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Department of Chemistry & Biochemistry

FLORIDA INTERNATIONAL UNIVERSITY

Phone: 305-348-4262
E-mail: reu@fiu.edu
http://chemistry.fiu.edu/undergraduate/reu/
REU Participants

Alaina McDonnell
Andrew Kalbach
Nathan Price
Jashaun Bottoms
Joseph McKillip
Brenna Walsh
Ingrid Lehman-Andino
Candace Norton
Carlos Paz
Aida Diouf

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Photographic Evidence of Reactions in Organic Chemistry: The Formation of Trans-Diols from Cyclohexene and Meta-Chloroperbenzoic Acid

Aida O. Diouf¹,², Dariana Trana¹ and J. Martin E. Quirke¹,*

¹Florida International University, Department of Chemistry and Biochemistry, 11200 SW 8th St., Miami, FL 33199
²Albright College, Department of Chemistry and Biochemistry, 1621 North 13th Street, Reading, PA 19604

We provide visual evidence for the transformation of cyclohexene into trans-1,2-cyclohexanediol via cyclohexene oxide. Cyclohexene reacted with pure meta-chloroperbenzoic acid (MCPBA) to form cyclohexene oxide and a precipitate of meta-chlorobenzoic acid (MCBA) byproduct. The cyclohexene oxide was identified by boiling point and by forming a green color with Reichardt’s dye. In addition, the cyclohexene oxide gave negative results on treatment with bromine and potassium permanganate. The MCBA was confirmed by comparison of its $pK_a$, 3.82, with that of MCPBA, $pK_a$, 7.52. Hydrolysis of cyclohexene oxide yielded trans-1,2-cyclohexanediol. This was confirmed by melting point, and rapid decolorization of the red complex of the reaction with ceric ammonium nitrate (CAN). The trans-1,2-cyclohexanediol complex oxidizes faster than those of simple alcohols, but slower than the cis-1,2-cyclohexanediol complex. Thus, this decolorization provides a novel way to confirm the reaction stereochemistry. All products were characterized by NMR and IR.
Mass Spectrometry Imaging of *Torpedo californica* Electric Organ Using MALDI FT-ICR MS

**Alaina McDonnell**1,2, Emily Schenk1, Mark Harlow3 and Francisco Fernandez-Lima1,*

1Florida International University, Department of Chemistry and Biochemistry, 11200 SW 8th St., Miami, FL 33199
2The University of Tampa, Department of Chemistry, Biochemistry and Physics, 401 West Kennedy Blvd., Tampa, FL 33606
3Texas A&M, The Department of Biology, College Station, TX 77840

The *Torpedo californica* is an electric ray capable of generating and discharging an electric current via its electric organ. The electric organ is composed of bundles of axons surrounded by stacks of electroplaque cells that assist in the production of the electric current. Mass spectrometry imaging by means a Solarix FT-ICR MS equipped with a MALDI source was used to analyze a tissue section approximately 1 mm x 0.5 mm in dimension from the *T. californica* electric organ. Ion density maps of the sample areas were generated to determine biomarkers characteristic to axon bundles or surrounding tissue. Possible compound identification of the biomarkers was made using LIPIDMAPS database, 3 ppm error threshold. Of the 152 and 211 lipids identified in the tissue corresponding to the bundle and surrounding tissue respectively, 54 were identified as being localized within the bundle region. For additional biomarkers observed in which a compound identification could not be made, mass-to-formula calculations using a 1 ppm error was utilized. Eight unidentified biomarkers were also detected using this approach. As a result of the high spatial resolution of this technique and the ability to detect ions simultaneously, the capacity to identify biomarkers in the tissue extends beyond the capabilities of a histological stain alone.
Here we report the functionalization of a zeolite-like metal organic framework of rho topology with two cationic dye molecules, methylene blue (MB⁺) and a ruthenium(II) tris bipyridine complex ([Ru(bpy)₃]²⁺). The spectroscopic properties of both molecules are influenced strongly by host-guest interactions within the cavities of the rho-ZMOF system. These strong interactions can be seen by observing the absorption and emission changes from the functionalized ZMOF with respect to the guest molecules free in solution. The absorption of MB-ZMOF is red shifted with respect to MB⁺ in aqueous solution, while the emission of [Ru(bpy)₃]-ZMOF is blue shifted with respect to [Ru(bpy)₃]²⁺ in aqueous solution. In the MB-[Ru(bpy)₃]-ZMOF, the presence of MB⁺ quenches the emission of [Ru(bpy)₃]²⁺ through an efficient energy transfer mechanism. Analyzing the lifetime of the [Ru(bpy)₃]-ZMOF reveals that there are four unique environments within the system, and increasing the concentration of MB⁺ in the MB-[Ru(bpy)₃]-ZMOF effectively quenches the [Ru(bpy)₃]²⁺ species.
Strain Promoted Click Chemistry Between 8-Azido-7-deazaadenosine Nucleoside Derivatives and Cyclooctynes

Brenna Walsh\textsuperscript{1,2}, Ramanjaneyulu Rayala\textsuperscript{1} and Stanislaw Wnuk\textsuperscript{1,*}

\textsuperscript{1}Florida International University, Department of Chemistry and Biochemistry, 11200 SW 8\textsuperscript{th} St., Miami, FL 33199
\textsuperscript{2}James Madison University, Department of Chemistry and Biochemistry, Harrisonburg, VA, 22807

Strain promoted azide-alkyne cycloaddition (SPAAC) reactions of 8-azido-7-deazaadenosine nucleoside derivatives (3) with various cyclooctynes in aqueous acetonitrile solution at ambient temperature resulted in the formation of the corresponding 1,2,3-triazole products (4). The novel 8-azido-7-deazaadenosine nucleosides (3) were obtained by aromatic nucleophilic substitution of the corresponding 8-bromo-7-deazaadenosine nucleosides (2) with sodium azide. We also report improved syntheses of the previously known 8-bromo-7-deazaadenosine nucleosides (2) from the parent 7-deazaadenosine nucleosides (1) under user friendly conditions in good to excellent yields.
Screening for novel leads towards antibacterial compounds targeting topoisomerase IA, a new target found in all bacteria.

Carlos Paz$^{1,2}$, Thirunavukkarasu Annamalai$^1$ and Yuk-Ching Tse-Dinh$^1$,*

$^1$Florida International University, Department of Chemistry and Biochemistry, 11200 SW 8th St., Miami, FL 33199
$^2$San Diego State University, Department of Chemistry and Biochemistry, 5500 Campanile Dr, San Diego, CA 92115

The need for new antibiotics cannot be overstated. New antibacterial mechanisms have not been developed in the last 30 years, and in all regions of the world common infections have developed very high rates of resistance to all existing antibiotics. Topoisomerases are enzymes found in all organisms, which play an essential part in every DNA function by regulating DNA topology via the rapid cleavage and religation of one or both strands of the DNA double-helix. Those that cleave one strand of the DNA during enzymatic action are referred to as type I enzymes, while type II enzymes cleave both strands. Topoisomerase poison inhibitors kill the cell by altering the cleavage-religation equilibrium, which normally lies heavily towards religation, so that the cleavage complex intermediate is stabilized. This causes the complex to accumulate to intolerable levels, becoming a poison to the cell. Topoisomerase poison inhibitors so far have been developed to target human topo I and II, and bacterial topo II, but bacterial topo I remains to be tapped as a therapeutic target. Here we use a screening assay to screen 60 compound mixtures from Torrey Pines Institute for Molecular Studies for novel candidates leading to topoisomerase poison inhibitors targeting topoisomerase IA, a new antibacterial target found in all bacteria. Of 60 mixtures, 13 were identified as having good relaxation inhibition activity, defined as an IC$_{50}$ of less than 50 µg/mL, while growth inhibition did not correlate to relaxation inhibition, indicating an additional mechanism of antibacterial action for these mixtures.
Nitro disulfonamide o-phenylenediamine derivatives for selective sensing of Pb(II) and other toxic metals

Ingrid Lehman-Andino\textsuperscript{1,2} and Konstantinos Kavallieratos\textsuperscript{1,*}

\textsuperscript{1}Florida International University, Department of Chemistry and Biochemistry, 11200 SW 8th Street, Miami, Florida 33199.
\textsuperscript{2}University of Puerto Rico Río Piedras Campus, Department of Chemistry, San Juan, PR 00931-3346.

Sensing of Pb(II) and other toxic metals based on selective extraction and complexation can lead to new techniques for addressing the challenging problem of toxic metal detection. Exposure of lead and its presence in the environment is a serious health concern. Researching the coordination properties of Pb(II) and other metals with sulfonamide ligands can give us the opportunity to design selective sensors, extractants, and complexes. In our research group we synthesize disulfonamide ion-exchangers derived from o-phenylenediamine. These derivatives can provide a versatile structure capable of sensing Pb(II) via complex formation and extraction in an organic solvent, which results in a change in fluorescent or UV-Vis spectroscopic properties. The 4-nitro-N,N'-bis-p-tolylsulphonyl-o-phenylenediamine ligand (1) and the Pb(II) complex (2) were successfully synthesized with 40\% and 78\% corresponding yields. Attempts to synthesize (1) and (2) by solvent-less methods are also described. The synthesis of the fluorescent dansylated o-phenylenediamine analog (3) was attempted. Extraction experiments showed that the mononitro analog (1) is not as capable for Pb(II) optical sensing as the previously studied dinitro derivative. Analysis by \textsuperscript{1}H-NMR, UV-Visible, and FT-IR of these compounds showing Pb(II) complexation will be elaborated.
Developing Paper Microfluidic Devices to Detect Drugs of Abuse

Jashaun Bottoms\textsuperscript{1, 2}, Ling Wang\textsuperscript{2}, and Bruce McCord\textsuperscript{2,*}

\textsuperscript{1}Florida International University, Department of Chemistry and Biochemistry, 11200 SW 8\textsuperscript{th} St., Miami, FL 33199.
\textsuperscript{2}Tuskegee University, Department of Chemistry, 1200 West Montgomery Road, Tuskegee, AL 36088

The existing presumptive narcotic test kits consist of colorimetric solution tests. The reagents used in these kits were adapted to paper microfluidic devices to improve specificity and the ease of use of the testing. The paper-based tests can provide doctors, law enforcement officers, and toxicologists with a rapid method for screening drugs of abuse at the point of care. The Scott, molybdic acid, and cobalt (II) thiocyanate reagents were successfully applied to the paper devices. A four-channel device was prepared to detect common drugs of abuse. Cocaine could be detected based on a blue color with the Scott reagent. Ketamine produced a lavender color with the basified Co(SCN)\textsubscript{2}, and codeine produced a red color with the molybdic acid reagent. Ephedrine produced a red color with the molybdic acid reagent but reacted inconsistently with the other reagents. The Scott and Co(SCN)\textsubscript{2} reagents were also screened against common drugs and substances that could act as interferences. Overall, the results of this work demonstrate the potential of paper microfluidic devices in detecting drugs of abuse at the point of care or in situations where rapid results are needed.
Fe₈-Based MRI Contrast Agents Targeted to Breast and Ovarian Cancer Cells

Joseph McKillip¹,², Evgen V. Govor¹ and Raphael G. Raptis¹,*

¹ Florida International University, Department of Chemistry and Biochemistry, 11200 SW 8th St., Miami, FL 33199.
²University of Wisconsin-Platteville, Department of Chemistry, 1 University Plaza, Platteville, WI 53818.

Fe₈-based MRI contrast agents (CA) are currently being studied for potential use in breast and ovarian cancer screening. Conjugation of Fe₈ with tyramine-modified hyaluronic acid has high potential to get a new targeted MRI CA specific to CD-44 receptors. We have synthesized [Fe₈O₄(4-Ph-pz)₁₂Cl₄] and further reacted it with 4-NO₂-PhOH, which led to a model compound - molecular 4-substituted complex [Fe₈O₄(4-Ph-pz)₁₂(4-NO₂-PhO)₄]. It was characterized by IR, ¹H NMR, UV-vis, and single crystal XRD, which gives fingerprints for identification of more complicated conjugates. We have attempted conjugation of Fe₈ with tyr-HA, and final conclusions require more characterization by mass and Mossbauer spectroscopies, ¹H NMR.
Phosphate removal from water is important in order to prevent eutrophication in aquatic systems. Presented here is an investigation of phosphate adsorption in aqueous solutions by using Humic Acid-coated magnetic nanoparticles (HA-MNP) as the adsorbent. Various parameters, such as temperature, pH, and ionic strength were tested, and adsorption kinetics and isotherms/mechanisms were explored. The adsorption capacity of HA-MNP was highest under room temperature while some desorption of phosphate occurred at higher temperatures. This can be explained by the fact that some decomposition of HA-MNP might take place at higher temperatures. The adsorption capacity was higher under acidic conditions than under neutral and basic conditions. Ionic strength had little to no effect on the phosphate adsorption. The adsorption kinetics fitted well to the Langmuir adsorption isotherm with monolayer coverage of phosphate on the HA-MNP surface. The overall adsorption process has been found to follow the second order reaction kinetics.
Formation of Thiolated Arsenicals through Reactions with Persulfides

Candace Norton\textsuperscript{1,2}, Szabina Stice\textsuperscript{1}, Andres Marin\textsuperscript{1}, Guangliang Liu\textsuperscript{1} and Yong Cai\textsuperscript{1,*}

\textsuperscript{1}Florida International University, Department of Chemistry and Biochemistry, 11200 SW 8th St., Miami, FL 33199.
\textsuperscript{2}Florida Gulf Coast University, Department of Chemistry and Physics, 10501 FGCU Blvd, South Fort Myers, FL 33965.

Glutathione persulfide (GSSH), a model compound for protein persulfides, was proven to be a potential sulfur donor to Dimethylarsinic acid (DMA\textsuperscript{V}) to form thiolated arsenticals such as Dimethylmonothioarsinic acid (DMMTA\textsuperscript{V}) and Dimethylthioarsinic acid (DMDTA\textsuperscript{V}). Recently, cystein persulfide (CysSSH) was discovered to be present in cells at prevalent concentrations and was found to regulate important cellular functions. We hypothesized that it is possible that CysSSH may be one of the thiol donors for the formation of toxic pentavalent sulfur containing arsenticals in human cells. We have successfully synthesized CysSSH and GSSH and developed a high performance liquid chromatography ultra violet (HPLC-UV) method for their quantitation. The produced CysSSH was reacted with DMA\textsuperscript{V} to observe its ability to donate the sulfur to form DMMTA\textsuperscript{V} and DMDTA\textsuperscript{V} using high performance liquid chromatography inductively coupled mass spectrometry (HPLC-ICP-MS). The abilities of CysSSH and GSSH to produce these compounds were compared and found to be comparable. Based on the experiments performed, we found that both protein persulfides and CysSSH are probable sulfur donors for arsenic under physiological conditions.
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Role of Trp13 and Trp133 in ligand migration in human neuroglobin

Camilo Varona\textsuperscript{1} and Jaroslava Miksovska\textsuperscript{1,*}

\textsuperscript{1}Florida International University, Department of Chemistry and Biochemistry, 11200 SW 8\textsuperscript{th} St., Miami, FL 33199

Desorption Electrospray Ionization Optimization for Analysis of \textit{Torpedo Californica} Electric Organ Tissue

Cynthia McCord\textsuperscript{1}, Junho Jeon\textsuperscript{2}, Emily Schenk\textsuperscript{2}, Paolo Benigni\textsuperscript{2} and Francisco Fernandez-Lima\textsuperscript{2}

\textsuperscript{1}Florida International University, Department of Chemistry and Biochemistry, 11200 SW 8\textsuperscript{th} St., Miami, FL 33199
\textsuperscript{2}University of West Florida, Department of Chemistry, 11000 University Pkwy, Pensacola, FL 32514

Application of fluorescent probes to monitor binding of hydrophobic molecules to DREAM and its oligomerization states

Norman Mayorga\textsuperscript{1}, Walter Gonzalez\textsuperscript{1} and Jaroslava Miksovska\textsuperscript{1,*}

\textsuperscript{1}Florida International University, Department of Chemistry and Biochemistry, 11200 SW 8\textsuperscript{th} St., Miami, FL 33199

Towards selective Pb(II) complexation and fluorescence sensing by a phenazine disulfonamide ligand

Natalli Bertolotti\textsuperscript{1}, Jessica J. Dela Cruz\textsuperscript{1} and Konstantinos Kavallieratos\textsuperscript{1,*}

\textsuperscript{1}Florida International University, Department of Chemistry & Biochemistry, 11200 SW 8th St., CP 304, Miami, FL, 33199
Synthesis of 6-N-substituted 7-deazapurine nucleoside antibiotics: Potential nucleoside transport inhibitors

Ramanjaneyulu Rayala¹, Patricia Theard¹, Heysel Ortiz¹, Sylvia Yao², James D. Young², Jan Balzarini³, Morris J. Robins⁴ and Stanislaw F. Wnuk¹.

¹Department of Chemistry and Biochemistry, Florida International University, Miami, FL, 33199
²Department of Physiology, The University of Alberta, Edmonton, Alberta, Canada T6G 2H7
³Rega Institute for Medical Research, KU Leuven, B-3000 Leuven, Belgium
⁴Department of Chemistry and Biochemistry, Brigham Young University, Provo, Utah, 84602.