapid separation and analysis of short lived isotopes. Short lived isotopes are currently being used in the radiopharmaceutical and nuclear medicine community and are being actively researched. Second, it will support applications to the super heavy element discovery research efforts that have been underway for some time in the field of nuclear chemistry.
AN "OPEN BOX" APPROACH TO FLUORESCENCE QUENCHING: USING AN IPAD SCREEN AND DIGITAL CAMERA TO MEASURE FLUORESCENCE INTENSITY

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Fluorescence quenching is an analytical technique as well as a common undergraduate laboratory exercise. Unfortunately, a typical quenching experiment requires the use of a $25,000 fluorometer that measures the fluorescence intensity of a single sample in a closed compartment, unseen by the experimenter. To overcome these shortcomings, we designed an “open box” fluorescence quenching method that is less expensive, utilizes common items, measures multiple samples simultaneously, has educational benefits, and provides accurate results. In this experiment, six fluorescein samples were prepared in 0.1 M NaOH with varying concentrations of the quencher, iodide, and transferred to plastic cuvettes. These cuvettes were then placed on an iPad screen, which served as the excitation source. A digital camera was used as the detector of the fluorescence intensity. A MATLAB program was designed to analyze the images and automatically generate a Stern-Volmer plot, which was then used to determine the quenching constant ($K_{SV}$). The $K_{SV}$ of fluorescein determined by this method was $8.98 \pm 0.13 \text{ L mol}^{-1}$, which agreed well with the fluorometer value of $8.97 \text{ L mol}^{-1}$ and the literature value of $9.0 \pm 0.2 \text{ L mol}^{-1}$. These results demonstrate that in addition to allowing the experimenter to visualize the chemical processes and better understand the concepts of fluorescence and quenching, this simple method provides quantitative results comparable in accuracy to the more expensive fluorometer.

SYNTHESIS AND CHARACTERIZATION OF BIODIESEL FUEL FROM ALGAE

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Energy demand is the single most critical challenge facing humanity today. Combustion of fuels provides the energy that sustains our modern way of life. Microalgae have emerged as an attractive feedstock for the large production of renewable bio-fuel, biodiesels in the recent decade. To evaluate the potential of algal biodiesel as renewable transportation fuels we report the energy content of the fuels from calorimetric measurements and compare to plant crops biodiesel and petroleum biodiesel.
SUGAR SACCHARIFICATION ANALYSIS FOR BIOMASS SAMPLES USING UPLC-CAD: A BIOMASS STORAGE COMPARISON

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With this research, an ultra-high pressure liquid chromatography (UPLC) using corona aerosol detection (CAD) was used to determine sugar concentration of saccharification samples prepared from switchgrass, a potential source of biomass used to develop biofuels. A study for the storage conditions of the biomass was performed where the biomass was kept at three different storage conditions, hooped, tarped, and uncovered, and then sampled at monthly intervals for 13 months. These samples were then subjected to pre-treatments and saccharification processes. Analysis with the UPLC-CAD generated data to determine the identity and concentration of sugars present and then correlate the effect of the storage conditions to sugar production. To analyze properly, calibration standards of known concentrations were tested and calibration curves were constructed based on detection level (peak area) versus known concentration. Samples within parameters of calibration curves were then measured to determine unknown sample concentrations. Samples were ran in duplicate and retention times were compared to the chromatograms of calibration standards. Glucose and xylose were determined to be the primary sugars present in samples. Using peak areas and calibration curves, individual sugar concentrations were calculated. Optimal chromatography conditions were as follows: 80°C column temperature, 0.250 mL/min 80% acetonitrile/20% water flow rate. This produced reliable analysis within 4 minutes per sample, Figure 1. This developed method allowed quality sample resolution and quantification while minimizing time required for each sample. Results with statistical analysis of these switchgrass saccharification samples after different storage conditions will be shown.

Figure 1. Chromatogram of a saccharification sample generated after switchgrass processing generated with a developed ultra-pressure liquid chromatography (UPLC) system with corona aerosol detection (CAD).
The Determination of Antioxidants in Juice and Tea Beverages Using High Performance Liquid Chromatography

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Antioxidants are species that have many health benefits and are found in fruits, plants, as well as tea and juice beverages. The Gallic Acid Equivalence Method measures the total amount of antioxidants in the wine industry (A.L Waterhouse. “Determination of Total Phenolics” in “Current Protocols in Food Analytical Chemistry”, I1.1.1-I1.1.8). Gallic acid, which is used as a measure of the total antioxidant content, quenches free radicals by getting itself oxidized, thereby reducing cell damage. A standard gallic acid calibration curve is prepared and is further used to measure the amount of gallic acid present in commercially available tea and juice beverages via High Performance (or Pressure) Liquid Chromatography. All samples are also left open for a week to measure the decomposition of gallic acid via air oxidation.

Figure 1. Oxidation of Gallic Acid into 3,5-didehydroshikimate
**GC METHOD DEVELOPMENT FOR OLEIC ACID IN OLIVE OIL**

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This study involved measuring the saponification value of olive oils, oleic acid and decanoic acid. Saponification value is a measure of the amount of base needed to saponify 1 g of fat. It serves as a way of determining the average molecular weight and, by extension, the average chain length of fatty acids in a sample. Samples of olive oil, oleic acid, and decanoic acid were found to have saponification values of 198, 207, and 326, respectively. Using decanoic acid as the internal standard, samples olive oil and oleic acid standards were methylated and quantified on a GC. Both the external calibration method and the standard addition method were used to quantify the oleic acid in olive oil. Oleic acid is the primary ingredient in olive oils.

**QUANTITATION OF MEDICINAL COMPOUNDS IN BLACK COHOSH BY HPLC-ELSD**

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Black cohosh (Actaea racemosa, formerly Cimicifuga racemosa) is a perennial forest understory plant, native to the mountains of the Southeastern United States and Southern Canada. Natural products extracted from black cohosh have recently gained widespread popularity as a safe and effective alternative for menopausal women to hormone replacement therapy. As one of the top ten selling herbal products, the production of black cohosh supplements has the potential to threaten wild black cohosh populations. Alternatives to wild harvest, such as field and forest understory cultivation are being explored as a means to protect wild populations of black cohosh. The optimization of cultivation conditions such as shading, soil composition, and soil fauna has the potential to enhance the concentrations of medicinal compounds in black cohosh root and improve the quality of commercial products. Although the active ingredients in black cohosh rhizomes have not been determined, rhizome...
Due to climate change it is becoming increasingly important to decrease atmospheric CO₂. One climate change mitigation strategy would be through the process of carbon sequestration. This poster will describe the methods used in the GSU Chemistry Department to measure the total organic carbon (TOC) content of soil samples generated during a collaborative study with the GSU Biology Department that will investigate the carbon sequestration potential of Switchgrass (*Panicum virgatum*). The TOC measurement method involves high temperature (900°C) heating of soil samples in an O₂ carrier gas flow to release organic carbon. A Pt catalyst converts all released organic carbon to CO₂, and the CO₂ is then detected by IR absorption. The instrument used is the Shimadzu TOC (V series) with Solid Sample Module (SSM). This poster will also describe plans to measure carbon isotopes using the Skidaway Institute Scientific Stable Isotope Laboratory (SISSIL) at the Skidaway Institute of Oceanography (Savannah, GA). A preliminary acid treatment will be performed on the samples to remove the inorganic carbon, and prepare them for the isotopic analysis Isotope-Ratio Mass Spectrometer. These results will determine the distribution of carbon isotopes in the soil before the Switchgrass is planted, and after it is harvested.
SYNTHESIS AND CHARACTERIZATION OF MICROEMULSION POLYMERIZATION OF CROSSLINKED POLYMETHYL METHACRYLATE-NET-POLYETHYLENE GLYCOL DIMETHACRYLATE ENCAPSULATED POLYSTYRENE

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The synthesis and characterization of microemulsion polymerization of crosslinked PMMA-net-PEGDMA encapsulated linear Polystyrene (PS) is represented. Microemulsion polymerization synthesis using a sodium dodecyl sulfate (SDS) solution was used to prepare the polystyrene within the micelles. The linear polystyrene within micelles was encapsulated by crosslinking PMMA-net-PEGDMA around the polystyrene. Polymer characterization techniques such as viscometry, gel-permeation chromatography, and static light scattering were used to analyze the polymer material. The purpose of encapsulating the polystyrene is to lower the free volume of the linear polystyrene. Lowering the free volume of the polystyrene in the encapsulation is theorized to lower the glass transition temperature of polymeric material. The encapsulated polymeric material may have novel, rubber-like properties at room temperature.

Figure 1. Synthesis in the encapsulation of the PS using microemulsion: a) Pzn of the linear PS b) Pzn encapsulation of the PS with the crosslinked PMMA-net-PEGDMA and c) surfactant removal.
SOL-GEL ENCAPSULATED HORSE RADISH PEROXIDASE: A PEROXIDATION EXPERIMENT IN SEARCH OF THE MOST SUITABLE ENVIRONMENT

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Sol-gels are porous and optically transparent glass monoliths that have various functions. Their applications and development in biomedicine have shown promise for new biosensors and artificial organs. Sol-gels can be synthesized from various starting materials including tetramethoxysilane (TMOS) and tetraethoxysilane (TEOS). These starting materials create different pore sizes and byproducts that will allow a comparison of which process is a more suitable environment for enzyme encapsulation. Several types of sol-gels doped with Horseradish Peroxidase (HRP) are synthesized and investigated. Effectiveness is gauged via UV-Vis spectroscopy and analysis of the affinity of HRP for hydrogen peroxide is measured using concentration values obtained from the Beer-Lambert law. The syntheses and characterization of these materials are highlighted in this presentation.

PEO-BASED HYBRID HYDROGELS WITH HAIRY NANOPARTICLES AS POLYFUNCTIONAL CROSSLINKER

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Hydrogels, consisting of a crosslinked 3-dimensional (3D) polymeric network swollen with water, are used in multiple applications such as drug delivery, chemical sensing, and tissue engineering. Synthetic hydrogels, however, tend to be brittle and lack toughness. It has been shown that both high network uniformity and the incorporation of nanoparticles can enhance the mechanical properties of hydrogels. This work is aimed at fabricating hybrid hydrogels with advanced mechanical properties using thiol-terminated polymer brush-grafted silica nanoparticles (hairy nanoparticles) as polyfunctional crosslinker to react with allyl end-functionalized poly(ethylene oxide) (PEO) via “thiol-ene” click chemistry. The first step, the functionalization of chain ends of PEO, is accomplished through a nucleophilic substitution reaction between hydroxyl-terminated PEO and allyl bromide. The hairy nanoparticles are synthesized by surface-initiated reversible addition fragmentation chain transfer (RAFT) polymerization from benzyl dithiobenzoate-functionalized silica nanoparticles, which are prepared by immobilizing a benzyl dithiobenzoate-terminated triethoxysilane onto the surface of silica nanoparticles. After the reduction of the chain ends of polymer brushes to thiol groups, the hairy nanoparticles are used to crosslink allyl-functionalized PEO via “thiol-ene” click chemistry to form a 3D network. By synthesizing these mechanically advanced hydrogels, new research, and thus technology, can begin to develop in many fields.
SYNTHESIS AND CHARACTERIZATION OF FUNCTIONAL POLYMERS BEARING AMINO-TRIAZINE

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Abstract:

In recent years, functional polymers are being widely used in different high-technology applications. Polymers bearing amino-triazine functionality are interesting materials in this regard. The amino-triazine functionality can lead to polymers that assemble to form supramolecular architectures having multiple hydrogen bonding. These polymers can be used in membranes for preferential separation of various substrates. In this investigation, 2-Vinyl-4,6 diamino-1,3,5 triazine (DVT) was homopolymerized and copolymerized with suitable monomers like styrene via free radical polymerization. Polymerization of DVT can also be carried out via controlled radical polymerization (CRP) using a suitable chain transfer agent (CTA) to obtain tailor-made polymers with controlled molecular weights and controlled functionality. These functional polymers will be characterized using NMR, FT-IR, size exclusion chromatography and Matrix Assisted Laser Desorption/Ionization Time-of flight Mass spectrometry. The thermal properties will be evaluated using differential scanning calorimetry and thermograviometric analyses.

Scheme 1. Copolymerization of (a) 2-Vinyl-4,6 diamino-1,3,5 triazine, (b) styrene via free radical polymerization.
Stimuli-responsive polymers or “smart” polymers are high-performance polymers that undergo reversible or irreversible, physical or chemical changes in response to small external changes in the environmental conditions such as pH, temperature, and light intensity. The responsive nature of these polymers can be brought about by the use of protecting group linkers. The use of light as a stimulus has attracted much interest because of its distinct advantages. Light characteristics can be remotely and accurately controlled, quickly switched, and easily focused into targeted areas. Also, these specific responses can be brought about and controlled from outside the system without the use of chemicals. The current study focuses on developing a hydroxyl photocleavable protecting group (PPG)-based photolinker that will be incorporated into a stimulus-responsive polymer chain. The hydroxyl PPG-based photolinker can be utilized in several fields such as biological research, biomedical engineering, and drug release.
INVESTIGATION OF THE HYDROSILYLATION OF VINYL PYRIDINE WITH TRICHLOROSILANE

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With the goal of creating multifunctional solid acid building block catalysts, the targeted incorporation of tethered pyridinium and imidazolium groups has been explored. The key aspect leading to such functionalized silicate matrices is the preparation of the ionic precursor via hydrosilation of vinyl pyridine with trichlorosilane. Organic synthetic techniques to produce 4-(2-trichlorosilyl) pyridine have been previously reported, which provide evidence that an ionic precursor has to be synthesized prior to the synthesis of 4-(2-trichlorosilyl) pyridine. We hypothesized that the experimental procedure for the synthesis would proceed without a metal catalyst. The synthesis of the 4-(2-trichlorosilyl) pyridine precursor without a traditional metal catalyst is described. We employed a wide-ranging variety of methods of organic synthesis by varying the temperature, solvent, and reaction time until the optimum conditions were established. Proton (\(^1\)H) and (\(^{13}\)C) NMR spectroscopic techniques was used to confirm the identity of the targets. We have found that the reaction requires a small amount of base to prevent proton transfer reactions. Additionally, our experimental design has provided a method to produce 4-(2-trichlorosilyl) pyridine precursor in high yields. Our studies have also proven that a coordinating solvent is needed, a non-coordinating base is required, and mild heating is required to produce the 4-(2-trichlorosilyl) pyridine precursor. These findings will be helpful for the breakdown of cellulose and can utilize renewable resources for bio energy, bio fuels, and other biodegradable chemicals. Future work will consist of the addition of sulfonic acid to the precursor of 4-(2-(trichlorosilyl) pyridine, incorporation into the silicate matrix, and catalytic testing.
SYNTHESIS OF NOVEL BIS-1,2,4-TRIAZINE LIGANDS FOR CHEMOSELECTIVE MINOR ACTINIDE EXTRACTION

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Nuclear energy continues to support increasing global energy demands at the expense of generating significant quantities of radioactive byproducts from spent fuel. Radionuclides derived from the lanthanides and actinides present risks to human health and the environment. Lewis basic donor ligands have been investigated for the effective extraction of minor actinides from lanthanides. The removal and transmutation of the minor actinides from spent nuclear fuel will greatly reduce storage time from thousands of years to hundreds of years, thus making nuclear power generation safer and more efficient. The goal of this project is to evaluate the significance of heterocycle conformational rigidity and overall ligand hydrophobicity towards the chemoselective coordination of minor actinides. Route scouting has provided access to a series of novel bis-1,2,4-triazine ligands via condensation of 1,2-dicarbonyls with [1,10]-phenanthroline-2,9-dicarbonitrile and 2,6-pyridinedicarbonitrile scaffolds. Alternative experimental conditions have been discovered that enhance conversion to the corresponding bis-hydrazonamides. Trituration and anti-solvent recrystallization methods have been developed to efficiently afford the desired ligands in good telescoped yield over two steps without additional purification. Ligands prepared in our lab derived from aromatic 1,2-dicarbonyls possessing a para-substituted halogen atom provide a strategic opportunity to afford functionalized derivatives via metal-mediated coupling experiments in an effort to produce materials with enhanced solubility. Evaluation of radiolytic and hydrolytic stability data collected from solubility and kinetic studies will provide guidance in the future approach for the synthesis of more effective ligands. The efficient synthesis and initial separations data of novel ligands based on a [1,10]-phenanthroline-2,9-dicarbonitrile scaffold will be presented.

SYNTHESIS OF COMPLEX HETEROCYCLES VIA NOVEL TRANSITION METAL-CATALYZED REACTIONS

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Functionalized heterocycles have played an increasingly important role in the development of novel pharmaceutical compounds. Aziridinones are of great interest due to their highly strained 3-membered heterocyclic ring structure. Based on the strength of the nucleophile, aziridinones can ring open at the C-2 and C-3 position to give a library of potential products. In 1984, Howard Alper converted aziridinones into azetidine-2,4-diones using rhodium and cobalt complexes providing the first example of metal insertion into these compounds, but the 3-membered heterocycles ring opening chemistry has yet to be explored. We believed that by inserting a metal into these aziridinones, the complexes formed could perform further chemistry with highly functionalized compounds. We have developed a new transition metal-catalyzed process for the N-functionilization of a variety of heterocyclic precursors. The benefit of the developed method is that complex heterocycles may be synthesized from strained heterocyclic precursors under mild reaction conditions in 25 minutes.
9 EFFORTS TOWARD THE ASYMMETRIC TOTAL SYNTHESIS OF HAMIGEROMYCN B

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Hamigeromycin B is an aromatic natural product isolated as a fungal secondary metabolite of the soil fungus *H. avellanea* found in Thailand in 2008. This resorcylic acid lactone has an extensively functionalized polyketide subcomponent and possesses structural features similar to molecules that display anti-malarial activity, selective cytotoxicity, as well as inhibitory action of HSP 90. Synthesis of the desired pyrone was accomplished utilizing a Jacobsen asymmetric hetero-Diels-Alder reaction between Danishefsky’s diene and an optically pure aldehyde prepared in two steps from chiral pool. Subsequent functionalization via conjugate addition and oxidation via the Rubottom protocol have been accomplished. Construction of the requisite aromatic synthon was realized in four steps from 2,4,5-trimethoxybenzoic acid. Completion of the total synthesis via a lactonization/ring-closing metathesis protocol highlights the proposed convergent preparation of the target in eleven steps for the longest linear sequence. The successful completion of the aromatic synthon and substantive progress towards the functionalization of the pyranone ring will be described.

10 SYNTHESIS OF D-GALACTOSE LIGANDS FOR NANOSTRUCTURES AND GLYCOSIDE ARRAYS

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The aim of the project is to develop a deeper understanding of the binding of carbohydrates to their cellular recognition proteins, which are known as lectins. Carbohydrates are found on the outer membrane of cells and help to distinguish one cell type from another and provide a means for pathogen recognition. The mechanism of cell recognition by lectins is not well understood as little research has been performed in this field. The current project focuses on the binding of mannose-binding lectin (MBL), which is a key protein in mammals for the recognition of fungi and yeast and so is an important part of the body’s immune system. Synthetic work is underway to explore the specific role sugars/configurations play in these events. By varying the sugars (e.g., mannose (Man) or galactose (Gal)), the binding constants can be determined for a specific interaction for a sugar–lectin complex. Significant progress has been made in the synthesis of α-D-Gal-(1,6)-α-D-Gal-disaccharide, α-D-Gal-(1,4)-α-D-Gal-disaccharide, α-D-Gal-(1,3)-α-D-Gal-disaccharide, and α-D-Gal-(1,2)-α-D-Gal-disaccharide. The glycosyl acceptor monosaccharides are under synthesis, and work is being conducted for the synthesis a glycosyl donor molecule that will be used to complete the coupling to synthesize the disaccharides for biological studies. In our case we will use immobilized sugars tethered to a solid support. The issues of sugar linkages (valency and structure) vs. sugar density can be determined using arrays of sugars immobilized to the solid support.
11 SYNTHESIS OF β-KETOESTERS THROUGH KETENE INTERMEDIATES

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β-ketoesters are used as building blocks for natural products and pharmaceuticals. The current synthesis of β-ketoesters is wasteful, toxic, and expensive with almost no stereospecificity. Ketenes can be generated at such low costs, but have never been used to synthesize ketoesters. Reactions of ketenes and Cinchona alkaloid derivatives form zwitterionic enolates that are readily able to attack esters in a Claisen-like Condensation reaction.

12 SYNTHESIS OF PHOTOACTIVE DAG ANALOGS VIA CLICK CHEMISTRY

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Diacylglycerol (DAG) is a lipid found in cellular membranes. It is involved in the composition of protein receptor regions on the cell surface. DAG functions to recruit and anchor important proteins, such as protein kinase C (PKC), to the membrane surface. This results in the activation of the bound protein. PKC is involved in cell growth and proliferation pathways and is aberrant in cancer cases. Due to the important biological properties of DAG, there is significant interest in understanding the proteins this molecule activates and the mechanism by which these interactions occur. To address this issue, an approach is taken in which a probe analog of DAG is developed to label and identify DAG-binding proteins from complex biological samples. In this project, we describe a synthetic pathway to produce an analog of DAG with a benzophenone crosslinker and an azide that can be derivatized by click chemistry. The benzophenone group undergoes a reaction that leads to insertion into the protein upon irradiation, strengthening the lipid-protein complex. The azide can be clicked to a fluorescent tag that can be imaged in an active system, thereby quantifying the target protein. By derivitizing the DAG lipids with these tags, it is proposed that specific proteins can be tracked in an active biological system. The lipid analogs can also be used to ‘fish’ target proteins out of cell extracts for further study. The following research was successful in synthesizing a specific photoactive tag, with further research aimed at complete synthesis of the target DAG analog.
STRUCTURAL STUDIES OF 1,Ν6 – (2-HYDROXY-3-HYDROXYMETHYLPROPA-N-1,3-DIYL)-2'-DEOXYADENOSINE, A MUTAGENIC ADDUCT INDUCED BY 1,2,3,4-DIEPOXYBUTANE

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1,2,3,4-epoxybutane DEB is the ultimate carcinogenic metabolite of 1,3-butadiene (BD) by cytochrome P450. Various industrial processes utilize BD, including the manufacture of tires, paints, hoses, and gaskets. Additionally BD is present in automobile exhaust and cigarette smoke (1). DEB reacts with deoxyadenosine to form the mutagenic lesion 1,Ν6 – (2-Hydroxy-3-hydroxymethylpropan-1,3-diyl)-2'-deoxyadenosine (1,Ν6-γ-HMHP-dA) (2).

Tretyakova’s group has shown that human polymerases (hpol) β was blocked, while hpol ι was able to place the correct base opposite this lesion without further extension. However, hpols η and κ and the archaebacteria polymerase Dpo4 did bypass the 1,Ν6-γ-HMHP-dA adduct, with correct base incorporation of 80%, 18%, and 59%, respectively. Other products included incorporation of adenine or guanine, as well as frameshift mutations (3).

The goal of our work is to elucidate the structure and stability of 1,Ν6-γ-HMHP-dA in a DNA duplex (5'- C1 G2 G3 A4 C5 Y 6 A7 G8 A9 A10 G11 –3': 5' C12 T13 T14 C15 T16 T17 G18 T19 C20 C21 G22 – 3', where Y is 1,Ν6-γ-HMHP-dA). In this duplex, thymine is paired opposite the adduct, which reflects the correct pair for error-free bypass even though the adduct prevents normal Watson-Crick base pairing. The modified and unmodified spectra were similar aside from alterations to the protons near the adduct, suggesting localized perturbation of the structure.

The largest NOESY chemical shift changes were observed for the adduct. UV melting studies demonstrated that the lesion destabilized the duplex.


FORMATION OF CYCLOHEXENYL CATION BY REACTION OF 3- AND 4-METHYLCYCLOHEXENE IN VARIOUS CONCENTRATIONS OF SULFURIC ACID

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Protonation of alkylated cyclohexenes in the 0.1 mM range using 70-96% w/w sulfuric acid in water gives rise to various cyclohexenyl cations absorbing in the range 280-330 nm, depending on position and number of alkyl groups. In order to understand the role of the acidity on this reaction, as well as position of the alkyl group relative to the π-bond, time-series absorbance spectra were obtained in the protonation of 3- and 4-methylcyclohexene (Figure 1) at various concentrations of sulfuric acid. Reactions were carried out at 60°C. Initial results showed that a strong absorbance band in the region expected for a cycloalkenyl cation was formed at sulfuric acid concentrations in the range 78-83% for 3-methylcyclohexene, and in the range 80-94% for 4-methylcyclohexene. At sulfuric acid concentrations above either of these ranges evidence for formation of the cycloalkenyl cation was not observed.

Fig. 1: Mechanism for acid-catalyzed disproportionation of 4-methylcyclohexene.
DEVELOPMENT OF NOVEL MITOCHONDRIALLY-TARGETED ELECTROPHILIC COMPOUNDS AS POTENTIAL ANTI-METASTATIC DRUGS IN BREAST CANCER CELLS

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When breast cancer is diagnosed with metastasis, the survival falls to 23%. Up to 40% of all patients who are treated for localized breast cancer develop metastasis. Currently, there is no therapeutic strategy for metastasis prevention or targeting and current treatments rarely lead to long-term survival of patients without disease recurrence. Thus, there is an urgent need to develop drugs which inhibit metastatic properties, including cancer cell adhesion and migration. Our laboratory has recently observed that a mitochondrially-targeted electrophilic compound (IBTP) inhibits cell adhesion, at concentrations which do not elicit overt cell death. The overall objective of this project is to rationally modulate the key chemical features of IBTP in order to improve its anti-adhesion activity. We have conducted studies changing the linker length as well as the leaving group present in IBTP. Synthesis, characterization and biological evaluation of these IBTP analogs will be presented.

EFFECT ON THE RATE OF AN ACID-CATALYZED DEHYDRATION BY VARYING THE COSOLVENT CONCENTRATION

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Acid-catalyzed dehydration of cyclohexanols in the 0.1 mM range using ~70-96% w/w sulfuric acid in water is known to give rise to cyclohexenyl cations which show a strong absorbance band (ε = ~10,000) in the region near 300 nm. Formation of the cyclohexenyl cation is attributed to hydride abstraction from previously formed alkene by the cyclohexanyl cation that forms upon loss of the protonated hydroxy leaving group. In order to understand the influence of the presence and position of alkyl groups on the hydride-abstraction cyclohexenyl cation, dielectric constant of the reaction medium was adjusted by replacing water with equal molar amount of methanol. Results from time-series absorbance spectra showed that increasing polarity of the solvent is used the pathway of the reaction is less likely to allow the persistence of a carbocation then when water is used.
THE INFLUENCE OF MOLECULAR STRUCTURE ON THE FORMATION OF EUTECTIC COMPOUNDS

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In order to understand the role of molecular structure in the formation of eutectic compounds, we measured the melting, crystallization, and glass transition temperatures of three sets of binary mixtures of lidocaine with saturated fatty acids of varying alkyl chain length (n = 10, 14, 18). We observed a decrease in the eutectic temperature and a strong shift of the eutectic concentration toward higher acid content as the length of the aliphatic tail was decreased. Furthermore, for the n = 10 fatty acid we observed a relatively wide range of “deep eutectic” compositions with no measurable melting or crystallization temperatures and practically identical glass transition temperatures. These results are discussed in the framework of current theoretical models of binary mixtures.

Fig. 1. Lidocaine: Saturated fatty acids mixtures of various concentrations
SYNTHESIS AND PHOTOPHYSICAL ANALYSIS OF POLYCYCLIC AROMATIC COMPOUNDS

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Various polycyclic aromatic compounds were synthesized via Pd-catalyzed coupling reactions such as the Suzuki, Sonogashira, and Stille reactions. The target molecules were good candidates for singlet fission, based on their ability to form stable di-radicals. Once synthesized, these compounds were purified using column chromatography and characterized using NMR and X-ray crystallography. Each compound was then subject to UV/Vis and fluorescence spectroscopy in order to observe the photophysical properties. The effects of electron-donating groups compared to electron-withdrawing groups were observed. The spectra showed that there is no significant difference between electron donating groups and electron withdrawing groups on these types of polycyclic aromatic compounds. Additionally, the spectra showed no indication of the process of singlet fission. In future studies, the push-pull electronics of polycyclic aromatics can be studied by having a combination of electron-withdrawing groups and electron-donating groups on a single molecule. This could promote further di-radical stabilization so that singlet fission would be more likely to occur.
19 STUDIES ON THE ORIGINS OF REAGENT-CONTROLLED ASYMMETRIC INDUCTION IN THE HETERO-DIELS ALDER REACTION OF CHIRAL β-ALKOXYALDEHYDES WITH ENANTIOPURE CHROMIUM (III) CATALYSTS

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The Jacobsen hetero-Diels-Alder reaction is an efficient manifold for creating chiral six-membered heterocycles. This project investigates the synthesis of pyrone adducts from protected chiral β-hydroxyaldehydes and Danishefsky's diene utilizing a variety of enantiopure chromium (III) catalysts. Experiments have been designed to probe the role that steric and electronic effects on the optically pure aldehyde influence towards “matched” and “mismatched” asymmetric induction. In synthetic routes where unsuccessful substrate control has been observed, selection of a suitable catalyst is critical. Studies evaluating chiral ligand, catalyst antipode and counterion, as well as the protecting group on the β-hydroxyaldehyde will be described. The results of this investigation will be leveraged towards the completion of the resorcylic lactone natural product hamigeromycin b.

20 SOLVATION ENTHALPIES OF ORGANICS INTO IONIC LIQUIDS

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Ionic liquids (ILs) are room temperature molten salts that have been used as non-volatile / non-polluting solvents. Although the solvation energetics of solutes can control their reactions (i.e. the S_n2 reaction in protic vs. polar aprotic solvents) almost nothing is known about the quantitative solvation of solutes in ILs. We have used solution calorimetry to measure such enthalpies for a wide range of organic molecules, into the thermochemical standard IL HMIM/Tf_2N. In comparison to the same quantity into water, there is a general parallel pattern, but interestingly the IL appears to be a better hydrogen bond acceptor than water, in spite of its weak basicity. The kinetics of dissolution have also been examined for a range of species.
SYNTHESIS OF 1,4-DI-[2'-(3'-HYDROXYCHROMONE)]BENZENE

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Recent results demonstrated that there is a significant transfer of substituent effects from the para position of the B ring to the 3-hydroxy-4-carbonyl position in flavonols (Fig. 1A). These results lead to the interesting prospect of significant electronic communication between two 3-hydroxychromone units across a benzene ring. Therefore, the synthesis of the novel title compound (Fig. 1B) was undertaken. It should also be highlighted that this new compound will form an interesting hydrogen bonding structure in the crystal.

In this presentation, the synthesis and characterization of the target compound will be described. In addition, the rationale for its synthesis including the recent results demonstrating significant communication of substituent effects from the 4' position of the flavonol B ring to the 3-hydroxy-4-carbonyl groups will be given. Lastly, some future studies involving the novel compound synthesized in this work will be described.

Fig. 1: (A) The structure of flavonols [2-phenyl-3-hydroxychromones] with numbering and ring labeling. (B) 1,4-Di-[2'-(3'-hydroxychromone)]benzene.
SYNTHESIS OF BENZOFURAN-2-CARBOXYLIC ACID DERIVATIVES
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3-Halocoumarins are readily converted into benzofuran-2-carboxylic acids via a Perkin (coumarin-benzofuran ring contraction) rearrangement reaction. Benzofuran-2-carboxylic acid derivatives are known for exhibiting various pharmacological activity such as anti-inflammatory properties, selective cytotoxicity against human cancer cells, human lymphoma cells U937, lymphoblastoid cells TK6, leukemia cells THP, and adenocarcinoma cells H441. Additionally, benzofuran-2-carboxylic acids bearing DNA-binding groups are structural subunits of synthetic analogues of some natural antitumor agents such as CC-1065, duocarmycin, dystamycin, and netropsin. This research focuses on the syntheses of benzofuran-2-carboxylic acid derivatives relevant to the development of novel solutions to immune system and radiation risks that have plagued the National Aeronautics and Space Administration (NASA) agency and its astronauts. We hypothesized that Benzofuran-2-carboxylic acid derivatives will prevent the immune dysfunction which occurs as a result of exposure to deep-space radiation, microgravity, and infectious agents from other crew members during long-term space flights. As a result, we have successfully optimized the synthesis of benzofuran-2-carboxylic acids and derivatives under mild conditions in good yield.
SECURING A RELIABLE SOURCE OF SHIKIMIC ACID

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Shikimic acid is vital to the production of Tamiflu\textsuperscript{TM}. As new strains of the flu virus surface, the demand for shikimic acid skyrockets to meet the need for Tamiflu\textsuperscript{TM}. Chinese star anise, the principal source of shikimic acid, has proven unable to meet the world demand during pandemics. Alternate sources such as microbial fermentation, chemical synthesis, and plant extraction are under intense investigation. The overall goal of our research is to secure a reliable source of shikimic acid by either finding a new plant source of shikimic acid or developing a cheaper shikimic acid synthesis. This poster presents our progress in identifying a new plant source of shikimic acid. Gingko, Loblolly Pine, Sweetgum, Kudzu, Mimosa, and Eastern Red Cedar were chosen as preliminary plants to be evaluated as dependable sources of shikimic acid. Ginko and Sweetgum are known to contain significant amounts of shikimic acid and served as controls to validate our chromatographic methods. Thin layer chromatography (TLC) and paper chromatography methods were sought as easy, rapid, and reliable techniques for detecting shikimic acid in plants. The paper chromatography method is still under development, but an 8:1:1:1 mixture of ethyl acetate, ethanol, acetic acid, and water that gave a 0.5 retention factor (Rf) for shikimic acid on silica gel TLC plates was found. High pressure liquid chromatography (HPLC) will be used to validate the paper chromatography and TLC methods and to quantitate the shikimic acid content of plant material.
A NEW SYNTHETIC APPROACH TO DISTAMYCIN A

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Distamycin A is a natural antibiotic and anticancer agent from which the lexitropsin family analogs are designed. Like other lexitropsins, it is an oligopeptide DNA-binding ligand which displays sequence-specific binding affinity. Distamycin A binds specifically to AT-rich sequences in the minor groove. While it can be obtained from the actinobacterium species Streptomyces distallicus, there are several synthetic approaches which are more convenient and cost-effective. Our research team aims to complete a new synthetic approach which starts from a commercially available N-methylpyrrole derivative, and, through optimized ordering of the introduction of pyrrole substituents and joining of these units, will allow for a larger scale production than what has been previously reported. This will advance studies of DNA binding both at UAB and abroad.

PROGRESS TOWARDS CO-CRYSTALLIZATION OF THE BROAD RANGE THERMOPLASMA ACIDOPHILUM NUCLEOSIDE KINASE (TANK) WITH SUBSTRATES

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The Thermoplasma acidophilum nucleoside kinase (TaNK) is involved in pyrimidine and purine biosynthesis pathways in bacteria, and has already been crystallized in its unbound state. However, there still remains much ambiguity as to how its active site residues correlate to its broad nucleoside substrate specificity. This challenge traces back to the wider dearth of knowledge on the protein structure-function relationships, as we are yet unable to confidently predict the ligand-binding interactions of proteins based on their structures alone. To address this issue, we propose to determine the TaNK protein–ligand interactions using two approaches: we will co-crystallize TaNK in the ligand-bound state and determine the effects of introducing specific mutations at the active site on TaNK activity. The former strategy would provide data on the specific interactions between TaNK and substrates. Specific mutations at the nucleoside-binding pocket that explore important functional groups through replacement and systematic variations will be analyzed with respect to TaNK’s kinetic properties. Defining the elusive tie between protein structure and function will provide a fundamental understanding for bioengineering and drug-discovery—as well as specific information about nucleoside kinase substrate specificity.

CHEMOENZYMATIC SYNTHESIS OF CHIRAL 4-AMINOALCOHOLS

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Amino alcohols are found in a wide variety of biologically active compounds and have been used as chiral ligands for transition metal catalysts and to induce chirality. Synthetic methodology that will allow for generation of both enantiomers of 2-alkyl-4-aminoalcohols is presented herein. Reduction of diethyl 2-benzylimalonate with LiAlH₄ yields a 2-benzyl-1,3-propanediol in good yields. To introduce the needed chirality, Bulholderia cepecia lipase was used to selectively acylate 2-benzyl-1,3-propanediol. The resulting acyl alcohol was used as a chiral intermediate from which both enantiomers of a 2-benzyl-4-amino-1-butanol can be synthesized. Synthesis of the (R)-enantiomer is accomplished through oxidation of the alcohol moiety to an aldehyde, a Wittig reaction, hydrogenolysis and a Curtius reaction. Synthesis of the (S)-enantiomer requires modification of the protecting group strategy. The free alcohol is first protected as a TBDMS ether and the acyl protecting group is removed by treatment with K₂CO₃. The alcohol can then be subjected to the same oxidation/Wittig/Curtius sequence as those used to make the R-enantiomer. The synthetic route outlined above produces good yields in each step and results in synthesis of both enantiomers of 2-benzyl-4-amino-1-butanol from a common acyl alcohol intermediate.

COMPARING PARTIALLY DENATURED AND NATIVELY UNFOLD PROTEIN STATES

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In the human genome, one in four proteins are predicted to contain a region of intrinsic disorder at least 30 residues long. These intrinsically disordered proteins (IDPs) are even more significant in human disease. For example, in neurodegenerative diseases, IDPs account for nearly 70% of the relevant human proteins. The structure of IDPs is not fully understood because the dynamic ensemble of structures in IDPs is extremely difficult to model accurately. This makes the design of IDP-targeted drugs very challenging. Our goal is to develop new experimental approaches for characterizing IDPs. Here, we investigate the similarities between IDPs and partially denatured proteins. Most IDPs are challenging to study because of their complexity; therefore, an appealing first step is the development model proteins capable of exhibiting intrinsic disorder under physiological conditions. Starting with GB3, a small globular protein, we have introduced mutations to create an artificial, IDP-like state. Using chemical denaturation, we have measured the thermodynamic stabilities of these variants. Circular dichroism spectroscopy was also used to assess secondary structure. These IDP-like variants are suitable for studies using NMR spectroscopy, and future efforts will focus on using NMR to measure the folding kinetics of these GB3 variants. Ultimately, this data allow us to compare how IDPs differ from conventionally denatured protein.
28  SHORT TERM DIRECT ELECTRIC CURRENT EXPOSURE DECREASES VIABILITY AND INCREASES CASPACE-3 ACTIVITY IN COLON CANCER CELLS

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Recently, treatment of tumor cells with electric current has been shown to induce apoptosis in human leukemic and oral mucosa cancer cells. Here we demonstrate anti-proliferative and apoptotic effects of direct electric current (DC) exposure on human SW480 and HCT116 colon cancer cells using a sophisticated electrochemical approach. Our experimental system uses microfabricated interdigitated platinum electrodes on silica chips in a three electrode configuration interfaced with an electrochemical potentiostat. The two interdigitated electrodes function as the working and reference electrodes while a folded Pt wire functions as the counter electrode. Cells were grown on electrode chips using RPMI media (SW480) and McCoy’s media (HCT116) contained within silicon gasket frames. Cells were exposed for 300 s (six controls, six test) to a DC field strength of 1.6-2.3 V/cm with current densities ranging from 0.05 -5 µA/cm². After 24 h the cells were tested for: 1) cell viability (2 x 10⁴cells/chip) using a tetrazolium/formazan assay and 2) apoptosis (2 x 10⁵cells/chip) using a caspase 3/7 assay. We find that caspase activities in HCT116 cells increased directly in proportion to electric current exposure and significant increases occurred at currents below those that adversely affect cell viability (<600 µA). Interestingly, significant differences in DC effects were observed between the two cell lines: SW480 and HCT116 cells exhibit 5-fold and 3-fold caspase induction peaks at 100 and 800 µA, respectively. SW480 and HCT116 cells begin to demonstrate loss of cell viability at 200 and 800 µA respectively. Compared to SW480 cells, HCT116 tolerate higher currents before exhibiting caspase induction or loss of cell viability.

29  INHIBITION OF MURA BACTERIAL ENZYME USING ORGANIC SYNTHESIS METHODS

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MurA is a key bacterial enzyme that catalyzes the first committed step in the formation of peptidoglycan in both Gram-positive and Gram-negative bacterial cell wall. So far there exists only one commercially available antibiotic, fosfomycin, that behaves as a MurA enzyme inhibitor. Unfortunately the effectiveness of fosfomycin has been reduced over the years. Based on the research done in the past, new potential inhibitors have been discovered, and such compounds can be synthesized by modifying Diels-Alder cycloaddition reaction adducts. These Diels-Alder adducts can be modified to form products that contain functional groups such as carboxylic acids, amides, and other functional groups that exhibit both polar and non-polar properties, allowing the compounds to function as prospective MurA inhibitors. The potential inhibitors that were synthesized are being tested in the presence of both Gram-negative and Gram-positive bacteria, as well as purified MurA enzymes for in vivo and in vitro results.
BIOLOGICAL VALIDATION AND COMPUTATIONAL MODELING OF DBM-GR INTERACTIONS IN HORMONE REFRACTORY PROSTATE CANCER

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Molecular Operating Environment (MOE) is modeling software that allows crystallized structures to be analyzed virtually to simulate drug interactions that occur in the body. This is an important step in the new age of drug development because it can give us preliminary data about how a drug interacts in a receptor before in vitro and in vivo testing. For cancers, like hormone refractory prostate cancer (HRPC), where an effective treatment has yet to be found, being able to test the effectiveness of potential anti-cancer drugs through computational methods could help speed up the discovery process. Current treatments being used for HRPC are glucocorticoid steroids such as dexamethasone (DEX). Although DEX has favorable effects on treatment of prostate cancer cells through glucocorticoid receptor (GR) signaling, its exact mechanism of action is unknown. Small molecules such as dibenzoylmethane (DBM) which potentially targets the GR signaling pathway may provide an effective treatment for HRPC. Computational and modeling data revealed that DBM (A) was able to find a binding site within the GR, without needing DEX (B) to conform. DBM was also found to be a more stable compound than DEX, based off binding energies, so it naturally fit better in GR. To further validate the computational data, in vitro studies were conducted. Cell proliferation assays showed growth inhibitory effects of HRPC cells (LNCaP) in response to 50 μM DBM and 20 nM DEX over three days. In order to see whether DBM can be used as a potential therapy for HRPC, GR protein expression in LNCaP will be examined by Western blotting. These data should demonstrate if DBM and DEX are working in a similar mechanism on the GR.

\[ \Delta E = 6058.050 \text{ kJ/mol} \]  
(DBM)

\[ \Delta E = 6378.234 \text{ kJ/mol} \]  
(DEX)

**Figure 1:** Docking Models of DBM and DEX in Glucocorticoid Receptor. The crystal structure of DEX and GR was obtained from the RCSB Protein Data Bank (PDB code 1P93 and 1NHZ, respectively). The three-dimensional structures of the DBM were generated using the software MOE 2010.11.
THE SYNTHESIS OF SIGMA RECEPTOR LIGANDS

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There are two different sigma receptors in the body, sigma-1 and sigma-2. Sigma-1 has received the most scientific attention to date. Previous research of sigma-1 receptors showed that various drugs act as ligands and bind to the sigma-1 receptor. These drugs are antipsychotics, neuroleptics, and neuroactive steroids. Sigma-1 receptors are located in various areas of the human body both centrally and peripherally. Sigma-1 receptors function as a modulator for dopamine, acetylcholine, NMDA, and opioid receptors. Sigma-1 receptors have potential application in the treatment of addiction as well as other neurological disorders such as Alzheimer’s and Parkinson’s. A common feature of sigma-1 ligands is an amine moiety, such as an N-alkyl, N, N-dialkyl, or N-aryalkyl. We are currently engaged in the synthesis of amide derivatives of benzofuran carboxylic acids via a DCC\DMAP condensation reaction in an effort to produce ligands that are selective for the sigma-1 receptor. The produced amide derivatives will be sent off to the National Institute of Mental Health-Psychoactive Drug Screening Program (NIMH-PDSP). Screening will take place over a panel of G-protein coupled receptors (GPCRs) and molecular targets. Compounds showing greater than 50% inhibition of radioligand specific binding at specific GPCRs and molecular targets are forwarded for additional screening to determine Ki values.

PROGRESS TOWARDS UNDERSTANDING OPAD INTERACTIONS WITH CEACAM1

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Isothermal Titration Calorimetry (ITC) is a fast, accurate and label free method of developing a quantitative understanding of thermodynamics of molecular interactions, such as binding affinities between proteins. We are using ITC to investigate the binding thermodynamics of opacity-associated (OpA) adhesion proteins, (found of the surface of Neisseria meningitidis and Neisseria gonorrhoeae) and carinoembryonic antigen-related cell adhesion molecules (CEACAMs, found on the surface of human host cells). CEACAM1 binding OpAD (from FA1090 N. gonorrhoeae bacterial strain) and non-CEACAM1 binding OpA50 (from MS11 N. gonorrhoeae strain) have successfully been expressed in BL21(DE3) E.coli cells and purified using metal affinity chromatography. Additionally, the N-terminal domain of human CEACAM1 has been expressed in MC1061 E.coli cells with a GST fusion tag. Following the cleavage of the fusion protein, CEACAM1 was purified using size exclusion chromatography. Methods for obtaining higher yields of CEACAM1 for ITC experiments are being investigated. Once higher yields of CEACAM1 have been obtained, OpA proteins will be folded into liposomes and ITC experiments will be performed. The invasion efficiency of Neisseria pathogens is mediated by the interactions between OpA and CEACAM proteins; however thermodynamic information of the binding between these proteins has not been investigated. An understanding of the OpA – CEACAM interactions will provide information about Neisseria pathogenesis and about how foreign bodies can invade human cells, which may be of interest in the development of therapeutic delivery systems.
OPTIMIZING BIOLUMINESCENCE IN HUMAN EMBRYONIC KIDNEY CELL LINE HEK 293 USING GIBSON ASSEMBLY TECHNIQUE TO CREATE NOVEL PLASMID CONSTRUCT PLUXABCDE.

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Non-invasive bioimaging techniques are important because they aid in visualizing the physiological functions of the body in vivo. One method that is at the forefront of bioimaging research is the use of bioluminescence for detecting biological phenomenon in mammalian tissues. While lux cassettes can be expressed in mammalian cells, the intensity of the luminescence produced is not sufficient for some applications. In this study, the lux cassette (luxCDABE) which is responsible for bacterial bioluminescence was genetically modified by reshuffling the order of the genes in the cassette to create a novel plasmid construct pluxABCDE, with the hope of increasing the bioluminescence in transfected mammalian cells. The NEBuilder software was used to generate 20 bp primer fragments of CMVfrp, luxAB and luxCDEA and these were annealed using a relatively new technique called the Gibson Assembly. The novel construct was amplified in competent E.coli cells and transfected into human embryonic kidney cells (HEK 293). A comparison between the amount of light produced by the wild type and the new plasmid construct in the HEK 293 cells as observed using the IVIS Lumina Imaging system showed that there was a reduction in bioluminescence in the novel construct. This suggests that although the genes in the lux cassette can be reshuffled and successfully expressed in mammalian cells, this order is not optimal for light production.

UNRAVELING AMINOTRANSFERASE SPECIFICITY: THE ACTIVITY OF TM1131, TM1698, AND TM1255

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TM1131, from Thermotoga maritima, was putatively identified as a PLP-dependent aminotransferase (AT) and hypothesized to catalyze the amino group transfer from L-aspartate (Asp) to 2-oxoglutarate to form oxaloacetate and L-glutamate. This annotation was based primarily on analysis of the crystal structure of TM1131. However, additional Thermotoga proteins (including TM1255) were proposed to be AspATs on structural comparisons, suggesting a surprising redundancy of function in the proteome of Thermotoga. Spectrophotometric assays were conducted to investigate substrate specificity and to establish kinetic parameters of TM1131. Together with studies of other aminotransferases (TM1255, TM1698) from Thermotoga, these assays allow for a more accurate functional characterization of aminotransferase proteins from T. maritima.
IMMOBILIZATION OF LACTATE DEHYDROGENASE

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The reaction kinetics of Lactate Dehydrogenase (LDH) is commonly measured in free state. The purpose of this research is to encapsulate LDH in calcium alginate beads to simulate the enzyme activity in vivo and to measure the activity in comparison with the free state. In this work, a commercial LDH enzyme was used. A new technique was developed to increase calcium retention in the calcium alginate beads in order to encapsulate/reticulate the LDH enzyme, using Tris as a buffer. Results show that the calcium alginate beads maintain their rigidity and storage stability. Utilizing a continuous flow method, containing a NADH and pyruvate solution, column results show that the immobilized state activity is limited by diffusion compared to the free enzyme.
Enzymes are critical components in the treatment of cancer. For purposes of drug delivery, enzymes that are capable of converting molecules into active drugs endogenously are of particular interest. NAD(P)H:quinone oxidoreductase isozyme I (NQO1) is a good candidate for drug delivery as it is up regulated in a number of cancer tumors and is known to reduce quinones. Prodrugs are macromolecules or molecular agents that contain functional groups that can be cleaved by environmental stimuli, such as enzymes. Absent these functional groups, the newly formed drugs will have been delivered to specifically desired sites. NQO1 is a homodimeric flavoprotein that catalyzes the direct two-electron reduction of various quinones using NADH or NADPH as a cofactor. NQO1 is dispersed throughout the cytosol of cells and has been reported in the nucleus, endoplasmic reticulum, cellular membrane, and mitochondria. Human NQO1 is overexpressed in certain cancer tumor tissues, including liver, lung, colon, and breast tumors, thus making it a valuable target for activating stimuli-responsive drug delivery systems of quinone derivatives.

The reduction of quinones is catalyzed by NQO1. In this study, the mechanism will be explored. To do this, the rate of quinone reduction using NADH and β-side NADD (deuterated form) will be compared. β-side NADD is capable of producing the stereo specifically deuterated nucleotide so that it could be coupled to an enzyme with the correct stereospecificity. To determine the rate-limiting step, possible kinetic isotope effects (KIEs) will be examined. KIEs are used to determine reaction mechanisms by determining rate limiting steps and transition states. In a KIE experiment, an atom is replaced by its isotope and the change in rate of the reaction is observed. A very common isotope substitution is when hydrogen is replaced by deuterium. This is known as a deuterium effect and is expressed by the ratio kH/kD (ratio of the reaction rate of H to D). A KIE is a mechanistic phenomenon wherein isotopically substituted molecules react at different rates. Interpretation of the rate differences will provide information on the nature of the rate-determining step.

References


In 2001, Murata-Kamiya and Kamiya identified a cross-link between Klenow Fragment and deoxyguanosine residues of a short oligonucleotide strand while in the presence of the methylglyoxal, an endogenous α-ketoaldehyde. Methylglyoxal is formed mainly as a byproduct of carbohydrate metabolism and is also found in many food products. Since the Murata-Kamiya and Kamiya publication, the Rizzo Lab has proposed a structure for the aforementioned cross-link, suggesting a lysine residue as the cross-linking site of the peptide. We have reexamined the methylglyoxal-induced DNA-protein cross-linking reaction by gel electrophoresis and mass spectrometric analysis. Cross-linked Klenow Fragment was prepared in the presence of methylglyoxal, magnesium, and a short, duplexed oligonucleotide strand with a run of single-stranded guanine residues. The cross-linked product was isolated via SDS PAGE and subjected to a tryptic digestion, followed by deglycosylation of the DNA in formic acid. Mass spectrometric analysis of the sample revealed the loss of 205 KD from two lysine residues (Lys-597 and Lys-601) in the thumb domain of Klenow Fragment. This mass loss corresponds to the loss of cross-linked guanine from the peptide. Crystal structures of Klenow Fragment and a related DNA polymerases reveal that upon binding DNA, the thumb domain, which affects processivity, more closely associates with the DNA, putting Lys-597 and Lys-601 in proximity (~10 Å) for cross-link formation.
THERMOPHILIC COUPLING ENZYMES: ENABLING FUNCTIONAL STUDIES AT PHYSIOLOGICAL TEMPERATURES

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One of the challenges facing biology is that with the rapid completion of genomic sequences of organisms today, there are far more gene products than functions we can ascribe. Sequence and structural comparison give only limited information, and so comprehensively characterizing the cellular and biochemical function of an uncharacterized gene product requires additional experimental investigations. Spectrophotometric assays is one approach used to investigate enzyme function. Frequently an enzymatic reaction is not readily observable spectrophotometrically and coupling enzymes can be used to allow the indirect monitoring of the first enzymatic reaction. Ideally, the enzymatic assays should be performed at physiologic temperatures. This study reports on the characterization of thermophilic enzymes isolated from Thermotoga maritima that may be used as coupling enzymes: TM1867, a putative L-lactate dehydrogenase (EC 1.1.1.27) and TM0208, a putative pyruvate kinase (EC 2.7.1.40). We report progress towards determining the kinetic parameters of these thermophilic coupling enzymes; and hence, their potential to be used for investigating the function of thermophilic enzymes at physiological temperatures.

STEM-LOOP DNA AS STARTING MATERIAL FOR SELEX

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An aptamer is a single-strand oligonucleotide that is capable of binding a target with high selectivity and specificity. There are well developed methods for obtaining an aptamer, the most common being a method called SELEX. Though SELEX is a well-developed and efficient process, it still has its problems when obtaining a DNA aptamer. The SELEX method includes an extra purification step in order to convert the double-strand DNA into single-strand DNA. This extra step can be very expensive, time consuming, and results in a low yield. Aptamers have many industrial uses such as drugs or diagnostic tools. So it is important to improve the method. In order to avoid the purification setup of SELEX, stem-loop DNA is used as the starting material. In order for this method to be tested, a stable stem-loop DNA structure needed to be designed, characterized, amplified, and produce the correct product after amplification. A SELEX procedure has been designed.

Fig. 1: Stem-loop Structure of DNA
A COLORFUL LOOK AT HNO: VALIDATION OF A FLUORESCENCE-BASED METHOD OF DETECTION BY PHOSPHINE PROBE

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Due to its unique biological and chemical profile separate from its oxidized and deprotonated counterpart nitric oxide (NO), nitroxyl (HNO) has been increasingly studied by scientists, and is suggested to play a role as a pharmaceutical agent for the treatment of cardiovascular dysfunction. As very little is known about whether it is endogenously produced, this study aimed to improve an established in vitro detection method for HNO to ultimately increase our understanding of its in vivo mechanisms. A fluorescent triarylphosphine probe that reacts with HNO to yield a specialized amide product and an activated fluorophore was used as the method of detection. Due to the intrinsic chemical reactivity of HNO and its tendency to dimerize, Angeli’s salt (AS) and 1-nitrosocyclohexyl acetate (NCA) were used as donor molecules. This reaction was measured using spectrophotometry to monitor fluorescence intensity of the activated fluorescein, as well as mass spectrometry (MS) to identify the amide and fluorescein products. Initial in vitro experiments showed both NCA and AS produce significantly higher fluorescence intensity when incubated with the fluorescein-phosphine probe, as compared to the control. Rat smooth muscle (A10) cells were then incubated with the fluorescein-phosphine probe and treated with Angeli’s salt (AS). Both lysate and intact A10 cells showed higher fluorescence intensity in response to increasing concentration of AS in the presence of the fluorescein-phosphine probe. The use of decomposed AS, which no longer releases HNO, as a control in these experiments proved that the results were due to the specific reaction of this phosphine probe with HNO. The experimental results validate the use of this fluorescein-phosphine probe as a successful detection method for HNO, and prove its efficacy in A10 cells. Further studies should utilize this detection method by treating cell samples with fluorescein-phosphine probe in presence of proposed pathways for endogenous HNO production.
THE CREATION OF AN ANTICANCER PRODRUG – COMBINING ASPIRIN WITH CISPLATIN

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Cisplatin is a chemotherapeutic drug which targets the DNA of cancer cells causing apoptosis. Treatment with cisplatin commonly demonstrates severe adverse side effects related to inflammation, such as nephrotoxicity and ototoxicity. Creation of a prodrug, Platin-A (Fig. 1); from the synthesis of aspirin and cisplatin, has been found to reduce the inflammatory complications and cytotoxic effects of treatment with cisplatin alone. These findings highlight the advantages of using a prodrug to decrease inflammation associated with the delivery of a chemotherapeutic agent.

Fig. 1:
Enzymes are ubiquitous in biological systems. They catalyze chemical reactions and are involved in many biochemical processes. The enzyme of interest is D-Arginine dehydrogenase (DADH). This enzyme is a relatively medium sized complex consisting of approximately 180 residues and a proposed catalytic site that has a high binding affinity for D-Arginine. DADH catalyzes the oxidation of D-amino acids into their corresponding imino acids by removing the main chain α-hydride and carboxyl proton using flavin adenine dinucleotide (FAD) as its cofactor. Following the redox reaction with FAD, the imino acid can either be hydrolyzed within the active site or after being released from the enzyme. Many enzymes have distinct specificity for their relative substrates. However, DADH has a broad specificity for D-amino acids, and the reason being is quite ambiguous. The difference in catalytic efficiencies between D-amino acids with DADH proposed an alteration in their corresponding binding energies. Molecular dynamics methods was applied to compare physical traits and properties of all the binding substrates, which included bond energies, partial charges, center of mass, entropy, and distance of residues inside the complex. Coupled with the previous knowledge from enzyme kinetics, more insights regarding extensive DADH/substrate behavior were provided.
SYNTHESIS OF NEW THERMOPLASTIC ELASTOMERS BASED ON BENZOFULVENE

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The novel elastomers have been prepared with different chemical compositions of polyisoprene, polybutadiene, polystyrene, polybutylacrylate, polymethylmethacrylate, etc. by emulsion, free radical, or anionic polymerization. This work represents the first synthesis of new thermoplastic elastomers based on benzofulvene (Figure 1A) and butadiene (or isoprene). For the development of improved elastomers, well-defined homopolymers and block copolymers containing benzofulvene blocks were synthesized by sequential living anionic polymerization in benzene at room temperature via high vacuum techniques (Figure 1B and 1C). The molecular weight and polydispersity by GPC and LS, thermal properties by DSC and TGA, Chemical composition by NMR, and micro-phase separation by TEM and AFM of resulting polymers were then characterized. Mechanical strength was measured by universal mechanical strength instrument (Figure 1D).

Figure 1: Outline of preparation of new elastomers. A) Synthesis of benzofulvene, B) Synthesis of controlled poly(benzofulvene) in benzene at room temperature C) Synthesis of block and grafting polymers by sequential living anionic polymerization, D) Characterization and measurement of mechanical strength
SILVER-POLYMER NANOCOMPOSITE MATERIALS WITH HIGHLY DISPERSED SILVER NANOPARTICLES

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Silver holds many possible uses within the field of medicine. Due to its antimicrobial properties, it may serve as a bactericide in implanted devices such as pacemakers. Additionally, silver could serve as a contrast medium for X-ray and similar radiographic technique. Because of silvers hydrophilic properties colloidal dispersions of silver nanoparticles (AgNPs) in non-aqueous media are currently limited to very low concentrations due to agglomerations of silver. This research presents a novel approach for the synthesis of silver/poly(methyl acrylate) nanocomposites (Ag/PMA) containing highly dispersed AgNPs of 20-100 nm diameter. The nanocomposites were obtained by a three step synthesis from bare silver and polyacrylic acid (PAA) (Fig. 1). The first step is modification of AgNPs by grafting 2-aminoethanethiol to the silver surface via thiolation. The alkyl chains on the surface of the modified silver aided with dispersion of silver in solution, but over time agglomeration occurred. The second step of the procedure utilizes a polymer to aid with dispersion of modified silver. PAA is covalently bonded to the AgNPs by condensation of carboxyl groups on the polymer with amino groups of the grafted aminoethanethiol using diisopropylcarbodiimide. After the second step, all samples contained fully agglomerated AgNPs which can be explained by the large number of free carboxyl groups able to form intermolecular and interparticle H-bonds. The third step was esterification of the remaining carboxyl groups using methanol with HCl as a catalyst. As the reaction was taking place, the solution became clear which suggest the silver became finally dispersed. Evaporation of the solvent resulted in a light-yellowish transparent composite material. Full colloidal dispersion of AgNPs was achieved up to a concentration of 1.4 wt% of silver (Fig. 2). The final product, Ag/PMA was studied by FT-IR, NMR, XRD, and TEM methods.
SYNTHESIS OF NEAR-INFRARED FLUORESCENT PENTAMETHINE CYANINE DYES FOR IMAGING SENSITIVE ENDOCRINE SYSTEM TISSUE

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Currently, the visualization of native endocrine glands is conducted by using positron emission tomography (PET) and single-photon emission computed tomography (SPECT) imaging modalities. These scans are a risk when used during surgery due to emission of harmful radiation and they place the patient and those around them in unsafe levels of exposure. Developing a contrast agent that avoids the use of these harmful techniques is of significant clinical importance, specifically during head and neck surgeries where avoiding the sensitive endocrine glands is of utmost importance. An intraoperative imaging technique being heavily researched utilizes near-infrared (NIR) fluorescence or the emission of light from a compound to selectively image a target region. This strategy is appealing for multiple reasons, including low native tissue absorption and low background interference. Pentamethine cyanine dyes represent a class of chemicals that may be used for NIR imaging due to their red-shifted optical properties. An electron deficient conjugated chain allows high fluorescence in the NIR region, which is highly desirable when designing imaging agents.

Designing endocrine specific near-infrared fluorophores (ESNFs) utilizing pentamethine cyanine dyes could be clinically important in allowing surgeons to visualize where the sensitive endocrine tissue is and to avoid that area in the surgical field. Predicted physicochemical values and a literature review of non-fluorescent endocrine-targeting compounds guided the synthesis of halogenated pentamethine cyanines. The study of pentamethine dyes was performed, with specific halogens as substituents on both the heterocyclic backbone and pentamethine-bridge. The hypothesis driving this study was that the extended conjugation of the pentamethine-bridge, as well as halogen incorporation, would influence biodistribution for developing cyanines that can be used in the medical field.

A set of pentamethine cyanine dyes were successfully synthesized, and those predicted to match hormonal compounds targeted the endocrine system. Through this study it was determined that the characteristics of effective hormone mimicking fluorophores include: (1) the planarity associated with the indolenine heterocyclic moiety mimicking the planar face of hormones, (2) the extended methine bridge and (3) terminal halogenation. Future work on this project will be to determine the exact molecular and cellular target of the fluorophores.
4. **New directions in nucleopalladation: efforts toward the synthesis of functionalized silyl-enol ethers from alkenes utilizing a catalytic Wacker type C-H activation reaction**

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   Conversion of alkenes to the corresponding ketone has been accomplished through the Wacker oxidation for sixty years. Recent advances in nucleopalladation have resulted in the preparation of Wacker-type products via C-H activation with a variety of nucleophiles leveraging catalysis by palladium (II) salts. The use of commercially available silanols for the preparation of functionalized silyl-enol ethers directly from the alkene oxidation state presents a unique opportunity to expand the scope of current C-H activation. A systematic study of catalyst, co-oxidant, solvent, ligands and additives, and temperature towards this objective was initiated. The observed results were quantified using NMR spectroscopy with an internal standard leading to a general process that with further optimization could potentially negate the need for the traditional three step process of oxidation, enolization, and O-alkylation. Efforts toward the catalytic preparation of these materials in a regioselective fashion without metal-mediated isomerization of the alkene substrate in concert with the utility of air as a co-oxidant will be described.

5. **CHARACTERIZATION OF BACTERIAL CHEMOTAXIS RECEPTORS SENSING AND SIGNALING**

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   Motile bacteria navigate in gradients of diverse chemical signals (toward attractants or away from repellents) by chemotaxis. Chemotaxis is essential for the adaptation of motile bacteria to changes in their environment. Bacterial chemotaxis depends on a functioning signal transduction pathway comprising several cytoplasmic proteins that form a phosphorylation cascade. Chemotaxis signal transduction is initiated via sensing cues by dedicated chemoreceptors that are localized in the membrane. The sensing activity of a bacterial chemotaxis receptor, named Tlp1 from *Azospirillum brasilense*, was recently shown to be regulated by binding to the second messenger molecule, c-di-GMP and a novel mechanism of sensory adaptation was proposed. To further characterize this mechanism, a polyclonal antibody against the C-terminal region of Tlp1 was purified. This antibody was then used to test whether it was c-di-GMP bound or c-di-GMP free. Tlp1 receptors could be distinguished, using the wild type strain and a mutant derivative over-expressing c-di-GMP. Biophysical methods such as X-ray crystallography are currently being used to characterize how c-di-GMP binding to the C-terminal region of Tlp1 affects conformational change and signaling activity of this receptor. Although chemotaxis receptors are essential for bacteria to monitor their environments, the sensory specificity of bacterial chemoreceptors is largely unknown (88% unknown function) despite the public databases harboring over 22,000 such chemoreceptors. Tlp2 is a chemoreceptor from *A. brasilense* with a periplasmic domain of unknown function. Genetic and behavioral evidence indicate that Tlp2 senses nitrogenous compounds (ammonium and nitrate). Further characterization of the sensory specificity of Tlp2 for these compounds is being conducted using Isothermal Titration Calorimetry to determine the affinity of the isolated and purified recombinant sensory domain of Tlp2.
THE EFFECT OF DIFFERENT 3’ BASES OF AFB1-FORAMIDOPYRIMIDINE (FAPY) ADDUCT ON DNA DUPLEX STRUCTURE

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Aflatoxins are a group of carcinogenic fungal metabolites found in agricultural products and aflatoxin B1 (AFB1) is the most toxic kind. AFB1 can be metabolized to epoxide in human body, and form a stable AFB1-foramidopyrimidine (FAPY) adduct when reacted with the guanine base in DNA. Our study shows that although the AFB1 moiety is intercalated on the 5’ end of the adducted guanine, the difference in the 3’ neighboring base causes different structural changes in the DNA duplex structure. In particular, NMR structural analysis has shown that the sequence with C as the 3’ neighboring base has two isomers, both in the form of $\beta$ anomer, while the sequences with A, T or 7-deazaG 3’ neighboring base only has one isomer, in the form of $\beta$ anomer as well. In terms of distinguishing between the E/Z rotamers of the different structures, E configuration is predominant in duplexes with A 3’ neighboring base while Z configuration is predominant in duplexes with T and 7-deazaG 3’ neighboring base. The major isomer of C 3’ neighboring base sequence has been identified as E rotamer while the minor isomer could be Z rotamer.

Crystals of the AFB1-FAPY adducted DNA, Sulfolobus solfataricus P2 DNA polymerase IV (Dpo4) and dNTP have been collected. The ternary system is used to imitate the DNA replication process in human body. Structures of DNA duplex with A 3’ neighboring base has been solved in previous experiment and we currently have crystallized the ternary complexes with T and 7-deazaG 3’ neighboring base. The crystal structures will be solved for to more directly compare the different effect of the damage on DNA replication of sequences with different 3’ neighboring bases including adenine, thymine, cytosine, and 7-deazaguanine.

This finding in the sequence specificity of AFB1-FAPY adduct in both solution environment and crystal lattice might be helpful in explaining the strong correlation of aflatoxin exposure and liver cancer incidence rate as opposed to other types of cancer, if a specific DNA sequence related to liver cells is more likely to be affected by AFB1-FAPY adduct.

Fig. 1: Expanded Structures of sequences with different 3’ neighboring bases to the AFB1-FAPY Adduct based on NMR analysis. (A): A$^{\text{FAPY}}$GA sequence, (B): A$^{\text{FAPY}}$GT sequence, (C): major isomer of A$^{\text{FAPY}}$GC sequence, (D): A$^{\text{FAPY}}$G (7-deazaG) sequence.
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