Ohio Photochemical Society Conference 2023

July 10th – July 12th

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OoPS Schedule

Monday, July 10th

2:00 - 4:00 PM	Registration and Check-in (Outside Eagle and Heron Meeting Rooms, 2nd Floor)
4:00 - 6:00 PM	Poster session (PICNICS, Undergraduates, and Graduate Students)
6:00 – 7:00 PM	**Buffet Dinner (Eagle/Heron Rooms)**
Session 1	**Chair: Austin Sartori**
7:00 - 7:10 PM	Opening Remarks **Malcolm D. E. Forbes and Jayaraman Sivaguru**

Memorial Symposium for Douglas C. Neckers (Founding Director, Center for Photochemical Sciences)

7:10 - 7:30 PM	**Alex Mejiritski**, Spectra Photopolymers, Inc., *Remembering Douglas C. Neckers*
7:30 - 8:00 PM	**Lisa Kelly**, University of Maryland Baltimore County, *Environmentally-Mediated Photochemistry of 4-Amino-1,8-Naphthalene Imides*
8:00 - 8:30 PM	**Samer Gozem**, Georgia State University, *Spectroscopy in the Condensed Phase: Connecting Theory and Experiments*
8:30 - 9:00 PM	**Rony Khnayzer**, Lebanese American University, *Tuning the properties of Ruthenium(II) Diimine complexes for using photoactivatable chemotherapy*
9:00 – 10:00 PM	Networking time

Tuesday, July 11th

8:00 – 9:00 AM	**Continental Breakfast** (outside meeting room)
Session 2	**Chair: Dipti Garg**
9:00 - 9:30 AM	**James Cassidy**, The University of Chicago, *Synthesis of Colloidal III-V Nitride Quantum Dots for Light and Photocatalysis Application.*
9:30 - 10:00 AM	**Sarah Sobeck**, College of Wooster, *Impact of Energy Transfer Pairs on the "Pop" and Fading of Daylight Fluorescent Pigment.*

10:00 - 10:30 AM	**James McCusker**, Michigan State University, *Excited-state Dynamics of First-row Metal Complexes in the Marcus Inverted Region, Or: How I Learned to Stop Worrying and Love Ligand-Field Theory.*
10:30 - 11:00 AM	**Coffee Break**
Session 3	**Chair: Siddhartha Thennakoon**
11:00 - 11:30 AM	**Prashant Kamat**, University of Notre Dame, *Overcoming Challenges in Photocatalysis and Electrolysis. Why Seeing is Not Always Believing*
11:30 - 12:00 PM	**Valentine Vullev,** UC-Riverside, *Managing Charge Transfer and its Effects on Molecular Photophysics*
12:00 - 12:30 PM	**Corey Stephenson**, University of Michigan, *Redox Catalysis Strategies for Complex Molecules*
12:30 - 1:30 PM	**Box Lunch and Panel Discussion**
Session 4	**Chair: Dedunu Senarathne**
1:30 - 2:00 PM	**Julie Peterson**, UC Santa Barbara and BGSU, TBA*, Designing biocompatible photoactive dynamic covalent systems.*
2:00 - 2:30 PM	**Mikhail Zamkov***,* Bowling Green State University, *Quantum Shells: An Emerging Class of 2D Colloidal Semiconductors.*
2:30 - 3:00 PM	**Natalia Lebedeva**, Syngenta Corporation, *When is Light Not Good for Plants?*
3:00 - 3:20 PM	**Vanessa McCaffrey**, Michigan State University, *Assessing the Broader Learning Outcomes and Participation Patterns of Undergraduate Research at Michigan State University.*
3:20 - 6:00 PM	Networking time
6:00-7:30 PM	**Dinner**
Session 5	**Session to honor the late R. Marshall Wilson (founder of OoPS)**
	Chair: Rashmita Dulal
7:30 – 7:45 PM	**Malcolm D. E. Forbes**, Bowling Green State University, *Remembering R. Marshall Wilson.*
7:45 - 8:30 PM	**Prashant Kamat**, University of Notre Dame, *Will AI Tools Make a Paradigm Shift in Scientific Publishing?*
8:30 – 8:45 PM	**Recognition of Sponsors and Poster Award Presentations**

8:45 – 10:00 PM	Networking time

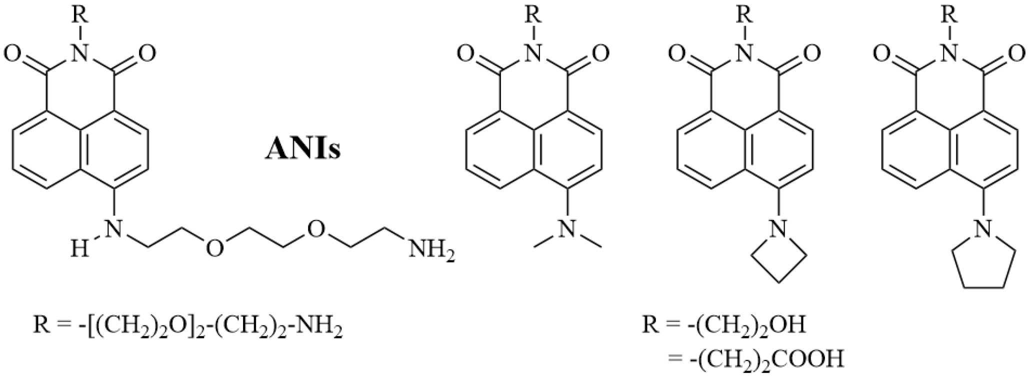
Wednesday, July 12th

Session 6	**Session Chair: Dulanjan Harankahage**
9:00 - 9:30 AM	**Dmitri Talipin**, The University of Chicago, *Can we revolutionize colloidal synthesis of semiconductor nanostructures using molten inorganic salts?*
9:30 -10:00 AM	**Len MacGillivray**, University of Iowa, *Building Molecules in Crystals Using Light: Green Chemistry to Sustainable Materials*
10:00 -10:30 AM	**Pravas Deria**, Southern Illinois University, *Excited state Dynamics in Porous Crystalline Assemblies*
10:30 -11:00 AM	**Coffee Break**
Session 7	**Session Chair: Lalita Shahu**
11:00 -11:30 AM	**H. Peter Lu**, Bowling Green State University, *Single-Molecule Spectroscopy and Force Manipulation Studies of Protein Dynamics and Signaling*
11:30 -11:45 AM	Closing Remarks, **Malcolm D. E. Forbes and Jayaraman Sivaguru**

Environmentally Mediated Photochemistry of 4-Amino-1,8-Naphthalene Imides

Dr. Lisa A. Kelly

The substitution of the aromatic core of 1,8-naphthalene imides (**NIs**) with amines and other nitrogen-rich species significantly alters their electronic properties. The class of compounds, herein called 4-amino-1,8-naphthalene imides (**ANIs**), has unique photoredox properties. Though **ANIs** have been shown to photoinitate tissue welding and protein cross-linking processes, the mechanism remains unknown. The aim of this work is to understand how the electronic properties of the **ANIs** are modified by structure and the environment in which they are in, towards the goal of understanding the photobiological mechanisms of action. Though there is a large body of literature on the use of **ANIs** as fluorescent sensors, the implications of tuning the structure and environment of **ANIs** for specific photochemical outcomes, including photoredox-initiated reactions, remains largely unexplored. The **ANI** excited states have been characterized and quantified using steady-state and time–resolved fluorescence spectroscopies, as well as nanosecond transient absorption. The interconversion between singlet, triplet and CT excited states is governed by the polarity of the medium. Furthermore, intermolecular interactions with co-dissolved amino acids and peptides appear to modify the **ANI** conformation and subsequent excited-state dynamics. The spectroscopies reveal both non-absorbing and dark excited states. Quantum yields of the dark states have been measured using methyl viologen as a redox trap. Preliminary evidence suggests that protein cross-linking likely occurs via both oxidative cross-linking and oxygen-dependent redox processes.



Funding provided by Alucent Biomedical and the National Science Foundation (CHE-1855467).

Spectroscopy in the Condensed Phase: Connecting Theory and Experiments

Dr. Samer Gozem

Molecules UV-visible and photoelectron spectra spectral line shapes encode important information about a molecule's electronic and molecular structure. Quantum chemical calculations may hold the key to deciphering the spectral signals into information about molecular structure and properties. However, connecting computed and experimental quantities is not always straightforward, especially for experiments in the condensed phase where the spectra are shifted and broadened by intermolecular interactions. This is discussed in the first part of the talk, which will serve as a pedagogical account of computational spectroscopy. In the second part of the presentation, I will discuss some recent applications of the Average Solvent Electrostatic Configuration (ASEC), a hybrid quantum mechanical/molecular mechanical (QM/MM) approach, to understanding the effect of a solvent (or a protein) on the spectroscopic properties of a solute (or cofactor).

Tuning the properties of Ruthenium (II) diimine Complexes for use in photoactivatable chemotherapy

Dr. Rony S. Khnayzer

The development of chemotherapeutic agents is reaching a bottleneck largely due to the side effects of anti-cancer drugs that are not specific. On the other hand, targeted immunotherapy for cancer treatment has been on the rise but is still limited to a few types of cancer. Photochemotherapy entails the use of light to improve the spatial and temporal control of prodrug activation yielding cytotoxic agent(s) only in cancer tissues. In this work, the rational design of strained Ru (II) complexes bearing polypyridyl ligands is discussed vis-à-vis their photoactivatable chemical and biological properties. A relationship between the photophysical properties and photochemical characteristics was elucidated using an array of spectroscopic techniques. Finally, a new series of Ru (II) complexes possessing 2,5-diamino-1,4-benzoquinonediimines (DABQDI) ligand exhibited photochemistry using lower energy light approaching the optimum optical window for photochemotherapy.

Synthesis of Colloidal III-V Nitride Quantum Dots for Light and Photocatalysis Applications

Dr. James Cassidy

Group III nitrides, particularly gallium nitride and indium gallium nitride, have become well-known for their technological importance in high-power electronics and blue light-emitting diodes. To date, there exists no stable blue emitting electroluminescent material capable of being employed in a non-epitaxially grown device, which is needed for bright high-resolution displays. Gallium nitride and indium gallium nitride quantum dots offer the potential to be both bright blue emitters and be patterned via non-epitaxial processes. Most recently, we have shown that gallium nitride can be grown from a biphasic molten salt and organic solvent mixture, in which the molten salt facilitates microscopically reversible growth, which is required for highly crystalline quantum dots. We have further developed our synthetic strategies by utilizing low order metal ammoniates as single source gallium and nitrogen precursors that allow for size-tunable synthesis of gallium nitride quantum dots. Additionally, by utilizing NMR and Raman spectroscopies we have gained crucial insight into the organo-gallium complexes that form during our reaction, furthering our understanding of the underly growth mechanism and allowing us to develop a robust synthetic protocol.

Impact of Energy Transfer Pairs on the “Pop” and Fading of Daylight Fluorescent Pigments

Dr. Sarah J. Schmidtke Sobeck

Daylight fluorescent pigments have been around for nearly a century and have found use in a range of applications ranging from industrial safety and military navigation to art and fashion. They are challenging materials for conservation due to their complex formulations consisting of a mixture of dyes and optical brighteners embedded in a polymer resin. Furthermore, these colorants are often intended to be displayed under blacklights accelerating photochemical breakdown of the dyes. Our studies seek to better understand the impact that specific combinations of dyes and optical brighteners has upon the appearance and light stability. We have identified dyes that can serve as energy transfer pairs in different pigments. Spectroscopically the enhancement of acceptor emission is evaluated as a function of donor concentration. The stability of the different fluorophores alone and in the presence of energy transfer partners is also assessed to evaluate how energy transfer may also contribute to the observed color changes as the pigments fade. Collectively understanding of the impact of different formulations on both the appearance and perceived fading is valuable to conservation. This can inform decisions for both display and storage of pieces featuring daylight fluorescent materials.

Excited-state Dynamics of First-row Metal Complexes in the Marcus Inverted Region, Or: How I Learned to Stop Worrying and Love Ligand Field Theory

Atanu Ghosh, Jonathan T. Yarranton, Micheal Alowakennu, and James K. McCusker*

Department of Chemistry, Michigan State University

The photophysical properties of transition metal-based complexes have been studied extensively for decades due in part to their pivotal role in light-enabled chemical processes ranging from solar energy conversion strategies to photoredox catalysis. Second- and third row transition metal complexes such as $[Ru(bpy)_3]^{2+}$ and $Ir(ppy)_3$, (where bpy is 2,2’-bipyridine and ppy is 2-phenylpyridine) have proven to be useful particularly in applications reliant on electron transfer because of their long-lived charge transfer (CT) excited states, where photon absorption results in the creation of a charge-separated state whose stored potential can be leveraged to drive a wide variety of reactions. Despite this success, recently there has been considerable attention placed on sustainability and scalability for chemical transformations; for transition metal-based chemistry, this involves shifting focus primarily to the first transition series whose members are characterized by natural abundancies that are significant larger and costs that are significantly lower than their heavier congeners. While this has resulted in exciting and potentially transformative developments in areas such as catalysis, replacement of chromophores based on Ru and Ir, for example, with first-row analogs to effect analogous excited-state chemistry has proven to be more challenging.

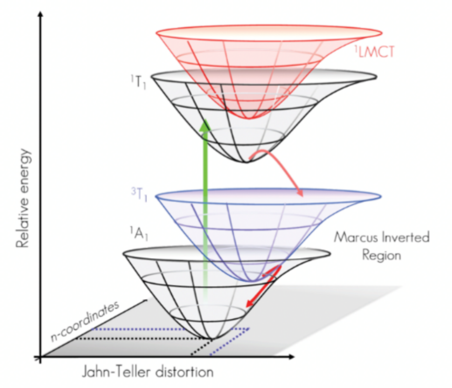


Figure 1. Schematic representation of the relevant potential energy surfaces for ground-state recovery dynamics in Co(III) polypyridyl complexes.

The primary difficulty with creating first-row chromophores that possess photophysical properties reminiscent of second- and third-row complexes stems from fundamental differences in electronic structure that impact non-radiative dynamics subsequent to light absorption.[1] In the case of compounds like $[Ru(bpy)_3]^{2+}$ and $Ir(ppy)_3$, both the absorptive and lowest-energy excited states of these compounds are charge-transfer in nature, whereas first-row metal complexes are typically subject to ultrafast deactivation of the absorptive charge-transfer excited state(s) due to the presence of low-lying ligand-field excited states. These excited states are localized on the metal center and are characterized by a rearrangement of electron within the d-orbital manifold as opposed to a formal separation of charge, which significantly changes the landscape in terms of the type of excited-state chemistry that can be anticipated.

Assessing ligand-field strength plays an important role in designing such ligand frameworks. This is difficult to do from an experimental perspective for Fe(II) complexes, for example, due to the fact that the strong MLCT absorption envelope obscures the far weaker d-d absorption bands that inform on ligand-field strength. This the presentation will go over a successful approach for addressing this problem that utilizes isoelectronic low spin Co(III) complexes.[2] Charge-transfer absorptions of Co(III) complexes – which are LMCT in nature – are significantly blue-shifted relative to their counterparts in Fe(II), thereby revealing previously obscured ligand-field absorption features and allowing for the creation of a spectrochemical series for low-spin, d^6 coordination complexes. This information was leveraged to interpret the ground-state recovery dynamics of a series of Co(III) polypyridyl complexes through the use of ultrafast time-resolved electronic absorption spectroscopy. Analysis of the data led to the unexpected conclusion that ground-state recovery for this class of chromophores occurs in the Marcus inverted region, a fact that has opened exciting new possibilities for the use of such compounds for applications in a wide range of settings, including photoredox catalysis.[3,4]

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[1] McCusker, J.K. *Science* **2019**, 363, 484 – 488.

[2] Yarranton, J.T.; McCusker, J.K. *J. Am. Chem. Soc.* **2022**, 144, 12488 – 12500.

[3] Alowakennu, M.; Ghosh, A.; McCusker, J.K., submitted for publication.

[4] Chan, A.Y.; Ghosh, A.; Yarranton, J.T.; Twilton, J.; Jin, J.; Arias-Rotondo, D.M.; Sakai, H.A.; McCusker, J.K.; MacMillan, D.W.C., submitted for publication.

Managing Charge Transfer and Its Effects on Molecular Photophysics

Dr. Valentine Vullev

Charge transfer (CT) is of fundamental importance for sustaining life on Earth and for making our modern ways of living possible. CT governs the optical properties of chromophores comprising electron-rich and electron-deficient components. In photoexcited dyes with an acceptor-donor-acceptor (A-D-A) or donor-acceptor-donor architecture, for example, CT breaks their quadrupolar symmetry. While the optical absorption of such quadrupolar chromophores is invariant to medium polarity, the CT-driven excited-state symmetry breaking yields dipolar structures manifesting pronounced solvatochromism. Our experimental and theoretical studies reveal that strengthening the donor-acceptor electronic coupling in A-D-A chromophores actually decreases the CT rates and overall, the propensity for symmetry breaking. As surprising this result is, it reveals effects of electronic coupling on the CT thermodynamics, which in its turn affects the CT kinetics. Another important outcome encompasses the tunability of the energy level of the CT state under intermediately strong donor acceptor electronic coupling. It permits conditions under which fluorescence from the locally excited states of the donor and acceptor accompanies the broad CT emission, producing spectral bands that spread through the whole visible range, i.e., producing white fluorescence. Overall, tuning the thermodynamics of the intramolecular CT of donor-acceptor chromophores controls their propensity to fluoresce. Nitroaromatic compounds, that inherently possess excited states with a CT character, illustrate this feature especially well. Enhancing the CT character of their excited states suppresses the nitrocompounds from undergoing intersystem crossing (ISC), which is a principal pathway of non-radiative deactivation responsible for their lack of fluorescence. Concurrently, as the CT character of an excited state becomes too strong, its energy level drops close to that of the ground state, opening efficient internal-conversion (IC) pathways for non-radiative decay via back CT. Tuning the CT char acter of nitroaromatic compounds has allowed us to decrease the rates of non-radiative decay by several orders of magnitude and make them fluoresce. Such electron-deficient fluorophores are especially important for the design of n-type organic electronic materials. Overall, understanding and managing the thermodynamics and kinetics of intramolecular CT offers a wealth of unexplored opportunities for molecular photonics and optoelectronics.

Designing biocompatible photoactive dynamic covalent systems

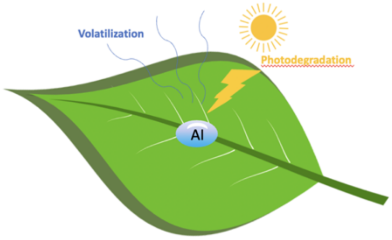
Dr. Julie Peterson

The use of dynamic covalent chemistry in networks for cell growth media with tunable stress-relaxation behaviors is a growing field for studying the interplay between cells and the mechanical properties of the extracellular matrix. The influence of changes in dynamic behavior of the matrix on cells is of particular interest. Changes in temperature, pH, and/or UV light are required to manipulate the behavior of most dynamic covalent bonds; however, these triggers also perturb biological processes. In contrast, low energy light is an ideal bioorthogonal stimulus that can be applied with high spatiotemporal precision to study and manipulate interactions between cells and their matrix. Recent advances in visible light photolabile moieties open opportunities for the design of networks with dynamic character that can be triggered with low energy light. As a starting faculty at BGSU, I will present my inspiration and research goals for designing biocompatible light responsive dynamic systems.

When is Light Not Good for Plants?

Dr. Natalia V. Lebedeva, Senior Research Scientist

To feed the planet, conventional agriculture uses sophisticated formulations to deliver herbicides, fungicides, and insecticides (pesticidal active ingredients (AIs)) to targeted sites for crop protection. After application, photodegradation of AIs is one of the most powerful loss mechanisms that limit crop protection. Most photochemical research in this area is driven by regulatory factors and often involves very standardized techniques to satisfy such requirements (e.g., soil and water persistence of AIs). For successful biodelivery, and hence bioperformance, different methodologies to study photodegradation should be implemented. In this lecture, the differences between these standard techniques and more realistic analyses of photodegradation



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Building Molecules in Crystals Using Light: Green Chemistry to Sustainable Materials

Dr. Leonard R. MacGillivray

The ability to reliably form covalent bonds in organic solids promises to provide access to product molecules that may be completely unavailable in solution. Critical covalent bonding forming process occur in solids without use of solvent and with the materials being accessible using mechanochemistry. Crystal packing, however, is a nemesis of the crystal engineer since covalent bond formations generally require reactive sites to be assembled and oriented in close proximity to react, which can be adversely affected by unpredictable intermolecular forces. In this presentation, a method to direct the formation of covalent bonds in crystals using principles of supramolecular chemistry is described. The main reaction of focus is the [2+2] photodimerization. The method relies on the use of small molecules, coordination complexes, and metal-organic frameworks as templates to assemble olefins via supramolecular synthons into geometries for inter- and intramolecular cycloadditions. The method gives rise to a toolkit that enables the synthesis of complex molecules such as [2.2] cyclophanes, cubanes, and ladderanes. Applications of the products as ligands in coordination-driven self-assembly are described. The relevance of the work to energy capture and release, as well as pharmaceutics, will also be discussed.

Excited-state dynamics in porous crystalline assemblies

Dr. Pravas Deria

Efficient heterogeneous photocatalysts can transform the basic understanding into deployable and scalable platforms for major kinetically and energetically challenging chemical reactions. Anchoring well-established molecular photosensitizers or photocatalytic ensembles on a solid surface can make a heterogeneous system but not an efficient one as energy must be delivered without molecular diffusion within the lifetime of its excited state. Of course, a triplet-based photosensitizer can solve this time issue, but it must have control over singlet oxygen generation if the reaction requires oxygen as an electron acceptor. Macromolecular and supramolecular systems provide opportunities to manipulate excited state dynamics and processes suitable for various optoelectronic utilities. Crystalline metal−organic frameworks (MOFs) can be viewed as a special solid-state polymorph of such ensemble -where the well-defined pores play a critical role in arranging the molecular chromophore (strut/linker) to define electronic and excitonic interaction as well as providing the required environment (e.g., dielectric modulation). We will discuss why MOFs are reminiscent of natural LHC harnessing unique photophysical properties in solid scalable assemblies. These include: (a) coupled oscillator in multi-strut exciton showing superradiance and controllable anisotropy in their migration (b) better control of S-T ISC and strategies to prepare triplet excitons, (c) strategy to generate charge carrier that maintains high potentials. Many of these processes and strategies are challenging in monomeric molecular systems, and therefore, MOFs provide a unique yet modular platform for solid artificial LH systems.

Student Poster Abstract

Probing Epidermal Growth Factor Receptor Extracellular Domain Dimers and Monomers in the Presence and Absence of EGF, under an External Compressive Force using Single Molecule Force Spectroscopy Measurements

H. Dedunu Senarathne, Lalita Shahu, H. Peter Lu*

Probing Epidermal Growth Factor Receptor Extracellular Domain Dimers and Monomers in the Presence and Absence of EGF, under an External Compressive Force using Single Molecule Force Spectroscopy Measurements H. Dedunu Senarathne, Lalita Shahu, H. Peter Lu* Bowling Green State University, Department of Chemistry, Center for Photochemical Sciences, Bowling Green, OH 43403 *Corresponding Author: E-mail: hplu@bgsu.edu Abstract: The investigation into the relationship between the structure and function of proteins when subjected to external compressive forces shows great promise and provides valuable insights.1-5 However, while there have been extensive studies on manipulating protein dynamics and ligand-receptor interactions under pulling forces, there has been relatively limited research on the detailed and quantitative analysis of protein conformational changes under compressive forces. In this study, we evaluated the response of unliganded EGFR monomers, liganded EGF-EGFR monomers, and dimers to an externally applied compressive force using a modified AFM setup equipped with an ultra-soft AFM tip. Our results demonstrate that EGFR exhibits spontaneous structural rupture behavior during ligand binding, characterized by a rupture event that has a gradual and a partial drop in force rather than an abrupt and a full force drop. Furthermore, the compressive forces measured in our study range from tens to hundreds of pN, which are within the biologically relevant range influenced by hydrodynamic stress, surface tensions, protein crowding, and cellular osmotic pressures.

Investigating neuronal cell membrane lipid bilayer disruption induced by central nervous system stimulant of methamphetamine.

Hashini R.S.Eheliyagoda, Lorena Alvarez and H. Peter Lu*

Investigating neuronal cell membrane disruption induced by central nervous system stimulant of methamphetamine is important due to the lack of knowledge of molecular level disruption of the lipid bilayer and underline effects caused by interacting these lipophilic drugs on the neuronal membrane. Even though, detection of these drug induced disruption of the neuronal membrane is technically challenging, we were able to measure the electrical current fluctuation changes of the HT22 neuronal cell membrane due to the interaction of methamphetamine using whole cell patch clamp and differential interference contrast microscopy. We observed that the fluidity and permeability changes of HT22 cell membrane has increased upon addition of methamphetamine, and it is also found that this permeability fluctuations of the cell membrane are concentration dependent resulting higher leaking states which has more electric conductance compared to the non-leaking states for higher methamphetamine concentrations. Also, analyzing electric current fluctuation dynamics of the cell membrane by fitting the autocorrelation function for the leaking vs non-leaking current activities allowed us to predict the leaking vs non-leaking confirmational dynamics and to speculate the possibility of these cells to survive from the temporary disruptions or the recovering rate of the lipid membrane from the perturbed disordered state. With this new approach we accomplished receiving real time permeability changes of the cell membrane due to cell membrane disruptions in the presence and in the absence of methamphetamine molecules which is important for crucial cellular functions.

Probing Intramembrane Amphiphilic drug molecule Concentration and Investigation of Temporal Penetration of Amphiphilic drug molecules inside Neuronal cells using Surface Enhanced Raman Spectroscopy

Udhari Deshapriya, Lorena Alvarez, Hashini R. S. Eheliyagoda, H. Peter Lu*

We gain valuable insights into the cellular and molecular processes by studying the mechanisms of the transportation of stimulant drugs through neuronal cell membranes. Surface Enhanced Raman spectroscopy is utilized to investigate the concentration of amphiphilic drug molecules retained within lipid membranes. We employ a home modified experimental setup consisting of Raman spectrometer coupled with a confocal microscope and interstitial method to probe the spatial distribution of Amphetamine and Methamphetamine molecules across the DOPC supported lipid bilayers. By acquiring Raman spectra at different points within the membrane, we can obtain valuable information regarding the drug concentration profile. By calibrating the Raman spectra with known drug concentrations, a reliable correlation between spectral features and drug concentration can be established. Furthermore, this study aims to understand the temporal dynamics of Amphetamine and methamphetamine molecule penetration and concentration inside HT22 live cells. A quantitative assessment of temporal concentration profiles of live cells contributes to a comprehensive understanding of amphiphilic drug penetration behavior through passive membrane diffusion driven by the concentration gradient.

Aqueous Warfarin and 4-Hydroxycoumarin Photodegradation Products and Yields from UV-B Exposure

Jeffrey M. Allison, Karl J. Feierabend

Warfarin is a pharmaceutical anticoagulant and common rodenticide. Due to these common applications, warfarin has been measured in trace quantities in environmental aqueous systems and can undergo photodecomposition when exposed to sunlight. 4-Hydroxycoumarin comprises most of the warfarin structure and is warfarin's primary chromophore. Equipped with such tools as UV-B photochemistry, HPLC, High Resolution MS/MS-QTOF, and fluorimetry we worked to determine the photoproducts formed from this compound's photolysis and characterize them. Three major photoproducts of 4-hydroxycoumarin and their associated yields have been identified: salicylic acid (3%), phthalic acid (86%), and 2,6-dihydroxybenzoic acid (3%). To determine the extent to which each parent compound photodecomposed, the photolysis quantum yields of warfarin (7.3×10^{-4} mol/einstein) and 4-hydroxycoumarin (1.27×10^{-2} mol/einstein) were determined as well as the fluorescence quantum yields of both (7.74×10^{-3} mol/einstein; 7.44×10^{-3} mol/einstein).

Earth abundant elements as photosensitizers; cyclometallation as a strategy for extending excited state lifetimes

Spencer Burton

In the search for clean energy, earth abundant elements such as iron, cobalt and nickel in the earth's crust make them attractive candidates for large scale industrial applications that are affordable and sustainable. In first row transition metals, low lying metal centered states exist which allows for ultrafast deactivation of excited states. This inhibits charge transfer ability, hindering their usefulness in many energy applications. An approach to overcome this problem is the destabilization of metal centered states such that they are above the energy of the useful charge transfer (CT) state, thus removing the states that promote ultrafast relaxation. To be presented is a computational and experimental study that employs cyclometallating 2-phenylpyridine ligand on cobalt(III) in efforts to destabilize low lying metal centered states. The complexes, that take the general form of Co(ppy)2L (ppy = 2-phenylpyridine, and L = 2,2'-bipyridine(bpy), 1,10-

phenanthroline (phen) or 1,12-diazaperylene(DAP)), have thus far been subjected to UV-Vis, cyclic voltammetry, and ultrafast transient absorption to characterize the complexes. The focus of the presentation is on preliminary computational data of the cyclometallated cobalt series, as well as synthetic schemes of the complexes and the initial data that has been collected.

Tethering Cobaloximes to Molybdenum Disulfide Photocathodes for Photoelectrochemical Water Splitting

Taylor Matthews

Dye-sensitized photoelectrochemical cells (DSPECs) consist of two spatially separated electrodes which capture, convert, and store solar photon energy in the form of solar fuels, such as hydrogen from the hydrogen evolution reaction (HER). Hydrogen gas can be evolved from metal oxide-based photocathodes with adsorbed layers of dye molecules coupled with HER catalysts. Molybdenum disulfide materials are a promising class of catalysts for the HER; however, the catalytic activity of platinum remains greater than MoS_2, motivating the need to improve the activity for practical applications. Catalytic activity can be improved by activating the basal plane and increasing the number of edge sites by covalently tethering HER catalysts to active MoS_2 sites. Cobaloximes have shown potential as catalysts and modifications of the axial pyridine ligand and equatorial ligand framework can tune the photoelectrochemical performance of MoS_2. The focus of this project is to chemically bond cobaloxime derivatives to the surface of MoS_2 photocathodes to improve the kinetics of the HER.

Heteroleptic dirhodium(II,II) paddlewheel complexes for photocatalytic proton reduction

Piyush Gupta and Claudia Turro

Bimetallic complexes have been shown to exhibit high electrocatalytic and photocatalytic activity owing to multiple redox active metal centers and high structural stability. Dirhodium compounds having a paddlewheel structure with a Rh-Rh bond have become promising candidates for photocatalytic hydrogen evolution with high turnover numbers and catalytic efficiency. Recently, dinuclear complexes with short metal-metal bond distance such as *cis*- $[Rh_2(DPhF)_2(bncn)_2]^{2+}$ (DPhF = *N*,*N*'-diphenylformamidinate; bncn = benzo[c]cinnoline) have been shown to possess long lived triplet excited states and work as a single molecular photocatalyst for proton reduction under red light with good turnover numbers. To further understand the mechanism of such compounds, the present work focuses on the studying similar complexes with uncapped axial sites and exchanging bridging ligands. Substituting the bridging formamidinate ligands with acetates alters the HOMO-LUMO transition and offer insight in the importance of two of these ligands each. This poster/talk aims to discuss the compare the series, *cis*- $[Rh_2(DPhF)_x(OAc)_{2-x}(bncn)_2]^{2+}$ (where x=0-2), along with their synthetic routes, spectroscopic, electrochemical and structural properties granting an insight into their lifetimes and mechanism for proton reduction.

Investigation of the Catalytic Cycle of Single Molecule Photocatalysts: [Rh2(DPhF)2(bncn)2] $^{2+}$

Santana Garcia, Claudia Turro*

As global energy needs rise each year significant efforts have been made to design photocatalysts which can efficiently convert solar energy into chemical fuel. The most advantageous of these photocatalysts are ones which can generate hydrogen from protons in solutions, as this would be a carbon neutral process. Dirhodium paddlewheel complexes are photocatalysts which can undergo this process. One of these known paddlewheel complexes is [Rh2(DPhF)2(bncn)2] $^{2+}$ (DPhF = N,N'-diphenylformamidinate; bncn = benzocinnoline). To elucidate the mechanism of this hydrogen generation, the singly reduced species was generated and studied photochemically. The single reduced species displays broadened absorption features, and is highly reactive in the presence of acid.

Ru(II) Polypyridyl Complexes with Extended π-System Ligands as Photodynamic Therapy Photosensitizer

Alexia Marques Silva, Claudia Turro

The achievement of long-lived excited states in ruthenium(II) polypyridyl complexes is of interest for photoactivated applications, such as photodynamic therapy (PDT). The development of complexes with a ligand-centered 3ππ* state below the traditional metal-to-ligand charge transfer (MLCT) excited state can result in longer-lived triplet excited states. 1,10-phenanthroline (phen) ligands were synthetically modified to contain aromatic groups in the position 2 and those were then coordinated to a Ru(II) metal center. The series cis–[Ru(bpy)(dppz)(2-R-phen)]2+, where R = phenyl (1), 2- naphthyl (2) and 1-pyrenyl (3), are currently being prepared, and were compared to the control series cis–$[Ru(bpy)_2(2\text{-}R\text{-}phen)]^{2+}$. Modification of synthetic methodology resulted in easier purification steps. TD-DFT calculation of complexes 1 – 3 are consistent with a metal centered highest occupied molecular orbital (HOMO) and a ligand-centered lowest unoccupied molecular orbital (LUMO). The emission spectra of the series at 77 K exhibit E00 ~ 16 000 cm-1 for 3ES. The π-stacking feature was observed through bidimensional NMR (COSY and NOESY) and the 3MLCT lifetimes were longer when compared to the control series by one order of magnitude. Emission and singlet oxygen quantum yields will be presented.

Investigating the spontaneous rupture of Calmodulin under direct mechanical compressive force using AFM-FRET Single-Molecule Nanoscopic approach

Lalita Shahu, H. Dedunu Senarathne, Shermi M. Katugampalage, H. Peter Lu*

Proteins control and regulate the vital biological processes in all living organisms. In the context of living cells, various factors such as molecular aggregation, molecular crowding, hydrodynamic stress, and cell osmotic pressure can give rise to mechanical forces that induce spontaneous rupture of proteins, consequently leading to significant conformational changes in their native structures.[1,2] This study aims to utilize AFM- FRET single-molecule nanoscopic approach to study the spontaneous rupture of calmodulin under a small mechanical compressive force. CaM is activated by Ca^{2+} and has the ability to bind to short peptides and proteins in a reversible or irreversible manner.[3] This method enables precise localization and mechanical manipulation of a specific dye-labeled protein within a wide observation area and allows the real-time monitoring of conformational changes in the targeted protein by recording individual FRET time trajectories at the single-molecule level simultaneously.[4,5] By the analysis of the acquired force curves and FRET trajectories, it can be scientifically validated that the protein undergoes a conformational change during the occurrence of the rupture event. Additionally, the threshold force for rupture is of Pico newton level which is accessible in physiological environments. Therefore, it is imperative to perform additional investigations in order to reveal the biological consequences that ensue from the application of compressive force within cells.

Cucurbit[n]uril-based Fluorescent Dye-Displacement Assays for Opioid Detection

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Opioid analgesics are widely used as analgesic, antitussive, and antidiarrheal drugs.[1] Even though they are considered essential for pain management, there are well-known risks associated with an opioid prescription, such as overuse, addiction, and overdose deaths.[2] Fluorescent dye-displacement methods are inexpensive, quick, sensitive, and quantitative to detect drugs.[3] In the present work, sensors are created based on different fluorophores and dyes, and receptors, such as cucurbit[7]uril (CB7) and cucurbit[8]uril (CB8). Fluorophores (pyridinium-coumarin based) are designed and synthesized to provide better interaction between dye and receptors. Fluorophores and dyes (acridine based) are used to give a turn-off system by adding receptors. Then analyte addition allows for displacement between dye and analyte; a turn-on system is obtained. Our results demonstrate that acridine yellow, acridine orange, and pyridinium-coumarin attached with CB8, and after the addition of four opioids such as oxycodone, codeine, dextromethorphan, and methadone replacement and turn-off-on system obtained with different responses.

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Correlating molecular-scale photochemistry to macroscale property changes in Metallosupramolecular polymers

Irene F. Baraza, Ankit D, Alexis D. Ostrowski

Modification of polymer chains with specific binding groups enables the coordination of different metals, improved temperature stability of the materials and in some cases tunable mechanical properties. In this study we have used curcumin to synthesize polymers of differing molecular weights and coordinated them to different first row transition metals. Introduction of different chains in the polymeric unit changes the degree of polymerization and how these polymer units arrange giving rise to differences in polymer strength. Preliminary results show that photoresponsive curcumin polymer has greater affinity to Cu^{2+} compared to Fe^{2+}. The artificial modification in the metal-ligand center surrounding affects the viscoelastic properties of the curcumin Metallosupramolecular polymer resulting in quenching the fluorescence as evidenced in the metal-polymer titration spectra results. Preliminary dynamic mechanical analysis of the material composites of the different curcumin metallopolymers with polyurethane shows the effects of metal coordination to the elasticity of the different materials. Continued studies on the effect of the metal-ligand bond and difference in molecular weight to the mechanical properties of the curcumin metallopolymers is being carried.

Photoisomerization of *trans*-4,4’-Azopyridine: Excited State-Specific Dynamics and Relaxation Mechanism

Laura Marie Obley

Ultrafast femtosecond transient absorption spectroscopy was utilized on *trans*-4,4’-azopyridine (4,4’-APy) to elucidate its earliest photoinduced dynamics and excited-state relaxation mechanism. 4,4’-APy was excited at 460- and 275-(290) nm, to access the S_1 n,π^* and S_2 π,π^* states, respectively. Upon excitation into S_1 n,π^*, a lifetime of 2.1 ps is obtained, which is assigned to a portion of the excited state population becoming trapped on a planar minimum (TM_1). The remaining fraction of the population travels further down to a second shallow planar minimum (TM_2, 300 fs lifetime) exiting into the S_0 state. After exciting into S_2 π,π^*, the state undergoes a very fast decay in 30-fs leading to a hot population buildup on n,π^* where the excited state species then proceeds along the surface similar to what is observed in direct S_1 n,π^* excitation. Formation of hot ground state species occurs nearly simultaneously as well. Exciting into these excited states reveals coherent vibrational modes, most notably 195 cm^{-1}, which is observed in both relaxation channels and is assigned to CNN bending. It was concluded that for both S_1 n,π^* and S_2 π,π^* the deactivation coordinates occur along a non-rotational pathway as well. However, upon higher excitation energy wavelengths (275- and 290-nm) the *cis*-isomer product yield is seen to increase, in contrast to what is observed in *trans*-azobenzene where there is a yield reduction. A possible explanation involves the presence of a seam along the planar conical intersection of $n,\pi^*/S_0$ of which higher lying levels become more easily accessible upon higher energy excitations, in turn, generating a larger yield of ground state *cis*-isomers.

Quantum Shell in a Shell: Engineering Colloidal Nanocrystals for a High-Intensity Excitation Regime

Jiamin Huang

The efficiency of many optoelectronic processes in colloidal semiconductor nanocrystals (NCs) tends to decline when subjected to high-intensity excitation. This decline is primarily attributed to Auger recombination, where multiple excitons result in the conversion of NC energy into excess heat. As a consequence, the efficiency and life span of NC-based devices such as photodetectors, X-ray scintillators, lasers, and high-brightness light-emitting diodes (LEDs) are negatively impacted. Although semiconductor quantum shells (QSs) have recently emerged as a promising approach to address Auger decay, their optoelectronic performance has been impeded by surface-related carrier losses. To deal with this issue, we propose the implementation of quantum shells with a CdS–CdSe–CdS–ZnS core–shell–shell–shell multilayer structure. The presence of a ZnS barrier effectively inhibits surface carrier decay, resulting in a significant increase in the photoluminescence (PL) quantum yield (QY) to 90%, while maintaining a high biexciton emission QY of 79%. Furthermore, the enhanced morphology of the quantum shells allows for one of the longest Auger lifetimes observed in colloidal NCs to date. The reduction of nonradiative losses in QSs also leads to diminished blinking in single nanoparticles and low-threshold amplified spontaneous emission. We expect that the ZnS-encapsulated quantum shells will be widespread across various applications in high-power optical or electrical excitation regimes.

Characterization of Co_3(II,II,II) as Electrocatalysts and Potential Photosensitizers

Erin Ramey

The global energy crisis is a major concern, specifically finding greener routes to produce fuel. An attractive approach combines renewable solar energy and hydrogen production in photochemical hydrogen evolution catalysis. Previously, ruthenium and rhodium photocatalysts have generated hydrogen through their triplet metal-ligand to ligand charge transfer (ML-LCT) states. However, exploring first row metals, such as cobalt, would be both novel and economical. Herein, tri-cobalt complexes with ligand-centered hydrogen evolution are explored. Although previous tri-cobalt complexes evolve hydrogen under electrocatalytic conditions, the lifetimes of the excited states are only up to 20 picoseconds; these lifetimes are not long enough for robust photocatalysis. To improve the lifetimes, a new cobalt complex is proposed. Based on computational data, a ligand scaffold including a benzo[c]cinnoline (bncn) moiety would center the HOMO on the bncn-like ligand and possibly extend the lifetime of the ML-LCT state. Additionally, protonation of bncn has been proposed as the mechanism for producing hydrogen in similar rhodium complexes. Modifying bncn to include an amine as a third coordination site would allow synthesis of novel tri-cobalt paddlewheel complexes and characterization of their new lifetimes and excited states.

Extended Excited State Lifetime Using Donor/Acceptor Ligand Design in Cobalt Centered Molecule

Aaron Martinez

As global demand increases for photoreactive compounds in areas from pharmaceuticals to energy applications, first row transition metals such as cobalt, copper, zinc, and iron are often choices to replace rare and expensive second row metals like ruthenium or rhodium at a fraction of the cost but often have decreased effectiveness due to the lifetime of the excited state being much shorter. One method for increasing effectiveness is increasing the electron-hole separation in the excited state to induce long lived excited states. This presentation is centered on the synthesis and photophysical characterization of a novel cobalt(III) complex expected to exhibit a long-lived ligand-to-ligand charge transfer excited state (LLCT). This complex will employ a tridentate donor ligand (nptpy) and acceptor (pyphen) ligand in order to create spatial separation of the electron-hole pair (nptpy = 4-([2,2':6',2''-terpyridin]-4'-yl)-*N*,*N*-diphenylaniline) and pyphen = 2-(pyridin-2-yl)-1,10-phenanthroline).

Hybrid Organno-silicon 3-D Printable Materials For Medical Devices

Ethan Chandler, Cory Simms, Dr. Joseph C. Furgal

Silsesquioxane materials are effective at absorbing fluids and can become polymerized via their functional groups on their corners. This research focuses on making a photo-responsive silsesquioxane polymer 3-D printable and more adaptable to modern technology.

Photophysical Properties of Perovskite Materials for Optoelectronics

Hamza Shaili and Clemens Burda*

Perovskites are a class of materials that have attracted wide attention in the past decade due to their exceptional properties that allowed for a wide range of applications. Perovskites possess unique features such as their ability to exhibit a diverse range of physical properties with facile solution processibility. Their unique properties make them highly suitable for numerous technological applications, particularly, in optoelectronic devices such as solar cells, light-emitting diodes (LEDs), photodetectors, and lasers. Perovskites have shown a promising advancement in the field of solar cells achieving astonishing power conversion efficiencies in a short period of time matching those of traditional silicon-based solar cells with a lower-cost fabrication process. However, in most devices, the hybrid organic-inorganic perovskite material has issues with instability, and device degradation, which affects their efficiency and the possibility of their commercialization. Therefore, a huge emphasis on our group's research is to investigate more stable alternatives that will permit the fabrication of highly efficient and stable devices. My poster will give an overview of my recent efforts in this area.

Structure and Solvation Dynamics of Deep Eutectic Solvents

Desiree Mae Prado[1], Rathiesh Pandian[1], Ibrahim Alfurayj[1], Xiaochen Shen[1], Carla Fraenza[2], Stephanie Spittle[3], William Brackett[3], Bryce Hansen[4], Kaylie Glynn[4], Yong Zhang[5], Brian Doherty[6], Robert Savinell[1] , Steve Greenbaum[2], Joshua Sangoro[4], Edward Maginn[5], Mark Tuckerman[6], and Clemens Burda[1, *]
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Deep eutectic solvents (DESs) are mixtures of hydrogen bond donor (HBD) molecules and hydrogen bond acceptor (HBA) molecules that are characterized by a significant depression of the melting point compared to that of its individual constituents. With their versatile properties, DESs hold great promise as next-generation electrolytes for electrochemical energy storage solutions. In this study, we investigate the influence of varying the HBA, HBD, HBA/HBD molar ratios, and co-solvents on the structure and dynamics of DES ethaline, a 1:2 molar ratio mixture of choline chloride (ChCl) and ethylene glycol (EG). When examining the influence of HBA/HBD molar ratio, femtosecond transient absorption spectroscopy reveals two distinct time components. Both components indicate that solvation dynamics are enhanced with increasing ChCl composition up to 16.67 mol% but are slowed down for 33 mol% ChCl. Additionally, molecular dynamics simulations shed light on the role of co-solvents, specifically water molecules, in DESs. Higher concentrations of water co-solvent promote longer Grotthuss mechanism chain lengths within the DES. The H_3O^+ ion, briefly stabilized by Cl^-, interacts with ethylene glycol, indicating a disruption of the hydrogen bond network in the DES.

Our results also reveal that substituting ChCl with ChF as the HBA enhances the relaxation dynamics of DES. The ^{19}F-NMR spectrum of ethalineF unveils two distinct chemical environments surrounding the fluoride ion, namely EG···F (freely dissolved F^- in EG) and Ch···F (choline-bound F^-). Consequently, by altering the O-H spacing and alkyl chain length of EG, it becomes possible to fine-tune the polarity and solvation dynamics of DESs.

Spectral Analysis of Dye Pairs in Daylight Fluorescent Pigments

George Belay, Sarah J. Schmidtke Sobeck

Daylight fluorescent pigments, developed in the 1930s, have found applications in safety and navigation products, as well as being featured in art and marketing since the mid-century. These materials are made by embedding fluorescent dyes and optical brighteners in a polymer matrix. Our studies examine the photophysical properties and stability of dye pairs used in commercial pigments. These dye pairs can serve as energy transfer partners with the acceptor's absorbance overlapping with the donor's emission. In this study we present analysis of how the ratio of the two components impacts the observed emission intensity and wavelength. Secondly the photostability of the dyes alone and in combination is evaluated under UV-radiation. This work helps to understand the impact of product formulation on the appearance of the daylight fluorescent material, as well as the potential impact of fading due to light exposure.

Beyond Moore's Law: Harnessing Nanomaterials for Technological Advancement

Md Sirajul Islam

As we stand at the brink of a significant technological paradigm shift, the conventional methods of fabricating semiconductor technologies have almost reached their physical limitations. Therefore, exploring alternative approaches to meet the growing demands for data storage and processing has become necessary. Nanoscale materials hold great promise in overcoming these limitations. Synthesis and study of these materials give us insights into their fundamental properties and interaction with light. This exploration of the 1-nanoscale realm presents abundant opportunities, empowering us to make significant improvements in three key areas: biosensing & healthcare, energy, and environmental research. Succeeding in these areas requires a smart, innovative approach to materials synthesis, analysis, and data handling. Among the various nanoscale materials, 2D MXene sheets exhibit interesting semiconducting properties. Through my research, I am investigating their properties for different applications like water splitting, photovoltaics, and photothermal treatment.

Photothermal Study of Nanodiamonds in Agarose Gels

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The photothermal properties of carboxylated nanodiamond (C-ND) particles in agarose gel base medium were experimentally investigated within a remarkably small volume percentage range: $6.55x10^{-5}$ - $2.29x10^{-2}$% (v/v) and two distinct particle sizes. Compared to base gels, laser-induced spot heating of gels containing trace concentrations of C-ND particles resulted in a significant increase in temperatures distant from the spot. These increases contradicted any thermal conductivity (TC) increases related to particle inclusion. Investigation of the UV-visible and Raman spectroscopies reveals that the considerable particle concentration as well as size-dependent changes in the optical scattering of particulate gels lead to this photothermal phenomenon. C-ND particles attach to the agarose polymer structure, resulting in enhanced optical scattering and entrapment in particle-loaded gels, according to structural analysis of the gels. We find that the inclusion of minimal amounts of nanodiamond particles in agarose gels results in structural modifications that highly influence the light scattering and trapping characteristics of the particulate gels. This finding proves that the rate and volume of heating could be controlled based on the intended application. The observed scattering/entrapment has a substantial effect on the photothermal characteristics of these gels, which have wide-ranging applications, including the ablation of tumors and photoelectronic materials.

Spectroscopic Investigation of Deep Eutectic Solvents and Added Co-Solvents: A Comparative Study with Water, Acetonitrile, and Dimethyl Sulfoxide

Desiree Mae Prado, Aaron Niño Gonzaga, and Clemens Burda*

Deep eutectic solvents (DESs) have gained considerable attention as promising electrolytes for redox flow batteries (RFBs), one of the most promising long-duration energy storage technologies that address the intermittent power generation of solar and wind renewable energies. DESs are an emerging class of solvent mixtures that are characterized by a significant depression of their melting point compared to that of the individual constituents. Despite some advantages, like low cost, environmental compatibility, DESs also have disadvantages, e.g. low ion mobility. To address these challenges, we explore the addition of co-solvents such as water, acetonitrile (ACN), and dimethyl sulfoxide (DMSO) to DES ethaline (a 1:2 choline chloride: ethylene glycol mixture) in order to gradually interrupt the intrinsic hydrogen-bonding network. Our FTIR results reveal that systematic addition of water leads to a blue shift of the O-H stretch at around 3300 cm-1 and to an increase in intensity of peaks at 2340 cm-1 and 2360 cm-1 that correspond to asymmetric O-C-O stretching. This means that there is a significant absorption of CO2 in ethaline. A blue shift in the O-H stretching band can also be observed with the addition of ACN and DMSO. Furthermore, a decrease in viscosity can be observed with the addition of co-solvents, suggesting that there is a weakening of intermolecular interactions between the DES components. An analysis of the results will be presented.

The Solvation Dynamics of Deep Eutectic Solvents

Rathiesh Pandian, Daniel Kim, Edward Maginn, Clemens Burda*

Li-ion batteries are excellent energy storage devices. However, they have environmental and safety issues that limit their future potential, with the primary cause for concern being their electrolyte system. As a result, there is a need to develop novel electrolytes to satisfy not just the health and safety issues, but also the ever-growing energy demands of the future. A class of electrolytes that may be robust enough to alleviate these issues are called deep eutectic solvents (DESs). They are binary mixtures made by combining a hydrogen bond acceptor (HBA) and hydrogen bond donor (HBD). In this work, choline chloride (ChCl) is used as an HBA and is combined with HBDs 1,2-ethanediol, 1,2-propanediol, and 1,3-propanediol to make numerous systems. To measure polarity on the ET(30) scale and solvent response dynamics by femtosecond transient absorption (fs-TA) spectroscopy, the negatively solvatochromic Reichardt's Betaine 30 (B30) dye was dissolved as a reporter molecule in each system. In addition to experimental measurements, classical molecular dynamics simulations were computed to better understand the solvation structure and hydrogen bond networks of these systems. 1,2-ethanediol, 1,2-propanediol, and 1,3-propanediol were selected as H-bond donors to investigate the effects of alkyl chain length and O-H spacing. Our findings indicate that when the solvent molecule (the HBD) increases in size, the solvent's solvation dynamics becomes progressively slower and its ability to act as a polar solvent, capable of dissolving significant quantities of charged Redox species, decreases. Thus, future battery electrolytes need to be constructed of small and stable molecules of high mobility.

Raman and Impedance Spectroscopy of Sodium Bismuth Titanate doped with transition metals

Stefane Lira,[1,2] Clemens Burda, [2] Adolfo Franco,[1]

Perovskite multiferroic materials are in the center of an industry that includes several applications nowadays such as non-volatile ferroelectric random-access memory (NVFRAM), ceramic capacitor material, ultrasonic transducers, actuators, etc. These applications are due inherent dielectric, piezoelectric, ferromagnetic and ferroelectric properties that these materials present. Obtaining these properties simultaneously at room temperature is yet a difficult task, however it was observed in some lead-based perovskite materials like PZT-Lead Zirconate Titanate, PbTiO3. However, replacing materials containing lead is a very pressing issue because of its toxicity, therefore lead-free materials have been for some time now the focus in the advanced materials research field. Similarly, to the structure of the lead-based materials lead free perovskites systems like sodium bismuth titanate, Na0.5Bi0.5TiO3 (NBT) are being pursued for its excellent dielectric properties, high Curie temperature 320 ºC and large remnant polarization (38 µC/cm). Nonetheless some drawbacks such as high dielectric loss and high conductivity are yet to be addressed. Doping sodium bismuth titanate with metals it is a good technique to improve the properties of NBT. Since most of these metals present more than one oxidation state they can produce several defects in the structure of the ceramic material possibly resulting in really interesting properties. Sodium bismuth titanate ceramic pellets with a composition of (Na0.5Bi0.5)x−1MxTiO_3 with x = 0 and 0.01 (1%) and M = Co^{2+}, Cr^{3+}, Mn^{4+}, Al^{3+}, Nb^{5+} were synthesized by a standard solid state reaction and sintering method. The observed peaks in the XRD measurement shows a single perovskite phase of rhombohedral symmetry and R3c space group. Calculations of Rietveld refinement were made using GSASII software and the output indicates that the doping ions entered the structure due changes in the unit cell parameters. Vibrational studies of FTIR and Raman spectroscopy showed bands characteristics of perovskites structures agreeing with the information obtained in the XRD. Through complex impedance spectroscopy measurements it was possible to obtain dielectric permittivity data and fit the right equivalent circuit revealing grain and grain boundary contributions. The dielectric constant measurement was made at room temperature in the frequencies range of 20 Hz–2.0 GHz and showed with the addition of transition metal ions that the dielectric permittivity values increased and dielectric loss decreased significantly when comparing with the pure sample.

Optical and Impedance Spectroscopic Study of the (Na0.5Bi0.5)x−1RExTiO3 system

Stefane Lira,[1,2] Clemens Burda, [2] Adolfo Franco,[1]

The use of lead-based materials in electronic equipment has always been a health and environmental hazard for the scientific community. After the restrictions imposed by the European Union involving lead in 2011 (2011/65/EU), researchers started working with the objective of developing a lead-free material to replace lead-based ones in several devices such as multilayer capacitors, transducers, actuators and random-access memories (RAM). Sodium bismuth titanate, Na0.5Bi0.5TiO3 (NBT) based materials are excellent candidates to replace lead based ferroelectric materials specially because of its perovskite crystal structure. Perovskite family materials display interesting phase transitions and outstanding ferroelectric, piezoelectric, dielectric and energystorage properties. Although Na0.5Bi0.5TiO3 presents a really promising dielectric material, it also suffers from high dielectric loss, large coercive field (7.3 kVmm−1) and high conductivity resulting in difficulties for the electric poling process. The modification of sodium bismuth titanate through doping with rare earth ions was found to be a suitable technique to minimize these problems. This work's purpose is to study the influence of rare earth doping perovskite A-site, rather than just doping the Bi3+ site, this work aims to observe the influence of doping on both A-site ions - Bi^{3+} and Na^{+}. Polycrystalline ceramic pellets of rare earths (Y^{3+}, Dy^{3+}, Yb^{3+} and Er^{3+}) doped NBT (Na0.5Bi0.5)x−1RExTiO_3 with x = 0 and 0.01 (1%) were synthesized by a conventional solid-state reaction and sintering method. The XRD patterns of all compositions are in good agreement with a single Perovskite phase of rhombohedral symmetry and R3c space group. Rietveld refinement showed small changes in the lattice parameters, volume, and density of the unit cell suggesting that the ions entered the crystalline structure. Raman and Complex impedance spectroscopy are two really important techniques that can give us information about structure and electric properties of the materials. Raman spectra of all samples display five Raman-active peaks characteristics of the rhombohedral structure around 136 cm^{-1}, 279 cm^{-1}, 541 cm^{-1}, 608 cm^{-1}, 797 cm^{-1} and indicate the introduction of defects as a result of the doping process. Diffuse reflectance (UV-Vis spectroscopy) shows that most of the doped samples have a smaller band gap than the pure one which can be explained by the introduction of new electronic states with doping and also because of oxygen vacancies. The dielectric constant measurement at room temperature in the frequencies range of 20 Hz–2.0 GHz yielded high values with the addition of rare earth ions for all samples in the ~103 range and the frequency dependency of the permittivity agreed with the Debye model. AC conductivity was calculated and the doping process resulted in lower conductivity for all samples. Impedance data were collected and fitted to the right equivalent circuit revealing grain and grain boundary contributions.

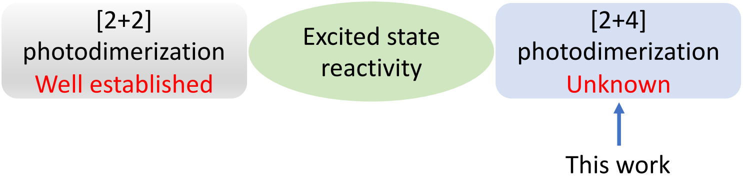
Enzyme-Targeted Phototherapy of Metastasis Using Gold Nanoclusters

Zoey A Lockwood, Michael Jirousek, James Basilion, and Clemens Burda*

Although advancements in cancer treatment have led to improved survival rates for various types of cancer over the years, it remains the second leading cause of death in the United States. Despite the progress made, current treatment methods often come with significant risks and adverse effects for patients. However, a promising avenue that shows great potential in mitigating these drawbacks is nanoparticle-based phototherapy. This innovative approach aims to induce cell death in cancerous tissue through combinational phototherapy. One key component of this therapy involves the utilization of indocyanine green (ICG), a near-infrared dye capable of generating reactive oxygen species or heat. To further enhance the effectiveness of the treatment, gold nanoparticles will be employed due to their exceptional light absorbance properties, surpassing those of normal tissue by several magnitudes. To ensure precise targeting of ICG to malignant tissue, a cathepsin inhibitor will be incorporated due to its overexpression in tumor cells. This project initially focuses on the synthesis of AuNCs conjugated with a ROS stimuli-responsive linker containing a cathepsin inhibitor and ICG. To achieve this therapeutic complex, it is essential to synthesize a carboxylated derivative of ICG. Once synthesized, the ICG and cathepsin inhibitor will be conjugated onto the thioketal linker, facilitating their delivery of cancer treatment.

Exploring the excited state reactivity of aryl maleimides and revealing a new photochemical [2+4] dimerization reaction by direct/sensitized excitation

Sruthy Baburaj, Lakshmy Kannadi Valloli, Spana Ahuja, Steffen Jockusch, Jayaraman Sivaguru



The study of how molecules and materials interact with light is crucial in understanding the transformations that occur, both in terms of chemical properties and physical phenomena. Photochemical [2+2]-dimerization is one of the thoroughly researched chemical transformations that has been utilized in both synthetic and material chemistry. Aryl maleimides are known for the well-established [2+2]-photodimerization when exposed to light. This presentation will highlight our investigation in circumventing the well-known [2+2] photodimerization to develop [4+2]-photodimerization reaction by both direct irradiation and by photosensitizer. Based on detailed photophysical and mechanistic studies the poster will highlight the rationale for the observed [2+4] photodimerization in aryl-maleimides.

Colloidal synthesis of PbS nanosheets and its optical properties

Megh Raj Khadka

Over the past decades, nanomaterials have greatly improved and developed. Infrared nanomaterials can be used in fiber optical communication, night vision, and sensing. PbS nanomaterials are a prominent option.

We developed two different techniques to improve the light-emitting efficiency of the PbS nanosheets: using organic ligands and inorganic shells. Both methods improved the photoluminescence quantum yield significantly. The nanosheets with improved quantum yield may find applications in photonic devices including light-emitting diodes, solar cells, and lasers.

Effectiveness of Commercial Enzymes in Isolating Microplastics from Substrate

Gabe

As microplastics continue to become an ever-increasing health hazard, it is imperative that new solutions are developed to prevent further contamination of food and water supplies. While filters that are capable of isolating microplastics do exist, their sheer cost and lack of versatility prevent them from being used on a large scale. The objective of this project is to determine whether meat tenderizer, Bio-Clean, or trypsin would be the most cost-effective enzyme at isolating microplastics found in environmental substrate for continued experimental use. Having the most efficient (cost to time) enzyme source will increase productivity for future projects.

Photophysical understanding of TADF molecules towards energy transfer mediated photocatalysis

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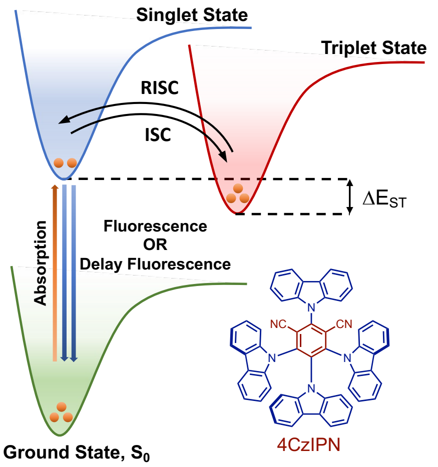
Photocatalysis using rare earth and transition metal based as well as organic photosensitizers has proven to be a useful tool to facilitate organic transformations with higher efficiency over traditional thermal synthetic methodologies. In some cases, this provides access to products which are not accessible via thermal methodologies. Due to scarcity of rare earth transition metals, the demand to develop organic photocatalysts has dramatically increased over a past few decades.[1] Among all the organic photocatalysts (PCs), a family of thermally-activated delayed fluorescence (TADF) catalysts with carbazole as an electron donor and dicyanobenzene as an electron acceptor are emerging as one of the most desirable and versatile photocatalysts due to its attractive features which include high molar absorption coefficients in the visible range, low toxicity profile and easiness with which these can be synthesized from inexpensive commercially available starting materials.[2,3] One such example is 2,4,5,6-tetra(carbazole-9-yl)benzene-1,3-dicarbonitrile (4CzIPN), which was first introduced by Adachi and co-workers in 2012.[4] Due to a small singlet – triplet energy gap (DE_{ST}), the family of catalysts are called as TADF molecules, the action of which is shown schematically in the figure.[4,5] Carbazole-based donor-acceptor photocatalysts are unique in their properties and, therefore, deserve to be studied. They show similar reactivity as rare 4d- and 5d-transition series metal complexes such as Ir(III) and Ru(II) complexes.[1] Light-induced electron transfer reactions has been extensively studied but detailed photophysical understanding is necessary to leverage these excited states in energy transfer mediated photocatalysis. The aim of the study revolves around the understanding of the photophysical properties of a series of TADF catalysts. Steady-state absorption and emission, along with time-resolved absorption and emission, provide unique information on the excited state which is targeted in the present study to use these catalysts for energy transfer. Mechanistic studies have shown compelling evidence of the energy transfer pathway from the excited state of the photocatalyst to the substrate.



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Photoexplosivity of 1-azido-2-nitrobenzene crystals

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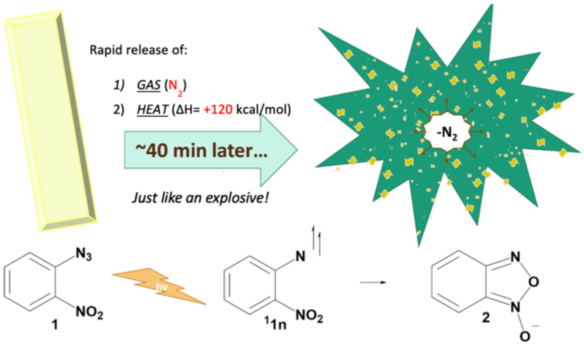

There is a need for safe high-density materials for explosives. While being the first to report the uniform photo-explosivity of **1** (~1 cm blast radius) in under 40 minutes, this work laid the basis for making safer explosives initiated by light. High energy density material, 1-azido-2-nitrobenzene **1,** with two explosophores has been studied extensively in solutions, we, however investigated its photo-response in crystals upon irradiation. Single crystals of azides **1** were irradiated with LED results in formation of benzofuroxan **2,** and the reactions takes place with explosions of the crystals as documented with digital microscope. Framework calculations identified both strong (27.4–39.8 kJ mol^{-1}) and weak (6.6-10.9 kJ mol^{-1}) intermolecular forces. By indexing the crystals of **1**, we can identify that the crystals crack at the weakest intermolecular forces, along the *c*-axis with minimal movement (τ = 37°) of **1** needed to form **2** and expulsion of nitrogen gas. This chemical reaction resulted in no change in space group (*P*-1, triclinic) as N_2 gas fills and strains the lattice forces. We will further explore whether changes in lattice structure from reactant to product is more important than N_2 gas release when it comes to dynamic responses of **1** and its derivatives.

Dynamic Work Using Light by Azide Crystal Derivatives

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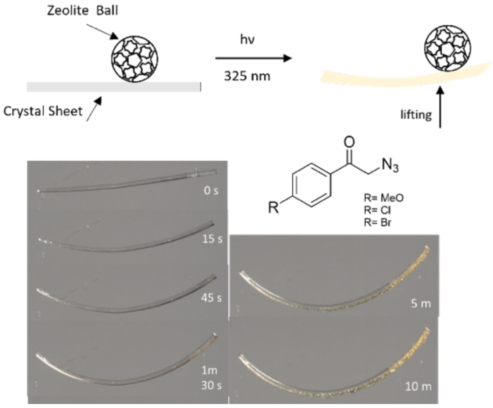

Photodynamic crystals are responsive to light depending on the crystal packing of the photosensitive species. Azides are a photosensitive substituent that can be irradiated to release nitrogen gas in an irreversible reaction. With varying organic azides, we can find the photomechanism from classical photochemical routes like laser flash photolysis, cryogenic UV/IR, and DFT calculations. In the solid-state, the X-ray Diffraction provided crystal packing showing the reaction points of a confined reaction.[1] Because having different substituents provides different packing, we looked at α-acetophenone azides where previously studied they had the same photomechanism.[2] Initially, the methoxy substituent as a needle or sheet crystal could lift a zeolite ball 50x its weight. With this knowledge, investigation continued with chlorine and bromine substituted organic azide to compare its photodynamic movements to the methoxy. Theoretical calculations in Crystal Explorer provided the intermolecular strengths within the lattice for a quantitative analysis of the movement. The chlorine had similar strengths to the methoxy but one strong bond held the lattice for a propelled surface reaction into a deglazing or when a needle caused a slight bend then slicing. The bromine had strong bonds causing a restricted bend which was able to push and slightly lift. With N_2 gas pressure build up, we can correlate the amount of intermolecular energy that must be overcome to break in a way that lifts weight mechanically. The advantages of this are no carbon-based gas byproduct, metals, solvents, or high heat, making it useful for advanced materials work./

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Photolithography on Full Hydrate Aryl Azides Inhibiting Photoconversion Allowing Beautiful Color Change

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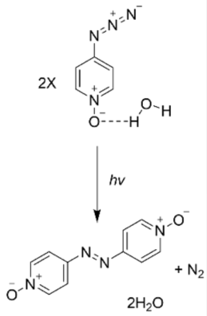

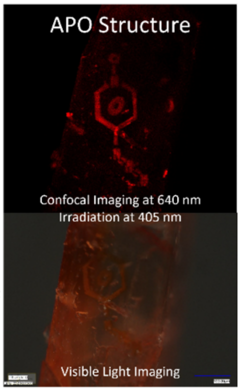

Azides have long been used for the formation of certain nitrogen containing compounds while aryl azides are continually reported in solution as forming azo-dimers.[1] We have also investigated the impact of photoirradiation of azides to release nitrogen gas through these chemical pathways and the induced photodynamic effects that this pressure causes within the solid-state.[2] Due to molecular confinement, differing chemical pathways and amounts of photoconversion. Previously reported 4-azidopyridine-1-oxide progresses when irradiated to a trans-azodimer through a triplet nitrene and release of nitrogen gas. In spite of a 4:5 nitrogen carbon ratio of the starting material it did not provide great photodynamic effects but, is very stable even upon fast surface reaction with only white light. Single crystal X-ray diffraction was conducted to explain this stability and provided context of the lack of movement through a full hydrate crystal packing with strong hydrogen bonding. The azide also confirms rules with aryl nitrene distances for dimerization where N_α-N_α needs to be within 4.5 Å, and the distance of 4.358 Å crosses over hydrate atoms causing less photoconversion to occur.[3] This very stable crystal with bright color change allows for photolithography, a technique used to convert surfaces or carve into materials.[4] In this case, we can draw into the crystal with the red dimer and only in the first layers of the soft crystal. This highly stable azide crystal shows great promise for photochemotherapy, biological phototrackers, and metal-free microchips.

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Organic Hydroperoxide for Releasing O_2 utilizing Photochemical Reactions

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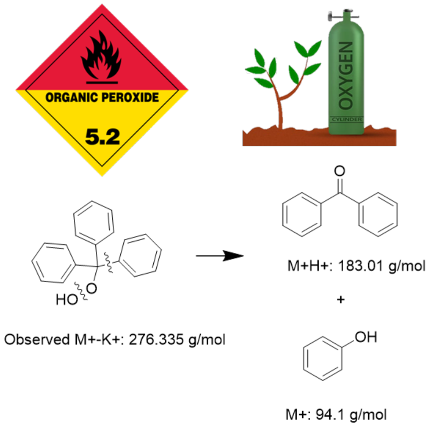

Solid-state photochemistry utilizes the most abundant reagent- *light*- and does not need organic solvents, while also progressing reactions using confinement, leading to highly selective reactions. To capitalize on this discipline, we investigate systems to create low thermodynamic gas release systems like nitrogen and oxygen gas in the solid-state using only light. It has been demonstrated that solid-state reactions can influence the packing to change upon exposure to light, while also resulting in photodynamic movements of the starting materials.[1] Using inert gas release we do not see any other effect to the reaction than intermolecular confinement change and pressure, but with oxygen or peroxides, they can react within the crystal lattice of the starting material creating new products. Endo- and hydroperoxides have been recorded as photosensitive for small organic molecules by the mention of pressure build up and decomposition without being studied for their photochemical pathways.[2] To investigate whether oxygen can be released in the solid state we studied a trityl hydroperoxide (THP **1**), and elucidate the solid state reaction mechanism and photodynamic behavior of the crystals. With a lab synthesized THP, we irradiate it with 325 nm laser to obtain two products: benzophenone (BePh **2**) and phenol (PhOH **3**). Laser flash photolysis shows a long lived intermediate at 320 nm and a short lived intermediate at 320, 520, and 620 nm. The crystal structure determined by XRD crystallography confirms the same packing as published before, the molecules pack into the crystal lattice in such a manner that they look like cups fitting into each other, so the release of the peroxide can reach another molecule before escaping the crystal lattice.[3] The applications of releasing oxygen from the solid-state include breathing cannulas, gas expansion, organic synthesis, and ROS biological drugs.

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Investigating the photodynamic behavior of azidobenzoic acid crystals

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In the present study, we are investigating the photodynamic behavior of the crystals of 3-azidobenzoic acid, 4-azidobenzoic acid and 2-azidobenzoicacid. Our objective is to understand the photodynamic behavior of the above mentioned azidobenzoic acid crystals and to correlate how gas release affects the crystal lattices.

For the study, 3-azidobenzoic acid crystals were grown separately in methanol: acetone (1:1) mixture and in ethyl acetate: acetone (1:1) mixture. Upon irradiating the crystals grown in the first solvent mixture with visible light, we observed that the crystals were turning yellow, and the color lines appeared through the vertical direction of the crystal. The crystals grown in the second solvent mixture twisted while turning yellow upon irradiation with visible light. X-ray crystallography was performed for these crystals, and we confirmed that we have the similar crystal packing pattern as the already published one. From the crystal packing pattern, we identified the strongest intermolecular interaction (79.4 kJ/ mol) and the weaker intermolecular interactions (5.8 – 11.4 kJ/ mol). In addition to that we figured out from face indexing that the color line appearing pattern through the vertical direction is possible on 001 face, since we have the shortest distance (3.712 Å) between the adjacent azide groups through that direction.

4-azidobenzoic crystals were grown in methanol: dichloromethane (1:1). Upon irradiating the crystals with visible light, we observed the crystals change their color into orange while jumping. In this case the color lines appeared approximately 43.43 degrees to the long axis. Here we did the force field calculations on the already published crystal structure and we identified the strongest intermolecular interaction (96.2 kJ/ mol) and the weaker intermolecular interactions (13.2 – 21.5 kJ/ mol). As future works, we need to do the face indexing to understand the color changing pattern. The thickness of the crystals must be important for their ability to bend or coil.

Batch vs. Flow Photochemistry of Flavanones

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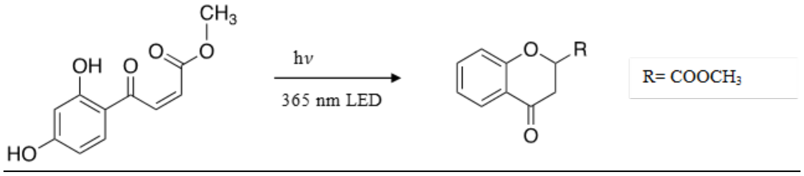
The integration of photochemistry with flow chemistry represents a powerful synergy that holds immense importance in the field of synthetic chemistry. Flow photochemistry combines the unique benefits of photochemical reactions with the efficiency and control offered by continuous flow systems. This innovative approach not only enables the development of new tools for synthetic applications but also paves the way for sustainable and environmentally friendly synthesis. By harnessing the energy of light, flow photochemistry offers precise control over reaction parameters, such as light intensity and exposure time, resulting in enhanced selectivity and yield. Moreover, the continuous flow setup allows for the efficient utilization of reagents and catalysts, minimizing waste generation and promoting cleaner processes. As a result, flow photochemistry emerges as a promising avenue for advancing synthetic methodologies, fostering the development of greener and more sustainable chemical processes.

In this study, we have demonstrated the remarkable capability of chalcone derivatives to undergo selective conversion into the corresponding flavanones utilizing visible light. The reactivity of chalcone, however, is highly dependent on concentration, necessitating a strategic approach to ensure the formation of photoproducts in excellent yields. To address this, we have implemented flow chemistry techniques, which have proven to be instrumental in achieving both selectivity and high yields consistently. By employing wavelength selective batch and flow photochemistry, we have been able to meticulously compare the selectivity and yields of the products. Moreover, the characterization of these products has been accomplished using Nuclear Magnetic Resonance spectroscopy (NMR), facilitating a comprehensive understanding of their chemical properties.



Elucidating the Mechanism and Understanding the Photochemical Behavior of (1-azidoethene-1,2-diyl)dibenzene and 2,3-Diphenyl-2H-azirine

Katrina Sumarli, Dinindu Mendis, Katrin Vilinsky, Jeanette A. Krause, Bruce Ault, Anna Gudmundsdottir*

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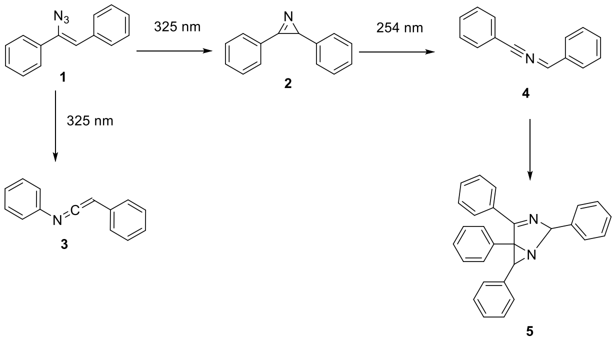
Herein we report on the photoreactivity and photodynamic behavior of (1-azidoethene-1,2-diyl)dibenzene **(1)** and 2,3-diphenyl-2H-azirine **(2)**. We used cryogenic matrices and laser flash photolysis to identify the reactive intermediates formed upon exposing **(1)** and **(2)** to light. In more details, irradiation of **(1)** with 325 nm laser at cryogenic argon matrices results in formation of azirine **(2)** and ketenimine **(3)**, whereas irradiation of **(1)** with 254 nm resulted in formation of more ketenimine **(3)** and ylide **(4)**. In contrast, laser flash photolysis of **(1)** in acetonitrile showed formation of triplet vinylnitrene **(^{3}1N)**. Photolysis of **(2)** in solution results in [3+2] cycloaddition to yield 2,4,5,6-Tetraphenyl-1,3-diaza-bicyclo[3.1.0]hex-3-ene **(5)**. Interestingly, upon irradiations the shape of the crystals **(2)** changed significantly, from needles to spherical crystals. We will discuss possible explanation for the photodynamic behavior of **(2)**.



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Elucidating the Wavelength Dependent Photochemistry of (1-azidovinyl)benzene and 2,3-diphenyl-2H-azirine

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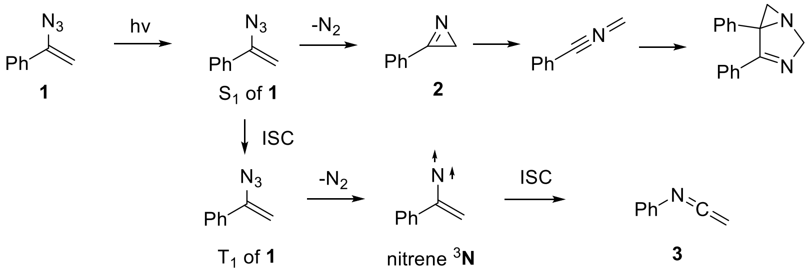
Wavelength dependent photochemistry is a way of forming distinct products from the same starting material by using different wavelength of light. In this work we studied the photochemistry of styrene azide (**1**) in solution and cryogenic matrices as a function of irradiation wavelength. Irradiation of **1** with light above 300 nm at cryogenic argon matrices and glassy mTHF matrices results in formation of azirine **2** and ketenimine **3**. In contrast, irradiation of **1** with light below 300 nm in cryogenic matrices resulted in formation of more ketenimine **3**. Furthermore, azirine **2** reacted further with short wavelength irradiation to form ylide **4**. At ambient temperature irradiation of **1** in argon- or oxygen saturated solution gave azirine **2**. Ultra-fast transient spectroscopy with 340 nm laser made it possible to detect the triplet excited state of ^{3}**1N** (l$_{max}$ ~ 474 nm, t = 608 ps). We will present and discuss the mechanism for the observed photoreactivity of **1** in solution and cryogenic matrices and support it with DFT calculations.



Exploring the Photodynamics of Pyrazolylphenyl Azides (PZA)

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Herein we present the photodynamic behavior of 1-(2-azidophenyl)-3,5-dimethylpyrazole (**1**) in crystals. The photochemistry of **1** in solution and in the solid-state has been reported previously.[1] Upon irradiation in solution **1** forms a singlet arylnitrene that cyclizes to 1,3-dimethylpyrazolo[1,2-a]benzotriazole. Furthermore, the singlet arylnitrene also intersystem crosses to its triplet configuration, whihc abstracts a hydrogen from a methyl group to form 1-methylpyrazole[1,2-a]quinozaline. We studied the solid-state photoreactivity by irradiating the crystalline **1** which yielded 1-methylpyrazole[1,2-a]quinozaline but at low conversion. We investigated the solid-state reaction mechanism of **1** by performing laser flash photolysis on the crystals to identify the intermediates formed within the crystal lattice upon exciation.
In addition, we showed with digital microscopy that irradiation of yellow needles of **1** crack both vertically and horizontally across the crystals surface, presumably due to product formation and release of N_2 gas within the crystals lattice. We used force field calculations and SEM images to attempt to correlate the photodynamic behavior with the crystal lattice of **1**.

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Exploring the photodynamic of 4-azido-2,6-dibromo phenol

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Crystals can show interesting photodynamic behavior upon excitation, the crystals can jump, split and fracture, and thus they turn light energy into motions. We prepared 4-azido-2,6-dibromophenol (1) is synthesized and grew single crystals from a mixture of ethanol and hexane. The crystals are formed as sheet. Within 15 minutes of irradiation with visible light the crystals first bend and broke and then burst into smaller pieces. To explain the photodynamic behavior of the crystals, we obtained its crystal structure. The force field calculations show that the crystal lattice has the strongest intermolecular bond due to π-π stacking of the benzene rings. In contrast the weakest bond is between bromine atoms. We will index the crystals so we can correlate whether the crystals break at the weakest interactions.

Solid-state rearrangement of 6,7-Dimethyl-2,3-Dicyano-1,4-Naphthoquinone

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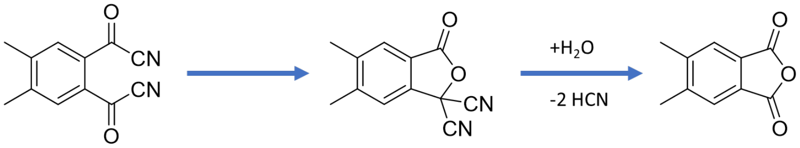
Reaction scheme:



Scheme 1.

The quest for environmentally benign chemistry has rekindled interest in solid state chemistry, that does not need solvents. We discovered that in the solid-state 6,7-dimethyl-2,3-dicyano-1,4-naphthoquinone rearrangement into 5,6-dimethyl-2-benzofuran-1,3-dione as shown in Scheme 1. Interestingly, the solid-state rearrangement of the 6,7-dimethyl-2,3-dicyano-1,4-naphthoquinone into 5,6-dimethyl-2-benzofuran-1,3-dione takes place without external activators. We will discuss a plausible mechanism for the rearrangement.

Crystal Engineering of Diboronic Acids Building Blocks for Assembly: Modularity in Organic Solid State

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Boronic acids are versatile building blocks for the construction of supramolecular architectures (e.g., saccharide sensors, pharmaceutics, porous, and photoactive solids.[1,2] This work examined the systematic study on the self-assembly of diboronic acids (1,3-benzenediboronic acid: **1,3-bdba**; 1,4-benzenediboronic acid: **1,4-bdba**; 4,4'- biphenyldibononic acid: **4,4'-bphdba**) and bipyridines (1,2-bis(4-pyridyl)ethane: **bpeta**; 1,2-bis(4-pyridyl)ethylene: **bpe**) in the organic solid state. Specifically, we demonstrate how subtle changes to the constituent components lead to broad diversification of supramolecular architectures and crystalline motifs of diboronic acids through conformational changes in the $B(OH)_2$ groups. The cocrystals comprise 1D, 2D, and 3D hydrogen-bonded frameworks with components that display reactivities upon cocrystal formation and within the solids. Our study involving [2 + 2] photodimerization in the solid state by Single-Crystal-to-Single-Crystal (SCSC) transformation and *in situ* linker reaction.[3]

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Photocycloadditions in Ionic Cocrystals: Case of a Boronic Acid

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The field of crystal engineering allows chemists to control properties of organic solid-state materials with the aim to develop functional materials. As part of our efforts to develop organic crystals that exhibit controlled photoreactivity, we describe here the development of an ionic cocrystal (ICC) that supports a [2+2] photocycloaddition reaction. Cocrystals are multicomponent solids that can provide an ability to integrate organic functional groups into organic solids in a highly modular way. Specifically, $[(\textbf{4-apba})_3(\textbf{bpeH})^+_4(\textbf{Cl})^-_8(\textbf{H}_2\textbf{O})_{7.5}]$ (where: **4-apba** = 4-aminophenylboronic acid) is characterized by single-crystal X-ray diffraction (**Figure 1**). The crystal lattice shows two different layers: one layer includes molecules of **4-apba**, $\textbf{H}_2\textbf{O}$ and $\textbf{Cl}^-$ ions and the second layer consists of monoprotonated $\textbf{bpeH}^+$ molecules (**bpe** = 1,2-Di(4-pyridyl)ethylene). The photocycloaddition occurs within the second layer A discussion on the application of ICCs to control reactivity in the solid state is also presented.

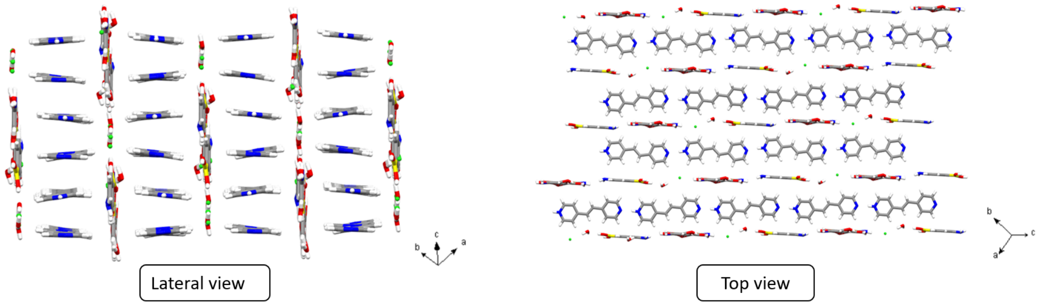

Figure 1. Layers of **4-apba**, $\textbf{H}_2\textbf{O}$ and $\textbf{Cl}^-$ ions orthogonal to π-stacked columns.

Crystal Engineering of Pharmaceutical Cocrystals with Alkenes: 2,4-Pyridinedicarboxylic acid as a Coformer with *trans*-Bis(pyridyl)ethylenes

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Materials designed through crystal engineering experience found applicability in areas such as pharmaceutics, energy storage, electronics, and catalysis. Cocrystals are single-phased crystalline solids comprised of two or more molecular and/or ionic components in a stoichiometric ratio. When one of these components is an active pharmaceutical ingredient (API), the solid is regarded as a pharmaceutical cocrystal. Our group has reported on an orange cocrystal of acetaminophen and 2,4-pyridinedicarboxylic acid (PDA). PDA serves as a zwitterion in the solid. Herein, we report pharmaceutical cocrystals of PDA with a series of *trans*-bis(*n*-pyridyl)ethylenes (where: $n = 2, 3$, or 4). The structures were characterized using powder X-ray diffraction (PXRD), single crystal X-ray diffraction (SCXRD) and Fourier transform infrared spectroscopy (FTIR). A main focus is the design of pharmaceutical cocrystals that exhibit solid-state photoreactivity. We are currently evaluating the physicochemical and pharmacokinetic properties of the solid forms.

Abstract

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Eumelanin is a dark, abundant mammalian pigment that acts as protection against ultraviolet radiation. It is the most extensively studied type of melanin, however, its secondary structure is still unknown. Eumelanin is polymerized from 5,6-dihydroxyindole (DHI) and 5,6- dihydroxyindole carboxylic acid (DHICA). One of eumelanin's most interesting characteristics is its stable, intrinsic radical population. These radicals play an important role in quenching reactive oxygen species and chelating toxic heavy metal ions in the body. It has been hypothesized that the source of these radicals is the comproportionation equilibrium between DHI and its oxidized form 5,6-indolequinone (IQ), forming the semiquinone radical (SQ). Direct study of this equilibrium is hindered due to the rapid oxidation and melanization of IQ in solution. In this study, protected monomers of DHI (DHI-Me) and IQ (IQ-Me) were utilized to stop polymerization and directly observe the radical formation. Formation of the radical species is examined via stabilization of the product (SQ-Me) of the comproportionation equilibria between IQ-Me and DHI-Me with zinc metal ions. Additionally, characteristics of IQ-Me in cyclohexane were studied. IQ is thought to associate with itself via hydrogen bonding in cyclohexane, which leads to proton-coupled electron transfer and disproportionation to SQ-Me and NQ-Me. This disproportionation is confirmed through two methods that inhibit IQ-Me's self-association: N-methylation to block the hydrogen bond donor of IQ-Me, and pyridine (Py) addition as a more favorable hydrogen bond acceptor than IQ. Both equilibria give insight into how eumelanin produces a stable radical population.