

4-23-2019

Department of Chemistry and Biochemistry 24th Departmental Symposium in Conjunction with the Petersheim Academic Exposition

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ROSE MERCADANTE SEMINAR SERIES

Department of Chemistry and Biochemistry 24th Departmental Symposium in Conjunction with the Petersheim Academic Exposition

Book of Abstracts

**McNulty Hall
Seton Hall Science and Technology Center
April 23, 2019**

Poster Setup: 5:00 – 5:30 PM, Mary Ann and Pat Murray Atrium

Refreshments: 5:30 PM

Lecture: 5:45 – 6:45 PM, Helen Lerner Amphitheater

Poster Session: 7:00 – 9:00 PM, Mary Ann and Pat Murray Atrium

7:00 – 7:45 Odd Numbered Poster Authors Present at Poster

7:45 – 8:30 Even Numbered Poster Authors Present at Poster

8:30 – 9:00 Open Discussions

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Keynote Lecture

Polymer Sensors: A Journey from the Academic Laboratory to a Commercial Product

Dr. Joseph BelBruno (SHU '74)

Department of Chemistry Dartmouth College, Hanover, NH 03755

FreshAir Sensor, LLC, Lebanon, NH 03766



The path from an academic laboratory experiment to a product that can be successfully introduced to commercial users is littered with roadblocks. Ideal conditions in the lab and the expertise of the researchers ease the path to the academic journal publication. However, when the same device is released in the wild, unforeseen, and sometimes unimaginable, results occur. This talk will describe the laboratory experiments and chemistry used to develop a molecule-specific tobacco smoke sensor, initially proposed as a research tool for child exposure to parental smoking. The device eventually became the

leading product of FreshAir Sensor, LLC and, with the addition of a marijuana-specific smoking sensor, is installed in hotels, rental housing and schools to eliminate smoking in areas where such activity is banned. The role (and the education) of the scientist in the formation of a viable company, which includes an extensive R&D effort in both chemistry and engineering, will be described.

Professor BelBruno is a faculty member in the Department of Chemistry at Dartmouth College. He graduated with a B.S. degree in Chemistry from Seton Hall University in 1974. After a short interval in industry, he enrolled in graduate school and received the Ph.D. in physical chemistry from Rutgers University in 1980. Subsequent postdoctoral research at Princeton University involved theoretical studies of chemical reaction dynamics with a joint appointment in the Departments of Chemistry and Mechanical & Aerospace Engineering. He joined the Dartmouth faculty in 1982, and early research focused on the spectroscopy of large molecules, leading to the use of lasers to deposit thin films and subsequently, since 2006, to thin film sensors and materials. He served, for a time, as the Director of the Dartmouth Center for Nanomaterials.

His sensor research is focused on the development of materials and complete sensing units targeted to a wide variety of targets. These target molecules include saccharide tumor markers, explosive residues, amino acids, and environmental pollutants. He has also developed solid phase extraction materials, based on the same polymer technology to reduce the levels of undesirable flavor components in foods and beverages, such as wine. He has worked with commercial companies under research agreements and has received support from diverse sources, including the American Academy of Pediatrics, the Flight Attendant Medical Research Institute, the National Institute of Health, the National Science Foundation, and the Norris Cotton Cancer Center. He has published more 140 peer reviewed papers and holds 12 patents in sensors and coatings. Joe co-founded FreshAir Sensor, LLC in 2013 and serves as Chief Technical Officer. FreshAir currently markets the only sensing systems to specifically detect tobacco and marijuana smoke in real time, providing rapid notification to property owners and preventing smoking in hotels, public housing and schools. A wide range of other sensors are currently under development at FreshAir Sensor, which hosts an active R&D program.

Dr. Cosimo Antonacci

1.

Vaccinia Virus Transcription Factor Expression and Purification for in Vitro Poxvirus DNA Binding and Poxvirus Early Transcription Inhibition Studies

Brian T. Reiss, **Christopher H. Beasley**, Cosimo Antonacci, D. Brian Nichols
Department of Chemistry and Biochemistry, Department of Biological Sciences
Seton Hall University, South Orange, NJ

Poxviruses are dsDNA viruses that transcribe viral DNA temporally with early, intermediate and late gene products. Early genes code for viral proteins that function in host interaction and viral genome transcription and replication. The conserved promoter sequence serves as the binding site for early transcription factors, enabling the downstream production of viral proteins. In Vaccinia virus (VACV), A7R and D6L transcription factors bind the E9L promoter region to the viral DNA polymerase, which catalyzes the replication of DNA. Within this region is a potential DNA secondary structure called a G-quadruplex composed of three stacked G-quartets that may function in transcriptional and translational regulation. G-quadruplexes are potential targets for drug binding. Binding of this region could prevent the production of the DNA polymerase thereby inhibiting the replication of DNA, which could lead to reduced virulence. This project aims to test potential inhibitory functions of a G-quadruplex binding molecule on the VACV E9L promoter sequence. The VACV E9L sequence was cloned into a pJET1.2 vector and transformed into bacteria cells to be replicated and harvested for DNA. Current studies are aimed at determining the conformational states adopted by these sequences using Circular Dichroism spectropolarimetry. The VACV A7 and D6 transcription factors were separately cloned into pET vectors and transformed into BL21 (DE3) *E. coli* cells to express useful quantities of protein. Transcription factors were run through a nickel resin gravity column to purify His-epitope tagged transcription factors. Future studies will be aimed at combining DNA and purified proteins to assess binding.

2.

Lipstick “Blooming” – W/O Crystallization Effects with DSC Analysis

Jessica Aragona, Cosimo Antonacci, Ph.D., James E. Hanson, Ph.D.
Department of Chemistry and Biochemistry
Seton Hall University, South Orange, NJ

Cosmetic lipsticks are commonly made with both basic and complex components, then are sold through various avenues to the mass-market. Oils and waxes make up the primary ingredients of lipstick formulas and it is this ratio that will be analyzed here. Many consumers have noted that their lipstick products seem to ‘sweat’ or ‘bloom’ when reaching a time period of roughly 6 months of being open and after first use. This blooming effect is the natural dispersion of the waxes, from within the oil emulsion, reaching the surface of the product and creating bead-like dots on the exterior. While there is no specific sanitary issue with this effect, as it is only the input waxes coming out of the formula, many consumers are concerned with the aesthetic look of their

cosmetics and the value for potential high-end products. The goal of this research is to perfect a formula in which a ratio of oils and waxes are present to minimize the blooming effect of stabilized long-term lipsticks, as well as still upholding customer satisfaction with the produced cosmetic.

3.

Developing Antioxidant Lipsticks Using Essential Oils

Ellora Haukenfrers, Cosimo Antonacci, Ph.D., Fr. Gerald Buonopane, Ph.D.

Department of Chemistry and Biochemistry

Seton Hall University, South Orange, NJ

As the industry of cosmetic chemistry rapidly adapts to the ever-changing world, it must stay current. The latest trend is products made using natural ingredients as opposed to those unknown to the average consumer, such as essential oils, which contain antioxidants. Antioxidants have radical scavenging activity, which helps to protect cells from the damage caused by free radicals. Free radicals are unstable molecules that are made in normal cell metabolism however they can collect and damage other molecules, leading to diseases, including cancer. Essential oils have proven to have an antioxidant quality in lipsticks, making them anti-inflammatory, immunomodulatory, and regenerative. We report here the testing of essential oils using 2,2'-diphenyl-1-picrylhydrazyl (DPPH) free radical scavenging method. Upon determination of the best essential oils exhibiting the highest antioxidant activity, lipstick formulations will be developed accordingly.

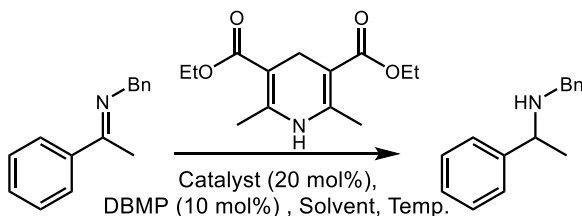
Dr. Joseph Badillo

4.

Title: Carbocation Catalyzed Imine Functionalization Through Asymmetric Transfer Hydrogenation

Presenters: Darwin Glynn, Michael Freddy, Kiraia Harris, and Joseph Badillo*

College: Department of Chemistry and Biochemistry



Abstract:

Chirality and Enantiospecificity play an important role in the treatment of diseases by producing a desired effect when targeting an intended biological target. However, if the wrong region of the receptor is stimulated then it can cause a cascade of various undesired side effects. One case of a drug producing debilitating side effects was seen in thalidomide. The (*R*)-enantiomer of thalidomide cures nausea, while the (*S*)-enantiomer prevents the development of major blood vessels during pregnancy that lead to multiple physical and mental complications of newborn infants.

This research evaluates the potential of Lewis acidic carbocations as catalysts for the asymmetric transfer hydrogenation of imines in order to produce chiral amines. We began by examining transfer hydrogenation of aryl ketone derived imines using Hantzsch ester as the hydride source. A range of achiral carbocation catalysts were investigated. The reaction was found to be temperature dependent and the highest yield for amine formation (76%) was obtained using 20 mol% tritylium tetrafluoroborate at 80 °C in 1,2-dichloromethane. A proton sponge was used in order to show the reaction is Lewis acid catalyzed and not catalyzed by adventitious acid produced under the reaction conditions. Future plans include the development of enhanced Lewis acid carbocation catalysts and the use of chiral counterions to promote enantioselective amine formation.

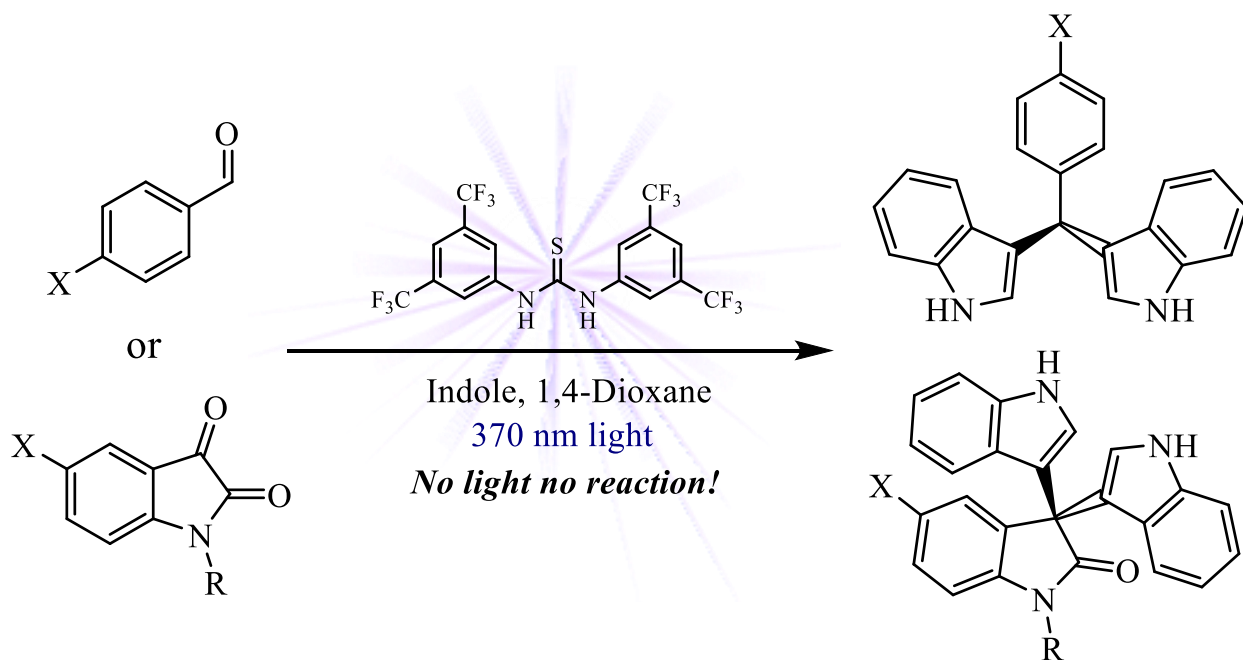
5.

Photoacid Catalyzed Friedel-Crafts Alkylation of Carbonyls

Zena Salem, Jason Saway, Samantha Chalet, and Joseph Badillo*

Seton Hall University, Department of Chemistry and Biochemistry, 400 South Orange Ave, South Orange, New Jersey 07079

Photoacids are molecules that become orders of magnitude more acidic upon the absorption of light. Here we show that a simple organophotoacid, such as Schreiner's thiourea, is capable of being engaged in hydrogen bonding catalysis through visible light excitation to enable the synthesis of numerous bis(indolyl)phenylmethanes. Bis(indolyl)phenylmethanes are interesting therapeutics for drug discovery due to their ability to interact with various ligand binding domains within cancer cells to either induce cellular apoptosis or inhibit cellular growth. Initial studies for the addition of π -nucleophiles to carbonyl compounds show that in the absence of light, the thiourea-catalyzed reaction is completely shut down. Specifically, we have demonstrated that excited state N,N'-bis[3,5-bis(trifluoromethyl)phenyl]-thiourea facilitates the double addition of indole to aldehydes and isatins to form the corresponding 1,1-bis(3'-indolyl)-1-phenylmethanes and 3,3'-bisindolyl oxindoles. Reaction conditions including solvents, light sources, photoacids, catalyst loading, and a range of electrophilic carbonyls and nucleophilic aromatics have been investigated.



6.

Photoacid Catalyzed Alkylation and Acetalization of Carbonyl Compounds

Jason Saway, Zena Salem, Samantha Chalet, and Joseph Badillo*

Seton Hall University, Department of Chemistry and Biochemistry, 400 South Orange Ave, South Orange, New Jersey 07079

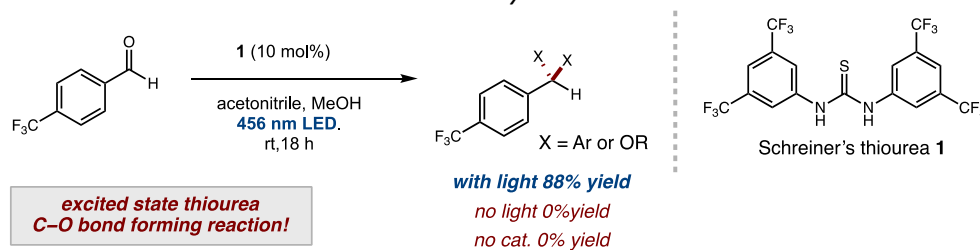


Photo-catalyzed synthesis strategies have recently gained interest in the pharmaceutical industry due to the use of visible light as a mild way to activate organic processes. Photo-catalysts can reduce reaction times and more importantly eliminate the need for environmentally harmful reagents and the production of waste products. We have observed that the visible light-excited state of Schreiner's thiourea facilitates product formation in a variety of reactions. First, we studied the alkylation of indole with aldehydes and isatins. Here a double addition of indole to the carbonyl of an aldehyde or isatin forms two new C-C bonds. The products from these reactions have been identified as potential probes for the study and treatment of cancer. We have also shown that Schreiner's thiourea catalyzes the formation of C-O bonds. Using 10 mol% photoacid catalyst enables the photoinduced acetalization of aldehydes with a range of alcohols. The acetals produced have been shown to be useful in the multistep synthesis of complex natural products and other biologically relevant products.

Fr. Gerald Buonopane

7.

Antioxidant Activity in Proline-Linolenic Acid Mixtures Using the DPPH Method

Sweta Rana, Giovanna Dabbagh, Mariez Aziz, Viral Shah, and Gerald J. Buonopane

Department of Chemistry and Biochemistry, Seton Hall University

Most processed and packaged foods often contain both a fat/lipid source and a protein/amino acid source. Fats can oxidize due to various environmental conditions, including elevated temperature and exposure to light. In particular, lipids that have oxidized can in turn react to oxidize amino acids and proteins within a food system. The resulting oxidized proteins are adversely affected in terms of their structure and function. Understanding the reactions of oxidizing lipids with proteins is important for determining reduction of nutritional quality of a food, as well as helping to predict quality deterioration during processing and storage. In this study, the amino acid proline and the polyunsaturated fatty acid linolenic acid were combined in model systems to study their interaction with one another. It is noteworthy that proline has been shown to exhibit antioxidant properties. Antioxidant analysis employing the stable radical DPPH was used to determine oxidation of the fatty acid and possible antioxidant protection from the proline. Three model systems were prepared in triplicate in 25-mL volumetric flasks with each containing 1) only proline (20 mg), 2) only linolenic acid (20 mg), and 3) both proline and linolenic acid (20 mg each). Samples were placed in an oven at 40°C for 12-16 hours. After incubation, the samples were brought to volume with methanol followed by preparation of serial dilutions in 10-mL volumetric flasks. Concentration ratios of linolenic acid/proline were 240, 160, 80, 40, and 16 µg/mL. Each of these was reacted with DPPH (0.3 mM) and then stored in the dark for 30 minutes. Absorbance of the samples was then measured on a MetaSpec UV/VIS Spectrophotometer at 518 nm. Samples containing only proline and those containing both proline and linolenic acid demonstrated antioxidant activity of proline.

Dr. Alexander Fadeev

8.

Adsorption and Wetting Study of Energetic Nitrocellulose

Henry Grau & Dr. Alexander Y. Fadeev
Department of Chemistry/BioChemistry
Seton Hall University

Abstract

In our previous work nitrocellulose was functionalized by a two-step process using the reaction of 3-(triethoxysilyl-propyl isocyanate followed by reactions with either alkyl-, fluoroalkyl, or phenyl silane producing NC surfaces ranging in lyophobicity^{1,2}. The wettability of the modified nitrocellulose was characterized by contact angle techniques, Chemical analysis, and solid state FTIR techniques.

In this work we study the sorption parameters of nitrogen and water on untreated NC and surface treated NC. We find the nitrogen adsorption on untreated 12.47% NC demonstrate a type IV isotherm attributed to distinct capillary condensation with narrow hysteresis, possibly of the H3 type. From these observations, we speculate the contribution of secondary porosity between the NC fibers. The initial comparison of untreated NC with alkylsilane gives low c-constant values using the BET equation. This may be related to the low surface energy of the treated NC compared to the more polar surfaces of untreated NC. For water sorption the treated NC surfaces adsorbed less water than the untreated NC. Initial studies show that NC treated with tetramethoxysilane vapor adsorbed less water than neat NC.

This study also involves utilizing nitroglycerin as a probe fluid on a number of known surfaces. In open literature there is very little data concerning the surface properties of nitroglycerin. We find that the measurement of NG surface tension was first measured circa 1934. The measurement of liquid surface tension is temperature dependent and is characteristic of the liquid. The surface tension of NG as a function of temperature, which may be of importance in several industries, is lacking entirely in literature. We performed an extensive literature search only to discover that we are unable to locate data related to the wetting properties of nitroglycerin. This is most likely due to the hazards of sensitivity and potential of explosion when isolating pure NG. According to previous studies, pure nitroglycerin has a surface tension of 50.5(mJ/m²) similar in value to methylene iodide. Methylene iodide is a common probe fluid used commonly by researchers in surface characterization. With few exceptions, NG should have similar wetting properties. In this study, we utilize NG as a probe fluid on a variety of surfaces. We compare NG and methylene iodide contact angles. We measure the surface tension of NG at variable temperatures up to 60°C after which degradation and increased vapor pressure starts to have direct influence on the measurements.

Reference:

- 1. Grau. H. Fadeev, A.Y. Methods for Modifying Nitrocellulose having Lyophobic Properties. U.S. patent number: 9856328. Date of Patent: January 2, 2018.**
- 2. Grau. H. Fadeev, A.Y. "Raincoat for Explosives": Surface Chemistry Approach to Control Wetting of Nitrocellulose with Nitroglycerin, *Journal of Colloid and Interface Science* (2019). Doi: <https://doi.org/10.1016/j.jcis.2019.03.063>**

9.

Nickel Phthalocyanine

Suazo, M., Pelmus, M., and Gorun, S. M.*

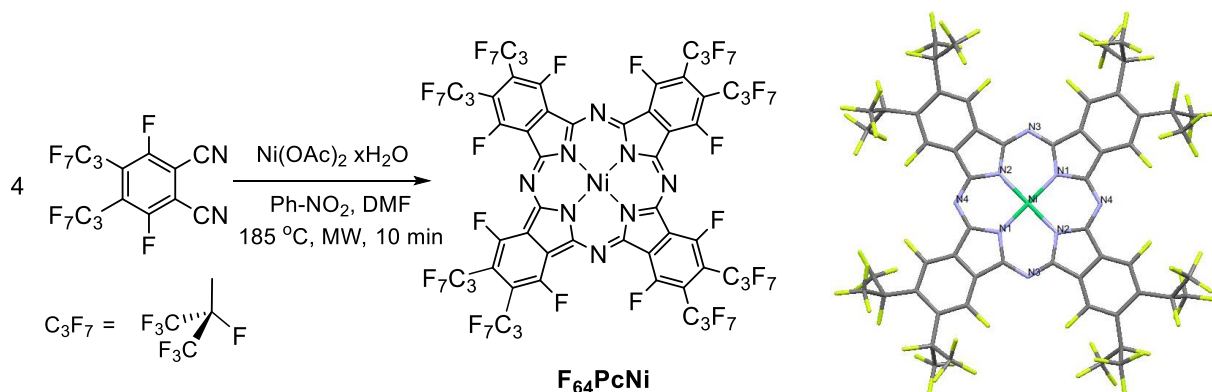
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Phthalocyanines (Pc) are chelating macrocyclic photo-catalysts that can convert O_2 from air into singlet oxygen and then reactive oxygen species (hydroxyl radicals, superoxide ions). The chelated metal can influence the photo-catalytic properties and impart redox characteristics making the complexes suitable for numerous applications in both the industrial and the medical field: as a dye in textiles, laser jet printing, in photodynamic therapy of cancer, as a catalyst in industrial systems and many more.¹

We report the synthesis of a perfluorinated nickel Pc, $F_{64}PcNi$, substituted with bulky perfluoroisopropyl ($i-C_3F_7$) groups to create a robust and stable Teflon-like shielded catalyst, resistant to decomposition and deactivation.² While there are extensive studies of PcM with $M = Cu, Zn, Co, Fe, Mn$, $PcNi$ have very minimally been investigated, except for efficient catalysis of reductions reactions.¹

$F_{64}PcNi$ was synthesized by the condensation of a perfluoroisopropyl-phthalonitrile precursor using a microwave reactor. The compound was purified *via* gravity column chromatography. Spectroscopic characterization of the compound included high resolution mass spectroscopy, ^{19}F NMR, FT-IR and UV-Vis.



X-Ray quality crystals were grown from acetone confirmed the proposed, $F_{64}PcNi(II)$, structure. Aggregation studies carried out in both non-coordinating (trifluorotoluene) and coordinating (ethyl acetate) solvents confirmed the lack of aggregation, and thus, ascertaining no possible deactivation of photo-catalysts by π - π stacking. The ^{19}F NMR virtually identical when $M = Zn(II)$ or $Ni(II)$ (but not for $d^7 Co(II)$ or $d^9 Cu(II)$) indicated that the $PcNi$ is also diamagnetic, low-spin $d^8 Ni^{2+}$.

Surprisingly, $F_{64}PcNi$ exhibits no fluorescence and no ability to generate singlet oxygen. The reason for this unusual behavior is under investigation by using singlet oxygen traps.

1. Sorokin A. *Handbook of Porphyrin Science* 2016 **189**: 193-322.
2. Trashin S. et al. *Nature Communications* 2017, **8**: 16108.

10.

Push-Pull Type Phthalocyanine

Xiao, O. C., Pelmus M., and Gorun S. M.*

Seton Hall University, Department of Chemistry and Biochemistry

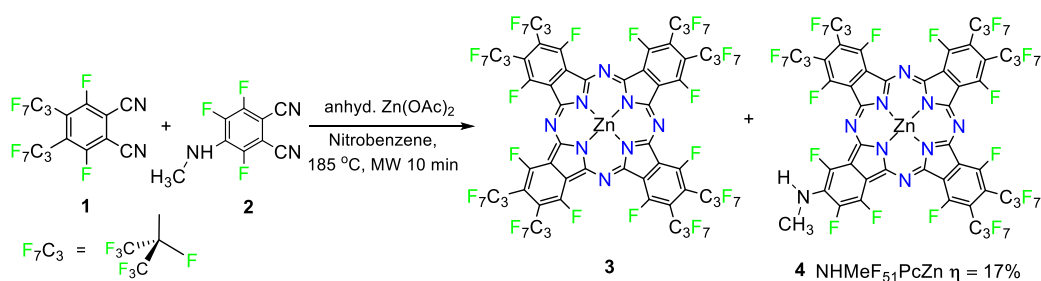
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Dye sensitized solar cells (DSSCs) sustainably capture the Sun's energy and convert it into electricity. DSSCs include a dye that uses Sun radiation to inject electrons into a TiO₂ semiconductor. Phthalocyanine (Pc) photosensitizers beneficially absorb in the red/near IR region, thus over half of the available solar energy,^[1] and are thermally and chemically stable. Planar Pcs favor aggregation, thus diminishing the capacity for photon capture.^[1]

Fluoroalkyl zinc (II) phthalocyanine, F₆₄PcZn, contains bulky peripheral fluoro groups on all its 4 quadrants. They hinder aggregation. We hypothesize that amino, 3 quadrants-hindered F₅₁PcZn, attached to TiO₂ might yield a hybrid material with electron injection capabilities.

The target NHMeF₅₁PcZn, **4**, was synthesized in a microwave (MW) reactor by combining two different precursors, **1** and **2**. F₆₄PcZn, **3** was also obtained.



The NHMeF₅₁PcZn, purified chromatographically exhibits the known UV-Vis, FT-IR, ¹⁹F NMR properties of **4** obtained more laboriously via conventional synthetic methods.^[2] Variable amounts of **4** were supported on relatively narrower and wider gap TiO₂ and SiO₂, respectively. Solid state fluorescence of the TiO₂-supported **4** was about 1/2 as intense as the equimolar **4** supported on SiO₂, while a linear UV-Vis absorption vs. concentration dependency was observed for both types of solid supports. The fluorescence quenching suggests an electronic communication between **4** and TiO₂, absent between **4** and SiO₂. The elucidation of the communication type is the aim of future work.

Acknowledgments

The SHU-New Jersey Space Grant Consortium and Center for Functional Materials (SHU) are kindly thanked for financial support.

References

1. García-Iglesias, M. *et al.* Effect of anchoring groups in zinc phthalocyanine on the dye-sensitized solar cell performance and stability *Chemical Science*, **2011**, *2*: 1145.
2. Patel, H.H. *Fluorinated metallo phthalocyanines for chemical and biological catalysis*, **2015**, Seton Hall University Dissertations and Theses (ETDs).

Dr. James Hanson

11.

Degradation of Organic Dyes on F₆₄PcZn supported on Silica

J. Bandala, A. Azeez, S.M. Gorun*, J. Hanson*

¹*Department of Chemistry and Biochemistry, ²Center for Functional Materials, Seton Hall University, 400 South Orange Avenue, South Orange NJ 07079*

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Abstract:

Metallophthalocyanines (PcM) are metal complexes that are structurally similar to porphyrins, found in nature. This study focuses on the properties of Pc containing zinc as the central metal ion. In this work, F₆₄PcZn is used as a catalyst embedded on superhydrophobic surface that are self-cleaning. The purpose of this research is to study the photocatalytic application of a catalyst for the degradation of dyes such as Rhodamine B, Evans Blue, Rose Bengal, Methylene Blue, Methyl Orange and Crystal Violet. The organic dyes will be irradiated under a broad spectrum of light to determine the kinetic activities of the photodegraded dyes. Cleaning the discharged wastewater is a serious environmental issue since the colored waste prevents the re-oxygenation of water by cutting out the penetration of sunlight, this promoted the study six dyes that are used commercially for industrial applications.¹ Many dyes are difficult to degrade since they are resistance to aerobic digestion and they cause allergic reactions and skin irritations.¹ The degradation of organic dyes over time is analyzed and the rate of degradation will be determined by UV-VIS, HPLC, and LCMS analytical techniques.

References:

1. Yurtoğlu, N. *Department of Applied Chemistry* 2013, 10(7), 241–264.

12.

Preparation and Photocatalytic Characteristics of Magnetically Reusable Fe₃O₄ nanoparticles coated with F₆₄PcZn

N. Jimenez, A. Azeez, S.M. Gorun, J. Hanson

¹*Department of Chemistry and Biochemistry, ²Center for Functional Materials, Seton Hall University, 400 South Orange Avenue, South Orange NJ 07079*

**Correspondence should be addressed to: Sergiu.Gorun@shu.edu and James.Hanson@shu.edu*

Abstract:

The preparation of core-shell nanoparticles has grown and with great interest for widespread potential applications in the areas of catalysis, chromatography separation, drug delivery, chemical reactors and protection of environmentally sensitive materials. The proposed research is to prepare Fe₃O₄ as a solid support coated with F₆₄PcZn as the catalyst. Fe₃O₄ magnetite nanoparticles (MNPs) as a good candidate for solid support and also for catalytic purpose due to its special property, notable as a magnetic catalyst and other properties include improved surface area, low toxicity and potential applications in various fields. [1] Originally, traditional separation methods in chemistry are always too expensive and can pose the greatest potential hazard including photocatalyst loss resulting to secondary pollution. The metal substituted phthalocyanines or in other words metallophthalocyanines (PcM) are a class of organic/inorganic dye material that is structurally similar to porphyrins, which are found in nature. Phthalocyanines are large, aromatic, organic compound that is composed of four isonidole units linked by nitrogen atoms. In this case, F₆₄PcZn will be studied under magnetite as it becomes magnetic catalyst. They can serve as catalysts and photocatalysts due to their high efficiency to generate free radicals and excited state species. With this study, the photocatalytic activities of the composites are evaluated using the degradation of methyl orange solution and potentially other dyes as case study for this research.

References:

- 1) Jin, X., Zhang, K., Sun, J., Wang, J., Dong, Z., and Li, R. (2012). Magnetite nanoparticles immobilized salen Pd(II) as a green catalyst for Suzuki reaction. *Catalysis Communications*, 26: 199-203.

13.

Hydrophobic Polymer Coatings

Daniel M. Goldman and James E. Hanson

Seton Hall University

Department of Chemistry and Biochemistry

Petersheim Conference 2019

Abstract

The general applicability of a method for preparing super hydrophobic polymer coatings was investigated. To simplify the evaluation, only those polymers soluble in DMF were studied. Selections of such polymers of different types (addition vs. condensation, vinyl vs. polyester, etc.) were prepared as DMF solutions. To each solution was added a volatile salt in varying amounts. The materials were coated onto substrates as films, and then heated to volatilize the salt. The hydrophobicity of the films was then evaluated using contact angle measurements.

14.

Formulation and Evaluation of Antibiotic microspheres against Gram-negative *Escherichia coli* and Gram-positive *Staphylococcus aureus*

Miguel Medico ^a, Ayuni Yussof ^b, Dr. Tin-Chun Chu ^b, Dr. James E Hanson ^{a,*}

^a Department of Chemistry and Biochemistry, Seton Hall University, USA

^b Department of Biological Sciences, Seton Hall University, USA

Plant-derived flavonoids are a large group of naturally occurring phenylchromones found in fruits, vegetables, tea, and wine. Flavonoids have shown to have a wide range of biological activities, including antiallergic, antibacterial, antiinflammatory, antimutagenic, antioxidant, antiproliferative, antithrombotic, antiviral, and hepatoprotective effects. A certain flavonol glycoside has antiplatelet, antiviral, antihypertensive properties, as well as strengthen the capillaries of blood vessels. These properties are potentially beneficial in preventing diseases and protecting the stability of the genome. Erythromycin (ERY) is a bacteriostatic macrolide antibiotic. ERY is effective against skin and the upper respiratory tract infections caused by Gram-positive bacteria. Poly (DL-lactide-co-glycolide) (PLGA) has been approved for several biomedical applications in humans and is widely used for drug delivery. PLGA has been successful as a biodegradable polymer because it undergoes hydrolysis in the body to produce the original monomers, lactic acid and glycolic acid, which are metabolized in the Krebs cycle to produce carbon dioxide and water. In this investigation, the antibacterial and biological properties of flavonoid-PLGA and erythromycin-PLGA microparticles were studied. Two types of bacterial strains, *Staphylococcus aureus*

and *Escherichia Coli* were chosen to evaluate the antibacterial activity of microparticles formed by solvent evaporation technique.

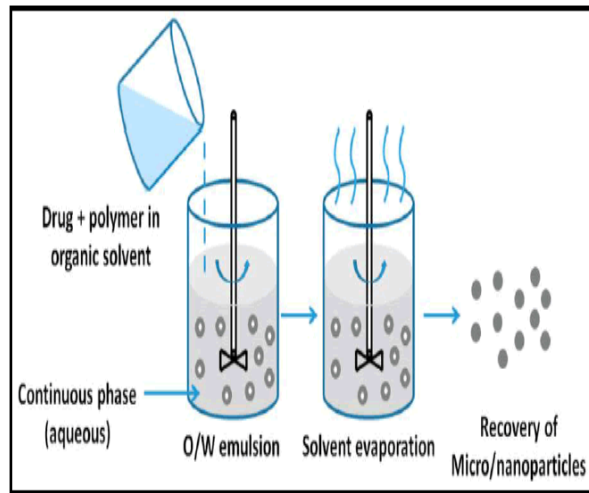
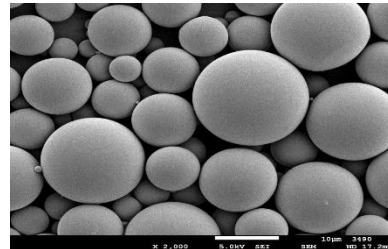


Figure 1: Solvent evaporation technique.



Dr. Yuri Kazakevich

15.

Non-Distractive Chromatographic Determination of a Surface-Area in Reverse Phase Chromatographic Columns

Margaret Figus¹, and Yuri V Kazakevich¹

¹*Department of Chemistry and Biochemistry, Seton Hall University, South Orange, NJ 07079*

One of the critical, but an underutilized parameter that affects chromatographic separation is an adsorbent surface area (SA). The analyte retention volume is proportional to the surface area of the packing material. Traditionally, the application of the Brunauer, Emmet, and Teller (BET) theory to the nitrogen adsorption isotherm is employed for the determination of the surface area in chromatographic columns; however, this is a complicated method, and it required expensive instrumentation. Herein we introduce a concept of direct determination of the SA in chromatographic columns by utilizing the Minor Disturbance Method and the application of the Standard Excess Adsorption Isotherm from acetonitrile-water and methanol-water binary mixtures for direct determination of the SA in chromatographic columns.

This undistracted technic was used to determine SA in five commercial columns including three different poroshell columns (Kinotex-C18, Ascentis C-18, and Halo C18), and four in-house made columns (C1, C-4, C-8, and C-18). Herein we are comparing SA results of traditional LTNA technic to the novel chromatographic method. The chromatographically determined SAs for nine columns are in excellent agreement with the traditional technique. The percent difference between the two technics is less than 10%.

Additionally, the amount of the packing material, chromatographically determined pore volumes, and bonding densities were also presented.

16.

Surface Characterization of Blended Silica and C18 Adsorbents and Mixed-Mode Adsorbents by Low Temperature Nitrogen Adsorption

Dinah Lee, Yuri V. Kazakevich

Department of Chemistry and Biochemistry, Seton Hall University

Mixed-mode chromatography is becoming increasingly popular in pharmaceutical and biopharmaceutical applications due to its unique selectivity and retention of a variety of compounds [1]. Adsorbents with surface bonded ligands of different nature are used in mixed-mode chromatography. Solutes interact with those ligands through more than one interaction mode or mechanism. It is because of these complex interactions, however, that it is difficult to predict chromatographic behavior of analytes on mixed-mode columns. Characterization of different mixed-mode columns on the basis of surface energy characteristics has not been explored.

We selected formalistic normalization and indexation approach for characterization of these adsorbents. The most universal energetic characterization for highly different surfaces arguably could be C-constant of BET equation. According to Gregg and Sing [2] C-constant represent the exponent of the excessive energy of nitrogen-surface interaction over its condensation energy at 77 K. The mixtures of silica and C18-modified silica (Luna 5 μ m Silica - Phenomenex), and C18 (Luna 5 μ m C18 – Phenomenex), in the proportions where their surface area was incremented by 10% for each indexation point was chosen as index scale. C-constant of these mixtures were measured using Micromeritics nitrogen adsorption system.

A variety of commercially available mixed mode columns were unpacked and the materials were analyzed by LTNA. Adsorption isotherms, surface area, and BET constants were obtained for all the blended materials in various ratios and the mixed-mode materials. A linear relationship between the BET C-constant and the blend ratio of silica has been observed. The results from the commercial mixed mode packing material showed similar surface energy characteristics to single mode C18 materials. This data suggests that the BET C-constant maybe a viable parameter that can be used to characterize mixed-mode columns on the basis of surface energy. Chromatographic characterization will be performed by studying the retention behaviors of model analytes to illustrate the hydrophobic and hydrophilic properties of the blended stationary phases.

Utilizing this surface energy scale in conjunction with the study of retention behaviors on mixed-mode material could lead to improvements in the understanding of method development on mixed-mode columns, allow the comparison of commercialized mixed-mode columns, and even predict retention behavior of an analyte in mixed-mode columns.

Reference:

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17.

Measuring Longitudinal Temperature Gradients under Ultra High-Performance Liquid Chromatography Conditions

Timothy Nowak, Alexey Makarov, and Yuri Kazakevich
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Seton Hall University

The usage of sub-2-micron particles in liquid chromatography is very popular in liquid chromatography since faster and more efficient chromatographic separations can be achieved in comparison to traditional (3 μ m, 5 μ m) particle size stationary phases. However, the reduction of the particle size leads to a significant increase in backpressure. In addition, heat is generated when the mobile phase passes through a column of finely packed particles. As the heat dissipates through the column, non-uniform temperature gradients can occur both along (longitudinal gradients) and across (radial gradients) the column. However, the environment surrounding the stationary phase bed influences the gradient temperature dissipation. In this study, we measure the longitudinal temperature gradients, while assessing its impact on the chromatographic behavior for several analytes.

18.

Intact Analysis of therapeutic monoclonal antibodies using Hybrid Hydrophobic Interaction Chromatography on poly (alkyl aspartamide) silica columns

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Developing mass spectrometry compatible HPLC methods to analyze therapeutic monoclonal antibodies (mAbs) has been a growing interest of pharmaceutical industry. Hydrophobic interaction chromatography (HIC) was found to be the most powerful and suitable analytical technique for separation of these biomolecules in their native form. However, due to the use of high concentrations of non-volatile salts in the mobile phases, HIC is incompatible with online mass spectrometry (MS).

HIC columns packed with poly (alkyl aspartamide) silica can be used in hybrid mode with low concentrations of MS compatible salts (ammonium acetate) and with a small portion of organic solvent to improve the separation while preserving the native structure of the molecule. Dual opposing gradients of decreasing salt and increasing organic offer a new dimension in hybrid HIC separation developments.

Presented research provide a good understanding on how elution conditions such as salt concentration, pH and organic modifier can influence the retention, efficiency and selectivity of the separations performed using poly (alkyl aspartamide) silica HIC materials. An overview of the role of stationary phases with different alkyl chain length in selectivity is given.

Dr. Stephen Kelty

19.

Using DFT to Determine the Stability of Cis and Trans Conformers of Proline and Modified Variations

Jeffrey Raab and Stephen P. Kelty

Short cyclic amino acid chains are starting to make waves in the drug development fields for a few reasons. One being that the degradation products of these drugs are nontoxic to the body because the degradation products are just amino acids which, obviously, pose no threat. Depending on what the drug is being designed to target, the cyclic nature of them helps to get them past the blood brain barrier, seeing as rotationally restricted molecules are more likely to pass through it. Synthesis of these molecules is not particularly hard and is well understood, but sometimes can be difficult because the two ends of the amino acid chain can either link to itself or to another chain, and thus ruining the structure of the drug. In order to limit this bond forming with other chains in solution, proline is often used to fold the chain back onto itself. Proline itself does this decently well but improvements could be made. In this work the stability of cis and trans conformations of proline were compared and then modifications were made to the proline to form this cyclic structure more readily. Density functional theory was used to determine the energies of each rotamer and after this had been established, the molecular orbitals of each rotamer, for each molecule, were compared to see where the differences in energy were. This helped to reveal why one rotamer was more favored than the other and to see what role double bond conjugation plays in the stability.

20.

Development of New NMR Methods for Structure Elucidation of Peptides

Ryan Cohen, Gary Martin, Monika Raj, and Stephen Kelty

Conventional NMR structure elucidation tools used for small molecules often have difficulty when applied to larger, medium-sized molecules. While biomolecular NMR methods for protein structure elucidation have been available for many years and are quite robust, they typically require uniform ^{13}C and ^{15}N isotopic labeling, which is often not an option for novel peptide structures. Thus, there exists a need to develop new tools capable of interrogating complex molecules at natural isotopic abundance. Towards this end, we developed band selective pure shift NMR methods that can provide high resolution for focused spectral regions without sensitivity losses. The new NMR pulse sequences allow for collapse of three-bond and long range proton J -couplings through real-time application of bilinear rotation decoupling (BIRD) pulses during the sampling of the free induction decay (FID). Band selective (bs) pure shift HSQC and bsHSQC-TOCSY pulse sequences were developed and applied for complete and unambiguous elucidation of several 1500+ Da cyclic peptide reaction products from a newly developed macrocyclization synthesis. In addition, the stereoconfiguration of a newly formed stereocenter was unambiguously determined using a combination of through-space correlations (ROEs) and comparison of predicted (via DFT) versus experimentally-determined carbon and proton chemical shifts.

Dr. David Laviska

21.

Biodiesel from renewable feedstocks: Leveraging chemical building blocks derived from plants for both teaching and research

Dominick Gamarro (undergraduate)

David A. Laviska

Department of Chemistry and Biochemistry

Abstract: During the summer of 2019, a new, greener experimental sequence for organic chemistry will be unveiled as part of the Green Chemistry Initiative (GCI) at Seton Hall. As an introduction to basic laboratory skills and the fundamentals of research, our research group has tested, developed, and/or modified experimental protocols for the new curriculum that will teach students about the essential tenets of green chemistry and sustainability. One common undergraduate experiment involves making soap (saponification), but this is not, typically, a green protocol. In addition to exploring greener saponification conditions, we have investigated a closely related reaction: transesterification to synthesize biodiesel. Several different starting materials (mostly plant-based) and solvents have been tested with variable results; pros and cons of the different options will be presented. In keeping with the idea of using renewable plant-derived building blocks, a separate experiment involving the extraction of pigments from spinach and other plants has been developed in order to provide a platform for teaching students about fundamental techniques in organic chemistry: solid-liquid extraction, thin-layer and column chromatography, and uv/vis spectroscopy. Additionally, this latter experiment addresses chemical exposure and waste, since conventional extraction techniques often utilize toxic and/or environmentally unfriendly solvents. As with the synthesis of biodiesel, a matrix of results along with analysis and conclusions will be presented.

22.

Development of greener laboratory experiments: Syntheses of acetaminophen and tetraphenylporphyrin

William Kohman (undergraduate)

David A. Laviska

Department of Chemistry and Biochemistry

Abstract: One component of the Green Chemistry Initiative (GCI) at Seton Hall involves assessing the current curriculum for the organic chemistry sequence and developing new or revised experimental protocols that more closely adhere to the principles of green chemistry. As part of this effort, two synthetic reaction sequences have been piloted for inclusion in the lab sequence beginning in the summer of 2019. The common analgesic acetaminophen has been synthesized from *p*-aminophenol and acetic anhydride through an acid catalyzed reaction, following a known protocol from the literature. Modifications have been introduced that customize the reaction conditions for our facilities and equipment at Seton Hall with an emphasis on green concepts including catalysis, minimal solvent use, and reduction of waste. In a separate

reaction sequence, tetraphenylporphyrin was synthesized from pyrrole and benzaldehyde in solvent-free conditions, using our new microwave reactor instead of conventional heating. The ring system formed in this reaction will be further exploited in metalation reactions which introduce a coordinated metal atom through the removal of two protons. These syntheses align with curricular concepts and analytical skills including atom economy, recrystallization, TLC, melting point analysis, uv/vis spectroscopy, and NMR; yields and purity of both products are excellent.

23.

Two-step “green” synthesis of furil from furfural, a renewable feedstock

Kyle Otto (undergraduate)

David A. Laviska

Department of Chemistry and Biochemistry

Abstract: In order to contribute to the on-going Green Chemistry Initiative (GCI) at Seton Hall, two different “green” experimental protocols were piloted involving the upgrading of the renewable chemical furfural through a two-step synthetic process to the desirable diketone furil. These reactions were chosen for piloting due their pedagogical value in two primary respects: first, they can be connected in series as an example of a multistep, synthetic process; second, the reaction sequence is a significantly greener alternative to the conventional, analogous process of synthesizing benzil from benzaldehyde. The first step of this sequence is modeled on a procedure taken from the primary literature and results in a coupling reaction yielding the alpha-hydroxyketone furoin from the furfural starting material. The catalyst for this transformation is the benign, biologically derived molecule thiamine hydrochloride. In the second reaction to synthesize furil from furoin, a novel method involving a significantly greener oxidation was developed using copper (II) as the catalyst. This second reaction is currently being adapted to utilize microwave rather than conventional heating. Both new protocols gave products in good yield and will be implemented during the lab sequence beginning in the summer of 2019.

24.

Greener Suzuki-Miyaura coupling and other carbon-carbon bond forming reactions

Anthony Rodriguez (undergraduate)

David A. Laviska

Department of Chemistry and Biochemistry

Abstract: As part of the Green Chemistry Initiative (GCI) at Seton Hall, two well-known carbon-carbon bond forming reactions have been pilot-tested that leverage the principles of green chemistry and provide organic chemistry students with new insights concerning sustainability and benign reaction conditions. The Suzuki-Miyaura coupling (SMC) reaction has become ubiquitous as a C-C bond forming protocol due to its versatility and ease of execution; it is one of the cornerstones of synthesis in the production of fine chemicals and pharmaceuticals. A highly green protocol was tested in which the reaction was completed in aqueous medium in preference to conventional organic solvents. This process gave high yields of biphenyl-type

products and will be implemented within the organic chemistry lab curriculum starting this summer. Unfortunately, we discovered that this method is restricted to a narrow range of aryl starting materials, so we are currently investigating different reaction conditions designed to accommodate heteroarenes such as pyridine and quinoline that will yield highly desirable coupling products for a separate research project involving optical devices. In addition to the SMC, we have successfully demonstrated the utility and flexibility of a green, solventless Aldol coupling reaction taken from the primary literature. Like the SMC, product yields from this latter experimental protocol are excellent; both coupling reactions align with curricular concepts and highlight analytical skills including recrystallization, uv/vis and IR spectroscopy, and NMR.

Dr. Cecilia Marzabadi

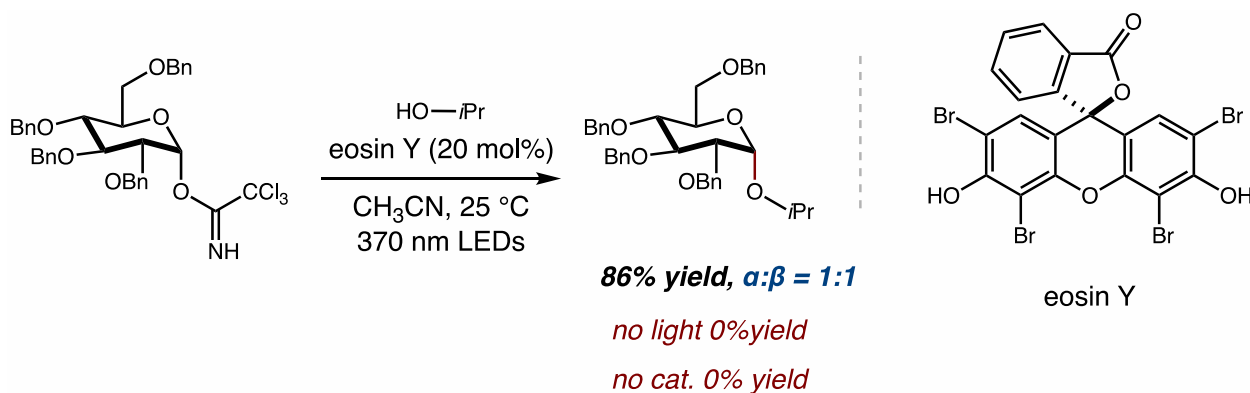
25.

Photocatalytic glycosylation of alcohols by eosin Y

Desiree Harris, Joseph Badillo*, and Cecilia Marzabadi*

Seton Hall University, Department of Chemistry and Biochemistry, 400 South Orange Ave, South Orange, New Jersey 07079

Carbohydrates are an essential part of biological processes, especially when in the form of simple sugars like glucose. The development and study of modified carbohydrates is important for the study of diseases such as diabetes. This poster describes the glycosylation of alcohols using organic photoacid catalysis under irradiation with visible light. Catalysts and solvents such as eosin-Y in acetonitrile and dichloromethane were effective in the photoinduced glycosylation of isopropanol with 2,3,4,6-Tetra-O-benzyl-D-glucopyranosyl trichloroacetimidate using 370 nm LEDs. Furthermore, the $\alpha:\beta$ stereoselectivity was found to be 1:1 (unoptimized). In the future the scope of alcohols and carbohydrates in a variety of solvents will be studied in order to fully explore the potential of this photoinduced process.



26.

Cycloaddition Reactions of Aromatic Imines with Tri-O-Acetyl D-Glucal

John Michael Benedict B. Unciano and Cecilia Marzabadi

Department of Chemistry and Biochemistry

We are interested in forming carbohydrate-quinoline complexes to act as potential intercalating agents for cancer DNA. We believe these will be useful compounds because human cells are able to ingest carbohydrates rapidly, while the quinoline (aromatic compound) acts as an intercalator which can fit in between the cancer DNA, preventing it from replicating, and eventually, stop the spread throughout the human body. Eventually, these cancer cells will die after not being able to replicate (National Human Genome Research Institute). The quinoline portion of the complex is synthesized by the addition of aniline to acetophenone to form an imine compound. The carbohydrate was synthesized from Tri-O-Acetyl-D-Glucal or was purchased commercially. The cycloaddition reaction was carried out with heating in triethyl orthoformate. A microwave synthesis will also be tried.

Dr. Wyatt Murphy

27.

Method Development of a Gas Chromatographic Separation of Polyaromatic Metabolites from Fish Oil

Adigun Andy Ajayi, Setrak Tanielyan, Wyatt R. Murphy, Jr.

A capillary gas chromatographic technique using flame ionization detection (GC-FID) was developed to separate and quantitate alcoholic metabolites of polyaromatic hydrocarbons. Such compounds, including 1-hydroxypyrene, 1- and 2-naphthol, 2-hydroxyanthracene, etc. have been detected via excitation-emission matrix spectroscopy (EEMS) in oil derived from menhaden livers. Parallel measurements of prepared samples have been analyzed by EEMS and GC-FID to validate the former technique.

28.

Evaluation of Microwave Reactors for Synthesis of Heteroleptic Ir(III) Ortho-metallated Complexes

Alexa Skalski, Paria Remolina, Alexander Serpico, Maggie Cosgrove, Allyson Dixon, Wyatt R. Murphy, Jr.

Microwave reactors from Biotage and CEM using both manufacturers supplied vessels and traditional standard taper glassware (CEM only). Known synthesis of $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+$ (ppy = 2-phenylpyridine; bpy = 2,2'-bipyridine) was tested on both reactors. The synthesis of the new complex $\text{Ir}(\text{ppy})_2(2,3\text{-DPhPz})$ (2,3-diphenylpyrazine) was tested. NMR and fluorescence data will be presented.

29.

Microbial Treatment Using Humimycin

Kazim Baynes and Wyatt R. Murphy

Drug research is an ongoing topic. New methods of synthesis are being developed daily, old drug formulations are always being looked at to see if they could be improved upon, and of course, new drugs are always being developed. Recently a new class of antibiotic drugs called Humimycins was discovered. This class of drugs inhibits the lipid II flippase and potentiates β -lactam activity against methicillin-resistant *Staphylococcus aureus* in mice. This new flippase method of treatment opens new way to treat microbial infections. The goal of this research is to look at the Humimycin class of peptides and to see if it can be improved upon. Some improvements would be what changes to the peptide can be made to increase its efficacy and to see if we can change the peptide and have it work against fungi. Using solid phase peptide synthesis, we will recreate and modify this humimycin peptide and see if these modifications increase the efficacy of this antimicrobial treatment and if this treatment is applicable to other microbial life such as fungi.

30.

The Green Chemistry Initiative: Preparing chemistry and biochemistry students for the future.

Wyatt R. Murphy, Jr., Robert Augustine, Cecilia Marzabadi, Setrak Tanielyan, David Laviska and Alexander Serpico

The startling growth in the teaching laboratory population prompted members of the chemistry department to evaluate how our laboratory experiments are taught. As a result of this evaluation, the Green Chemistry Initiative was formed to incorporate the principles of Green Chemistry into our programs. An analysis of the enrollment trends and consequences for laboratory resources, with predictions for 2020 will be presented. The progress made to date on minimizing waste disposal, excess reagent usage, and inculcating green principles into the chemistry curriculum will be communicated as well.

31.

Evaluation of Microwave Reactors for Synthesis of Heteroleptic Ir(III) Ortho-metallated Complexes

Alexa Skalski, Paria Remolina, Alexander Serpico, Maggie Cosgrove, Allyson Dixon, Wyatt R. Murphy, Jr.

Microwave reactors from Biotage and CEM using both manufacturers supplied vessels and traditional standard taper glassware (CEM only). Known synthesis of $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+$ (ppy = 2-phenylpyridine; bpy = 2,2'-bipyridine) was tested on both reactors. The synthesis of the new complex $\text{Ir}(\text{ppy})_2(2,3\text{-DPhPz})$ (2,3-diphenylpyrazine) was tested. NMR and fluorescence data will be presented.

32.

Evaluation of Microwave Reactors for Synthesis of Homoleptic Ir(III) Ortho-metallated Complexes

Victoria Saniko, Florian Balan, Alexander Serpico, Caitlin Patt, Amanda Taylor, Samantha Reed, Wyatt R. Murphy, Jr.

Microwave reactors from Biotage and CEM using both manufacturers supplied vessels and traditional standard taper glassware (CEM only). Known synthesis of $\text{Ir}(\text{ppy})_3$ (ppy = 2-phenylpyridine) was tested on both reactors. The synthesis of the new complex $\text{Ir}(\text{dpp})_3$ (dpp = 2,3-di(2'-pyridyl)pyrazine) was tested. NMR and fluorescence data will be presented.

Dr. David Sabatino

33.

THE RATIONAL DESIGN, SYNTHESIS, CHARACTERIZATION, AND BIOLOGICAL EVALUATION OF CANCER-TARGETING IMMUNOSTIMULATORY PEPTIDES

¹Nelson Casanova, ²Rachel Montel, ²Keith Smith, ²Constantine Bitsaktsis, ³Dante Descalzi, ³Robert Korngold and ¹David Sabatino

¹Department of Chemistry and Biochemistry, ²Department of Biological Sciences, Seton Hall University, 400 South Orange Avenue, South Orange NJ 07079, ³Department of Biomedical Research, Hackensack University Medical Center, Hackensack, NJ, USA

With the advent of cancer immunotherapy and synthetic biologics, there has been a steady decline in the incidence of cancer. Despite this trend, there is still an anticipated 1,762,450 new cancer cases and 606,880 cancer deaths projected to occur in the United States in 2019. Therefore, the call for continued efforts in creating more effective treatment options are in high demand. In this presentation, several cancer-targeting immunostimulatory peptides activating NK and cytotoxic T cell lymphocytes are presented. These synthetic biologics are hypothesized to activate NK and T cells' effector functions enabling tumor cytolysis. While the multiepitope inducers have the ability to provoke multi-peptide-specific cytotoxic responses in solid and hematological tumors. Using Fmoc-SPPS, we have generated a library of peptides that were isolated and characterized using RP-LC/MS and UV/Vis spectroscopy. Using flow cytometry, the preliminary data confirmed peptide binding and activation of NK92-MI cells. We anticipate the specific binding of the peptides to their intended targets will provide the best candidates for translating our cancer immunotherapy approach *in-vivo*.

34.

siRNA Nanotechnology and Bioconjugation for Silencing the Glucose Regulated Chaperones in Cancer

Christopher N. Cultrara¹, Sunil S Shah¹, Gina L Antuono¹, Adah E. Beck¹, Claudia J. Heller¹, Jenny Zilberberg, PhD² and David Sabatino, PhD^{1,*}

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The Glucose Regulated Proteins are resident chaperones of the endoplasmic reticulum and master regulators of the unfolded protein response under physiological and pathological cell stress conditions. They are also found to be overexpressed and cell surface localized in many cancers making them clinically relevant biological targets. Gene therapy has re-emerged as a

promising precision nanomedicine in the treatment of cancer. At the forefront of its efficacy are short-interfering RNA (siRNA), that have silenced oncogenic mRNA expression leading to cancer cell death through the RNA interference (RNAi) pathway. In this presentation, the design, development and biological evaluation of siRNAs silencing the expression of the Glucose Regulated Proteins are described. Our design and development strategies focuses more specifically on: 1) covalently attaching a fluorophore, fluorescein isothiocyanate (FITC) as well as 2) the incorporation of fatty acids, which respectively assists in monitoring cell uptake and for direct transfection applications. Furthermore, the incorporation of cationic cell penetrating and cell targeting peptides (CPP and CTP) are discussed for targeted siRNA delivery applications. Taken together, these new siRNA constructs represents the next generation of more efficient siRNAs for screening important oncogene targets for cancer gene therapy applications.

Reference:

Cultrara CN, Shah S, Kozuch SD, Patel MR, Sabatino D. Solid phase synthesis and self-assembly of higher-order siRNAs and their bioconjugates. *Chem Biol Drug Des.* **2018**, doi: 10.1111/cbdd.13448. [Epub ahead of print].

**Structural and Electrical Properties of Pulsed Laser Deposited Yttrium Doped Zirconium
Oxide Thin Films Stabilization**

Erica Wiley and M. Alper Sahiner
Department of Physics

Solid Oxide Fuel Cells, SOFC's, are devices that convert chemical energy from fuel into electricity from a series of electrochemical reactions. These fuels can be hydrogen, carbon monoxide, oxygen, etc. with a high conversion efficiency of conversion. Comparing SOFC's to coal powerplants, the SOFC's produce a higher electrical conversion efficiency. SOFC's are possible candidate of energy production. However, SOFC's high temperatures (800-1000°C) create a lower ionic conductivity of the electrolytes. This ionic conductivity creates limitations of SOFC's applications. When decreasing the temperatures, the ohmic resistance as a thin-film. An Yttria-Stabilized Zirconia, YSZ, layer is produced from the fine dimple grain structure allowing high flow of oxygen mobility. This ion mobility increases the ionic conductivity and decreases the ohmic losses. The goal of our research is to optimize the Yttria Stabilized Zirconia thin-film synthesis conditions which lead to minimum ohmic resistance in these films. We will also use different substrates and monitor the effect of the choice of the substrate on the YSZ thin film properties. These thin-films will be characterized through electrical measurements such as 4 pt. probe resistivity measurements, Hall Effect characterization, and structural and compositional characterization such as AFM, SEM, and EDX.

Dr. Nicholas Snow

36.

Post-Blast Residue of Single-Base Smokeless Powders

Amara Borchers, Department of Chemistry and Biochemistry
Seton Hall University, South Orange, NJ
Federal Bureau of Investigation
Laboratory Division: Explosive Chemistry Groups

Smokeless powders can be used easily in the making of an improvised explosive device and are readily available commercially. Their commercial applications primarily can be seen with the use of firearms, which is why smokeless powders can be bought from many hobby and outdoor stores in the country. There are three types of smokeless powders. The first, and the main focus of this project, is a single base smokeless powder whose main component is nitrocellulose, which currently does not have any known detection methods. The second, is a double-base smokeless powder whose two main components are nitrocellulose and nitroglycerin. The last is a triple base smokeless powder whose three main components are nitrocellulose, nitroglycerin, and nitroguanidine. The double-base smokeless powders can be analyzed using methods that are tuned to search for nitroglycerin. The triple base smokeless powders currently do not have established methods of detection based on nitroguanidine. With single-base smokeless powders, there is the question of whether or not certain additives that make up a minute percent of the overall composition can be detected using various analytical instruments. The additives that were focused on in this project were diphenylamine, methyl-centralite, and ethyl-centralite. These are organic nonpolar compounds. These additives were run on the GC/ECD, LC/MS, and GC/MSD to determine limits of detection for the three compounds. The ultimate goal was to find out if we could see these additives and how we could fine tune those analytical methods to give the best opportunity to extract the necessary information as needed from post blast residue. This project adds on to previous work done by John A. Mathis and Bruce McCord in 2004 [2] as well as other articles that were done on these additives also found in gun residues.

37.

FINITE DIFFERENCE STUDIES OF THE CONCENTRATION EFFECTS ON PEAK SHAPES AND SIMULATION OF PEAK TAILING IN CHROMATOGRAPHY

Nicole Charles
Mentor: Dr. Nicholas Snow
Department of Chemistry and Biochemistry (Seton Hall University)

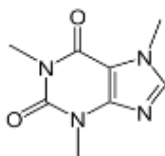
HPLC and GC both use the same principle that heavier molecules will elute more slowly than lighter ones. Polarity also plays a role in elution time in these chromatography techniques. However, they are both susceptible to issues and limitations. Common problems are related to selectivity, sensitivity, and resolution depending on the nature of the sample. Finite difference simulations have been used previously to model surface adsorption effects in partition chromatography. Previous studies also

suggested that nonsymmetrical peaks usually indicate that some interaction has taken place during the chromatographic process [1,2]. In fact, it is well established that the position and shape of peaks in chromatography depend directly on the adsorption between a compound and interactions between the stationary and the mobile phase either liquid (HPLC) or gas (GC).

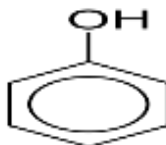
A novel VBA software has been developed in-house [3,4,5] to run in Excel and to generate a numerical representation of the chromatographic peak shape. This software uses four dimensionless input parameters. Statistical moment analysis is employed to compute the retention time and variance of each peak along with tailing factor. [1-3]. In this study, we hope to demonstrate how this program compares with other HPLC and GC simulations programs. Therefore, chromatographic data will be acquired for caffeine and phenol as they have previously shown to exhibit HPLC tailing peaks [2] within the right conditions. Results obtained will be compared with outputs from the readily available Restek EZGC simulation software [6]. Quantitative agreement between simulation and experimental data will be examined to further understand the VBA chromatographic simulation software and confirm its validity for separation studies.

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Caffeine



Phenol

38.

Performance of Nitrogen as a GC carrier gas

By: Brittany Handzo and Nicholas H. Snow, Seton Hall University
Department of Chemistry and Biochemistry

Gas chromatography (GC) is one of the most widely used analytical techniques for the separation and analysis of volatile compounds. Solids, liquids, and gases, organic and inorganic materials, and large molecular weight compounds can all be analyzed via this technique. GC separations are fast, accurate, and reliable. One of the main reasons why these separations are so efficient is because of the carrier gas. The purpose of the carrier gas is to carry the injected sample through the column. It is known as the mobile phase and does not interact chemically with the sample.

Common carrier gases include helium, hydrogen, and nitrogen. Helium is the most frequently used gas, but increased demand has caused a worldwide helium shortage. This has forced scientists to look for alternative carrier gases and study how much they influence separation.

The purpose of this research is to explore the performance of nitrogen as a GC carrier gas. In previously published literature, Van Deemter plots prove that nitrogen has the smallest optimum linear velocity and therefore the longest retention times. However, nitrogen is also known to have the most efficient separations and is more cost-effective compared to helium. This research focuses on the comparison between nitrogen and helium in order to conclude which carrier gas is the most effective. Compounds such as alkanes and programmed test mixtures such as Grob's and PAH's have been analyzed, fundamental calculations were performed, and Van Deemter plots were completed. In the end, nitrogen was able to give excellent separations and should be considered a reasonable alternative as a carrier gas in GC.

39.

Column Performance in Comprehensive Two-dimensional Gas Chromatography

Sean McCann and Nicholas H. Snow
Department of Chemistry and Biochemistry

Gas chromatography is a common separation technique used by many chemists where a compound serves as the stationary phase and an inert gas acts as the mobile phase. A sample can be injected into the inlet where it is vaporized and carried throughout the column via the mobile phase and interacts with the stationary phase to cause separation of the sample. This analytical technique has been expanded upon with two-dimensional gas chromatography, where two columns are connected via a modulator and allows for two dimensions of separation for a sample. This experimental research delves into the nature of two-dimensional separation with various column sets with a focus on ionic liquid columns in the second dimension. A test mix was prepared that includes Grob's Mix reagents, McReynold's reagents, and a homologous series of alkanes. 1 μ L of the mixture was injected and the various peaks of the analytes were theoretically analyzed, as well as with calculations, to study how the stationary phase and its polarity determine the chromatography.

40.

Retention Indexes on Polar and Non-polar Stationary Phases in Gas Chromatography

Hetal Rana and Nicholas H. Snow
Department of Chemistry and Biochemistry

In gas chromatography, retention times are converted into system independent constants known as retention indices(RI) and its calculations is based on two internal standards(n-alkane),one shortly eluting before and the other shortly eluting after the compound of interest. This term was introduced by Kovats in1950s. However, RI is dependent on kind of stationary phase used. In the present experimental research, RI is calculated for five probes namely benzene,1-butanol,2-pentanone,1-nitropropane and pyridine on following column SH-Rxi-5Sil MS, ionic liquid column. And it is proved that RI value is larger for ionic liquid column than Rxi-5Sil, meaning analyte will interact more with the stationary phase and retained longer, leading to better efficiency and resolution.

Dr. Weining Wang

41.

Conductivity and Work Function Study of PEDOT:PSS with Different Shaking Times

Charity Diamonon, Sebastian Valbuena and Weining Wang

College of Arts & Sciences, Department of Physics

Conducting polymers are recognized because of their ability to replace expensive and often heavy metals and semiconductors on solar cells because of their high conductivities and high work functions. They have shown much potential because they are transparent, inexpensive, and easy to create as well as work with. Conducting polymers and the research towards improving them also improves the fields of optoelectronics and renewable energies. The purpose of this research is to discover two relationships: the relationship between the shaking time and the conductivity of the polymer solution and the relationship between the shaking time and the polymer solution's work function. Studying these relationships between the polymer and its resulting conductivity and work function will help to create more efficient, new generation solar cells. The conducting polymer at the focus of this research is poly(3,4 - ethylenedioxythiophene):poly(styrenesulfate) (PEDOT:PSS), which is mixed with dimethyl sulfoxide (DMSO) to create the polymer solution (PEDOT:PSS/DMSO). The dopant, DMSO, is known to increase the polymer's conductivity. The experiment consists of shaking polymer solution for a total of four hours; a sample of the solution is taken at every one-hour interval. Various techniques were utilized to measure and calculate the resulting conductivities and work functions—spin-coating, spectrophotometry, thermal vacuum evaporation deposition, and Kelvin Probe method. From these measurements, both the conductivity and the work function increased as the total shaking time of the polymer solution increased. Therefore, a direct relationship was observed between the shaking time and the resulting conductivities and work functions.

Dr. Gregory Wiedman

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Aptamers Towards Anti-Tuberculosis Drugs

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Single stranded oligonucleotides known as aptamers that bind with high affinity and specificity to a target molecule can be developed to measure the concentration of anti-tuberculosis drugs. Tuberculosis, one of the world's deadliest diseases, is usually treated with carefully scheduled dosages of a multi-drug prescription primarily composed of Isoniazid, Rifampin, and Pyrazinamide. Focusing on the Pyrazinamide drug, multiple rounds of synthetic evolution of ligands through exponential enrichment (SELEX) was used to isolate a specific sequence of ssDNA that bonded to the drug through the magnetic bead affinity method. Polymerase chain reaction (PCR), then, was utilized to amplify this sequence along with a NanoDrop Spectrophotometer to measure the DNA concentration. Further experiments with a competitor molecule tested the specificity and accuracy of the Pyrazinamide aptamer. More research with other anti-tuberculosis drug aptamers such as Isoniazid and Rifampin, would allow the Pyrazinamide aptamer to be potentially an important tool for Tuberculosis treatment.