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Petersheim Academic Exposition

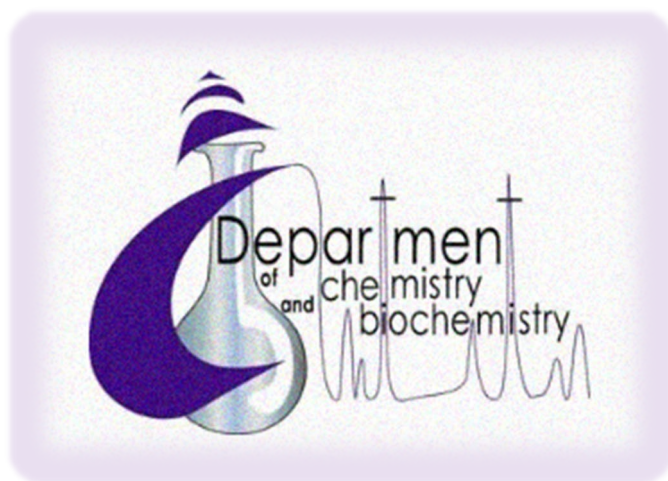
Petersheim Academic Exposition

4-25-2023

Book of Abstracts

Seton Hall University

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ROSE MERCADANTE SEMINAR SERIES

Department of Chemistry and Biochemistry

28th Departmental Symposium

in conjunction with

The Petersheim Academic Exposition

Book of Abstracts

Hybrid Poster Symposium

April 25 2023

Foreword

Over 25 years ago, Dr. Matthew Petersheim had the idea that there should be an event each year when the Academic Excellence of the University was celebrated. He believed that a period of focus on research and scholarship and a celebration of academic excellence was the least that could be done to reward those pursuing this fundamental goal of Seton Hall University. The result of this idea was the Academic Exposition. After his untimely death in 1998, the Exposition was named in his honor. Each year, the Academic Exposition continues to reinforce Dr. Petersheim's vision.

The Department of Chemistry and Biochemistry has held a Research Symposium each year since the initial Petersheim Academic Exhibition. Dr. Petersheim was our colleague and Chair of the Department, so his vision of a celebration of research and scholarship is one that we share.

The past few years, the Academic Exposition has faced unique challenges. COVID-19 resulted in unforeseen changes in teaching, scholarship and research. The Department of Chemistry and Biochemistry rose to meet these challenges, and combined our traditional in-person poster session with virtual poster sessions to allow those members of our community who could not attend in person to share in the celebration of scholarship. This year, although all posters are presented in person, we continue to generate an online repository of posters as a way of increasing access. In this book, you will find Abstracts of all of the posters presented at the symposium, organized by research mentor. The online poster session can be found at the Chemistry Biochemistry Graduate Student Blackboard site, as a collection of Wikis, also organized by research Mentor.

Hazard Zet Forward!

Dr. James E. Hanson
Director of Graduate Studies
Department of Chemistry and Biochemistry
Seton Hall University

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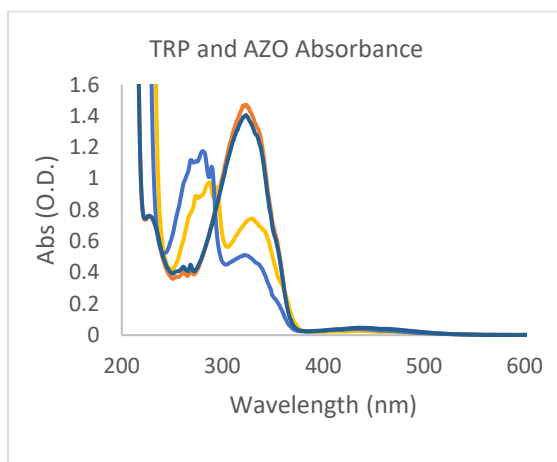
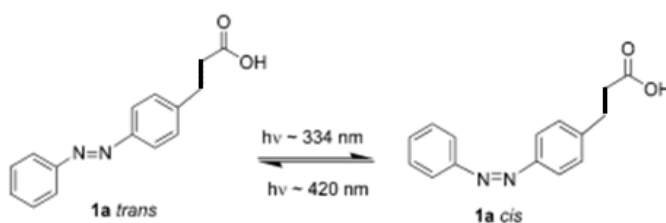
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Keynote Presentation

Charnette Frederic

Innovative Fluorescence-Based Techniques for the Identification of Small Biomolecules

Understanding fluorescence-based techniques for identifying small biomolecules is an important area of research studies. Rifampicin (Rif) is an antibiotic used to treat several types of bacterial infections, including tuberculosis (TB). Using the Systematic Evolution of Ligands by Exponential enrichment (SELEX) process, aptamers were developed from a nonspecific 40-mer Deoxyribonucleic Acid (DNA) library to interact with its target, Rif, which provided a simple method of detection. Recovered nucleotides were amplified using Polymerase Chain Reaction (PCR), and the process was repeated until the most selective aptamers were found. Finding Rifampicin-target aptamers and understanding the capacity to attach to the target Rifampicin were the primary goals of this research. Additionally, photoswitchable molecules were investigated to determine the interaction of azobenzene moiety on nearby aromatic amino acids, tryptophan. When irradiated at 365 nm, the photo-switching behavior favors the *cis*-isomer and is visibly fluorescent. This is the first evidence to suggest that primary protein structure could affect photoswitch activity. The knowledge gained from this research will help to further the understanding of photo-switches as they are used in biomolecules.

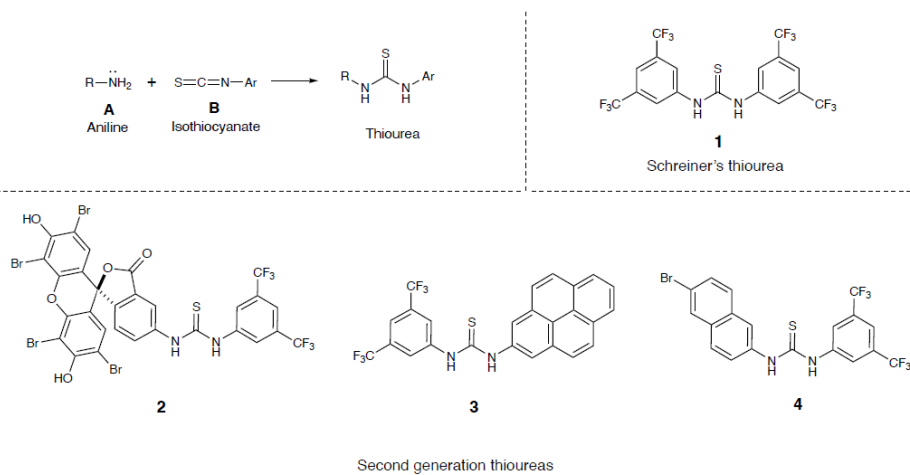


Title**Synthesis of Second-Generation Thiourea Photoacids****Authors**

Daniela S. Noguera-Urbina, Ashlyn E James and Joseph J. Badillo*

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

The design and synthesis of photoacids is an intriguing area of research due to the structure-activity relationship inherent to their photochemistry. Here we present progress toward the development of strategies for the synthesis and study of novel photoacids. Specifically, this presentation will discuss second-generation thioureas' synthesis, acidity, and photophysical properties. The use of these photoacids as catalysts for organic transformations will also be presented.



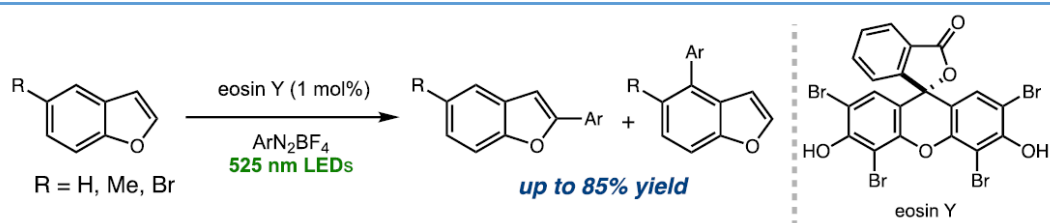
Title

Photoredox-Catalyzed Meerwein Arylation of Benzofurans

Authors

Shreya Rawat and Karen Liu

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

Abstract

In recent years, photoredox catalysis has emerged as a potent tool for molecular synthesis. The Meerwein arylation, which involves the coupling of an aryldiazonium salt with an alkene, is often performed using transition metals and a strong base. This presentation will discuss the development of a photoredox-catalyzed Meerwein-type arylation with benzofurans and various substituted aryl diazonium salts to synthesize 2-aryl benzofurans and 4-aryl benzofurans. This strategy provides an alternative, energy-efficient protocol that proceeds at room temperature without the need for transition metals and strong bases.

Title

Photoacid Generator Catalyzed Michael Additions

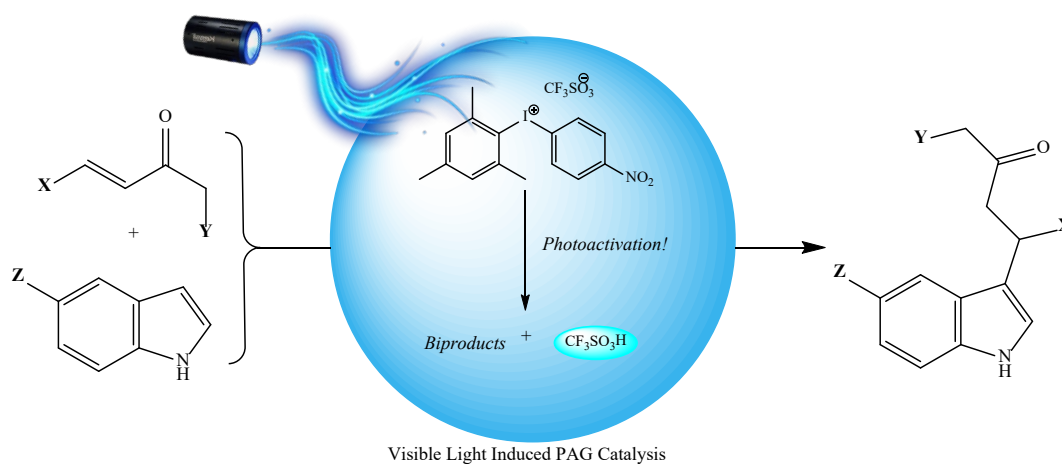
Authors

Zena M. Salem

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

Abstract

Photoacid generators (PAGs) have recently accelerated in interest in the science community due to their various applications in stereolithography, microfluidics, capsule release in medicine, and photobiology. This project demonstrates that multiple PAGs, primarily emphasizing mesityl(4-nitrophenyl)iodonium triflate, can catalyze Michael additions between various substituted indoles and a wide range of α,β -unsaturated carbonyls to form the corresponding β -indolyl carbonyl derivatives. Mechanistic studies show that light is required for reaction initiation.

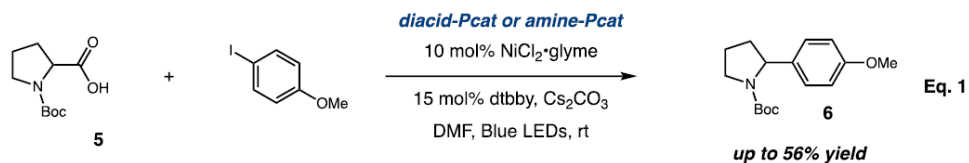


Title**Development of Solid-Phase Photoredox Catalysis****Authors**

Isaiah D. Torres and Joseph J. Badillo*

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

A major challenge in photoredox is that transition metal photocatalysts can be incredibly expensive. Ruthenium and iridium are two of the most common transition metal catalysts used and are both very expensive. Here we present the development of a reusable iridium-based photocatalyst to mitigate the cost of these powerful catalytic tools. I decided to take inspiration from solid-phase peptide synthesis (SPPS) and attach an iridium-based catalyst to an SPPS-type polystyrene bead, which we could recover and reuse without loss of efficiency. This presentation will discuss the development of a novel solid-phase photoreactor to enable iterative use of the solid-phase photocatalyst. The optimization and synthesis of various bead-bound photocatalysts, including organophotocatalysts, will also be discussed.



Photocatalyst beads can be recovered and used without loss of efficiency!

Title

Water Activity of Selected Dry Foods and Oxidative Stability of Linolenic Acid-Proline Mixtures

Authors

John-Joseph Rieger, Aladeen Eewshah, and Dr. Gerald J Buonopane

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

Abstract

This study was carried out in two phases, first to determine the water activity of a variety of dry foods and second to assess oxidative stability of linolenic acid-proline mixtures using the DPPH method. It was anticipated that this research would lead to further understanding of the relationship of chemical reaction rate (e.g., lipid oxidation) and water activity (aw) in foods.

In the first phase involving water activity three temperature model systems were prepared with seven different dry "snack" foods (incl. crackers with peanut butter or cheese filling and pretzels). One set of dry foods was left out in weigh boats at room temperature; another set was stored in an oven at 37°C; and a third set was stored in a freezer at -14°C. The samples were held at their set temperature respectively for a total of 7 days with water activity measured on day 1, 3, 5, and 7 using a dew point water activity meter.

The second phase involved the determination of antioxidant activity in mixtures of fatty acid and proline in model systems. The resulting oxidized proteins are adversely affected in terms of their structure and function. Studying the reactions of oxidizing lipids with proteins is important for understanding the reduction of the nutritional quality of a food, as well as helping to predict quality deterioration during processing and storage. In this study, the amino acid proline and the polyunsaturated fatty acid linolenic acid were combined in model systems to study their interaction with one another stored at 37°C for 7 days. Proline has been shown to exhibit antioxidant properties. Antioxidant analysis employing the stable radical DPPH was used to determine oxidation of the fatty acid and possible antioxidant protection from the proline. Preliminary results show that proline has high antioxidant activity when used with linolenic acid, particularly at higher concentrations. These results combined with the results of phase 1 provide interesting preliminary data toward establishing solid conclusions.

Title

A Study of Peroxide and Conjugated Diene (CD) Formation, Accumulation, and Stability with Methyl Linoleate and Proline Interactions in Dry Model Food Systems at Different Storage Temperatures and Times.

Authors

Viral Shah, Amber Chaudhary, and Dr. Gerald J Buonopane

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

Abstract

One prominent challenge food chemists face with the quality and stability of dry foods is lipid peroxidation. The lipid peroxidation reaction releases deleterious and harmful intermediates, significantly contributing to food degradation. Two primary oxidation products are peroxides and conjugated dienes (CD).

This study investigated the formation of peroxides in dry model food systems consisting of methyl linoleate (ML) and proline in various time and temperature storage conditions. The ML and proline (1:5 and 1:10 moles), including control samples, were stored in the freezer, refrigerator, room temperature, 37°C, and 65°C for five days to monitor primary lipid oxidation products. Peroxide and CD results were summarized to understand their formation, accumulation, and stability in initial stages of ML oxidation in the presence and absence of proline under different temperature conditions and storage times.

Xylenol orange assay and UV analysis were utilized to determine peroxide formation with ML. Each sample test solution was analyzed with a UV spectrometer at 560 nm wavelength.

The results show that the peroxide formation was less in samples with proline present than when compared to the ML samples kept at the same temperature conditions and time point for five days without proline, while CDs were stabilized up to the third day at 37°C in ML and proline mix samples. Results indicate that proline's presence affects ML's CD and peroxide formation.

Title

Adsorption of Fluorinated Zinc Phthalocyanines at Liquid-air Interface

Authors

Ester E. Carrera, Jonathan Z. Pinnock, Alexander Y. Fadeev

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

Abstract

In this work, the adsorption of fluorinated zinc phthalocyanines at the air-liquid interface was studied using a tensiometer. The solutions of two perfluorinated phthalocyanines ($F_{16}PcZn$ and $F_{64}PcZn$) were prepared in three solvents (formamide, 1,4-dioxane, and water) and their surface tensions were measured using pendant drop and capillary rise techniques. For all the solvents, the surface tension of solutions showed a significant decrease with the solute concentration demonstrating positive adsorption of amphiphilic phthalocyanine molecules at the air-liquid interface. The surface tension data were treated with the Gibbs adsorption equation and the adsorption isotherms were generated. From the adsorption isotherms plateau, the molecular cross-sections of phthalocyanine molecules in the adsorbed layers were estimated. This work was in part supported by DTRA.

Title

Temperature Dependence of the Solution Adsorption of Fluorinated Zinc Phthalocyanines on Metal Oxides

Authors

Benjamin T. Hajek, Jonathan Z. Pinnock, and Alexander Y. Fadeev

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

Abstract

This study was carried out to analyze the effect of temperature on the solution adsorption of perfluorinated zinc phthalocyanines on metal oxides. The adsorption of two phthalocyanines $F_{16}PcZn$ and $F_{64}PcZn$ on three metal oxides including silica, alumina, and aluminosilicate mineral Halloysite was studied at 253, 298, and 323K from the ethanol solutions under static conditions. The adsorption was monitored by the UV-vis absorbance of the solution phase and the adsorption isotherms were generated. The isotherms were of sigmoid shape with the plateau roughly corresponding to monomolecular adsorption. Based on the amount adsorbed, the strength of the adsorption interactions of $F_{16}PcZn$ and $F_{64}PcZn$ followed the range: alumina > Halloysite > silica. For each metal oxide, the adsorption increased as the temperature decreased. From the temperature dependence of the adsorption, the adsorption enthalpies were estimated to be negative 10-20 kJ/mol. The authors acknowledge partial financial support by DTRA.

Title

**Non-Covalent Immobilization of Fluorinated Zinc Phthalocyanines
in Matrices of Metal Oxides**

Authors

Kai N. Hansen, Jonathan Z. Pinnock, Alexander Y. Fadeev

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

Abstract

This work focused on the immobilization of fluorinated zinc phthalocyanine $F_{64}PcZn$ on metal oxides via non-covalent, steric interactions aiming to improve the stability of solid supported catalysts. Two synthetic strategies of building “bottle around the ship” were explored. The first approach included synthesis of ordered mesoporous silicas SBA-15 and SBA-16 in presence phthalocyanine. Alternatively, the phthalocyanine was incorporated in the metal oxides during the cross-coagulation of the colloidal sols of silica, alumina, titania, and zirconia. The incorporation of $F_{64}PcZn$ in the solids was evident from the formation of intensely colored precipitates. Solid state UV-vis and the solubility tests demonstrated that the structure of the incorporated $F_{64}PcZn$ was intact, yet it could not be extracted from the solids suggesting its entrapment in the pores. As assessed by the transmission electron microscopy (TEM), the distribution of phthalocyanine throughout the metal oxide matrices was uniform. The prepared catalysts showed activity in the photocatalytic oxidation of model thioethers demonstrating accessibility of the pore-immobilized phthalocyanine to the substrate. This project was in part supported by DTRA.

Title

**Fluorinated Zinc Phthalocyanines Supported on Halloysite:
Adsorption and Catalysis**

Authors

Jonathan Z. Pinnock, Alexander Y. Fadeev

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

Abstract

This work investigates the adsorption of the perfluorinated Phthalocyanine ($F_{64}PcZn$) on Halloysite and the use of these materials in oxidation photocatalysis. Halloysite is an aluminosilicate clay mineral with a chemical formula of $Al_2Si_2O_5(OH)_4$. This material has tubular structure. The nanotubes have different chemistry, Alumina on the inner and Silica and outer surface. The sample of halloysite used in this work had a surface area of $34\text{ m}^2/g$, as determined by the adsorption of Nitrogen at 77K using the BET equation. The deposition of Pc into Halloysite was done by the "Wet Cake" Method. This method includes saturation of the pore volume of an ethanol solution followed by the vaporization of ethanol. This method renders the deposition of F_{64} microcrystals in the pore space of Halloysite. The phthalocyanine loaded samples were characterized by solid state UV-Vis, TGA and Zeta Potential. The morphology and the uniformity of deposition of the $F_{64}PcZn$ microcrystals in the halloysite particles were verified by Transmission Electron Microscopy (TEM). To ensure the stability of the prepared catalyst, the samples of halloysite with loaded $F_{64}PcZn$ were kept by the reaction with TEOS. Lastly, all created powders were tested in catalysis at room temperature and yielded high activity which was demonstrated on organosulfur modelled compounds. The authors acknowledge partial financial support by DTRA.

Title

Dendritic and Branching Surface Interactions of Pigmented Suspensions and Kaolin Colloids

Authors

Diana Malenkova & Jacob Goldsmith

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

Abstract

Mocha diffusion is a ceramic surface decoration technique that is characterized by dendritic pattern formation. It is presumed that the technique originated in the 18th century when potters accidentally spit chewing tobacco onto a clay slip, creating branching designs. Recipes were trade secrets, making it difficult to explore mechanisms of dendritic pattern formation. The technique involves chemical interactions between substances based on particle size, acidity, composition, gravity, zeta potential, and viscosity. Household, potter-available chemicals (such as apple cider vinegar, ethanol, water, soap, lemon juice, etc.) were utilized for the creation of oxide suspension mixtures. The pigments come from chemicals such as iron oxide black, rutile, copper oxide (red), cobalt(II) dinitrite, titanium oxide, and others. The current research design seeks to find an ideal combination of clay and dendritic slip in which a dendritic arrangement is prominent. Clay slip colloid is poured over a semi-dry test tile, and the acid-color mixture applied dropwise on the surface to produce the design. After the pattern reaches an aesthetically pleasing dendrite, the test tile is fired in a kiln to cone 6 (or 1200°C) to ensure color retention in the formulation. Herein, we report on two formulations that showed reproducibility and color preservation throughout the entire firing process. The two working oxide solutions were made with iron (II, III) oxide (black) and cobalt(II) dinitrite (blue) pigments.

Publicly available recipes were used for slip formulations. The set of experiments explored oxide suspensions, pH of suspensions, concentration of oxide in suspension, particle size in slip, and pre- & post-firing results. Results were obtained through morphological observations and diffusion radii measurements. A higher oxide loading produced more prominent, darker dendritic patterns. Oxide suspensions that are too high in either acidic or basic content resulted in loss of dendritic patterns and smaller diffusion radii. Particle size was an important factor limiting dendritic branching. Pre-fired and post-fired test tile results were compared to observe the effects of firing on final color intensity. Firing produced different results for varying oxides- optimized iron oxide pattern lost nearly all coloration while cobalt oxide became more vibrant after firing. Although these two pigments yielded reproducible results, there are other color formulations to discover.

Title

Photoactive Non-Metallic Perfluorinated Phthalocyanine Silicon Coordination Complexes

Authors

Alfredo DiPaola & Sergiu Gorun

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

Abstract

Silicon-centered fluorinated phthalocyanines have been prepared starting with Cadmium-centered fluorinated phthalocyanine, followed by the removal of Cd with H₂SO₄ and insertion of Si using HSiCl₃. Characterizations using UV-Vis, NMR, and X-ray crystallography confirmed the proposed compositions. Generation of ¹O₂ has been preliminarily demonstrated. The financial support of DTRA is gratefully acknowledged.

Title

Photooxidation Kinetics: Dependency on Wavelength and Light Intensity

Authors

Mary Elias, Mary Chioma Okorie and Sergiu M. Gorun

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

Abstract

The light intensity influence on the ability of fluorinated non-functional, $F_{64}PcZn$, and functionalized, $F_{48}H_7(COOH)PcZn$, phthalocyanines photocatalysts to generate singlet oxygen, 1O_2 , and other reactive oxygen species (ROS) using visible light was investigated. While the production of 1O_2 is light dependent, the effects of the intensity of the illumination variation are less understood. The kinetics of thioether oxygenation to sulfoxides, measured using both dissolved and supported catalysts, reveal that (i) compared with Solar light intensity, an order of magnitude lower levels of light are sufficient for efficient reactivity by selective excitations in the 650-800 nm, Q-band, region, and (ii), the reactions using supported catalysts are about an order of magnitude slower compared with the reactions in solution. Interestingly, the 1O_2 oxygenations reaction rates vary linearly with the exciting light intensity, a finding that may help optimize catalysts and their utilization. The financial support of DTRA is gratefully acknowledged.

Title

Perfluorinated Silicon Phthalocyanines

Authors

Joshua I Korn-Heilner, Foster S. Tenkorang, Abigail G. Hall, Sanskruti S. Brahmabhatt, Michael Eckel Santos, and Sergiu Gorun

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

Abstract

We preliminarily report the first Silicon perfluoroalkylated phthalocyanines, $F_{64}Pc^{(-n)}SiX_m$, $m = 2$, $X = F, OH$, $n = 2$; $m = 4$, $n = 0$. The $Pc^{(-2)}$ species exhibit the typical electronic spectra observed for related $PcSi$, their Q bands occurring at 688-694nm with additional peaks at 900 nm, within the $PcSi$ 678-714 nm range. ^{19}F NMR signals occur at -71.20 ppm, -101.19 ppm, -102.56 ppm, -164.72 ppm for $F_{64}PcSiF_2$ and -71.31ppm, -103.96ppm, -164.64ppm for $F_{64}PcSi(OH)_2$, vs. the same signals obtained for $F_{64}Pc^{(-2)}Zn$: -71.55ppm, -103.30ppm, -164.70ppm. The Q-bands for the $Pc^{(-4)}$ molecule appear at 694nm, the absorption at 900 nm being of equal intensity. Single crystal X-ray structures of $F_{64}Pc^{(-2)}SiF_2$, and $F_{64}Pc^{(-4)}Si$ document the expected structures and reveal atomic-level details. Mass spectrometry results for $X = OH$ confirmed its composition. Preliminary heterogeneous reactivity studies of the supported, reduced Pc , $m = 4$, $n = 0$ reveal the production of 1O and the oxygenation of thioethers. The financial support of DTRA is gratefully acknowledged.

Title

Functionalized Fluoro Phthalocyanines in Heterogeneous Catalysis

Authors

Mary Chioma Okorie, Abdul Azeez and Sergiu M. Gorun

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

Abstract

*A third generation functionalized fluorinated phthalocyanine R_fAPcZn , R_f = a combination of 8 aromatic F and 8 alkyl i-C₃F₇ groups, A = –COOH, exhibits the robustness of the parent, non-functionalized R_fPcZn , while retaining its photophysical and singlet oxygen generating properties. We report that $F_{48}H_7(COOH)PcZn$ can be anchored on metal oxides without incurring leaching, and that a supported photocatalyst, $F_{48}H_7(COOH)PcZn$ – **Metal Oxide**, **photooxidizes a chloroalkyl thioether mainly to its sulfoxide using visible light. The degradation rate is 2X faster in a slurry relative to the case when solvents are not present. Anchoring groups, such as –COOH, may allow the design of new, supported photocatalytic materials. The financial support of DTRA is gratefully acknowledged.***

Title

Semiconductor-supported functionalized fluorophthalocyanine oxygenates -S-groups

Authors

Deborah O. Sosanya, Mary Chioma Okorie, Sergiu Gorun

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

Abstract

Phthalocyanines generate singlet oxygen ($^1\text{O}_2$), which decays to form reactive oxygen species (ROS), including hydroxyl ($\text{HO}\cdot$) and superoxide ($\text{O}_2^{\cdot-}$) radicals. We report a semiconductor-anchored, heavily fluorinated functionalized Pc, $\text{F}_{48}\text{H}_7(\text{COOH})\text{PcZn}$, that photo-oxidizes a chloroalkyl thioether using air and visible light. $\text{F}_{48}\text{H}_7(\text{COOH})\text{PcZn}$ on $\text{TiO}_2(\text{P90})$ used as a slurry produces mainly the sulfoxide following 1st order kinetics, but the catalyst has limited stability. Similar products are obtained in the absence of solvents, following 0th order kinetics, and the catalyst is stable. Anchoring groups, such as the $-\text{COOH}$ group may allow the production of new, supported photocatalytic materials. The financial support of DTRA is gratefully acknowledged.

Title

Photodynamic Therapy: Fabrics incorporating Phthalocyanines to kill micro-organisms

Authors

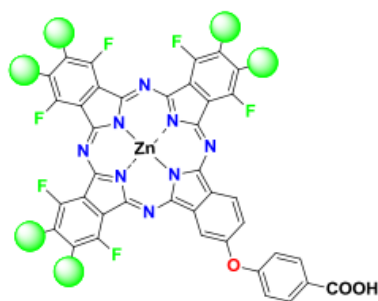
Razi Abbas, Sergiu Gorun and James E. Hanson

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

Abstract

Phthalocyanines (Pc) are large aromatic, macrocyclic organic compounds with a formula $(C_8H_4N_2)_4H_2$ that can coordinate a transition metal in the center. These compounds have a unique color with functional groups that can be used in a variety of applications depending up on the nature of material surface. Pc are colorful functionalized compounds based on which they were initially introduced as industrial dyes, but now they are being used in many states of the art devices such as solar cells, and photodynamic therapy agents and photosensitizers.

Phthalocyanine compounds can be synthesized as with different functionalized materials by synthesizing Pc with different functional groups or linkers that can help Phthalocyanine to be more diverse functional materials. $F_{48}H_7(COOH)PcZn$ reported to be a first functionalized fluoroalkyl phthalocyanine. It is synthesized with a functional -COOH linker to make the Pc more polar compound so that it can attach to the polar surface with a strong bond. The complex is reported to be generated 1O_2 affording long lasting photooxidation of an external substrate without self-decomposition. $F_{48}PcZn-(COOH)$ will be used as a photosensitizer in Photodynamic therapy (PTD) where it could attach the synthetic fabric or surface where it generates reactive oxygen species, ROS (e.g. singlet oxygen, 1O_2) that could potentially kill microorganisms.



Title

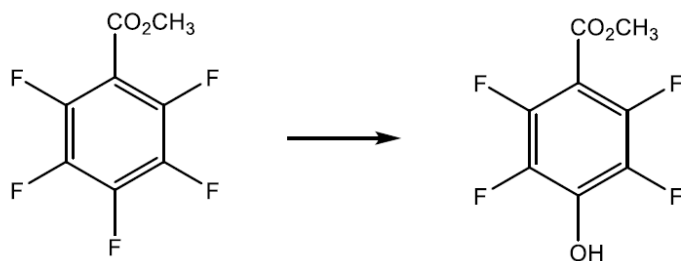
Synthesis of precursor for new symmetrical carboxy phthalocyanine

Authors

Mailani Aguila, Usha Kalra, James E. Hanson

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

Phthalocyanines are heterocyclic aromatic organic compounds that are widely used for their multiple properties. These versatile features make phthalocyanines popular in various fields such as photovoltaic solar cells, semiconductor materials, dyes, coatings, catalytic reactions, functional porous materials etc. In this report, we describe two synthetic approaches for preparation of a precursor for new tetrakis carboxylic acid substituted perfluorophthalocyanines. The first approach converts methyl pentafluorobenzoate in N-methyl-2-pyrrolidine (NMP) at elevated temperatures to produce methyl 2,3,5,6-tetrafluoro-4-hydroxybenzoate. The second approach attempts a similar conversion in dioxane at room temperature. TLC is used to monitor the progress of the reaction, and the resulting product is analyzed using IR and F-NMR after work-up. The differences in yield and side products between the two approaches will be presented.



Title

Titania Supported Perfluorinated Phthalocyanines as Oxygenation Photocatalysts using White Light Irradiation

Authors

Anahi Flores, Usha Kalra, Sergiu Gorun & James E. Hanson

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

Abstract

The reactivity of the perfluorinated F64PcZn supported on P90 TiO₂, F64PcZn - P90 hybrid, was investigated for the photooxygenation of thioethers as a slurry and in the absence of solvents. Diffuse reflectance UV-vis spectroscopy and reactivity data indicated the stability and favorable reactivity of the thermally treated hybrid under white light illumination treatment, but only the absence of solvents ensured full catalytic stability. GC-MS and GC-FID revealed the formation of sulfoxides as the major product, but also sulfones and vinyl sulfoxides. The financial support of DTRA is gratefully acknowledged.

Title

Chromatography of Star Polymers

Authors

Daniel Goldman and James E. Hanson

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

Abstract

The method of Abiko, Yano and Iguchi was used to explore the application of star polymer branching with cyclic sugars and multi hydroxy aromatic compounds as the core center.

Phloroglucinol, D-Glucose and D-Lactose were reacted with glutaric anhydride via a ring opening reaction to form the individual star-shaped polymer with carboxylic acid terminal groups.

The number of polymer arms formed depended on the reaction conditions as well as the size and the chemistry of the core molecule. The terminal end of each individual arm possesses a carboxylic acid function group resulting in a highly polar molecule with the absence of chromophores.

This chemistry presents unique analytical and purification challenges that were evaluated by hydrophilic interaction liquid chromatography. using a graphed diol phase bonded to silica.

Title

Synthesis & Characterization of a Novel Cationic Porphyrin via Click Chemistry

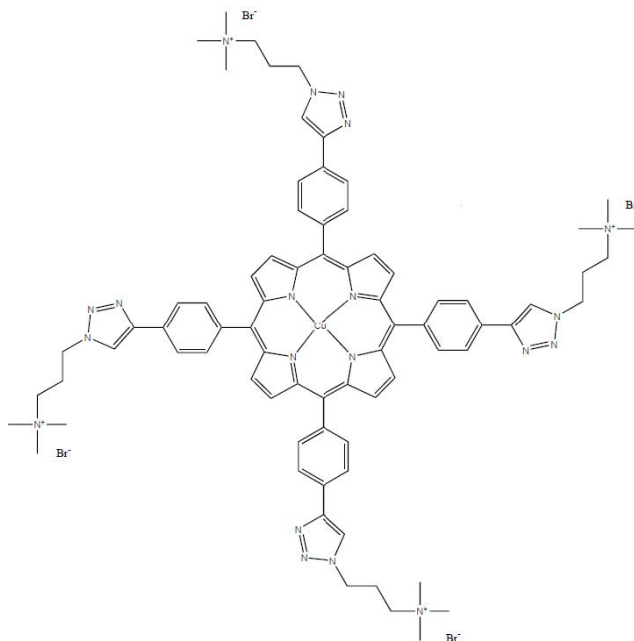
Authors

Jason Guzman, Oluwabusayo S Faseru, James Hanson

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Abstract

The preparation of water-soluble cationic porphyrins is an area of interest for both biochemical studies as well as bio-sensing applications. These molecules are particularly suited to binding to G quadruplex DNA which are thought to play widespread biological roles. Using click chemistry, we have prepared a novel meso substituted tetra cationic porphyrin via a copper catalyzed azide alkyne cycloaddition (AA()). Click chemistry has become a powerful tool for the design and synthesis of a wide range of compounds under fairly mild conditions. This work will present the click chemistry preparation and spectroscopic characterization of a new meso substituted tetra cationic porphyrin namely meso-5, 10, 15, 20-tetra-(4-(3-1 H-1, 2, 3-triazol-1-yl)-N, N, N-trimethylpropan-1-aminium) phenyl porphine tetra-bromide.



Title

Supported Perfluorinated Phthalocyanines as Oxygenation Photocatalysts

Authors

Usha Kalra, Abdul Azeez, Sergiu Gorun and James E. Hanson

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Abstract

Phthalocyanines (Pc) are photosensitizing dyes that can generate singlet oxygen ($^1\text{O}_2$) and other reactive oxygen species (ROS). We report the synthesis of a $\text{TiO}_2\text{P90}$ and Al_2O_3 supported bulky, photoreactive fluorinated phthalocyanines, F_{64}PcZn , $\text{F}_{64}\text{PcZn} \cup \text{TiO}_2\text{P90}$ and $\text{F}_{64}\text{PcZn} \cup \text{Al}_2\text{O}_3$, respectively, their stability and thioethers oxygenation reactivity. $\text{F}_{64}\text{PcZn} \cup \text{TiO}_2\text{P90}$, which produces singlet oxygen and oxidizes thioethers mainly to sulfoxides, is stable and reusable using red light illumination. Catalytic stability is also observed using white light, but only in the absence of solvents. In contrast, $\text{F}_{64}\text{PcZn} \cup \text{Al}_2\text{O}_3$, is stable and catalytically reactive, with/without solvent present, in any light conditions, thus revealing the destabilizing effect of TiO_2 in the presence of UV light. Sulfoxides are also the major product formed. The financial support of DTRA is gratefully acknowledged.

Title

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

Authors

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Abstract

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

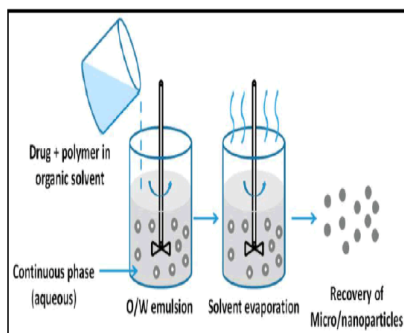
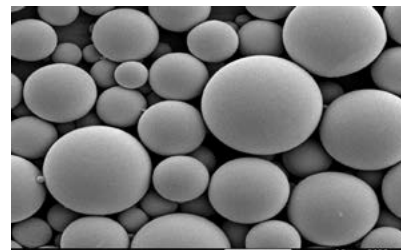


Figure 1: Solvent evaporation technique.



Title

Titania Supported Perfluorinated Phthalocyanines as Oxygenation Photocatalysts using Red Light Irradiation

Authors

Reva Pavithran, Usha Kalra, Sergiu Gorun and James E. Hanson

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Abstract

Fluorinated phthalocyanines photosensitizer, supported on titania, $F_{64}PcZn \cup TiO_2P90$, generates a singlet oxygen and oxygenates thioethers. The hybrid is unstable in the presence of solvents when while light is used, but when the shorter wavelength radiation is eliminated, the $F_{64}PcZn \cup TiO_2P90$ catalyst is stable as a slurry, and reusable, thus underscoring the destabilizing role of UV-activated TiO_2 . The reaction produces mostly sulfoxides. The financial support of DTRA is gratefully acknowledged.

Title

Singlet oxygen-based oxygenation of chlorothioethers with a perfluorophthalocyanine in homogeneous as well as heterogeneous system using

Authors

Sean J. Scally, Usha Kalra, Abdul Azeez, James E. Hanson

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Abstract

Chloro thioether (2-chloroethyl methyl sulfide) oxygenation reactions are of interest for mitigating environmental and other issues. Non-toxic, “green” oxidants are preferred in catalytic oxygenations. A fluorinated phthalocyanine, R_fPcZn , R_f = a combination of 8 aromatic F and *iso*- C_3F_7 groups photo produces singlet oxygen that oxygenates functionalized thioethers, while resisting self-oxidizations due to the absence of C-H bonds. Here, we report the use of the Pc in transforming the S-containing substrates. The photodegradation reaction follows 1st order kinetics in homogeneous as well as in heterogeneous catalysis. The homogeneous catalysis displaces a faster reaction rate as compared to heterogeneous catalysis in solvent rich system. For heterogeneous catalysis, catalyst complex is prepared by thermally assisted adsorption of Pc on monoclinic ZrO_2 . Additionally, heterogeneous catalysis is also conducted in solventless system which leads to significant degradation of 2-chloroethylmethyl sulfide (CEMS) with half-life of only 13 min in visible light and 19 min in red light. Products formed are significantly less in both lights. The kinetics of photodegradation are evaluated using GC-FID.

Title

Epoxy-Siloxane Self-Cleaning Surfaces Functionalized with F₆₄PcZn

Authors

Edrice Sediq, Brandon Pineda, Abdul Azeez, Sergiu Gorun and James E. Hanson

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Abstract

The incorporation of a photocatalytic composite powder incorporated into a siloxane epoxy polymer matrix has been shown to be an efficient self-cleaning material. The composite powder is developed by coating a phthalocyanine photosensitizer (F₆₄PcZn) at 3% w/w onto a nano-particle powder (TiO₂), which is also photocatalytic in nature. The resulting powder of F₆₄PcZn on P25-TiO₂ was then incorporated into a siloxane epoxy polymer matrix and used for photo-induced degradation of surface contaminants, such as methyl orange dye. The photo-activity of the F₆₄PcZn/P25 TiO₂ powder within the matrix is shown to be more effective as compared to unmodified P25 TiO₂. The modified composite powder is expected to produce singlet oxygen (¹O₂). The singlet oxygen (¹O₂) is generated from the F₆₄PcZn, this is believed to be the primary species responsible for the observation of increased photoactivity. The coating material was analyzed in conjunction with various surface contaminants and photoactivity along with surface integrity was evaluated.

Title

An Attempt to Improve Dissolution and Dissolution Profile Samples Analysis Throughput using Open Tubular Hydrodynamic Chromatography

Authors

Timothy Breuninger and Yuri Kazakevich

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Abstract

Dissolution analysis is a pharmaceutical product critical quality attribute for both routine commercial and R&D development activities. The analysis of dissolution sample requires various analytical techniques including HPLC. The timeliness and efficiency of analyzing the dissolution samples can accelerate R&D development and product throughput. An inefficient and labor intensive off line UV spectrophotometric analysis was optimized using open tubular Hydrodynamic Chromatography concepts to meet the unsolved efficiency problem. An HPLC coupled with a PDA using a Waters RXN column successfully meet the efficiency need for that specific sample matrix and target analyte. The chromatographic conditions were further investigated using known polystyrene standards under strict hydrodynamic conditions. The study determined that the Waters RXN column did not meet the Reynolds Number requirement for hydrodynamic chromatography conditions and that the chromatographic separation was not observed.

Title

The Influence of Pressure and Frictional Heating Influencing Retention in Reversed-phase Chromatography

Authors

Timothy Nowak, Alexey Makarov and Yuri Kazakevich

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Abstract

The usage of sub-2-micron particles in liquid chromatography is very popular in liquid chromatography since faster and more efficient chromatographic separations can be achieved in comparison to traditional (3 μ m, 5 μ m) particle size stationary phases. However, the reduction of the particle size leads to a significant increase in backpressure. In addition, heat is generated when the mobile phase passes through a column of finely packed particles. As the heat dissipates through the column, non-uniform temperature gradients can occur both along (longitudinal gradients) and across (radial gradients) the column. However, the environment surrounding the stationary phase bed influences the gradient temperature dissipation. The impact from both the increased backpressure and increased temperature caused by the frictional heating both influence the retention of the analyte. In this study, we study retention behavior of different analytes varying in molecular weight as both backpressure and flow rates are modified.

Title	Synthesis of a novel saccharide with TLR-4 agonist activity
Authors	Sahan Theegala, Navya Gutti, & Dr. Cecilia Marzabadi

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

Abstract

The saccharide we have been synthesizing was previously prepared by Dr. Vikram Basava and was proven to act as an immunostimulant in mouse and human cell lines. This saccharide was synthesized using three small units: two saccharide derivatives (one which was derived from glucosamine, one that was derived from galactose) and a cyclohexane diol. The cyclohexane diol connects the two sugar derivatives together. This saccharide analog was found to jumpstart the production of pro-inflammatory cytokines using a TLR-4 dependent mechanism. The saccharide was made to imitate the function of TLR-4 agonists in producing immunological effects. TLR-4 signaling proves to be significant in immunological processes as it regulates and induces inflammatory cytokines in response to stimulation from LPS.

We have been working towards modifying and synthesizing compounds made by Dr. Bassava to further optimize the reaction and to assess the efficacy of these organic compounds as vaccine adjuvants. Currently, we have completed **Scheme 1. Synthesis of Donor 2** in the reaction and are currently working on **Scheme 2. Synthesis of Donor 3**. The result of work as of now was the formation of sugar subunit **2**, thioethyl-2-phthalimido-3,4,6-tri-O-acetyl-b-D-glucopyranose and an intermediate molecule that will result in a specific thiophenyl glycoside donor **3** respectively. After the synthesis of these two molecules, we will proceed to **Scheme 3. Preparation of Analog 1**; in this final procedure, we will create our final saccharide molecule and move on to testing for TLR-4 agonism and other novel properties in mouse and human cell lines.

Title

Gaussian Modeling of Heteroleptic Iridium(III) Cyclometalated Complex Emission Spectra Using Excel

Authors

Erin E Barno, Rawan Y. Dahhan, Nia S. Mullengada, Arta Boljevic, Allyson Dixon and Dr. Wyatt Murphy

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

Abstract

The complex absorption and emission spectra of ionic transition metal complexes (iTMCs) often require deconvolution to discover information about the singular bands within them. In a recent publication by DeLuzio, et. al., deconvolution of heteroleptic Ir(III) cyclometalated complexes was used to assign the complexes to one of four categories based on the number of Gaussians were used to fit the complex ion emission spectra. The degree of Metal-To-Ligand Charge Transfer vs Ligand Centered character responsible for the emission was correlated with the number of Gaussians necessary to fit the emission spectra. Our work will be building upon previous research with ionic transition metal complexes containing iridium(III) (Ir-iTMCS) which serve as a primary emitter Organic Light Emitting Diodes, or OLEDs. Our group has recently synthesized a broad range of new OLED candidates. Additional parameters of individual bands, such as the wavenumber, bandwidth and contribution to the emission can be assessed. The goal of this project will be to use advanced data analysis packages within Excel (a more assessable environment than Mathematica used by DiLuzio), along with Excel Macros and VBA, to properly resolve spectral data of iridium complexes into individual Gaussian components. Results of our analysis will be reported.

Title

Investigation of radiative and non-radiative decay pathways in greenly synthesized iridium based ionic transition metal complexes

Authors

Allyson D. Dixon, Wyatt R. Murphy, Jr.

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Abstract

A series of heteroleptic, iridium based ionic transition metal complexes (Ir-iTMCS), with purpose to serve as potential components of OLED and LEC devices, were synthesized through a green, combinatorial based approach. We have utilized a microwave reactor in order to bring our research into closer alignment with the tenets of green chemistry. The aim of this research was to assess the effects of structural differences, specifically steric crowding, on the photophysical characteristics of the complexes. The radiative quantum efficiencies (Φ_f) and excited state lifetimes (τ) of the series of Ir-iTMCS were investigated. The rates of radiative (k_r) and nonradiative decay (k_{nr}) were calculated and yielded interesting results; the energy gap law was not followed. Of the eight Ir-iTMCS, two complexes exhibited quantum efficiencies close to 100% and lifetimes within desirable range for applications in OLEDs and LECs. The rate of radiative decay was larger than that of the nonradiative decay for the two complexes of interest. As a result, focus should be shifted onto k_r as opposed to k_{nr} for highly efficient Ir-iTMCS with applications in OLEDs and LECs.

Title

Synthesis and Characterization of Six-Membered Ring System of Iridium (III)

Authors

Daniela Moncada, Nataly Areosa, Allyson Dixon, Wyatt R. Murphy Jr.

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Abstract

Organic Light Emitting Diodes (OLEDs) are electronic devices that employ a series of thin, light emitting films composed of various heavy metal complexes found in cell phones, televisions and computer screens. One group of metal complexes used are cyclometalated complexes of iridium. The cyclometalating ligands have a traditional dative bond and a bond to an anionic carbon. These ligands are indicated by C[^]N such iridium complexes can involve three cyclometalated ligands or two cyclometalated ligands, and a dative ligand (N[^]N) using nitrogen donor atoms. In our research group, significant progress has been made in the greener synthesis of such complexes utilizing microwave heating. As such complexes are widely used in cell phone screens, lowering environmental impact of preparing these complexes by using less energy and enhancing the atom economy of the reaction methodology will have significant societal benefits. We proposed to investigate a dative ligand known as neocuproine – [Ir(bzq)₂ (2,9-dimethyl-1,10-phenanthroline)]PF₆⁻. The goal of the research was to prepare the compound in high yield to determine the purity of the compound as well as atom economy. Throughout the investigation there were different conclusions that were drawn for the [Ir(bzq)₂ (2,9-dimethyl-1,10-phenanthroline)]PF₆⁻. Once synthesized, further examination was conducted which included UV-Vis, quantum yield, lifetime, and NMR.

Title Photophysical Characterization of ROS Generating Iridium (III) Complexes in Relation to Photodynamic Therapy

Authors Jessica Wasik, Shaan N. Patel, Allyson Dixon, Roksana Najjar, Wyatt R. Murphy, Jr.

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

Abstract

Photodynamic therapy (PDT) employs light-sensitive reactions between a photosensitizer and molecular triplet oxygen to generate the reactive oxygen species (ROS) of singlet oxygen, $^1\text{O}_2$. ROS generating iridium (III) complexes are a useful implementation in PDT due to their long radiative excited-state lifetime, relatively high quantum yield, and their ability to cause cell death to diseased cells. In particular, cyclometalated iridium(III) complexes such as Ir(ppy)-dihydroxy (ppy = 2'-phenylpyridine; dihydroxy = 4,7-dihydroxy-1,10-phenanthroline) may be successful in producing singlet oxygen, and therefore pose as a promising photosensitizer. The excited-state lifetime and quantum yields are used in assessing the efficiency of the complex at producing ROS, while the complex itself is synthesized using microwave heating which reduces the synthesis procedure from twenty-four hours to forty minutes while simultaneously abiding by green chemistry principles established by the American Chemical Society as it minimizes harmful chemical waste, reduces time of synthesis, and through atom economy – a process adapted from Monos by Dixon and Skalski (manuscript submitted). By tethering this photosensitizer complex to a cell targeting peptide, the goal is to kill the particles of a particular coronavirus of murine hepatitis a59 (MHV-A59) through its spike protein – an aspect further explored by the biochemical research group in a collaboration with Professor Weidman's research group.

Title

Gas Chromatography-Vacuum Ultraviolet (GC-VUV): Method Parameter Development of the LUMA VUV Detector

Authors

Alexander J. Bulsiewicz and Nicholas H. Snow

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

Abstract

Gas chromatography is a separation technique for volatile compounds. Separation occurs in the column where the mobile phase, carrier gas, moves the analyte through the column. The stationary phase interacts with the analyte and causes the analytes to elute at different times. The analysis of these compounds can be achieved with a variety of detectors. This work was conducted with the LUMA Multi-Channel Vacuum Ultraviolet Detector. Vacuum Ultraviolet (VUV) is the range of wavelengths from 125-240 nm which allow for the electronic transitions of chemical bonds from the ground state sigma to the excited sigma*, $\sigma \rightarrow \sigma^*$. Almost all compounds have a unique spectral fingerprint in the VUV range. This makes the detector for GC-VUV a universal detector as the only compounds that are not absorbed are the carrier gases Helium, Nitrogen, and Hydrogen. In this work, using caffeine as the analyte of choice, various method parameters such as make up gas, system gas, sampling rate were investigated to achieve optimal sensitivity and working conditions for the LUMA VUV detector.

Title

Analysis of Common Active Pharmaceutical Ingredients (APIs) Using Gas Chromatography-Flame Ionization (GC-FID)

Authors

Toni-Ann B. Grant, Prasidh Pradeep, Alexander J. Bulsiewicz, James D. Mizvesky and Nicholas H. Snow

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Abstract

Since the 1980s High-Pressure Liquid Chromatography has been the analysis method of choice for Active Pharmaceutical Ingredients (APIs) over Gas Chromatography. This was mainly due to the limitations at the time associated with column technology. Gas Chromatography theory was originally developed using packed columns which minimizes the possible analytes to extremely volatile compounds, as eluting these compounds would require the column to be well above the boiling points of the analytes. As many APIs are polar in nature, this would place their boiling points well above possible working condition without causing degradation to the analytes themselves. With the advancement of column technology, specifically capillary columns, using High-Temperature Gas Chromatography for APIs is revisited in this work. A method for the analysis of many common Pharmaceutical APIs using GC-FID was developed and demonstrates that it is possible to elute and analyze compounds with significantly high boiling points.

Title

Gas Chromatography-Flame Ionization Detector (GC-FID) System Linearity Effects on Limit of Detection Calculations

Authors

James D. Mizvesky and Nicholas H. Snow

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Abstract

The construction of an analytical calibration curve within a specified range is a requirement for all analytical methods and from which values are taken to calculate Limits of Detection (LODs). The curve is a plot of the signal, $r(x)$, vs analyte concentration, x , with the relationship between the two obtained by a linear regression analysis generating a sensitivity or slope, m , and y-intercept value, b , $r(x) = mx + b$. LODs are calculated based on these linear regressions. One of the most common, adopted in 1975, is the IUPAC definition of LOD which is the lowest concentration of an analyte that an analytical process can reliably detect, $C_L = \frac{k s_B}{m}$. C_L is the lowest analyte concentration that will generate a reliable signal; k is a numerical factor chosen in accordance with a desired confidence level; s_B is standard deviation of blank responses; m is the slope of the analytical calibration curve. Therefore, slope, m , is an important value that must be well defined because it is highly dependent on the working concentration range and individual chemical measurement system itself. Using GC-FID, the linearity of the coupled system was investigated using Dodecane and Pentylbenzene at concentrations ranging the dynamic range of the detector. The values generated were then pooled into various calibration curves representing different working ranges. LOD calculations were performed using three calculations methods and compared to the experimental LOD.

Title	Manual Synthesis and Characterization of CDC50 Antifungal Peptides
Authors	Reesha Hora, Yogarupa Das, Ishan Sharma, Zena Karam, Dr. Gregory Wiedman

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

Abstract

Continuing last semester's antifungal studies, elements of the CDC50 loop region in fungal pathogen *C. Neoformans* were once again used to develop a series of flippase inhibitors to be used and tested as antimicrobial agents. After identifying the relevant biophysical properties of the peptides previously synthesized, several sequences in the CDC50 loop which are similar to the original in terms of hydrophobicity, net charge and isoelectric point were developed. It is hypothesized that the peptides with the most similar properties will be the ones which behave most similarly. Solid phase peptide synthesis was used to synthesize the 15 amino acid long peptides, beginning with the furthest sequence away from the original, labeled QY-15ii. Although it was hypothesized that microwave synthesis could be used to make a pure antifungal peptide, mass spectroscopy only showed M+2H and M+3H peaks. After several failed attempts using a microwave reactor, two peptides were instead synthesized manually. One of these peptides was lipidized with a myristic acid tail and one was made without. Mass spectroscopy and High-Performance Liquid Chromatography were once again utilized in the detection and isolation of the pure product.

Title

Peptide FQ15 and FQ15MA

Authors

Miryam Kikhwa and Dr. Gregory Wiedman

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

Abstract

Cryptococcus neoformans is a crucial fungal pathogen that causes severe meningitis in immunodeficient people, which is extremely resistant to the drug caspofungin. We know from previous that *Cryptococcus* flippase is essential for the caspofungin resistance of the fungus. Therefore, continuing the antifungal studies regarding the elements of the CDC50 loop region in fungal pathogen, *Cryptococcus neoformans* will be used to develop a series of flippase inhibitors to be used and examined as antimicrobial agents. Since all 15 amino acid long sequences in the CDC50 loop have the same characteristics in terms of hydrophobicity, net charge, and isoelectric point, it is hypothesized that the peptides with the most similar properties will be the ones that behave most similarly. Solid Phase Peptide Synthesis was used to synthesize the 15 amino acid long peptide named “FQ15” and “FQ15MA”, which is a peptide with a myristic acid added to the N- terminus with the same amino acid sequence. They were both synthesized to identify which peptides can make the fungus sensitive to caspofungin by blocking the flippase function. Mass Spectroscopy and High-Performance Liquid Chromatography were used to analyze the detection and isolation of the peptide respectively. Mass Spectroscopy was used to confirm the detection and isolation of the synthesized peptide after the isolation of peptide fractions on the HPLC.

Title	Antimicrobial Activity of ATCUN Peptides
Authors	Akilah I. Mateen and Gregory R. Wiedman

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

Abstract

Since their discovery in the 1980s, antimicrobial peptides (AMPs) have been investigated as promising alternatives to traditional antibiotics and antifungals. Considered a major class of membrane active peptides, they form the first line of defense as part of the innate immune response to pathogens and have been observed to evade microbial resistance mechanisms, which are linked to the widespread use of antimicrobial medicine and pesticides. Despite the broad diversity of structural features, they are categorized based on their secondary structure. Many AMPs form random coils in aqueous environments; however, they assemble into an identifiable secondary structure in nonpolar environments, such as the hydrophobic core of cell membranes.

Although AMPs are ubiquitous throughout the six kingdoms of life, the level of defense they provide against exogenous microbes is often subject to host regulatory pathways. Therefore, *de novo* designs of AMPs are of particular interest to the biochemical research community. Many current design strategies incorporate naturally occurring peptide motifs that induce certain mechanisms of action as a response to non-commensal bacteria or fungi. A well-studied example is the ATCUN, or amino-terminal copper and nickel, binding motif. First observed in albumins, this motif is characterized by the conserved sequence $H_2N-X-X-His$, where X represents any amino acid. The coordination of the nitrogen atoms in the presence of Cu^{2+} and Ni^{2+} ions produce reactive oxygen species (ROS).

By inserting an ATCUN motif into a cell-penetrating peptide, ROS can be generated intracellularly, causing damage to membrane-bound organelles and exhibiting antimicrobial activity comparable to AMPs. Using TP2 (PLIYLRLRLGQF) as a template, an ATCUN-containing translocating peptide was synthesized with a pure yield of 71% using standard Fmoc-based solid-phase synthesis strategies. The antimicrobial efficacy of ATCUN-TP2 will be evaluated against various *Candida* species in minimum inhibitory concentration (MIC) and cell viability assays in comparison to clinical drugs.

Title

The Illuminative Photobuforin II

Authors

Cristina Ventura, Gregory Wiedman

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Abstract

Buforin II is a highly potent cationic antimicrobial peptide. Its proposed mechanism of action is translocation across the cell membrane and subsequent binding to DNA. The sequence of buforin II is identical to a portion of core histone protein H2A. The central proline in buforin II creates a helix-hinge-helix motif that has been found to play an important role to its ability to translocate across the cell membrane. To study the structure-function relationship of this proline residue this study has replaced P11 with a meta-substituted azobenzene amino acid (Z). The resultant peptide, Photobuforin II, retained the secondary structure and membrane activity of the naturally occurring peptide while gaining new spectroscopic properties. Photobuforin II can be isomerized from its *trans* to *cis* isomer upon irradiation with ultra-violet (UV) light and from its *cis* to *trans* isomer upon irradiation with visible (VL). Photobuforin II is also fluorescent with an emission peak at 390 nm. The intrinsic fluorescence of the peptide was also used to determine binding to the membrane and to DNA. Photobuforin II provides insights into the importance of structure function relationships in membrane active peptides while also demonstrating that azobenzene can be used in certain peptide sequences to produce intrinsic fluorescence.



Dr. Matthew Petersheim
1953-1998