1

DETERMINING WHAT STUDENTS KNOW PERIODICALLY

Eve Aldridge, Senior, Chemistry, University of Kentucky

Abstract:

The overall goal of this research is to develop an understanding of the capacity of students to learn, retain, recall, and apply information that is fundamentally important to developing a working knowledge of basic chemistry. The short-term goal is to determine what students remember of the periodic table throughout their education careers, with a particular interest in undergraduates who are majoring in chemistry. In this study, approximately 800 students from University of Kentucky, in approximately eight different chemistry courses, took an in-class survey of all 118 elements to determine which elements they remembered. The courses spanned the breadth of the chemistry program, from large service courses (general and organic) to small graduate-level courses (inorganic and physical). The periodic table surveys were provided to the students unannounced so that students were not able to study beforehand. This data, therefore, will help us determine what elements (and their associated symbols) the students are retaining throughout the program. The surveys were comprised of a randomized list of all element symbols, for which the students had up to 15 minutes to handwrite in the associated element names. In this poster, we present preliminary data that supports the parsing of the elements into three categories: those elements that students generally retain well, those elements that students do not retain or retain poorly, and those elements for which retention changes as the students' progress through the chemistry program. The implications of these results with regard to increasing student retention will be discussed.

2

SPERM NUCLEAR VACUOLES: NATURE'S INDICATOR OF SPERM DNA INTEGRITY

Danielle Berkowitz, Junior, Chemistry, University of Kentucky

Abstract:

Chromatin within somatic cells is packaged by histone proteins. Within sperm nuclei, chromatin is remodeled, and DNA histones are replaced with short arginine rich peptides known as protamines. These protamines condense the DNA into a near crystalline packaging density. This tight packaging serves not only to condense the DNA into an extremely compact space, but also protect the paternal genome from damaging agents. Within sperm chromatin, small cytoplasmic inclusions are sometimes visible, these inclusions are known as ‘sperm nuclear vacuoles’. The exact etiology of these vacuoles has yet to be conclusively proven. Prior studies have suggested that the presence of these vacuoles is indicative of either defects in sperm chromatin integrity or as a result of high levels of DNA damage to the paternal genome. In this study, the goal was to better characterize these sperm nuclear vacuoles and offer a potential explanation for their presence within sperm nuclei. Recent developments by the DeRouchey group have determined that sufficient DNA condensation is dependent on disulfide bond formation within eutherian protamines. Using Small Angle X-Ray Scattering (SAXS) techniques as well as DNA damage assays, this study will show that sperm nuclear vacuoles form as a result of poor disulfide bond formation within sperm protamines. This poorly condensed DNA is more susceptible to damaging agents, explaining the link between sperm nuclear vacuoles greater incidences of DNA damage.

3

ANALYSIS OF VOLATILE COMPOUNDS IN BOURBON HEADSPACE USING SPME

Joshua Betts, Senior, Chemistry, University of Kentucky

Abstract:

American bourbon whiskey is one of the more recognizable products that come from our region. There are numerous brands and variants of this product. Using solid phase microextraction (SPME) to collect the volatile compounds that are present in the headspace of various bourbon samples and using GC-MS to identify the compounds that are present. In addition to this a set of standards was made using volatile compounds known to be present in bourbon. A series of solutions were made at various concentrations so a standard curve could be made. This allows for the determination of the concentrations of the identified compounds. The purpose of this is to characterize and understand how these compounds affect both the flavor and aroma profiles of Bourbon.

4

CONVERSION OF CELLULOSE ACETATE INTO CELLULOSIC BIOMASS AND THEN INTO BIOFUEL (ETHANOL)

Courtany Brown, Senior, Chemistry, Berea College
Adan Martinez, Chemistry, Berea College

Abstract:

Cellulose is a complex carbohydrate, composed of a long repeating glucose chain. Cellulose is the main component of cell walls, some examples of abundant cellulose sources are cotton, hemp, and wood. Cows have a special stomach to digest this carb while humans do not. If it’s nonedible, then what should be done with the waste? Another source of cellulose is from one of the main debris most commonly thrown out the window and on the ground – cigarette butts. Through Saponification, Hydrolysis, and Fermentation we can turn this trash into Ethanol. Ethanol is a green energy source, the combustion engine in automobiles can run off of this fuel. In this presentation, Acid vs. Enzymatic Hydrolysis, DNS, Benedict ’s reagent, Phenol-Sulfuric reagent, Jones’s Reagent, Gas Chromatography-Mass spec and Green chemistry will all be discussed. This research is important because on a worldwide bases many scientists are working on the same problem, where to find a new energy source, and while this may not be new, it is still worth taking the time to learn more about and use as a multipurpose reaction.

5

ANALYZING AND DEFINING CARBOHYDRATE BINDING MODULES FOUND IN GLUCAN WATER DIKINASE OF THE RED ALGA, CYANIDIOSCHYZON MEROLAE

Cassadi Cordea, Senior, Chemistry, University of Kentucky
Corey Brizzee, Molecular and Cellular Biochemistry, University of Kentucky
Andrea Kuchtová, Molecular and Cellular Biochemistry, Univ. of Kentucky
Matthew Gentry, Molecular and Cellular Biochemistry, University of Kentucky

Abstract:

Objective: This project is based on the biochemical characterization of a putative Glucan Water Dikinase (GWD) orthologue that has been identified in a unicellular, thermophilic red alga, Cyanidioschyzon merolae (Cm). The goal of this experiment is to study the functioning of three carbohydrate binding modules (CBM) of family 45 contained in the sequence of CmGWD.
Significance: Glucan water dikinase is involved in starch metabolism through phosphorylation. The carbohydrate binding modules are thought to be critical for the enzyme's ability to efficiently phosphorylate starch. The role of CmGWD in starch metabolism is of interest because of potential industrial applications.
Methods: Bioinformatics to design primers to mutate certain tryptophan, tyrosine, or phenylalanine residues to alanine in three CBM45s. Polymerase chain reaction (PCR) to amplify the mutations. Transformation into chemically competent E. coli cells to grow cultures containing a large number of cells. A two-step purification scheme using affinity chromatography and fast protein liquid chromatography (FLPC). Carbohydrate binding and differential scanning fluorimetry (DSF) assays to test the ability of the CBMs to bind substrate.
Results: We were not able to purify some mutations of CmGWD. The assays that were performed showed reduced binding ability. We observed that mutations of critical amino acid residues did affect the overall binding ability of the CBMs.
Conclusion: On the CAZY server, the family CBM45 consists of 89 eukaryotic members, and all are found in GWDs. This project focused on the three CBM45s found in CmGWD. Knowing which amino acids alter the binding ability of CBM45s can help us determine the amino acids that are essential for the phosphorylation of starch by CmGWD.

6

SYNTHESIS OF STABLE AND SOLUBLE ORGANIC ELECTROLYTES FOR NON-AQUEOUS REDOX FLOW BATTERIES

William L. Eubanks, Senior, Chemistry, University of Kentucky

Abstract:

The fluctuation of renewable energy sources such as solar and wind has become a topic of concern in the scientific community as these renewables increase in proportion on the electrical grid. Large scale grid energy storage systems are under investigation to remedy this problem. Aqueous vanadium flow cells are the most well-researched of these storage systems, but suffer from a limited voltage window due to the electrolysis of water. The Odom Group is participating in the development of non-aqueous redox flow batteries (NAqRFBs) for grid energy storage applications. Commercialization of NAqRFBs is prevented by low energy efficiency, poor voltage, and rapid capacity decay. These are due to faults with the electroactive organic species, among them limited stability of oxidized/reduced forms and poor solubility. This project reports the large-scale and efficient syntheses of stable and soluble phenothiazine and viologen derivatives (and their tetrafluoroborate radical cation salts, where applicable) for use as NAqRFB electrolytes.

7

UNMANNED AERIAL SYSTEMS FOR PARTICLE GATHERING AND OFFLINE ANALYSIS OF OXYGENATED POLYAROMATIC HYDROCARBONS FROM BIOFUEL

Anna Fatta, Freshman, Chemistry, University of Kentucky
Travis J. Schuyler, Chemistry, University of Kentucky
Md Sohel Rana, Chemistry, University of Kentucky
Marcelo I. Guzman, Chemistry, University of Kentucky

Abstract:

In 2018, a record 1.9 million acres of land were lost to wildfires in California alone (California Department of Forestry and Fire Protection). In the same period of time, about 700 billion kilograms of coal were burned at power plants (U.S. Energy Information Administration). The smoke produced by these biofuels carries chemical compounds that cause cancer, and particulates that decrease the albedo of the atmosphere. A concerning byproduct of biofuel burning events is the production, and atmospheric aging, of oxygenated polyaromatic hydrocarbons (oxy-PAHs). Oxy-PAHs are photoactive and produce environmentally persistent radicals with complex chemistry. To better attribute the effects of oxy-PAHs produced from biofuel burning, a novel particulate collection device has been fitted to an unmanned aerial vehicle (UAV), or drone. The small unmanned aerial system (sUAS) is used to safely collect smoke particulates produced from biofuel burning events for offline analysis. The oxy-PAHs were solvent extracted from the filter and characterized with the following techniques: UV-Vis spectroscopy, attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), reverse phase high pressure liquid chromatography (HPLC), a photodiode array (PDA), and electrospray ionization mass spectrometry (ESI-MS). The results provide an estimate of the environmental impact of oxy-PAHs from biofuel burning.

8

COLLOIDAL SILVER NANOPARTICLES: A MORE EFFECTIVE BACTERIOCIDAL AGENT THAN CHLORINE AGAINST WATERBORNE GRAM NEGATIVE BACTERIA

Alex Gilman, Senior, Chemistry, Wright State University
Marjorie Markopoulos, Chemistry, Wright State University
Ashley Wilcox, Chemistry, Wright State University
John Ryan, Chemistry, Wright State Univeristy
Ioana Pavel, Chemistry, Wright State University

Abstract:

The main aim of this study was to determine the antimicrobial and bactericidal activity of unfunctionalized, silver nanoparticles (eAg) of ~10 nm in diameter against well-established water indicator organisms: Escherichia coli, Klebsiella variicola, and Pseudomonas aeruginosa. This was achieved by determining the Minimum Inhibitory Concentration (MIC) and Minimum Bactericidal Concentration (MBC) of eAg, which were synthesized electrochemically, size-selected, concentrated, and purified by tangential flow filtration. The MIC values for E. coli, K. variicola, and P. aeruginosa were 0.75-4.02, 1.09-4.08, and 1.55-5.39 mg L-1, respectively. The MBC values for the same bacteria were 1.51-3.96, 1.55-5.39, and 2.18-4.99 mg L-1, respectively. When tested against chlorine, the MIC values increased 1000-, 2000-, and 3000-fold, respectively, for mentioned bacteria. The MBC values increased 1000-, 1500-, and 1500-fold, respectively. CytoViva hyperspectral imaging was performed to confirm the proposed mechanistic aspects associated with the attachments of the negatively charged eAg to the cellular membrane and their subsequent structural disruption.

9

CHARACTERIZATION OF NANOMATERIALS AND SOLAR CELL ELECTRODES BY ATOMIC FORCE MICROSCOPY

Kelsi Goshinsky, Sophomore, Chemistry, Ball State University
Cody Leasor, Chemistry, Ball State University
Zhihai Li, Chemistry, Ball State University

Abstract:

As one of the most powerful tools in nanoscience and nanotechnology, atomic force microscopy (AFM) has been widely used in many fields including biology, chemistry, physics and materials. In this poster, we first introduce AFM principle, i.e., how AFM can image surface morphology, and continue to describe the procedure of how to carry out an AFM experiment in our lab. Then, we will present some experimental data on the characterization of different nanomaterials (such as NiWO4, TiO2) and solar cell electrodes using taping mode AFM imaging technique. The high-resolution AFM images show that morphology and size of NiWO4 nanomaterials can be determined. AFM images also reveal different surface morphology before and after depositing TiO2 and platinum nanomaterials on solar cell electrode surface.

10

ON THE ASYMMETRIC SYNTHESIS OF EXO-1-ACETAMIDOPYRROLIZIDINE

David Harris, Senior, Chemistry, University of Kentucky
Robert Grossman, Chemistry, University of Kentucky

Abstract:

Previous attempts at the asymmetric synthesis of exo-1-acetamidopyrrolizidine (AcAP) have been unsuccessful due to the racemization of a synthetic intermediate. Using the precursor of enantioenriched endo-1-hydroxypyrrolizidine generated by way of a chiral ruthenium-BINAP catalyst as characterized by Genet et al, it could be possible to substitute the tosylate for an exo-azide. Reduction via Curtius rearrangement and acetylation could yield enantioenriched AcAP for use in characterization of the enzymatic oxidation to form the 2,7 ether bridge in the conversion to N-acetylnorloline (NANL).

11

OPTICAL ENHANCEMENT OF CDSE AND INP QD/ CINNAMATE LIGAND COMPLEXES

Collan Henderson, Senior, Chemistry, Transylvania University
Kyle Schnitzenbaumer, Chemistry, Transylvania University

Abstract:

The effect of surface ligands on the molar absorptivity of InP and CdSe quantum dots (QDs) was studied. InP QDs were synthesized via a green synthesis with oleylamine ligands, while CdSe QDs were synthesized with oleic acid ligands and exchanged for a series of cinnamate ligands. Cinnamate ligands with a wide range of electronic structures were selected to probe the relationship between the ligand optical gap and QD molar absorptivity. UV-Vis spectroscopy was used to determine the enhancement in absorptivity relative to the native ligand/QD system. The results can be used to further increase our knowledge of the ligand/QD system and allow for the selection of ligands optimized for specific applications.

12

SYNTHESIS OF PHOSPHINE-BEARING TRICOORDINATE AU (I) COMPLEXES AND EVALUATION OF CHEMOTHERAPEUTIC POTENTIAL

William Jennings, Senior, Chemistry, University of Kentucky
Tyler Mertens, Chemistry, University of Kentucky
Sean Parkin, Chemistry, University of Kentucky
Samuel Awuah, Chemistry, University of Kentucky

Abstract:

Since the advent of cis-diamminedichloroplatinum(II) (Cisplatin), transition metal complexes have been critical in the effective treatment of a variety of cancers. However, this field has been traditionally dominated by Pt(II) based drugs. The presence of cancer lines resistant to Cisplatin and similar Pt(II) compounds makes the consideration of non-platinum anticancer metal complexes highly important. Recently, Au(I) and Au(III) based complexes have been investigated as potentially effective chemotherapeutics, especially for cisplatin-resistant cancers. However, the physiological stability of gold complexes has typically been problematic. Here, we report the synthesis and chemotherapeutic potential of a class of tricoordinate Au(I) complexes bearing N,N-bidentate and tertiary phosphine ligands. X-ray crystallographic studies reveal interesting structural properties of these compounds including variable Au-N bond lengths likely attributable to a second order Jahn-Teller distortion. MTT assays reveal appreciable cytotoxicity which may be related to the unique structural features of this class of compounds, though, solution stability remains an issue. This work provides insights into the relationship between the structure, stability, and cytotoxicity of tricoordinate Au(I) anticancer agents.

13

ENZYMATIC TREATMENT OF BOURBON BARRELS TO AFFECT AROMA AND TASTE OF SPIRITS

John Klein, Senior, Chemistry, University of Kentucky

Abstract:

American white barrels are used in the production of aged spirits. The barrel’s biopolymers are released into a solution during whiskey maturation and influence the aroma and taste of the distilled spirit. The biomass enzyme xylanase can be added to a barrel to amplify the degradation of the hemicellulose present in the barrel by creating more biopolymers. Model whiskey solutions of wood chips treated with xylanase were created to test for increased biopolymer production over a maturation period. To evaluate chemical changes in the model solutions, solid phase microextraction (SPME) and gas chromatography–mass spectrometry (GC-MS) were used to determine if aroma was affected by measuring and identifying volatile compounds in the model solutions.

14

EFFECTS OF SMALL MOLECULE INHIBITORS ON NITRIC OXIDE SYNTHASE

Alysia Kohlbrand, Senior, Chemistry, University of Kentucky

Abstract:

Nitric Oxide Synthases (NOS) are enzymes used in the body to catalyze the production of nitric oxide (NO), a very important signaling molecule which plays a central role in human biology. There are three types of NOS expressed in mammals, endothelial NOS (eNOS), involved in vascular tone and blood flow, inducible NOS (iNOS), involved in inflammation and immunity, and neuronal NOS (nNOS), involved in signal transduction in the brain. The regulation of each of these types of NOS is very important and can have serious health consequences when the proper balance of these enzymes is unachievable, for example, iNOS is involved in many autoimmune inflammatory diseases such as multiple sclerosis, rheumatoid arthritis, and asthma. Inhibitors could be used to stop or slow down the production of NOS if inhibitors specific to individual forms of NOS can be identified it would provide new avenues of treatment for diseases associated with nitric oxide production. In order to visualize NOS and NO activity, reporters are a necessity. Dendra2 is a fluorescent protein that can be used to examine the half-life of NOS in mammalian cells through photo-switching, the protein fluoresces green and irreversibly switches to fluoresce red when exposed to blue or UV light. Using Dendra2 as a technique to monitor NOS and NO production provides a quick, cheap, and high throughput assay to assess small molecule inhibitors of NOS.

15

EFFECT OF SOLIDAGO NEMORALIS ON OXIDATIVE STRESS LEVELS IN FETAL ALCOHOL SYNDROME RAT MODEL

Allison Lane, Senior, Chemistry, University of Kentucky
D.A. Butterfield, Chemistry, University of Kentucky

Abstract:

Fetal alcohol syndrome is caused by prenatal exposure to alcohol, and results in permanent mental and physical developmental abnormalities. Currently there are no approved drugs to treat or prevent fetal alcohol syndrome. Intermittent ethanol exposure with periods of binge drinking and periods of withdrawal are particularly harmful because of microglial activation during withdrawal. Extract from Solidago nemoralis, or Goldenrod, acts as a nicotinic acetyl choline receptor (nAChR) agonist. nAChR activation has been demonstrated in vitro to reduce neuroinflammation and excitotoxicity. Solidago nemoralis research may provide insight into potential treatment or prophylaxis when a fetus is exposed to ethanol. The human third trimester corresponds in rats to the first week after birth, allowing assignment of pups from a single litter to different treatment groups. We examined the oxidative stress levels in brain homogenate of rats treated with alcohol and Solidago nemoralis extract. It is expected that treatment of ethanol-exposed rat pups with Solidago nemoralis extract will reduce the levels of 3-nitrotyrosine, 4-hydroxynonenal, and protein-bound carbonyls when compared to non-Solidago treated ethanol-exposed counterparts.

16

HETEROGENEOUS OXIDATION OF PYROGALLOL BY OZONE

<u>Jacob Morris, Senior, Chemistry, University of Kentucky</u>
Md Sohel Rana, Chemistry, University of Kentucky
Marcelo Guzman, Chemistry, University of Kentucky

Abstract:

Natural and anthropogenic combustion emissions contribute precursors to the formation of atmospheric secondary organic aerosols (SOAs). SOAs, which affect climate and human health, could be potentially generated from phenolic compounds such as pyrogallol present in these emissions. This work shows how pyrogallol reacts at the air-solid interface with variable O3(g) mixing ratios (100 ppbv to 25 ppmv) at a relative humidity of 70%. The results show not only the expected products from the reaction with O3, but also those from the chemistry of hydrogen peroxide (H2O2) and hydroxyl radicals (HO•). The reactions are monitored using Fourier-transform infrared (FTIR) and UV-visible spectroscopy, and the products are identified using electrospray ionization-mass spectrometry (ESI-MS) and ion chromatography-mass spectrometry (IC-MS). The spectroscopic changes observed in the IR spectrum include the broadening of the ν(O-H) peaks between 3100 and 3400 cm-1, the decrease in absorbance for the ν(C=C) peak at 1525 cm-1, and the increase in absorbance for the ν(C=O) peak at 1710 cm-1. In the UV-visible spectra, there is a significant increase in absorbance between wavelengths of 300 and 500 nm, with a peak of □max (310 nm) having a mass absorbance coefficient MAC of 2.1633 m2 g-1, which is comparable with field sample measurements The main organic acids identified as anion by mass spectrometry are formic acid (m/z 45), glyoxylic acid (m/z 73), glycolic acid (m/z 75), butenoic acid (m/z 85), oxalic acid (m/z 89), maleinaldehydic acid (m/z 99), malonic acid (m/z 103), maleic acid (m/z 115) and 2-hydroxy-cis,cis-muconic acid (m/z 157). In addition, polyhydroxylated compounds, such as 1,2,3,4- and 1,2,3,5-tetrahydroxybenzene (m/z 141), benzenepentol (m/z 157), and benzenehexol (m/z 173), are formed by hydroxylation, along with heavier polyhydroxylated biphenyls (m/z 297 and 311) from coupling reactions of semiquinone radicals (SQ). The overall experimental results are used to propose reaction mechanisms showing the two main reactivity pathways of the aromatic ring: (1) oxidative cleavage by O3, involving Criegee intermediates, and (2) hydroxylation involving SQ and HO•. In conclusion, this research provides new understanding of the atmospheric oxidation of pyrogallol at the air-solid interface.

17

IMPROVEMENTS TO THE PERFORMANCE AND STABILITY OF PEROVSKITE PHOTOVOLTAIC DEVICES

Jonathan Nelson, Senior, Chemistry, University of Kentucky
Alex Boehm, Chemistry, University of Kentucky
Kenneth Graham, Chemistry, University of Kentucky

Abstract:

Photovoltaic devices are used to convert the sun's light into usable electricity. Research has revealed inorganic-organic halide perovskites as a low-cost and high-performing alternative to other common materials used for the active layers of the cells. Starting in 2009 the maximum percent conversion efficiency (PCE) was 3.9% but the highest recorded PCE to date is around 23%. This means that the perovskite based devices can compete with the performance of standard polycrystalline silicon devices. An emerging issue in the field is finding an alternative to lead (Pb) as the B-site cation. The main problem with the Pb-based devices is the scalability of production due to the innate toxicity of lead. Tin is a great alternative because it is an abundant and harmless element that acts very similar to lead. In the following experiments attempts were made to increase the stability of perovskite photovoltaic devices. Various pure and blended samples of perovskite films were analyzed by UV-Vis and photoluminescence (PL) spectroscopy in order to determine their relative photoluminesce. The A-site cations that were varied were Cesium (Cs), Formamidinium (FA), and Methylammonium (MA). The best performing sample was determined to be the mixture of FACsSnI3 as it had the most uniform morphology and the highest relative PL. Once the best performing sample was determined an experiment was carried out to test what concentration showed the best morphology and highest PL intensity. Next, the procedures for annealing, antisolvent treatment, and drying procedures were varied in order to increase the maximum PCE. When the annealing temperature was raised to 130 degrees Celsius the consistency and performance of the films increased. When the antisolvent treatments were added improvements to the PCE were observed immediately. When anisole was initially used it boosted the group's maximum PCE over 1 percent. Finally the stability of the precursor solution was tested. Four different Lewis bases were added to the precursor solution in order to prevent the oxidation of tin in solution. Improvements to tin stability were observed for the solutions containing pyridine and Tertahydrothiophene (THT) but not for the solutions containing anisole and pyrazine.

18

EVIDENCE OF PEROXIDASE CATALYSED FORMATION OF CYSTEINE-TYROSINE AND DITYROSINE CROSS-LINKING IN MAMMALIAN SPERM PROTAMINES

Christian Powell, Senior, Chemistry, University of Kentucky
Daniel Kirchoff, Chemistry, University of Kentucky
Jason DeRouchey, Chemistry, University of Kentucky
Hunter Moseley, Molecular & Cellular Biochemistry, University of Kentucky

Abstract:

Spermatogenesis is the process in which germ cells develop into spermatozoa in the testis. Sperm protamines are small peptides (<50 amino acids) which mediate DNA condensation during the spermatogenesis process. The protamines of eutherian mammals have an arginine-rich region which binds to DNA and multiple cysteine residues which facilitate intramolecular folding and intermolecular bonding between protamines. Protamines replace DNA histones during spermatogenesis allowing DNA to achieve a more condensed state. This further condensed DNA state allows for a smaller nucleus and facilitates the formation of the sperm head. Most metatherian sperm protamine lack cysteine but perform the same function. This lack of dicysteine cross-linking sites has made the mechanism behind metaherian protamines folding unclear. In order to investigate this phenomenon, protamine sequences from UniProt's TrEMBL and SwissProt databases were pulled down and sorted into eutherian and metatherian groups. Multiple sequence alignments (MSAs) for these groups were then generated with MUSCLE 3.8.31. The MSAs were then iterated through position by position and a gap weighted relative entropy score calculated for each position. This analysis showed that the cysteine containing positions were the most highly conserved within the eutherian alignment. For the metatherian alignment, the tyrosine containing positions were determined to be the most highly conserved and corresponded to the cysteine positions in the eutherian alignment. The high conservation implies that these positions are likely functionally/structurally important residues in the metatherian protamines and the correspondence with cysteine positions within the eutherian alignment implies a similarity in function. One explanation is that the metatherian protamine structure relies upon dityrosine cross-linking between these highly conserved tyrosines. Also, the human protamine P1 sequence has a substitution of tyrosines in a position eutherian mammals are expected to have a cysteine. The position is also thought to be involved in intramolecular dicysteine cross-linking. One explanation is the formation of a rare cysteine-tyrosine cross-linking to facilitate folding.

19

SYNTHESIS AND CHARACTERIZATION OF TWO ANIONIC PHTHALOCYANINE METAL COMPLEXES

John Quinn, Senior, Chemistry, University of Cincinnati
Rebecca Silva, Chemistry, University of Cincinnati
Peng Zhang, Chemistry, University of Cincinnati

Abstract:

As methicillin-resistant Staphylococcus aureus (MRSA) strains develop increasing resistance to traditional antibiotics, research into alternative treatments has gained momentum. Photosensitization using singlet oxygen producing complexes, commonly known as photodynamic inactivation (PDI), offers a method of treatment of MRSA that is inherently less susceptible to the development of drug resistance pathways. Phthalocyanine metal complexes as a class show promise as photosensitizing agents due to the ability of many to produce singlet oxygen upon irradiation. However, one obstacle to their use as photosensitizers is their general hydrophobicity, which renders them incompatible with aqueous distribution. In this project, two anionic phthalocyanine metal complexes were synthesized in a one-pot synthesis using either Zn(II) or Pd(II) metal centers. These complexes were then purified and characterized by UV-visible and infrared spectroscopies. The fluorescence properties of these metal complexes and their ability to generate singlet oxygen were also investigated.

20

UNDERSTANDING THE INFLUENCE OF ZINC ON SPERM CHROMATIN STRUCTURE

Kathryn Sandum, Senior, Chemistry, University of Kentucky
Daniel Kirchoff, Chemistry, University of Kentucky
Jason DeRouchey, Chemistry, University of Kentucky

Abstract:

During spermatogenesis somatic chromatin is remodeled and DNA histones are replaced with short arginine rich peptides known as protamines. This tight packaging serves to condense the large paternal genome into a space 1/6th the volume of the somatic nucleus. This massive reduction in size results in the sperm chromatin existing at a near crystalline packing density. Prior studies have demonstrated that a significant fraction of zinc is present in both mature sperm and the seminal fluid, but the exact etiology of the zinc fraction has not yet been conclusively proven. Mammalian sperm typically contains two protamines, P1 and P2, which have disulfide bonds that allow them to function. In humans, each P2 protamine has been shown to chelate one zinc atom with its disulfide bonds. This study attempts to discern the role of zinc in sperm nuclei packaging with salmon protamine, which has no cysteine residues to cause disulfide bonds, and in bull sperm nuclei, which has only protamine P1. In this study, zinc levels within isolated bull and salmon sperm nuclei were determined by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). Significant amounts of zinc were found in both bull sperm nuclei and salmon sperm nuclei. Packaging characteristics in both actual sperm nuclei and reconstituted protamine-DNA samples were examined by Small Angle X-ray Scattering (SAXS) techniques. The relationship between zinc concentration and DNA packaging density was determined by the addition of two different chelation agents, EDTA and porphine, to mature salmon nuclei, as well through the addition of excess zinc. Effect of specificity on DNA interaxial spacing was determined by the addition of several different cations to isolated salmon nuclei.

21

PELTIER FREEZER APPARATUS

**Taylor Secrest, Senior, Chemistry and Biochemistry,
Rose-Hulman Institute of Technology**

Abstract:

The freezing of water is a thermodynamically interesting phenomenon, with ice being capable of freezing into at least 20 different crystal structures. In particular, introducing salts with water can affect the type of freezing mechanism that the solution undergoes, allowing water to be supercooled well below its freezing point. I have created a Peltier freezing apparatus that can supercool water to -27 °C when in the presence of concentrated salts (calcium chloride for my research), with a focus on how the phase transition of water from a liquid to a solid is altered when salts are mixed with pure water. Additional concerns about the clarity of ice when salts are present was also a main highlight of my research. Several crystal structures of water have been observed depending on the rate of cooling applied. Variation of concentration in 5 calcium chloride standards has also affected the overall clarity of the ice to be more amorphous, with the calcium potentially preventing crystal packing of water, allowing for further supercooling of the water before freezing occurs. Other deliverables of this project include coding in C++, using Arduino software, as well as data logging directly into Excel, and knowing some wiring and other electrical components. Lastly, I can conclude that the presence of calcium chloride in increasing amounts allows for an increasing value for the freezing point depression (final freezing temperature) in comparison to pure water.

22

TOWARDS INHIBITORS OF D-ALANYLATION OF LIPOTEICHOIC ACIDS FROM GRAM-POSITIVE BACTERIA USING FRAGMENT-BASED DRUG DISCOVERY

Muna Shakhashiro, Junior, Chemistry, University of Kentucky
Konstantin Korotkov, Molecular and Cellular Biochemistry, Univ. of Kentucky

Abstract:

The dlt operon encodes four proteins (DltA-D) that are involved in the biosynthesis of lipoteichoic acids (LTA) in bacterial cell walls. Teichoic acids are essential for the growth and virulence of bacterial pathogens. They consist of glycerolphosphate polymers that are modified with D-alanines which are incorporated by the proteins DltA-D. While the functions of DltA and DltC have been established, the exact function of DltD remains unknown. Proposed models suggest DltD is a membrane protein that facilitates ligation of D-alanine to LTA. Studies have also shown that disruption of the Dlt gene increases bacteria's susceptibility to antibiotics, which is vital for targeting increasingly resistant pathogens.

In this study, we attempt to solve the structure of the DltD protein homologs from the bacterial pathogens Streptococcus pneumoniae, S. pyogenes, S. mutans, S. thermophilus, Staphylococcus aureus, and Enterococcus faecalis. In doing so, we can better understand the catalytic mechanism of DltD and potentially find small molecule inhibitors using fragment-based drug design. Through protein purification and X-ray crystallography methods, the structure of DltD from Enterococcus faecalis was successfully determined.

23

IRON-CATALYZED SUBSTITUTION OF SECONDARY ALCOHOLS

Julie Simon, Senior, Chemistry, Indiana University
Paul Marcyk, Chemistry, Indiana University
Silas Cook, Chemistry, Indiana University

Abstract:

Alcohols are attractive electrophiles for alkylation as they are widely available, stable, and easy to prepare. The Cook Lab has had great success with using the combination of FeCl3 and AgSbF6 to activate secondary alcohols for stereospecific nucleophilic substitution by sulfonamides as well as for the hydroamination and hydroetherification of unactivated alkenes. I was interested in investigating the extent of the utility of this catalytic system, particularly by examining intramolecular substitution of secondary alcohols with phenol nucleophiles to create a carbon-oxygen bond. Optimized reaction conditions were identified for the reaction with a model substrate. Additionally, the reaction was found to quantitatively transfer the stereochemical information of the starting alcohol, suggesting a stereospecific mechanism. Future work will involve analysis with additional substrates.

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HEAVY METAL CAPTURE AND DETECTION USING COLORED SYNTHETIC DITHIOL

Anna Soriano, Junior, Chemistry, University of Kentucky
Shashika Bandara, Chemistry, University of Kentucky
Sean Parkin, Chemistry, University of Kentucky
David Atwood, Chemistry, University of Kentucky

Abstract:

In our group, we synthesized a series of synthetic dithiol molecules which are able to precipitate by forming strong covalent bonds with heavy metals and metalloids as L-M. The parent synthetic dithiol molecule B9= N,N'-bis(2-mercaptoethyl)isophthalamide, common name “benzenediamidoethanethiol” was found to have unique ability, to immobilize heavy metals Cd, Hg, Pb and As from water to below the detection limits of ICP-OES and CVAAS by the formation of strong covalent S-M bonds which are exceedingly stable with metal leaching but occurring only at very low and high pH.

Figure 1 will show chemical structure, crystal structure, and the dimeric crystal structure of B9.

The synthesis of B9 is carried out by combining isophthaloyl chloride with two equivalents of cysteamine (to make B9, scheme 1.), cysteine (to make AB9), cysteine methyl ester (to make MB9) and cysteine ethyl ester (to make EB9).

Scheme 1 will show the synthesis of B9 in one step. Isophthalolyl chloride and cysteamine-HCl are the reactants.

However, the insolubility of the B9-M compounds has precluded structural characterization by single-crystal X-ray crystallography. Thus, a series of new dithiol molecules was synthesized as carboxylic acid derivative of B9; AB9= 2,2'-(isophthaloylbis(azanaediyl))bis-3-mercaptopropanoic acid, the methyl ester MB9= 2,2'-(isophthaloylbis(azanaediyl))bis-methyl 3-mercaptopropanoic acid and EB9= ethyl ester 2,2'-(isophthaloylbis (azanaediyl))bis-ethyl 3-Mercaptopropanoic acid are other synthetic dithiol molecules which are able to form M-L bond.(Figure 2.) expecting similar bonding possibilities as B9, give new functianility through various functional groups, expanding the solubility for X-ray crystallographic analysis. Thus, they maintain the same binding of B9-M as S-M-S with different functional groups attached to the main carbon backbone providing different inductive effects towards the CH2CH2SH group.

Figure 2 will show the chemical structures of AB9, MB9, and EB9.

These synthesized molecules show several advantages over conventional methods. These include odorless, no toxic byproducts, cost-effective, no excess precipitating agent needed, the heavy metal removal >60 % (under normal/uncontrolled pH and open to air synthesis from a stock solution of each heavy metal). Moreover, the sulfur providing starting material are resistance to get oxidized, which prevents the formation of disulfide bonds, immediate precipitation and resistance to release the bound heavy metal under wide pH range and long time. Thus, these systems are ideal for studying the covalent bonding to heavy metals and determining the effects, characteristics, and stability of M-S bonds.

Several modifications to the existing ligands were also made. Thus, a new class of colored compounds using Anthraquinone and Anthracene achieved by conjugated aromatic system backbone containing pendant thiolate groups. So, colored acid chloride instead of colorless isophthaloyl chloride was used. The interactions between anthracene/anthraquinone units and/or with the metal ions provide quantification via colorimetric methods, efficient identification of wastewaters and natural waters contamination and obtaining a crystal structure for L-M are main objectives.

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OPTIMIZATION OF SINGLET OXYGEN SENSOR GREEN FOR THE PURPOSE OF MEASURING CELLULAR REACTIVE OXYGEN SPECIES

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Abstract:

Singlet Oxygen Sensor Green (SOSG) is a commercially available fluorescence-based detection agent that is selective for singlet oxygen. Singlet oxygen is a form of reactive oxygen species (ROS) that can bind to DNA and cause damage to the cell due to oxidative stress. Therefore, compounds that produce ROS, called photosensitizers, have been used in antibacterial, antiviral, and anticancer treatments in the form of photodynamic therapy. Since high levels of ROS can be very detrimental to biological systems, a method of detection for such species would be most helpful. SOSG has been used predominantly in vitro to quantify the amount of singlet oxygen. In order to apply SOSG to cell-based assays, we have identified optimal conditions for using SOSG with human cell lines. To do this, SOSG was tested in different buffers to find the optimal buffer that produced the lowest amount of background fluorescence and then we tested the ability of SOSG to get into cells. Also, we studied the degradation of SOSG when exposed to indigo light by electrospray ionization mass spectrometry (ESI-MS). Finally, we tested the efficiency of SOSG by comparing its signal to the signal of direct singlet oxygen detection by fluorimeter.

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SYNTHESIS OF 1,2- AND 1,2,6,7-SUBSTITUTED PYRENE MOLECULES

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Abstract:

Organic semiconductors are compounds that have great value in organic materials, such as OLEDs, solar cells, and OFETS, due to their electronic and optical properties. That said, it is important develop semiconductors with higher charge carrier mobilities to increase efficiency of these devices. The purpose of this research is to develop a synthetic path for designing molecules that utilize pyrene from the 1,2 and 1,2,6,7 positions for extending chromophores. With these molecules, there are many hurdles to the synthetic process, most importantly scalability. As a result, the synthesis is extensive. This poster provides the synthesis to date of pyrene-based molecules, including to optimization of the synthetic process.