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ROSE MERCADANTE SEMINAR SERIES

Department of Chemistry and Biochemistry 23rd Departmental Symposium in Conjunction with the Petersheim Academic Exposition

Book of Abstracts

McNulty Hall
Seton Hall Science and Technology Center
April 24, 2018

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

From Small Organic Precursors to Fluorinated Phthalocyanine-Peptide Conjugates for Theranostic Applications

Erik N. Carrión

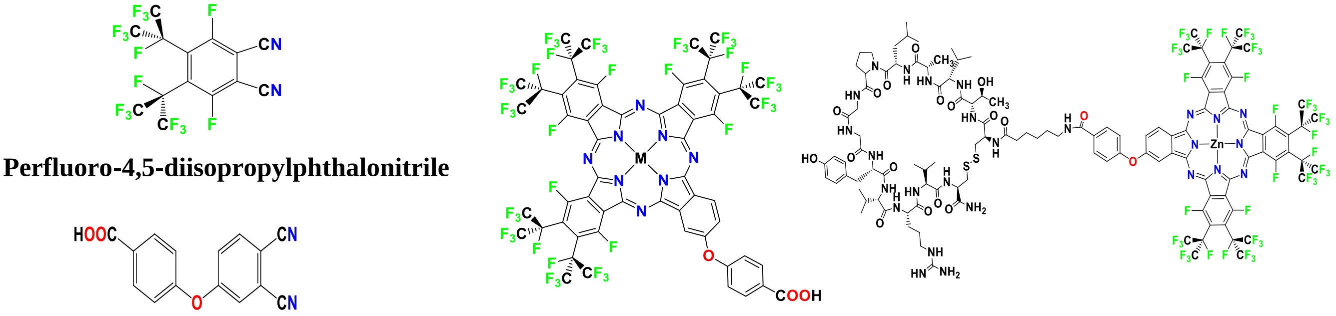
Department of Chemistry and Biochemistry, Seton Hall University, South Orange, NJ 07079
Final PhD Seminar – Mentor: Dr. Sergiu M. Gorun

Hydrocarbon-based therapeutics and imaging agents are prone to chemical oxidation and degradation resulting in loss of activity and limited functional utility. Thus, new materials are required to achieve long-lasting therapeutic effects. Phthalocyanines (Pcs) and their metal complexes (PcMs) can be utilized as photosensitizers requiring only renewable energy resources namely, air and light, for cancer therapy and diagnostic (theranostic) applications related to photodynamic therapy (PDT). However, hydrocarbon-based Pcs have limited therapeutic potential in PDT due to their poor bioavailability, chemical stability and therapeutic index. The replacement of the C-H bonds in the Pc scaffold with a combination of fluoro and perfluoroisopropyl groups has resulted in stable yet reactive oxidation catalysts and fluorescent materials of biological significance and importance.

For example, $F_{64}PcZn$ lacks tumor-cell specificity and solubility in aqueous media which limits its full therapeutic potential in PDT applications. However, the condensation of 4-3,4-dicyanophenoxybenzoic acid and perfluoro-4,5-diisopropylphthalonitrile may be used to generate asymmetric carboxyl-functionalized fluorinated metal phthalocyanines, $F_{48}H_7COOHPcM$ (M = Zn, Cu) for potential theranostic applications (**Figure 1**).

$F_{48}H_7COOHPcZn$ was conjugated to Pep42 and its polyarginine derivatives with capability of tumor-cell recognition towards an oncoprotein cell-surface receptor, Glucose Regulated Protein of 78 KDa (GRP78)

In addition to the diamagnetic Zn complexes, $F_{48}H_7COOHPcCu$, which is paramagnetic, unexpectedly produced singlet oxygen ($^1O_2$). $F_{48}H_7CONHPcZn$-AHX-Pep42, like $F_{48}H_7COOHPcZn$, still performed $^1O_2$-mediated substrate oxidation and showed fluorescence after peptide attachment. Pc labeling did not affect the cargo delivery capabilities of Pep42 towards Hep2 cells. $F_{48}H_7CONHPcZn$-AHX-Pep42-R_9 and $F_{48}H_7CONHPcZn$-PEG_6-Pep42-R_9 were biocompatible and demonstrated sufficient uptake into the Hep2 cells. Under dark and light conditions, the $F_{48}H_7CONHPcZn$-AHX-Pep42 showed moderate cytotoxicity in both cases unrelated to $^1O_2$ production. The work herein highlights that the developed, catalytic, fluorine-based PcM-peptide conjugates may be useful as potential theranostic agents.



Perfluoro-4,5-diisopropylphthalonitrile

4-3,4-dicyanophenoxy benzoic acid

$\mathrm{F_{48}H_7COOHPcM}$ (M = Zn/Cu)

$\mathrm{F_{48}H_7CONHPcZn}$-AHX-Pep42

Figure 1. Schematic representation of 4-3,4-dicyanophenoxybenzoic acid and perfluoro-4,5-diisopropylphthalonitrile, $\mathrm{F_{48}H_7COOHPcM}$, and GRP78-targeting fluorinated PcZn bioconjugate, respectively. AHX = 6-aminohexanoic acid.

About the Keynote Speaker

Erik N. Carrion is a PhD candidate in the Department of Chemistry and Biochemistry at Seton Hall University. He attended Lehigh University from 2009-2013 and obtained a BS in Biochemistry. After college, he joined the Department of Chemistry and Biochemistry at Seton Hall University in 2013 and I began studies towards a doctoral degree in the labs of Dr. Sergiu M. Gorun and Dr. David Sabatino. We explored the use of functional fluorinated diamagnetic and paramagnetic metal phthalocyanines for cancer therapy and diagnostic (theranostic) applications.

Publications:

- **Carrión, E. N.**; Santiago, J.; Sabatino, D.; Gorun, S. M. Synthesis and Photophysical and Photocatalytic Properties of a Highly Fluorinated and Durable Phthalocyanine-Peptide Bioconjugate for Potential Theranostic Applications. *Inorg. Chem.* **2017**, 56, 7210-7216
- **Carrión, E. N.**; Loas, A.; Patel, H. H.; Pelmus, M.; Ramji, K.; Gorun, S. M. Fluoroalkyl phthalocyanines: Bioinspired catalytic materials. *J. Porphyrins Phthalocyanines* **2018**, *22*, 1-27 (*invited contribution*)
- Pelmus, M.; **Carrión, E. N.**; Colomier, C.; Santiago, J.; Gorun, S. M. Group III perfluoroalkyl perfluoro phthalocyanines. *J. Porphyrins Phthalocyanines* **2016**, 20, 1403-1408 (*invited contribution)*
- **Carrión, E. N.**; Dang, A.; Gorun, S. M. Synthesis and X-ray structure of a fluorinated 1,1-dialkoxy-3-iminoisoindoline acetal, an elusive phthalocyanine precursor. **2018**, manuscript submitted for publication.

US Patent:

- Sabatino, D., Gorun, S. M., Borland, E., Patel, H., Patel, P., **Carrión, E.N.**, **2017**, "Functionalized Fluorine Containing Phthalocyanine Molecules" US Patent 9,572,898, filed 09/2014, 2014, issued 02/2017

Book Chapter:

- Rana, N.K.; Phillips, M.; **Carrión, E. N.**; Luisi, G.; Sabatino, D. Peptide Biomarkers and Assay Development. Drug Discovery Series No. 59, Peptide-based Drug Discovery: Challenges and New Therapeutics, RSC, 76-115, **2017**

Dr. Cosimo Antonacci

1

UV-Vis NIR Analysis of Cosmetic Powders

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

UV-Vis NIR absorbance spectra can be particularly challenging to obtain for powders. It can be prone to variability based on the sample holder utilized. In these studies, the application of sample powders to Scotch Tape proved to be an efficient and inexpensive sample analysis method to determine the percent transmittance in conjunction with a diffuse reflectance instrument attachment. Results from the analysis of a variety of cosmetic powders using UV-VIS NIR spectra are presented herein.

2

Identification of compounds that target poxvirus early promoters

Younghoon Park, **Baily Randolph**, Omkar Gandbhir, Taryn Heiser, Victoria Blakey-Padilla, Daniel Brian Nichols, Ph.D, Cosimo Antonacci, Ph.D.
Department of Chemistry and Biochemistry; Department of Biological Sciences, Seton Hall University

Poxvirus early genes code for viral products involved in host interaction, immune evasion, replication and transcription of the viral genome. These viral early genes contain a unique and conserved promoter sequence that is recognized by early transcription factors (ETFs). The working hypothesis is pharmacologically targeting the structure of the poxvirus early promoters can inhibit transcription of poxvirus early genes. To this end, we have identified a novel compound H_2TMPYP that has binding specificity for the vaccinia virus (VACV) E9L promoter compared to a scrambled promoter sequence. As E9L codes for the viral DNA polymerase, inhibition of E9L transcription would prevent replication of the vaccinia virus DNA during infection. To assess, potential antiviral activity of the compound we are developing an in-vitro system to identify compounds that prevent binding of ETFs to target promoters. Using VACV ETFs (VETFs) as a model system, we have cloned the genes containing VETFs, A7L and D6R, into a bacterial expression vector with a His epitope tag for purification. We have successfully optimized expression and detected both VETFs in bacterial cell lysates via immunoblotting with anti-His antibodies. Currently, we are optimizing protocols for large-scale purification of viral proteins to use the in vitro assay. Upon optimization, these VACV VETFs will be tested by an in vitro binding assay to determine, if these VETFs can bind to the E9 early promoter in the presence or absence of the compound. The drug compound absorbs light in the visible and yields a fluorescence spectrum. As such we will be utilizing titrations of the DNA to determine binding affinity spectroscopically. When successful, this assay will provide a low cost and safer means in

which to screen compounds for the ability to bind early promoter sequences and prevent binding of VETFs, which can be later validated for antiviral activity in cell cultures with live virus. The assay described here does not require the initial use of live virus and can be safely performed in a BSL-1 level facility, thus providing an opportunity to engage both graduate and undergraduate students in the initial stages of antiviral testing and drug design.

Dr. Joseph Badillo

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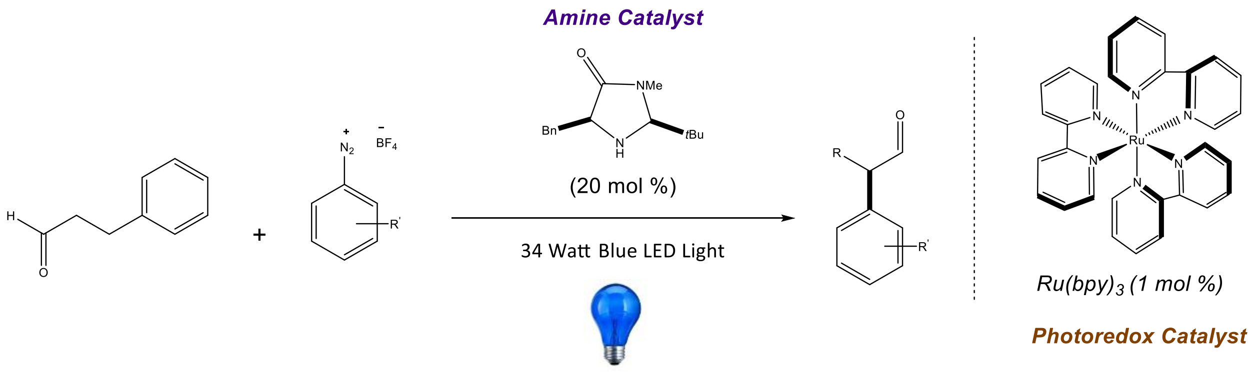
Asymmetric Photoredox Catalysis: A Method for α-Functionalization of Carbonyls

Samantha M. Chalet, Amani K. Gooden, Desiree M. Harris, and Dr. Joseph J. Badillo*

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

In organic chemistry, a recently growing field of photoredox catalysis has been prospering for its innovation in useful reaction mechanisms. Photoredox catalysis uses approaches that rely on the ability of metal complexes to convert visible light into chemical energy by engaging in a single-electron transfer with organic substrates. These reactive intermediates can be utilized in a variety of ways for organic reactions. The goal of this study is to develop strategies for the enantioselective synthesis of carbonyl compounds via the merger between photoredox catalysis and traditional asymmetric modes of activation, such as amine and Lewis acid catalysis. Initial studies use the photocatalyst $Ru(bpy)_3^{2+}$, reacting with an amine catalyst and aryl diazonium to synthesize α-arylated aldehydes. Several conditions have been investigated in order to optimize the reaction including light sources, potential photo catalysts, and usage of activated aryl diazoniums. So far this method has achieved >5% yield as determined by NMR.



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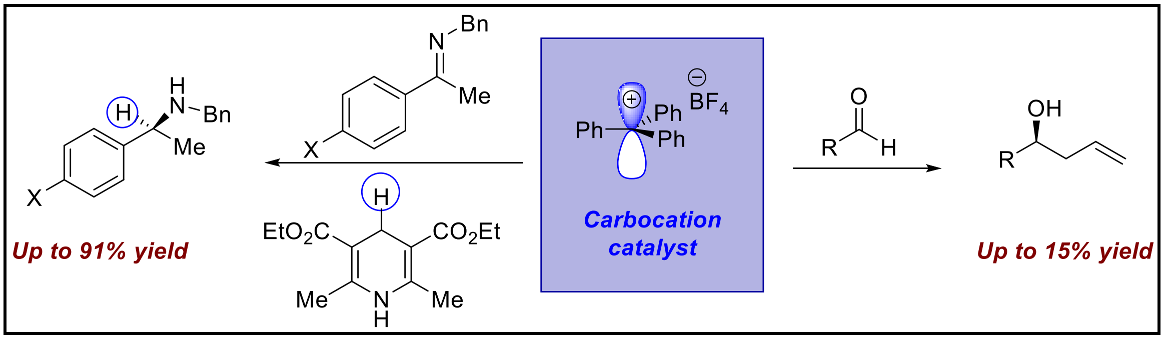
Carbocation Catalyzed Reduction of Imines and Allylation of Aldehydes

Zilma P. Muneeswaran, Darwin C. Glynn, Michael Freddy, Victoria S. Shahinian and Joseph J. Badillo*

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

The triphenylmethyl cation (trityl cation) is known to function as a Lewis acid. Here we show that trityl cations catalyze both the transfer hydrogenation reaction of imines to the corresponding chiral amines as well as the Hosami-Sakurai allylation of aldehydes. Specifically, we have demonstrated that catalytic tritylium tetrafluoroborate enables the reduction of *N*-benzyl-1-phenylethan-1-imine by Hantzch ester (diethyl 1,4-dihydro-2,6-dimethyl-3,5-pyridinedicarboxylate) with good yield. The Hosami-Sakurai reaction often uses catalytic titanium tetrachloride, an extremely toxic and moisture sensitive reagent which reacts in air to form hydrochloric acid and other metal biproducts. By utilizing trityl cation as a Lewis acid, we take on a “green-chemistry” approach by eliminating the need for such a toxic catalyst. The long-term goal of this work is to replace the achiral tetrafluoroborate anion with a chiral phosphate in order to induce asymmetry via asymmetric counterion directed catalysis (ACDC).



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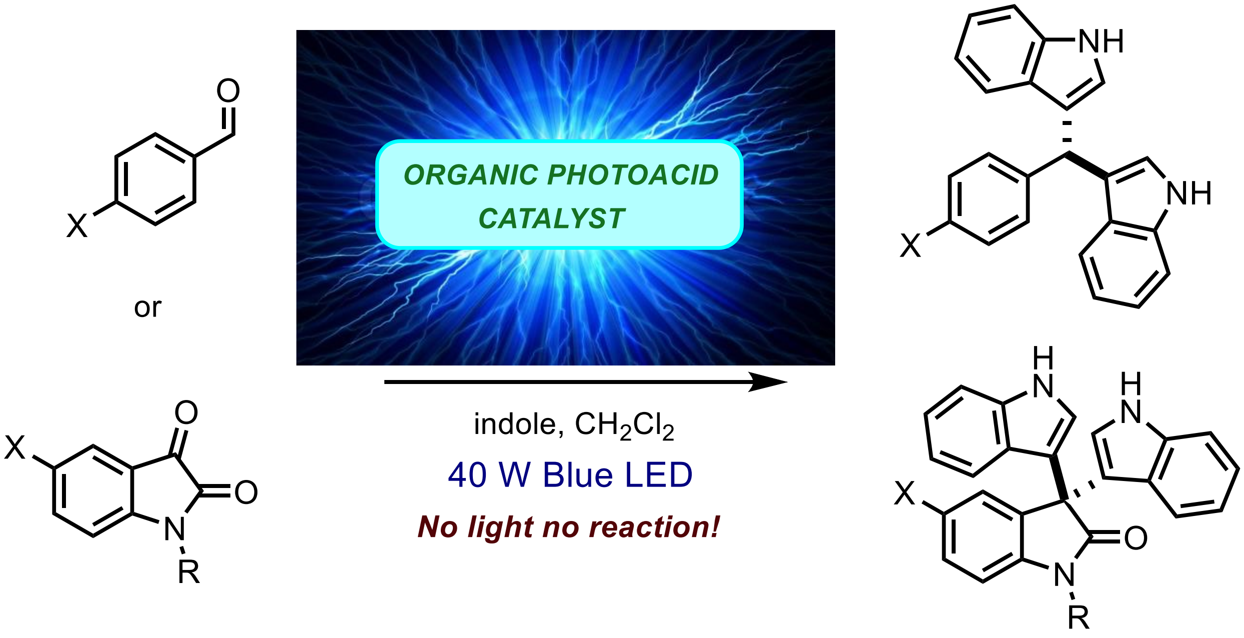
Organophotoacid Catalysis Enabled by Visible Light

Zena M. Salem, Zilma P. Muneeswaran, Darwin C. Glynn, and Joseph J. 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 when excited with 456 nm wavelength light, such as Schreiner's thiourea, is capable of being engaged in hydrogen-bonding catalysis through visible light excitation. 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. Additionally, initial studies for the photoacid-catalyzed allylation of alkyl aldehydes with allyltrimethylsilane is also discussed. Reaction optimization conditions including solvents, light sources, potential photoacids, catalyst loading, effects of water and oxygen, and a preliminary range of carbonyl compounds have been investigated.



Fr. Gerald Buonopane

6

Comparison of the Effect of Cold Plasma Processing on the Essential Oils of Sweet Basil (*Ocimum basilicum*) Grown in Two Different Aeroponic Systems

Alexandra Brielmaier, Stephen Grams, Sauvelson Auguste, Daniel Guerrero,
Setrak K. Tanielyan, Ph.D., Jose L. Lopez, Ph.D., and Rev. Gerald J. Buonopane, Ph.D.

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

In this study, sweet basil (*Ocimum basilicum*), grown in two different aeroponic systems was treated with cold plasma using an Atmospheric Cold Plasma Jet (ACPJ). Prior to planting, in their respective aeroponic system, the basil seeds were exposed to different durations of plasma treatment. In one of the groups, the seeds were mass treated: 500 seeds treated simultaneously for 5 minutes. In the other group seeds were individually treated with a direct stream of plasma for 30 seconds. The two groups of treated seeds were then planted in a rockwool housing. Once the seeds sprouted, they were transferred along with the rockwool into their respective aeroponics system. The aeroponics system was a tower that dispensed a nutrient-water solution to the basil for periods of 30 minutes on and 15 minutes off throughout the plant cycle. Upon harvesting of the basil, essential oils were extracted from the plants using Soxhlet extraction. The extracts were then analyzed by gas chromatography/mass spectrometry (GC/MS) to identify and quantitate the components of the essential oils. In addition, extracts were analyzed for antioxidant activity using the DPPH assay, which incorporates UV-Vis spectrophotometry (518 nm wavelength)[1]. The results from the GC/MS analysis showed that the individual seed treatment yielded higher production of the essential oil components (eugenol, linalool, and estragole) than the mass treated seeds. Results from the DPPH assay of mass treated and individually treated seeds will be compared.

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Effect of Cold Plasma Processing on the Chemical Components of Sweet Basil (*Ocimum basilicum*) Essential Oils and their Antioxidant Activity

Kedene Clarke, Sweta Rana, Sauvelson Auguste, Daniel Guerrero, Setrak K. Tanielyan, Ph.D., Mary J. Berger, Ed.D., Jose L. Lopez, Ph.D., and Rev. Gerald J. Buonopane, Ph.D.

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

This study was carried out to determine the effect of cold plasma processing on the essential oils of Sweet Basil (*Ocimum basilicum*) and their chemical components, including estragole, linalool, ocimene, and eugenol. Basil was grown in soil with fertilizer fortification. Study samples included the non-treated control sample; the seed treated sample, where only the seed was treated with cold plasma; seed treatment followed by the plant body treatment once a week; and seed treatment followed by the plant body treatment twice a week. All basil groups were grown under artificial LED light. Following harvesting, the basil was air dried and separated into its various body parts, including leaves, stems, and flowers. The weight of the fresh and dry basil changed under the conditions of treatment with cold plasma. Essential oils were extracted from the basil using Soxhlet extraction. The plasma had some effect on the plant which results in the effect on the quality of the essential oils. Essential oil extracts were analyzed using Gas Chromatography/Mass Spectrometry for identification and quantitation of their organic compounds. Extracts were also analyzed for antioxidant activity using the DPPH assay.[1] GC/MS analysis of the leaves revealed that eucalyptol, linalool, estragole, and cinnamic acid methyl ester (CAME) were present in all groups, except that the seed-treated sample that had no trace of eugenol. Leaves receiving body treatment twice a week had the highest amount of eucalyptol, linalool and estragole. In the stems, there was no trace of eucalyptol, linalool, estragole, eugenol and CAME. In the flowers, the most differentiation can be seen among the components. Eucalyptol was around the same amount throughout all the conditions. Antioxidant activity of the various treatment groups will be compared.

References

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Dr. Tin Chun Chu

8

Analysis of DRD2

John Murzaku &Tin Chun Chu
Seton Hall University, Department of Biological Sciences, 400 South Orange Avenue, South Orange, NJ 07079

Substance abuse and addiction to substances is an epidemic sweeping the country and affecting millions of people regardless of their age. The biological reason for substance abuse being a problem is that narcotic substances act on the dopamine receptors of the brain by flooding the receptors with signals to create more dopamine. A percentage of drug addicts tend to also be schizophrenic, and this is because the gene encoding the dopamine receptors is also associated with schizophrenia depending on how it is transcribed. This gene that encodes the dopamine D2 receptors in the brain is the DRD2 gene. Depending on how the DRD2 gene is transcribed or its structure, the rate of schizophrenia is higher. Drug addicts also have a change in D2 receptor structure because of the flood of the receptors. The aim of this project is to determine if drug addiction and use leads to higher rates of schizophrenia, Using the BrainCloud database and analyzing post mortem gene expression data, a statistical analysis regarding drug addiction and schizophrenia rates will be done. Using the R programming language, a graphical representation of drug addicts with schizophrenia will be shown too, all in relation with the DRD2 gene and D2 dopamine receptor.

Dr. Alexander Fadeev

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CONTROLLABLE WETTING OF NITROCELLULOSE WITH ENERGETIC PLASTICIZER

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

Abstract

The present study involves a surface chemistry project with the primary goal of creating a controllable or tunable interface on the surface of nitrocellulose (NC) for inhibiting energetic plasticizers. The functionality of the controllable/tunable surface is designed to provide an NC surface that has a degree of lyophobicity dependent on a specific application. The research goal is to create surfaces that demonstrate various degrees of wetting when in contact with energetic plasticizer. We have accomplished this by initially functionalizing the NC surface with 3-(triethoxysilylpropyl) isocyanate as a primer layer and therefore, adding various structures termed "parent compounds" that are known in literature to provide various degrees of phobicity on a surface. The work performed to date involves the surface functionalization of NC by esterification of hydroxyl groups with 3-(triethoxysilyl) propyl isocyanate and dibutyl tin dilurate as the reaction catalyst. The isocyanate reacted nitrocellulose is then further functionalized with various organosilanes of general formula $RSiX_3$ (R=alkyl-, phenyl-, fluoroalkyl-; (X=Cl or CH_3O) producing a series of lyophobic NC materials.

Currently, we are working on methodology to obtain surface functionalized NC by means of vapor condensation methods using tetramethoxysilane and dimethyldichlorosilane. This method gives a direct surface modification of powder and formed bulk surfaces of NC without compromising the explosive and burning properties of military grade NC. To date, we have successfully modified the surface of NC with tetramethoxysilane $(CH_3O)_4Si$ which reacts to form more hydroxyl groups for the attachment of lyophobic silanes.

The degree of surface lyophobicity is typically demonstrated by measuring advancing/receding contact angle measurements by observing a probe fluid on a flat surface. We have developed a method to obtain contact angle measurements using the liquid high explosive nitroglycerin (NG) as a probe fluid. Microscopy pictures of NC fibers demonstrate adequate lypophobicity of functionalized NC fibers to NG. FTIR/ATR methods were used to verify silane functionalization on the surface of NC crystals/fibers. Differential Scanning Calorimetry (DSC) was utilized to confirm onset temperatures of decomposition in relation to baseline NC. Future work will involve continuing to optimize solid surface reactions to obtain thin films on the surface of nitrocellulose to achieve tunable lyophobicity.

Reference: **Methods for Modifying Nitrocellulose having Lyophobic Properties**. **U.S. patent number:** 9856328. **Date of Patent:** January 2, 2018.

Dr. Sergiu Gorun

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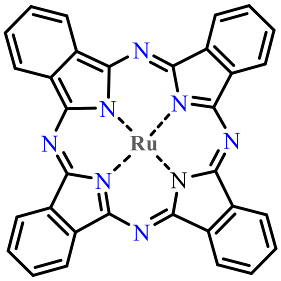
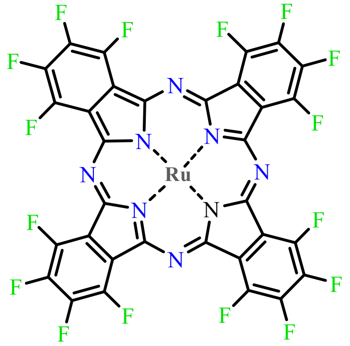
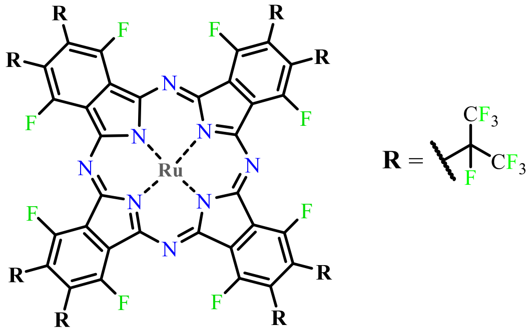
Ruthenium Phthalocyanine Based Heterogeneous Photocatalysts

Da Costa M. T., and Gorun S. M.*
Seton Hall University, Department of Chemistry and Biochemistry, 400 South Orange Ave, South Orange NJ 07079
**correspondence should be addressed to: sergiu.gorun@shu.edu*

Generation 1, 2, and 3 ruthenium phthalocyanines (RuPc's) were produced by a novel route of synthesis, utilizing one set of reaction parameters, then characterized by various spectrometric techniques. The RuPc's were supported on various substrates (i.e. alumina and glass) and will be tested for their catalytic abilities.







H_{16}PcRu ***Generation 1***	**F_{16}PcRu** *Generation 2*	**F_{64}PcRu** *Generation 3*

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Light and Air Based Decomposition of Model Pollutant Methyl Orange

Foglia III, R., Pelmus, M., and Gorun, S. M.*

Seton Hall University, Department of Chemistry and Biochemistry
400 South Orange Avenue, South Orange NJ 07079
**correspondence should be addressed to: sergiu.gorun@shu.edu*

In a world with 7 billion people, the demands on industrial production and, consequently, the reduction of their generated pollutants are directly proportional. As a result there is a strong driving force in industry and in society for "green" environmentally friendly processes. To reach this goal, the elimination of industrial waste products from water is extremely important. The aim of this project was to design a heterogeneous photo-catalyst to break down pollutants in water (simulated with methyl orange, a model azo dye). A fluorinated phthalocyanine (Pc) was chosen due to its ability to utilize the visible light spectrum and its high stability. A functionalized silica gel [SiO_2-$(CH_2)_3$-NH_2] was chosen as the solid support because SiO_2 is an inert inorganic material and doesn't absorb light in the visible region. The photo-sensitizers F_{16}PcZn and F_{64}PcZn were synthesized, purified and covalently attached to the functionalized silica *via* nucleophilic substitution to form two hybrid materials: SiO_2-$(CH_2)_3$-NH_2@F_{16}PcZn and SiO_2-$(CH_2)_3$-NH_2@F_{64}PcZn, respectively. Acetylation activates the amino substituted Pcs toward the production of singlet-oxygen.[1] The resulting hybrid materials were characterized *via* UV-Vis, FT-IR and TGA.

Photo-degradation studies were performed in aqueous suspensions, pH = 7, at 25 °C. The reaction kinetics, followed by UV-Vis analysis, Figure 1 and HPLC, reveal that the hybrid material completely degrades Methyl Orange (MO) in 10 h. Preliminary results indicate that SiO_2-$(CH_2)_3$-NAc@F_{64}PcZn exhibits the highest activity, paralleling the higher photo-activity of F_{64}PcZn *vs.* F_{16}PcZn (tested in homogeneous systems).[2]

The reusability of the catalyst was tested in successive photo-degradation cycles (1 cycle = 10 h run). The catalyst was stable for at least 3 cycles, Figure 1, exhibits constant degradation rates.

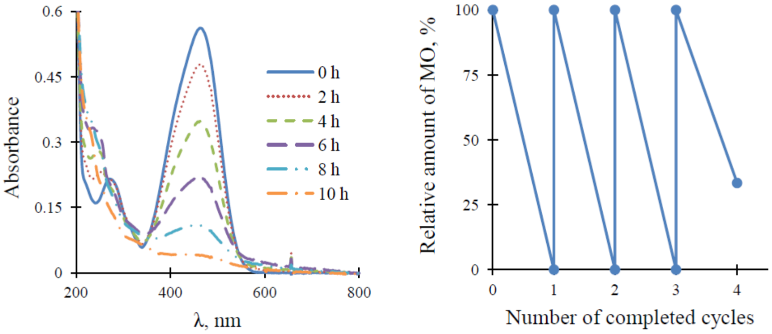

Figure 1. MO photo-degradation with SiO_2-$(CH_2)_3$-NAc@F_{64}PcZn. Left: UV-Vis monitored degradation of MO. Right: repeated cycles of catalysis with fresh MO

Taking into consideration the stability and efficiency of the hybrid material one could view it as a promising photoactive catalyst for green heterogeneous processes.

1. M. Pelmus, unpublished results. In-depth studies to follow.
2. Patel, Hemantbhai H., "Fluorinated Metallo Phthalocyanines for Chemical and Biological Catalysis" (2015). *Seton Hall University Dissertations and Theses (ETDs)*. 2104.

The Center for Functional Materials at Seton Hall University and NASA-NJSGC are thanked for their financial support.

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Physical Vapor Deposition Study of Fluorinated Phthalocyanines and their Metal Complexes

Korn-Heiler, J.[1], Kalantarov, D.[1] Gorun S. M.[1]

[1]*Department of Chemistry and Biochemistry, Center for Functional Materials, Seton Hall University*
400 South Orange Ave. South Orange, NJ 07079
Division of Mathematics, Engineering, Technologies, and Computer Science, Essex County College
303 University Ave, Newark, NJ 07102

Correspondence should be addressed to: sergiu.gorun@shu.edu

Phthalocyanines (Pcs) and their metal complexes (PcMs) have been utilized for a myriad of applications consisting of but not limited to dyes, optical limiters, photosensitizers for cancer therapy, imaging, and catalysis. Their enhanced thermal stability and high sublimation points can facilitate film deposition on surfaces for energy storage applications. Halogenated phthalocyanines, such as $F_{16}PcM$, are ideal candidates as p-type materials but can be subject to π-back bonding which may hinder electron transfer.

In this work, a highly lewis acidic perfluoroisopropyl phthalocyanine, $F_{64}PcH_2$ and its metal complexes (M = Zn^{II}, Cu^{II}) is proposed. The perfluoroisopropyl groups in the $F_{64}Pc$ ligand removes π-back bonding thus rendering the metal center electron deficient.[1] Their electronic properties with respect to conductivity, voltage, capacity, charge/discharge rate, cycle life and efficiency remain to be elucidated and will evaluate their use as potential p-type materials for energy storage applications.

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C-H Bond Free Platinum Drugs with Dual Modality: Anti-Cancer and Imaging

Santiago, J.[1], Gerdes, R.[2], Carrión, E. N.[1] and Gorun S. M.[1]

[1] *Department of Chemistry and Biochemistry, Center for Functional Materials, Seton Hall University*
400 South Orange Ave. South Orange, NJ 07079
[2] *Department of Chemistry, NJIT, University Heights, Newark, NJ 07102*

Correspondence should be addressed to: sergiu.gorun@shu.edu

Phthalocyanines (Pcs) are a unique class of metal-organic materials that generate singlet oxygen, $^1O_2$, and other reactive oxygen species and/or fluoresce upon irradiation using near infrared (600-800 nm) light. These properties are advantageous in many areas, including the photodynamic therapy (PDT) of cancer. Platinum-based anti-cancer drugs, such as cisplatin, have been utilized as DNA intercalators ultimately disrupting oncoprotein production. Platinum is also an NMR active nuclei (S = ½) for ^{195}Pt-NMR-based imaging applications. Platinum porphyrin complexes[1] have been utilized in ^{195}Pt-NMR but platinum phthalocyanines (PcPt), especially fluorinated, are not reported.

As previously elucidated, the perfluoroalkyl platinum phthalocyanine (F_{64}PcPt) is an efficient and durable catalyst for PDT capable of oxidizing an external substrate using only renewable energy resources, air and light. Although F_{64}PcPt has no fluorescence emission, a consequence of spin-orbit coupling, it can serve as a chemical reporter, due to its NMR active center. However, F_{64}PcPt's solubility in a broad range of solvents, especially deuterated, is insufficient for ^{195}Pt-NMR. Efforts are currently underway to develop next generation amino-functionalized fluorinated PcPt complexes, F_{51}NRR'PcPt (R/R' = H/H; H/CH_3; CH_3/CH_3) to enhance sample concentrations suitable for platinum-based imaging applications.

Reference:

1. Milgrom, L. R.; Zuurbier, R. J.; Gascoyne, J. M.; Thompsett, D.; Moore, B. C. Platinum porphyrins – V. Multinuclear NMR of some platinum(IV) porphyrins. *Polyhedron* **1994**, *13*, 209-214.

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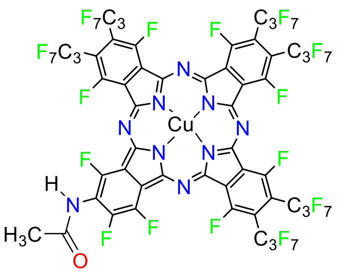
Synthesis and Characterization of Perfluoaroalkyl Copper Phthalocyanines

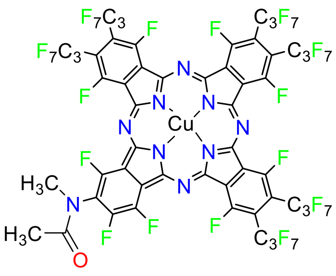
Suazo, M., Pelmus, M., and Gorun, S. M.*

Seton Hall University, Department of Chemistry and Biochemistry, 400 South Orange Avenue, South Orange NJ 07079
**correspondence should be addressed to: sergiu.gorun@shu.edu*

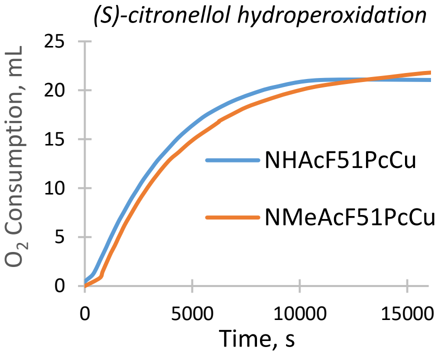
Phthalocyanines (Pcs) are chelating macrocyclic photo-catalysts that can covert, in the presence of light, O_2 from air into reactive oxygen species (singlet oxygen, hydroxyl radicals, superoxide ions). Their favorable photo-catalytic properties render them suitable for numerous applications in both the industrial and the medical field.[1] The synthesis of metallated Pcs with paramagnetic centers is of special interest due to their potential application in the medical industry as theranostic bio-conjugates. The target Pcs have paramagnetic Cu(II) centers, are fluorinated, and have been designed to show what the influence of anchoring upon activity will be in homogeneous systems. This study will be used further in heterogeneous applications.



NHAcF$_{51}$PcCu



NMeAcF$_{51}$PcCu



Chemical structures of the synthesized molecules. *Photo-catalytic activity.*

The acetamido-fluoroalkyl CuPcs (NHAcF$_{51}$PcCu and its methyl homologue NMeAcF$_{51}$PcCu, Ac = acetyl) were synthesized by the condensation of phthalonitrile precursors using a microwave reactor. The resulting mixtures of CuPcs were separated by automated flash chromatography. The identity of obtained compounds was ascertained by high resolution mass spectroscopy, NMR (Evans method), FT-IR and UV-Vis. Aggregation studies were carried out in ethanol and chloroform in order to confirm that there was no stacking, which could have deactivated the catalysts. Catalytic studies, performed using (*S*)-(–)-citronellol as the substrate, in EtOH on a Dosimat automatic gas titrator demonstrated that the Pcs with paramagnetic Cu(II) centers have the ability to function as efficient catalysts. While the rates of O_2 consumption are lower than that of their Zn analogues, their activity is still sufficient enough for further applications in heterogeneous systems. Future work will involve anchoring the CuPcs onto solid supports and testing their reactivity as heterogeneous catalysts which are more readily separated and reused for repeated reactions.

1. Sorokin, A.B. Chem. Rev. **2013**, 113 (10), 8152–8191.

Acknowledgements:
The Independent College Fund of New Jersey (ICFNJ) and the Center of Functional Materials are kindly thanked for their financial support.

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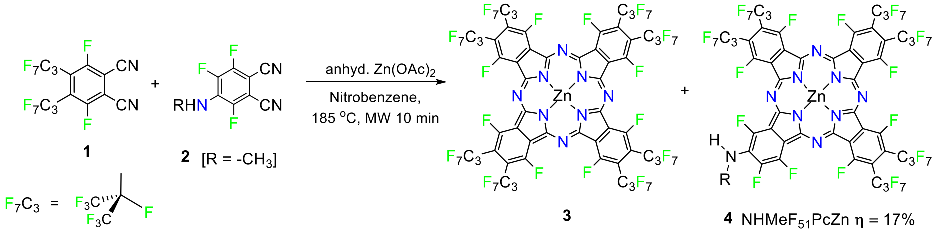
Covalently Bonded Phthalocyanine Heterogeneous Photocatalysts

Xiao, O., Pelmus M., and Gorun S. M.*
Seton Hall University, Department of Chemistry and Biochemistry
400 South Orange Ave, South Orange NJ 07079
**correspondence should be addressed to:* sergiu.gorun@shu.edu

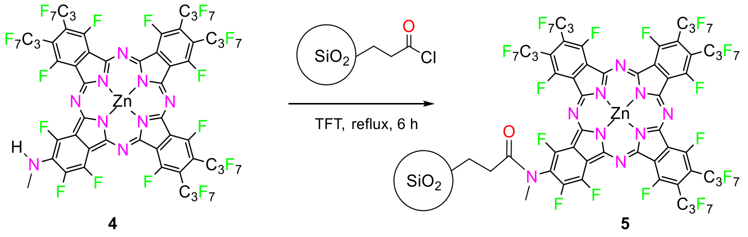
Heterogeneous catalysts have as main advantages robustness, easy separation and reusability.[1] Fluoroalkyl zinc(II) phthalocyanines (PcZn) are visible light sensitizers characterized by high stability and non-aggregation. We hypothesize that the combination of these two features with using a support to give a hybrid material may result in a visible-light solid photo-catalyst. The synthesis of the Pc was performed in a microwave (MW) reactor by combining two different precursors, **1** and **2**, which conducted to a symmetrical, **3**, and an asymmetrical, amino-functionalized sensitizer, **4**. The Pc of interest (**4**, NHMeF$_{51}$PcZn) was purified through column chromatography and characterized by UV-Vis, FT-IR, ^{19}F NMR. Its spectroscopic properties agree with the literature.[2]



Scheme 1: Synthesis of amino functionalized ZnPc: ***NHMeF$_{51}$PcZn***

Homogeneous photo-catalytic studies showed a low photo-activity for the amino Pc but acylation to form an amido Pc restores the photo-activity. Considering these results we proceed to attach the amino Pc to propionyl chloride functionalized silica solid support by the formation of an amide bond. The amide bond was expected to insure both the formation of a strong covalent bond and to restore the activity of the photo-catalyst.

The synthesis of the hybrid material, **5**, was carried in trifluorotoluene under inert atmosphere. The solid support was colored green and the Pc didn't leach out from the support upon washing with ethanol proving that the Pc, **4**, was covalently bonded to the functionalized silica. The solid UV-Vis absorbance showed the presence of the Q band (specific absor



Scheme 2. Synthesis of the hybrid material ***SiO$_2$-C$_2$H$_4$-CO-NMe-F$_{51}$PcZn***

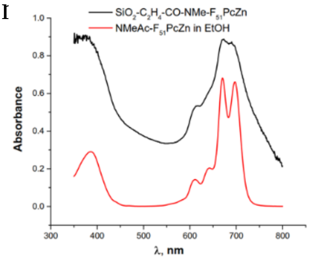


Figure 1. UV-Vis absorption of the hybrid material ***SiO$_2$-C$_2$H$_4$-CO-NMe-F$_{51}$PcZn*** vs ***NMeAc-F$_{51}$PcZn***

The photo-catalytic and catalytic efficiency of the hybrid material will be evaluated in the future.

1. Sorokin, A.B. *Chem. Rev.* **2013**, *113* (10), 8152–8191.
2. Patel, H. H. *Fluorinated Metallo Phthalocyanines for Chemical and Biological Catalysis*, **2015**, Seton Hall University, PhD Dissertation.

The Center of Functional Materials at Seton Hall University is gratefully acknowledged for financial support.

Dr. James Hanson

16

Heterogeneous Fluorinated Cobalt Phthalocyanines for Catalytic Applications

A. Aiello[1], J.M. Dufresne[1], M. Pelmus[1,2], S.M. Gorun[1,2], J. Hanson[1]

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

Abstract:

Phthalocyanines (Pc) are classified as aromatic macrocyclic compounds, with many varying uses both physically, chemically, and biologically depending on the metal ion in the center of the structure. Hemoglobin and Chloroplast both are related with the Pc core structure, which are four nitrogen rings linked in a complete circle. Pc are present in many pigments for plastics, dyes, green and blue automotive paints, solar cells, gas monitors, and inks. A representative largely used in dyes, pigments, and inks is PcCu for its strong blue coloring. The metal center has an important role in the catalytic and photocatalytic properties of these aromatic macrocyclic compounds.[1] In the present research, we have placed cobalt into the center of a fluoroalkylated Pc using perfluoroalkyl phthalalonitrile (Bis 1) with amino precursors (NH_2F_3PN or $NHMeF_3PN$) and cobalt acetate.[2] The reagents were mixed in a molar ratio of 2 Bis 1 : 2 NH_2F_3PN or $NHMeF_3PN$: 1.5 cobalt acetate and put under microwave irradiation (185 °C, 10 min). The resulted amino PcCo are catalytic under consideration for immobilization on Nafion support. Catalytic properties of the heterogeneous catalyst are expected for oxidation reactions.

References:

1. Yilmaz, Y., Phthalocyanines and Some Current Applications; Ed.; InTech: Rijeka, Croatia, **2017**.
2. Patel H. Fluorinated Metallo Phthalocyanines for Chemical and Biological Catalysis, Ph. D. Dissertation, Seton Hall University, South Orange, NJ, August **2015**.

17

Polymeric Materials for Additive Manufacturing

Alison Arissa, Brandon Pineda, Edrice Sediq, James E. Hanson

Additive manufacturing, more commonly known as 3D printing, is a manufacturing technique growing in popularity. We are developing new materials for additive manufacturing based on a variety of engineering plastics, designed to have high strength and high temperature resistance. The inspiration for our material is the engineering plastic material known as Noryl, which is a blend of polystyrene and “polyphenylene oxide” (which is actually poly(2,6-dimethylphenylene oxide). In our modification, polystyrene is replaced with styrenemaleimide copolymers, which required synthesis of the maleimide monomers and copolymerization, while the polyphenylene oxide is replaced with polyphenylene oxides derived from polymerization of phthalate

derivatives. The synthesis, polymerization, and evaluation of the individual copolymers and preparation of polymer blends will be described.

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Synthesis of Solid-Supported Fluorinated Ruthenium Phthalocyanines for Catalytic and Photocatalytic Applications

A. Beck[1], C. Del Castillo[1], M. Pelmus[1,2], S.M. Gorun[1,2]*, J. Hanson[1]*

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

Abstract:

Phthalocyanines are conjugated macrocycles similar in structure to the porphyrin rings found in biological proteins such as hemoglobin. When coordinately-bound to a transition metal cation, these enzyme mimics are capable of catalytic and/or photocatalytic function. Ruthenium-based phthalocyanines have been shown to perform both catalytic and photocatalytic functions. However, phthalocyanines are highly reactive and decompose in the catalytic process, rendering the compound no longer a catalyst of the reaction, but a reactant.[1] Partially fluorinated metal phthalocyanines equipped with several bulky groups prevent decomposition and aggregation, resulting in a reusable catalyst. Most organic reactions that require catalysis occur in either the liquid or gaseous phases, so heterogeneous catalysts bound to solid support are the optimal choice for its simple removal from the reaction system. The described fluorinated phthalocyanine rings are formed by the combination of two types of precursors: bis-perfluoroisopropylphtalonitrile (Bis I) and amino substituted fluorophthalonitrile ($NHRF_3PN$, R = H or CH_3).[2] To allow for covalent bonding between the phthalocyanine and the solid support, nucleophilic substitutions of tetrafluorophthalonitrile (TFPN) to form primary and secondary amine groups on C4 were performed to yield two alternatives for the second precursor. Each synthesized precursor molecule was separately reacted with Bis I and ruthenium trichloride to form $F_{51}PcRuNH_2$ and $F_{51}PcRuNHMe$ by microwave synthesis. Column chromatography and thin-film liquid chromatography were used to separate impurities and isolate the desired products. Further attachment on Nafion type resin is currently underway. Previous studies have shown fluorinated ruthenium phthalocyanines to catalyze hydrogenation and cyclopropanation of several compounds with lower cost and higher yields as well as the production of singlet oxygen, which can potentially be used in photodynamic therapy for cancer treatment.[1]

References

[1]. Rawling, T.; McDonagh, A. *Coord. Chem. Rev.* **2007**, *251*, 1128-1157.
[2]. Patel H. Fluorinated Metallo Phthalocyanines for Chemical and Biological Catalysis, Ph. D. Dissertation, Seton Hall University, South Orange, NJ, August **2015**.

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Synthesis and characterization of Fluorinated Nickel Phthalocyanines and immobilization on Nafion support

N. Jimenez[1], J. Bandala[1], M. Pelmus[1,2], S.M. Gorun[1,2]*, J. Hanson[1]*

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

Abstract:

Metallophthalocyanines (PcM) are metal complexes that are structurally similar to porphyrins, found in nature. The metallo Pc can easily be obtained by heating phthalonitriles with a metal salt, which results in a tetramerization of the starting material. This study focuses on the properties of Pc containing nickel as the central metal ion. In this work, the C-H bonds are replaced by fluorine and perfluoroalkyl groups, which yield models of catalysts that don't aggregate and are very stable.[1] F_{64}PcNi was synthesized as well as amino derivatives by microwave synthesis and the products were purified by column chromatography. The purification process was monitored by TLC, products were characterized by UV-vis spectroscopy and NMR. In parallel a study for immobilization of aminophthalonitrile on Nafion was performed and the leaching experiments showed a large amount of precursor not being bonded. The amino PcNi derivatives treated with Nafion are under study for stronger interactions.

References:

1. Patel H. Fluorinated Metallo-Phthalocyanines for Chemical and Biological Catalysis, Ph. D. Dissertation, Seton Hall University, South Orange, NJ, August **2015**.

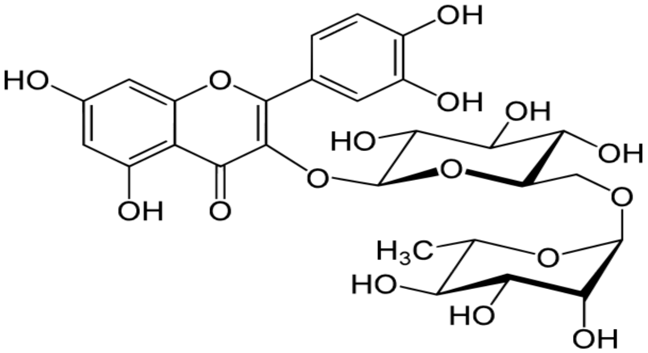
20

Novel PLGA-Rutin Polymer-Based Microparticles Assays of Antibacterial Activity for Gram-negative *Escherichia coli* and Gram-positive *Staphylococcus aureus*

Dr. James E. Hanson[a], Dr.Tinchun Chu[b], Miguel Medico[a]

[a] Department of Chemistry & Biochemistry
[b]Derpartment of Biologicals Sciences
Seton Hall University, South Orange, NJ 07079

Among the flavonoids, rutin, a kind of flavonoid glycoside, is known as vitamin P and has antiplatelet, antiviral, and antibacterial properties, as well as strengthen the capillaries of blood vessels, which are the results of its high radical scavenging activity and antioxidant capacity. These properties are potentially beneficial in preventing diseases and protecting the stability of the genome. Rutin is the most abundant antioxidant found in the human diet. Low aqueous solubility of rutin limits its bioavailability and hence therapeutic effects. Therefore, the aim of the present study is to develop a poly (lactide-co-glycolic acid) (PLGA) polymer-based microparticles of PLGA-Rutin with a view to improve its aqueous solubility and examine the effect on its antibacterial assays for both Gram-negative Escherichia coli and Gram-positive Staphylococcus aureus. Biodegradable PLGA microparticles have been widely studied as controlled release of drugs, peptides and proteins. PLGA is synthesized by means of ring-opening co-polymerization of two different monomers, the cyclic dimers (1,4-dioxane-2,5-diones) of glycolic acid and lactic acid. 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.



21

Zinc Phthalocyanines based Heterogeneous Photo-Catalysts

S. Reed[1], A. Borchers[1], M. Pelmus[1,2], S.M. Gorun[1,2]*, J. Hanson[1]*

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

Abstract:

Limitations presented by easily broken C-H bonds restrict the efficiency of commonly used catalytic materials in terms of oxidation-resistance; however, studies reveal that fluoroalkyl-substituted fluorophthalocyanines are ligands in which a combination of fluoro- and perfluoroalkyl groups replace all C-H bonds in the compound. This reaction yields porphyrin-bioinspired catalytic models.[1] Phthalocyanine metal complexes (MPc's) are used throughout nature in processes such as catalytic aerobic oxidations and peroxide destruction. Their structural resemblance to the porphyrin complexes, affordability and simplistic preparation make them highly sought-after catalysts, especially regarding large-scale industrial processes.[2]

In this realm of research, the preparation of the perfluoroisopropyl-substituted zinc phthalocyanine and amino derivatives as functionalized catalysts was performed via microwave synthesis and verified through Thin Layer Chromatography. Theoretically, the catalyst

heterogenization should yield an active hybrid material that performs an easy separation from the reaction mixture and be recycled through successive reactions, given that the catalyst retain its catalytic properties.[2] The zinc metal has a high triple state quantum yield and the long triplet lifetimes required for efficient photosensitization and the incorporation of $^1O_2$ in the C-H bonds of allylic derivatives.

References:

[1] Carrion E.N. *et al*. *J. Porphyrins Phthalocyanines*, **2018**; *22*: 1–27
[2] Sorokin A. *Chem. Rev.,* **2013**, *113* (10), 8152–8191

22

Rock-Polymer Composites for Architectural 3D Printing

Alison Arissa, Brandon Pineda, Jason Saway, Edrice Sediq, Ziwen Wang, James E. Hanson
Department of Chemistry and Biochemistry
Seton Hall University, South Orange NJ

In preparation for the NASA Mars Habitat Challenge, we evaluated rock-polymer composites for use in architectural 3D printing. In accord with the requirements of the challenge, we prepared composites using crushed rock and a variety of polymers. The polymers were selected from a list of materials expected to be available as recycled spacecraft components. Polymers were melted and blended with the crushed rock, and the resulting composite materials were evaluated based on melting temperature, ease of flow of the molten mixture, and strength of the final composite.

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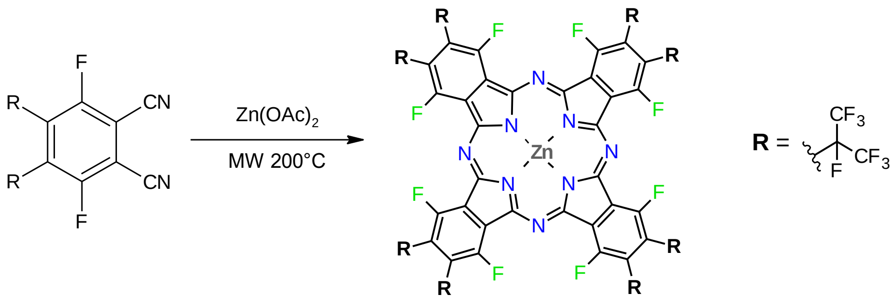
Zinc Perfluorophthalocyanine: A Reactive Oxygen Species- Induced Regulation of Microbial Growth.

Prabh J Jassal; Abdul Azeez; Mario T Da Costa;
Dr. Sergiu M. Gorun; Dr. James E. Hanson

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

Research Abstract

The prevalence of microorganisms causing infectious diseases cannot be over emphasize in our daily lives. The need for prevention include antibiotics, however, depending on the bacterial strains, resistance to these drugs vary. In this study, nonplanar perhalogenated metallophthalocyanine (zinc perfluorophthalocyanine) was synthesize based on previous research. This fluorinated phthalocyanine is photoactive and has the capacity to produce singlet oxygen a family of reactive oxygen species (ROS) when irradiated with visible light. Microwave method was used for the synthesis of the fluorinated phthalocyanine in the presence of zinc acetate and perfluoro-(4,5-di-isopropyl)phthalonitrile in a 4:1 ratio, resulting to a stable [$F_{64}PcZn$] molecules. Initial UV- vis spectroscopy analysis of the crude product revealed a Q-band at 688 nm, indicating the presence of the phthalocyanine moiety. Thin-layered chromatography (TLC) plate analysis in a 30% acetone- hexane solution was used to determine the bands and were confirmed by earlier literature. The focus of this project is the reduction and elimination of a family of microorganisms and macro organisms such as bacteria and algae growth common within the interior of a fish-tank due to fouling. The coated surface produce radical oxygen species (ROS) such as singlet oxygen when illumination with visible light in their excited state, the production of singlet oxygen has been tested on organic dyes and great results were produced, the current phase of the project is to investigate this coated surface on living organism.



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Evaluation of magnetic and photooxidative properties of zinc perfluorophthalocyanine nanocomposite

Jason Saway; Abdul Azeez; Dr. Sergiu M. Gorun; Dr. James E. Hanson

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

Abstract:

Solid support chemistry has played a major role in the development of new techniques to improve methods in areas of research including chemistry. The goal of this research is to design a magnetic photooxidative catalytic material that can easily separate the heterogeneous catalyst from the degraded compound. A sol-gel method was adopted to synthesize magnetite nanoparticles (Fe_3O_4) a composition of iron (II, III). The magnetite was further coated with silicon oxide (SiO_2), titanium oxide (TiO_2) and finally the nanocomposite-coated oxides were treated with zinc perfluorophthalocyanine ($F_{64}PcZn$) a photoactive catalyst. The final material produced a robust magnetic photocatalyst (Fe_3O_4-SiO_2-TiO_2-$F_{64}PcZn$) composite. Our coated magnetic nanocomposites materials were characterized with reflectance UV-Vis spectroscopy, magnetic stair plate was used to determine the magnetic properties, compound microscopy was also use to determine the preliminary surface properties, further characterization will be done with transmission electron microscopy, X-ray diffraction, field energy-dispersive X-ray spectroscopy, vibrating sample magnetometry, scanning electron microscopy and Brunauer-Emmett-Teller (BET). Preliminary activities of the photocatalyst magnetic nanocomposite were tested in methyl orange solution; the solution was degraded under visible light illumination. From the preliminary data acquired, photooxidative activities was revealed and the catalyst retained its magnetic properties. The experiment, revealed easy separation of catalyst from the treated solution using an external magnet. Our future objective is to conduct an optimization studies to determine the kinetic properties with respect to degradation and the efficiency of the magnetic photocatalyst.

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The Control of Microbial Growth using the effects of Zinc Perfluorophthalocyanine as a Photosensitizer under Visible light

Lauren Polio; Abdul Azeez; Dr. Sergiu M. Gorun; Dr. James E. Hanson

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

Abstract

A dual self-cleaning surface was created by embedding metallophthalocyanines doped with titanium dioxide as photo oxidative material in PVDF polymer matrix. This present research is to investigate the reactivity of a photoactive coated polymer surface, embedded in it is a photosensitizer, $F_{64}PcZn$, for the production of a radical oxygen species (ROS) against a family of microbes. (*Staphylococcus aureus* and *Streptococcus mutans*) Previous research demonstrated our photoactive coated surface has the ability to mineralize organic dyes such as methyl orange by completely bleaching into a colorless solution. With this knowledge, we propose that the production of ROS, in particular, singlet oxygen from our photoactive coated surfaces, in the presence of visible light, will lead to the deactivation of microorganisms. Our goal is to create a harmless hydrophobic coated surface that will disinfect the family of microbes such as *Staphylococcus aureus* and *Streptococcus mutans* under the presence of visible light illumination. We expect the results to show a limited growth of bacteria on the coated PVDF surface, embedded with TiO_2-$F_{64}PcZn$.

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Surface Re-engineered Reactive, Robust Polymer Hybrids

Abdul Azeez; Dr. Sergiu M. Gorun; Dr. James E. Hanson

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

Abstract

Polymers that incorporate inorganic materials capable of generating reactive oxygen species (ROS) using only visible light illumination and air also exhibit controlled surface properties that impart high hydrophobic and possible oleophobic properties is our current research. This research stands to address an unprecedented, universal, "green", self-cleaning surface re-engineering. Atmospheric O_2 activation by energy transfer from perfluorinated photosensitizer ($F_{64}PcZn$) demonstrated the production of singlet oxygen ($^1O_2$) by visible light illumination, both in solution and in supported metal oxide. Our research also highlighted surface re-engineering due to modification of surfaces to modulate hydrophobicity; a partially hydrophobic PVDF surface with water contact angle ~ 92^o re-engineered to superhydrophobic surface with higher water contact angle ~159^o. This achievement was due to the generation of roughness on the appropriate scale; usually about 1-100 microns, this micro scale resulted from the use of volatilizable ammonium bicarbonate (NH_4HCO_3) crystals, a non-toxic salt that decomposes to water, carbon dioxide and ammonia starting at about 37 ^oC, this resulted in voids throughout the film matrix, including surface roughness. The incorporation of a photosensitizer coated on TiO_2 or SiO_2 embedded onto the re-engineered polymer matrix resulted to the bleaching/decomposition of methyl orange (MO) in aqueous solution, a known contaminant model, which also serves as a pH indicator. These photosensitizers are thermally resistant to 300 ^oC, which makes them very resistive and robust. The roughening channels possibly would provide additional pathways for ROS formation via inward diffusing of oxygen and outward migration of activated oxygen, toward the surface, thus enhancing the desired ROS concentration on surfaces. Additionally, due to the 3D nature of the channels, the partial abrasion of the coating, a normal process of wear, may result in neither a decrease of surface roughness, nor a loss of reactivity. This feature represents a significant practical advantage in our research.

Dr. Yuri Kazakevich

27

Size Exclusion and the Void Volume of HPLC Columns

Mathias Kant, Yuri Kazakevich, Department of Chemistry and Biochemistry, Seton Hall University, South Orange, NJ 07079

Size exclusion chromatography is a popular technique for the analysis of polymer molecular weight. Chromatographic retention is usually associated with the logarithm of the polymer molecular weight. The exclusion process is usually understood as the inability of polymer molecules to penetrate into pores that are smaller in diameter than the size of the polymer. Column void volume is the volume of the liquid phase in the column. The exclusion could be expressed as the product of the polymer gyration radius and adsorbent surface area. In this case the polymer retention should be proportional to the $\sqrt[3]{M}$.
We verified this hypothesis and found that chromatographic retention of polymers at size-exclusion conditions is linearly dependent on the cubic root of its molecular weight. There are two distinct sections on $\sqrt[3]{M}$ vs. V_R dependence. The first linear section with a smaller slope is for low molecular weight polymers that show complete penetration in all pores. The second larger slope portion represents polymer samples with high molecular weights, in which molecules are completely excluded from adsorbent pores.
The propagation of these lines to their intercept with the retention volume axis represents the void volume value for the first line, and the interparticle volume of the column for the second line.
These results have been verified on ten different columns, using 32 polymer standards with molecular weights varying from 600 to 2,700,000 Da.

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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 und 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 over its condensation energy at 77 K. The mixtures of silica and C18-modified silica (Luna 5 um Silica - Phenomenex), and C18 (Luna 5 um 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 also 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 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 Constant maybe a viable parameter that can be used to characterize mixed-mode columns on the basis of surface energy. 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:

1. K. Zhang, X. Liu. J. Pharmaceutical and Biomedical Analysis. 128 (2016) 73-88.
2. S.J.Gregg, K.S.W. Sing, Adsdorption, Surface Area and Porosity, AP, London, 1982.

Dr. Stephen Kelty

29

Electron Density Dispersion of Amines Adsorbed on Pd(111) Surfaces

Frank Hung
Mentor: Dr. Stephen Kelty* and Dr. Robert Augustine**
*The center for Computational Research
**The center for Applied Catalysis
Department of Chemistry and Biochemistry
Seton Hall University
April 24, 2018

Abstract

Benzylcyclohexylamine (BCHA) containing para -methyl, -methyloxy, -perfluoromethyl, -isopropyl and meta -methyl, -methyloxy substituents on the benzyl group were investigated using density functional theory (DFT) calculations with Vienna Ab initio Simulation Package (VASP) in an effort to find a correlation between experimentally determined hydrogenation rates and the physical properties of the reactant. It has become clear that the well-known Hammett Free Energy Relationships offer little predictive information for many metal catalyzed hydrogenation reactions. In this study, we have used molecular dynamics followed by single point energy calculations and Bader Charge Analysis to investigate and compare observed hydrogenation reaction rates of a set of substituted BCHA reactants with variation in various physical properties of the reactants while adsorbed on Pd (111). The results show little change in the C-N charge difference compared to the previous results for benzylamine (BA) on Pd(111) surfaces using direct Geometry Optimization. We will do geometry optimizations based on the molecular dynamics results which will include van der Waals interaction functionals. We anticipate that these calculations will provide a better understanding of the crucial physical properties of the reactants that help offer prediction of the observed reactivity.

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Computational Investigation of Polypeptides as Candidates for Cyclization

Sara Lamcaj and Stephen P. Kelty, Department of Chemistry and Biochemistry, Seton Hall University, South Orange, NJ 07079

Proline and two modified versions of proline (U-PRO) (P-PRO) were studied to determine if it will stabilize in a conformation that would lead to a hairpin (HP) loop in the peptide backbone. Formation of a HP-loop is desired for subsequent cyclization of the peptide for therapeutic drug applications. Molecular Dynamics (MD) simulations were carried out to determine if certain

modifications of proline will lead to more frequent occurrences of HP loop structures. These studies were done using classical force fields with the Visual Molecular Dynamics (VMD) and Nanoscale Molecular Dynamics (NAMD) software packages.

Normal proline is composed of a ring of CH_2 groups starting at the alpha carbon and circling back to the nitrogen atom (Figure 1). The modified prolines contain oxygen substitutions and additions as shown in Figures 2 and 3.

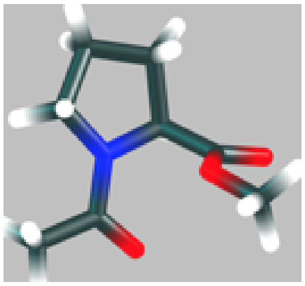

Figure 1: Proline (N-PRO)

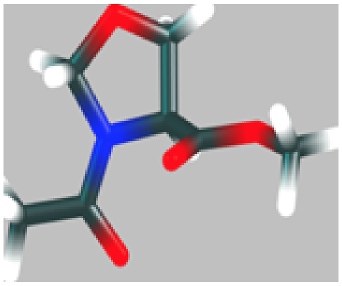

Figure 2: Psuedo-Proline (P-PRO)

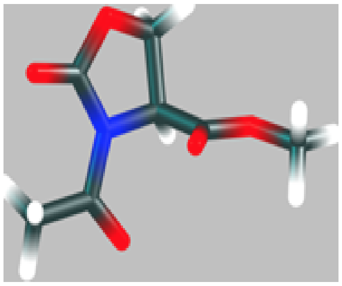

Figure 3: Urethane Proline (U-PRO)

The goal of this project is to predict if the modified versions of proline will lead to the formation of a hairpin loop turn in a peptide containing the modified proline more frequently compared to normal proline.

Methods:

The protein consisting of a 5 amino acid peptide sequence (FGXFG, X = N, P, or U-PRO) was created and solvated in explicit water with ions to resemble a cellular environment, implicit water, or implicit dimethylformamide. All MD simulations were run at 300K temperature and 1 atm pressure for 350 ns. Simulation trajectories were recorded for each system at a sampling rate of 70,000 data points (frames) per system.

Analysis:

The simulations have been completed and the distance between the leading and ending nitrogen atom will be measured to determine if a hairpin loop has been formed in the five-member peptide during the simulation. A plot of N-N pair correlation will be made for (N-PRO),(U-PRO), and (P-PRO) and will be included in the final report.

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Studying the Effect of Human Telomere Conformations on Porphyrin Binding

Rory Vander Valk, Jeffrey Raab, Stephen P. Kelty, Cosimo Antonacci
Center for Computational Research, Department of Chemistry and Biochemistry
Seton Hall University, South Orange, N.J.

The study of porphyrin binding on human telomeric DNA is of present interest in the treatment of cancer cells. The telomerase enzyme is overexpressed in over 80% of cancer cells and acts as a tumor promoter by extending cell life. The binding of small ligands to telomeres has been shown to inhibit the activity of the telomerase enzyme. The human telomeric DNA sequence $(TTAGGG)_4$ is known to favor the formation of a (3+1) G-quadruplex fold stabilized by potassium ions in solution. This structure contains a core of 3 stacked plates of G-tetrads linked together with TTA side chains. The (3+1) fold contains one reversed loop followed by two lateral loops. The arrangement of reversed and lateral side chain loops affect the stability of the structure in solution. In addition, the structure of the individual side chains around the G-tetrad core can form unique conformations of the entire (3+1) fold. The leading 5' TTA chain is also free in solution to adopt various structures interacting with the side chains or nearby tetrad face. These various interactions can interfere with the strongest binding mode of porphyrins, stacking on exposed G-tetrads. Here we study the stability of various conformations of the 5' TTA chain folding and its effect on the binding of the porphyrin H2TMPyP.

Dr. Joseph Maloy

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

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

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.

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]. This novel software is useful to compute the chromatographic peak asymmetry when both partition and adsorption simultaneously control the distribution on the column.

In this study, we hope to demonstrate how specific adsorption sites control peak tailing in analytical scale separation with the Excel based program. Therefore, chromatographic data will be acquired for a cationic amphiphilic dye 1,1-dioctadecyl-3,3,33-tetramethylindocarbocyanine perchlorate (DiI) in order to understand the tailing behavior of this cationic probe in analytical-scale reversed phase chromatography at different concentrations [6]. Caffeine and phenol will also be studied as they have previously shown to exhibit HPLC tailing peaks [6,7,8] within the right conditions. Results obtained for all analytes will be compared with outputs from the developed VBA program to investigate the extent of tailing of these specific compounds and to correlate experimental data to the simulation software. The effect of concentration variation on peak tailing and retention factor will be then examined as well as quantitative agreement between simulation and experimental data in order to further understand the VBA chromatographic simulation software and confirm its validity.

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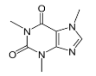

Figure 1: Caffeine, Caffeine is moderately soluble in water. It is also moderately soluble in ethanol. It is weakly basic (pK_a = ~0.6) requiring strong acid to protonate it.

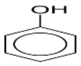

Figure 2: Phenol. Phenol is appreciably soluble in water and slightly acidic.

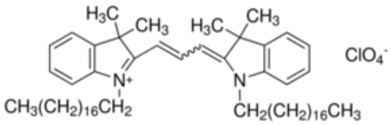

Figure 3: 1,1”-didodecyl:3,3,3’3’-teramethylindocarbocyanine perchlorate (DiI)

Dr. Gary Martin

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New Methods for Macrocyclic Peptide Structure Determination

Ryan D. Cohen,[a,b] Hader E. Elashal,[a] Heidi E. Elashal,[a] Chuhan Zong,[c]
James Link,[c] Monika Raj,[d,*] and Gary E. Martin[a,b,*]

[a:] Department of Chemistry and Biochemistry, Seton Hall University, South Orange, NJ 07079
[b:] Department of Process Research and Development, Merck & Co., Inc., Rahway, NJ 07065
[c:] Department of Chemical and Biological Engineering, Princeton University, Princeton, NJ 08544
[d:] Department of Chemistry and Biochemistry, Auburn University, Auburn, AL, 36830

Macrocyclic peptides are important drug discovery candidates and include the antibiotic, vancomycin, and immunosuppressant, cyclosporin. Advantages relative to their linear analogs are enhanced stability, potential for targeting protein-protein interactions, improved cellular permeability, and stronger ligand-binding ability. However, one disadvantage is that their structures are not easy to elucidate. There are several reasons for this: 1) common sequencing approaches, such as protealytic cleavage and Edman degradation, will not work and 2) NMR spectra are often complex (e.g., signal doubling) with broad line shapes. New methods to simplify structure determination and thus better enable discovery efforts are desirable.

In the first research project, we developed a broadly-applicable chemical cleavage methodology to selectively open the macrocyclic ring, which simplified mass spectrometry sequence determination. A high-throughput ion mobility mass spectrometry method paired with *de novo* peptide sequencing software was then used to analyze large combinatorial libraries.

In the second research project, we applied new NMR methods to simplify complex 2D spectra. Pure shift NMR, which removes proton-proton couplings, was combined with generalized indirect covariance (GIC) processing, which allowed for pure shift spectra reconstruction in cases where the pure shift methodology cannot be implemented directly as part of the pulse sequence. Pure shift GIC variants of HSQC-TOCSY, ROESY, and HMBC exhibited enhanced resolution and allowed for accurate assignment of all signals for a benchmark macrocyclic peptide, aureobacidin.

Dr. Cecilia Marzabadi

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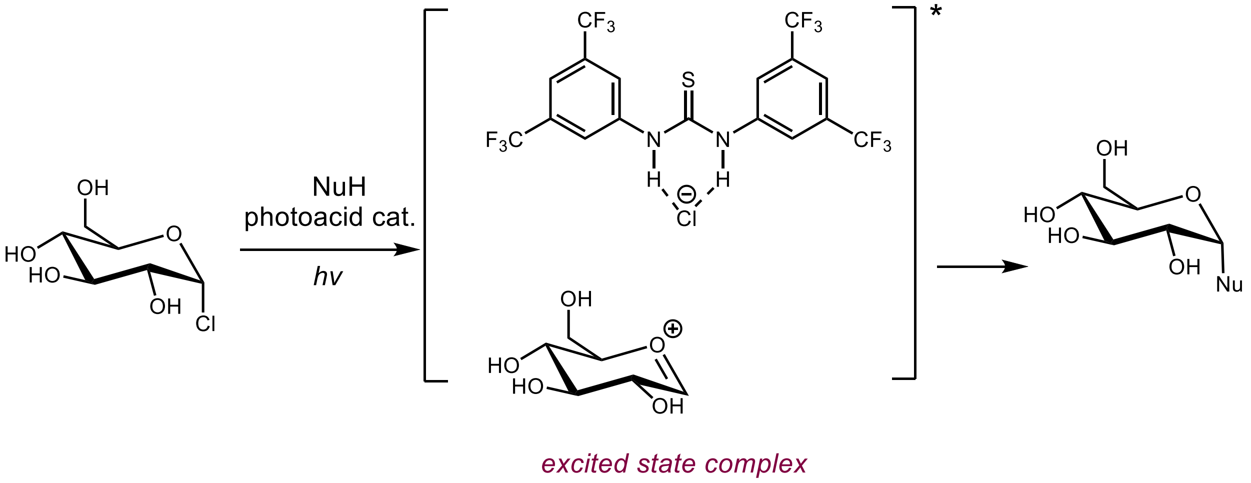
Organophotoacid Catalyzed Formation of Substituted Carbohydrates

Luis R. Alicea, Joseph J. Badillo* and Cecilia H. Marzabadi*

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

A photoacid is a molecule which exhibits enhanced acidity upon exposure to visible light. In this study, we will use organophotoacid catalysis to facilitate substituted carbohydrate formation. This strategy has the potential to become a powerful synthetic tool for the synthesis of substituted sugars. In addition to substrate scope and product selectivity, the nature of the photoacid structure and function relationship will be investigated.



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Optimizing Esterification Chemistry

Daniel M. Goldman and Cecilia Marzabadi, Department of Chemistry and Biochemistry, Seton Hall University, South Orange, NJ 07079

Abstract

Under the aegis of the current research to develop glycoconjugate antimetabolites to inhibit cancer metabolism, we have focused on the introduction of an ester bond at the C-3 position of an unprotected D-Glucal via a Yamaguchi esterification reaction. Under the conditions, we attempted to regioselectively direct the esterification reaction with a series of carboxylic acids.

Whereas bulky acids gave good regioselectivity, smaller acids gave mixtures of esterified product in these reactions. One of key goals is to optimize yields at the C-3 position for smaller acids with the goal conjugating fluorinated enzyme substrates to D-Glucal. The goal will be to optimize the pharmacokinetic properties of absorption, distribution, metabolism, and excretion.

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Site-Selective Bioconjunction

Yonnette Sim, Cecilia Marzabadi, Monika Raj, Department of Chemistry and Biochemistry,
Seton Hall University, South Orange, NJ 07079

Chemical modification of biomolecules is a critically important tool with a broad range of applications, including assays, therapeutic protein engineering, imaging, biosensors, drug delivery, and diagnostics. Convention bioconjugation methods are non-specific and produce heterogeneous mixtures of conjugates by utilizing surface-exposed side chain of lysines or cystines. Over the last two decades a number of bioconjugation methods have been developed which enable the site specific modification of biomolecules in a control manner. New methods for carrying out specific modifications at one particular amino acid or at one unique defined site on the biomolecules are highly desirable and very challenging. Even more challenging is the development of the method that works under mild biological conditions without the use of any catalyst. Recently, site-selective modification of a protein containing proline at the N-terminus has been attempted using o-aminophenol and potassium ferricyanide, but this method lacks specificity to modify a single amino acid on the protein. We have developed a novel site-specific method for labeling biomolecules containing proline at the N-terminus under biological conditions. This method will be used for site-specific conjugation of a polymer, dye, peptide and drugs to a N-terminal proline containing biomolecule and will be utilized for making glycoproteins. The long-term goal of the project is to apply this methodology for the synthesis of stable antibody-drug conjugates (ADCs) for targeted therapies.

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Dr. Wyatt Murphy

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Investigation of Polyol Induced Extraction of Recovered Polyaromatic Hydrocarbons

Denise T. Donnelly, Caitlin C. Patt, Wyatt R. Murphy, Jr., Department of Chemistry and Biochemistry, Seton Hall University, 400 South Orange Avenue, South Orange NJ 07079.

A recently developed sample extraction technique called polyol induced extraction (PIE) has been described by Sowa, et. al. where miscible solvents such as acetonitrile and water can be separated by addition of glycerin and cooling. Previous work by Del Mastro has shown that improved isolation of essential oils from botanical sources can be obtained with this method. The work reported here are preliminary studies on the use of PIE to recover polyaromatic hydrocarbons (PAHs) from biological sources such as fish oil. The studies aim to improve the percent recovery of model samples above 60% while retaining or enhancing differential isolation of the PAHs and metabolites from biopolymers. Parameters such as acetonitrile/water ratios, temperature and amount of glycerin added will be varied to optimize the recovery and differentiation of model PAH-metabolites 1-pyrenol and 1-naphthol from solutions containing bovine serum albumin as a test protein.

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Polyol Induced Extraction for Evaluation of Polycyclic Aromatic Hydrocarbons

Luke Harding, Alex Garrett & Varoon Dave
Seton Hall University, Department of Chemistry , 400 South Orange Avenue, South Orange, NJ 07079

Polyol Induced Extraction is a specialized technique for separation of an analyte from two miscible liquids. The essential goal was to separate an analyte in a solution of acetonitrile and glycerol. This method of extraction is much cheaper and easier compared to other methods of extraction. Better results are trying to be achieved through this method to increase the percent yield and have a more efficient process of extraction. One future use for Polyol Induced Extraction would include separating fragrances out of plants, or other materials, for perfumes and other aerosol products. This extraction method can also be used to separate oils that are being removed from polluted fish to determine the degree of contamination. A 2-napthol mixture was combined into a solution of acetonitrile and glycerol at a 10:2 ratio respectively. The solution was then chilled and allowed to separate for about 15-20 minutes. During this process, the 2-napthol separated from the glycerol and was contained in the acetonitrile. The acetonitrile and 2-napthol was then extracted from the addition flask and analyzed under the spectrophotometer. Then, the Solver program in Microsoft Excel was used in order to analyze the data. This extraction method and analysis was also used for 1-napthol and phenathrene.

Dr. Rhonda Quinn

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Determining $^{87}Sr/^{86}Sr$ isotope ratios in teeth samples of unprovenienced human remains by using laser ablation

Authors: Alexandr Trifonov[1], Rhonda L. Quinn[1,2]

[1]Anthropological Isotope Laboratory, Seton Hall University; [2]Department of Earth and Planetary Sciences, Rutgers University.

Reconstructing the geographical and dietary histories of unprovenienced human remains using stable isotope analysis plays an important role in historical archaeology and forensic anthropology. Analysis of $^{87}Sr/^{86}Sr$ isotope ratios in tooth enamel reflects the geochemical provenance during enamel formation. Consequently, measuring $^{87}Sr/^{86}Sr$ of teeth reflects snapshots of geographic location during infancy, childhood and adolescence depending on the specific tooth sampled. In this study, we determined strontium isotope ratios ($^{87}Sr/^{86}Sr$) by laser ablation ICP-MS and compared the results to previously measured stable oxygen isotopic ($\delta^{18}O$) data from three unprovenienced human teeth. We compare the $^{87}Sr/^{86}Sr$ and $\delta^{18}O$ results to established strontium and oxygen isoscapes of the region to determine correspondence between the two methodologies and to estimate geographic location of each individual.

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Forensic applications of carbon and nitrogen isotopic analyses of hair samples: Reconstructing dietary practices

Leyla Durmus & Rhonda L. Quinn, eton Hall University, Department of Anthropology, 400 South Orange Avenue, South Orange, NJ 07079

Forensic anthropology has recently expanded its tool kit to include geochemical analyses of human tissues. In some forensic cases, traditional methods of establishing the identity of human remains either through DNA analysis or dental records fail. Geochemical techniques have been added to standard methodologies of establishing a biological profile in order to determine a person's geographic region of origin, residential mobility, and dietary practices. Specifically, the abundance ratios of the bio-elements (H, O, C, N, S) and geo-elements (Sr, Pb) have been measured in living populations from known regions in order to build isoscapes for interpretation of human remains of unknown identities. These isotope ratios are mainly derived from human tooth enamel, bone, hair, and nail tissues. In this research project, hair strands from known individuals were analyzed for $\delta^{13}C$ and $\delta^{15}N$ values and compared to documented dietary practices and geographic locations. We compared our results to samples of unknown identity and to a worldwide isotopic database.

Dr. David Sabatino

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Cancer Gene Therapy using siRNA Nanotechnology and Bioconjugation

Stephen D. Kozuch,[1] Christopher N. Cultrara,[1] Sunil Shah,[1] Adah E. Beck,[1] Claudia J. Heller,[1]
Jenny Zilberberg, PhD[2] and David Sabatino, PhD [1,*]
[*]Correspondences should be addressed to: david.sabatino@shu.edu

1 Department of Chemistry and Biochemistry, Seton Hall University, South Orange, New Jersey 07079, United States
2 John Theurer Cancer Center, Hackensack University Medical Center, Hackensack, New Jersey 07601, United States

Gene therapy has re-emerged as a promising precision nanomedicine in the treatment of cancer. At the forefront of its utility are the applications of short-interfering RNA (siRNA), that have silenced oncogenic mRNA expression leading to cancer cell death through the RNA interference (RNAi) pathway. Our research is focused on the siRNAs that have been designed to target and silence the expression of the Glucose Regulated Protein of 78 kilodalton (GRP78). GRP78 is overexpressed in cancer cells where it functions as a signaling receptor for oncogenic activity, making it a clinically proven therapeutic target. In order to potentiate their therapeutic efficacy, we are developing methods for incorporating modifications and chemical functionality. Covalently attaching a fluorophore, fluorescein isothiocyanate (FITC), will allow for monitoring cell uptake, co-localization and biological activity of siRNAs. Covalent linkage with a fatty acid, palmitic acid, can improve siRNA cellular uptake in the absence of an additional transfection reagent. The latter would combine a molecular scaffold capable of cellular internalization. Ultimately, we aspire to develop targeted forms of cancer gene therapy by condensing siRNAs with a positively charged cancer targeting peptide that may target and internalize selectively within cancer cells. This presentation will serve to highlight the synthesis, characterization and biological evaluation of siRNA nanoparticle formulations and their modified bioconjugates.

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Identification of Mutational Variants in the *HSPA5* Gene As a Biomarker in the Development and Progression of Multiple Myeloma

Rachel A. Montel[1], Christopher Cultrara[2], Geber Peña[4], Robert Donnelly[3], David Sabatino[2], Jenny Zilberberg[4]

[1]Department of Biological Sciences, Seton Hall University, South Orange, NJ, USA
[2]Department of Chemistry and Biochemistry, Seton Hall University, South Orange, NJ, USA
[3]Molecular Resource Facility, Rutgers University New Jersey Medical School, Newark, NJ, USA
[4]Department of Biomedical Research, Hackensack University Medical Center, Hackensack, NJ, USA

Multiple myeloma (MM) is a B cell malignancy characterized by a clonal proliferation of malignant plasma cells in the bone marrow, the presence of high levels of monoclonal serum antibody, and the development of bone lesions. Although genetic changes are widespread as primary and secondary translocations may be present, the role of mono-variants has yet to be determined. Therefore, an important unmet clinical need is to develop precision treatment approaches based on an individual genetic and phenotypic makeup.

The 78 kDa glucose-regulated protein (GRP78) is a chaperone protein that serves as main sensor for misfolded proteins in the endoplasmic reticulum and triggers the unfolded protein response (UPR). In cancer, GRP78 is over-expressed and cell surface localized, where it exhibits a variety of signaling pathways associated with cancer initiation, proliferation, adhesion and invasion leading to metastatic spread in many cancer types, including MM.

To elucidate the role of GRP78 in MM, we performed genomic analysis of the *HSPA5* gene responsible for the production of GRP78 as a means of identifying single nucleotide polymorphisms (SNPs) and other genetic variations potentially responsible for the development of drug resistance and relapse in MM. By *HSPA5* sequencing in 4 human MM cell lines (MM.1S, MM.1R, RPMI-8266 and U266), 15 variants were identified for which 5 variants, including upstream and intronic SNPs: c.-107C>T, c.355-20delA, c.354+68delT and c.354+63T>C, were previously reported by 1000 Genomes and dbSNP NCBI databases. In addition, the previously reported missense SNP c.1019A>C/G was observed as a single nucleotide deletion, c.1019delA (K340S), in MM1.S and MM1.R. To the best of our knowledge, this is the first study to provide evidence for the potential role of variants in *HSPA5* which may influence causation and clinical pathological features in MM.

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THE RATIONAL DESIGN, SYNTHESIS, CHARACTERIZATION, AND BIOLOGICAL EVALUATION OF CANCER-TARGETING IMMUNOSTIMULATORY PEPTIDE-PROTEIN CONJUGATES AND TRIPEPTIDES

[2]Keith Smith, [2]Rachel Montel, [2]Andrieh Darwich, [2]Constantine Bitsaktsis, [3]Dante Descalzi, [3]Robert Korngold and [1]David Sabatino

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

With the advent of cancer immunotherapy and synthetic biologics, there has been a steady increase in treatment options over the past decade. Despite this, 1.7 million new cancer cases with an estimated 610,000 deaths are anticipated in the US by the end of 2018. Therefore, the call for continued efforts in creating more effective treatment options are in high demand. In this presentation, the rational design of a cancer-targeting immunostimulatory peptide-protein—using N-succinimidyl carbamate chemistry to conjugate synthesized Pep42 and recombinant B7H6 are described. Also presented are several cancer-targeting immunostimulatory tripeptides. These synthetic biologics are hypothesized to enable drug specificity by binding to cell surface GRP78—a phenotype found exclusively in several cancers. Moreover, they are also anticipated to activate NK cell effector functions enabling tumor cytolysis. Using Fmoc-SPPS, we have generated a library of tripeptides that were isolated and characterized using RP-LC/MS and UV/Vis spectroscopy. Using flow cytometry, the preliminary data confirmed tripeptide-GRP78 binding of the HepG2 cells and tripeptide-NKp30 binding in NK92-MI cells. We anticipate the specific binding of the tripeptides to their intended targets will provide the best candidates for translating our cancer immunotherapy approach *in-vivo*.

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Possible Immunotherapy for Multiple Myeloma through Cancer Targeting Peptides

Lachelle S. Dufresne, Vanessa E. Colmenares & Dr. David Sabatino
Seton Hall University, Department of Chemistry/ Biochemistry, 400 South Orange Avenue, South Orange, NJ 07079

Multiple Myeloma (MM) is a rare form of cancer that attacks the bone marrow by affecting the nature of plasma cells, a type of white blood cell. Once the disease has infiltrated the body, symptoms such as low red blood count, kidney complications, and low functionality of the immune system arise, all of which can be fatal. MM's complexity stresses the importance of early and feasible prognosis, while also advocating for the development of effective treatment strategies. In this study, a potential cancer targeting peptide (CTP), namely the DKTY peptide sequence, has been selected from docking studies in between the BAFF and BCMA receptors localized on the cell surface of malignant plasma cells such as MM. The DKTY sequence has been synthesized by Fmoc-based solid phase peptide synthesis (Fmoc-SPPS) and functionalized

at the N-terminus with fluorescein isothiocyanate (FITC) for monitoring peptide cell biology. When treated with MM cells, FITC-DKTY did not bind to the MM cells, however, changes in MM cell populations were detected by flow cytometry upon peptide treatment. The development of BCMA targeting peptides may lead to the generation of drug delivery vectors that can target MM.

Dr. M. Alper Sahiner

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PANI and PEDOT:PSS Dip-Coating on CdS/CdTe Solar Cells

Michael Patullo, Nnamdi Ene, Quinn Szanyi and Dr. M. Alper Sahiner

Seton Hall University, Department of Physics
400 South Orange Avenue, South Orange, NJ 07079

The ever-increasing importance of solar energy in today's green initiative creates an immense demand for the continual improvement of photovoltaic technologies, particularly thin film solar cells. The Advanced Materials Synthesis and Characterization Laboratory wishes to produce a more advanced solar cell by dip-coating high-conductive grade polyaniline (PANI) and poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) onto pulsed laser deposited cadmium sulfide/cadmium telluride substrates. In our previous studies, we have determined that depositing and dip-coating these particular substrates and polymers on indium tin oxide glass improves the photovoltaic conversion efficiency due to a reduction of the Schottky barrier resistance. In this study, we focus on optimizing the application of PANI and PEDOT:PSS solutions by experimenting with dip-coating procedures. The thin films are characterized by ellipsometry, scanning electron microscopy, and energy dispersive x-ray spectroscopy techniques. Electrical conductivity tests are also performed using a Keithley SourceMeter, and structure and efficiency results are discussed.

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

Matthew Melfi, William Cockerell, Joshua Steier, Rory Vander Valk, Dr. Stephen Kelty, &
Dr. Mehmet Sahiner
Seton Hall University, Department of Physics, 400 South Orange Avenue, South Orange, NJ
07079

Solid oxide fuel cells, or SOFC's, are electrochemical conversion devices that produce electricity and potentially a strong candidate to produce clean energy for the future. We are attempting to lower the operating temperature of SOFC's to minimize startup times and mechanical/chemical issues, yet preserve electrical efficiency. This can be achieved by lowering the solid oxide electrolyte resistivity in between the anode and cathode of the SOFC. This electrolyte compound of Yttrium Zirconium Oxide (Y_2ZrO_5) or known as Yttria Stabilized Zirconia (YSZ), is what causes the electrochemical conversion for the cell, but is also responsible for the operating temperature of the cells from 800–1000 ^{o}C. Our research goal is to determine the relationship between the surface structures. This includes roughness, periodicity, and molecular structure.

The resistivity changes due to these characteristics are observed. After production of samples by pulse laser deposition, structural characterization is performed using ellipsometry, scanning electron microscopy equipped with an energy dispersive x-ray spectroscopy, and x-ray diffraction. Electrical properties are analyzed by using four-point probe conductivity measurements. Structural versus electrical properties will be discussed.

Dr. Mitra Shojania-Feizabadi

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Studying Microtubules’ Physical Properties in Vitro

Jane Breslin & Ibukunoluwa I Akintola
Seton Hall University, Department of Physics, 400 South Orange Avenue, South Orange, NJ 07079

Microtubules are key components of the cytoskeleton. They are intrinsically dynamic, displaying potent instability in which they randomly switch between a phase of growing and shrinking both in vitro and in vivo. In order to study the specifications of individual microtubules, we will monitor their behavior in the laboratory without the influence of other proteins that can be found inside the cell. During this project, we practiced to polymerize and visualize microtubules from porcine tubulin in the lab. The goal is to use polymerized microtubules to further understand the intracellular functions of a cell such as cellular motility, as well as dynamics of microtubules and electrostatic functionality of cellular microtubules. In this work, we will discuss the methods that we implemented to polymerize porcine tubulin and the associated results. This project demonstrates our first training steps that we took to further study biophysical properties of microtubules.

Dr. Nicholas Snow

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Chromatographic Performance of an Ionic Liquid Column

Liem Pham, Brittany Handzo, Sean McCann and Nicholas H. Snow, Department of Chemistry and Biochemistry, Seton Hall University, South Orange, NJ 07079

The separation of vapor mixtures into their constituent molecules can aid chemists in their understanding of complex solutions, achievable through gas chromatography. Gas chromatography is a common separation technique used by many chemists where a liquid serves as the stationary phase while the inert gas will serve as the mobile phase. The experimental research proposes the concept that an ionic liquid capillary column will serve as a highly polar stationary phase with helium as the mobile phase in order to efficiently enhance the separation of a homogeneous vapor. A 1μL solution of toluene, ethyl benzene, meta-xylene, and para-xylene hexane is injected into the gas chromatograph where it will be vaporized and pushed into the columns via the carrier gas. Inside the column, the salts in the ionic liquid will attract the more polar molecules while the more nonpolar molecules will travel with the inert gas where a flame ionization detector will be used in order to detect the compound. From the chromatogram, the values of retention time, retention factor, distribution coefficient, selectivity, efficiency, and resolution will be obtained and used to evaluate the effectiveness of the ionic liquid column. Therefore, it is expected that the Ionic Liquid Column will result in a better separation between the compounds.

Dr. Weining Wang

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Conductivity and Work function Study of PEDOT:PSS with DMSO

Madison Guerrero & Weining Wang

Seton Hall University, Department of Physics, 400 South Orange Avenue, South Orange, NJ 07079

Conducting polymers have the electrical and optical properties of semiconductors or metals, but also have the properties of polymers (being easy to process, flexible, and less expensive), making them the popular candidate for many applications such as solar cells, light-emitting diodes, sensors, and other photo electronic devices. Among them, poly (3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) is the most widely-used conducting polymer because of its high conductivity. It has been shown that higher conductivity can be achieved by adding Dimethyl sulfoxide (DMSO) into PEDOT:PSS. In this work, we show our study on the conductivity and work function of PEDOT: PSS as a function of DMSO content percentage and its potential application as solar cell contact materials. Conductivity and work function are the two main criteria for choosing the contact materials for solar cells. Our study will allow us to determine the best ratio of PEDOT:PSS and DMSO as the contact material for different solar cells applications.