24th Inter-American Photochemical Society Meeting

January 1-4, 2015, Sarasota, Florida
We gratefully thank all our sponsors for their generous support for this conference!

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The Nick Turro Award

November 24, 2014

Dear Friends, Colleagues, Students and Admirers of Nicholas J. Turro:

Professor Nick Turro passed away on this day two years ago. As Nick’s friends / colleagues / students / admirers we have often reminisced about him and the impact he has had on our lives through his groundbreaking scholarship, his impassioned teaching, and his steadfast mentorship. Nick touched our lives in various ways and played a seminal role in supporting us in our endeavors, regardless of disciplinary emphasis or career path. He was a consummate teacher-scholar. He was a caring mentor who always wished success for his students and colleagues and cared about their careers. To pass Nick’s legacy to future generations of scientists, the Inter-American Photochemical Society has graciously agreed to consider a “Nicholas J. Turro award” if we are able to raise enough capital to establish a memorial fund in his honor. In this context we are writing this mail and request you to consider contributing to this fund. Donations can be made at http://www.i-aps.org/turrofund/

Keeping in mind all of Nick Turro’s characteristics that exemplified his indomitable scientific spirit, the award will honor someone who has not only made seminal contributions to the broadly defined area of photochemical sciences, but who also played the important role of mentor in helping others succeed. Many of us are present at this year’s I-APS meeting and if you have any questions or suggestions please feel free to talk to us.

Sincerely,

On behalf of I-APS: Malcolm D. E. Forbes
24th Inter-American Photochemical Society Meeting
Lido Beach Resort, Sarasota FL
January 1-4, 2015

Thursday, January 1, 2015
Registration
5:00 – 7:00 pm

Opening Comments from the Organizers,
Clemens Burda & J. Sivaguru
7:00 – 7:05 pm

Session 1. Emerging Investigators Symposium
Session Chair: Malcolm D. E. Forbes, University of North Carolina at Chapel Hill
7:05 – 9:20 pm

1. Ryan McCulla, St. Louis University
Title: The Role of Electron Transfer in the Oxidation of Thiols by Photoactivatable Atomic Oxygen Precursors.
7:05 – 7:35 pm

2. David Nicewicz, University of North Carolina at Chapel Hill
Title: Photophysical Studies on the Photoredox Catalysis of Alkene Anti-Markovnikov Hydrofunctionalization Reactions
7:40 – 8:10 pm

3. Mahesh Hariharan, IISER, India
Title: Strategies to Reduce the Rate of Charge Recombination
8:15 – 8:45 pm

4. Barry Dunietz, Kent State University
Title: Photoinduced Electron transfer through Molecular-resolved Interfaces: Insight by ab-initio Modeling.
8:50 – 9:20 pm

Reception and poster session, Sunset Lounge, Lido Beach Resort
9:20 – 11:30 pm

Full listing of poster abstracts available at http://i-aps.org
Friday, January 2, 2015

Continental Breakfast, Lido Beach Grill and Lounge  7:30 – 8:30 am

Session 2. Modern Molecular Photochemistry  8:30 – 10:10 am
Session Chair: Jack Saltiel, Florida State University

5. Igor Alabugin, Florida State University  8:30 – 9:00 am
Title: Alkyne photochemistry: from DNA cleavage to stereoelectronics

6. John Porco, Boston University  9:05 – 9:35 am
Title: Chemical Synthesis and Biological Studies of Antitumor Natural Products

7. Anna D. Gudmundsdottir, University of Cincinnati  9:40 – 10:10 am
Title: Towards understanding the unique reactivity of triplet vinyl nitrenes

Coffee Break  10:10 – 10:30 am

Session 3. Application of Photochemistry and Photophysics  10:30 – 12:25 pm
Session Chair: Jack Saltiel, Florida State University

2014 I-APS Fellow Award  10:30 – 10:35 am

8. Richard Givens, University of Kansas  10:35 – 11:15 am
Title: Spatiotemporal Control of Biological Reactions: Applications of Excited State Chemistry

9. David Whitten, University of New Mexico  11:20 – 11:50 am
Title: Biosensing with Charged Phenylene Ethynylene Oligomers

10. Alexander Greer, CUNY, New York  11:55 – 12:25 pm
Title: Phase Separation of Singlet Oxygen with Compartmented Sensitizers: Aspects Bordering on Photodynamic Therapy and Water Disinfection

Lunch  12:25 – 2:00 pm

Session 4. Supramolecular and Nanoscale Photochemistry  2:00 – 3:30 pm
Session Chair: Fred Lewis, Northwestern University

11. Linda Shimizu, University of South Carolina  2:00 – 2:30 pm
Title: Functional Materials from Self-Assembled Bis-Urea Macrocycles
12. Cornelia Bohne, University of Victoria, Canada  
Title: Bile Salt Aggregates as Adaptable Host Systems  
2:35 – 3:05 pm

13. 2014 Gerhard L. Closs Student Award: Albert King, 
Ohio University, Supervisor: Jeffery Rack  
Title: Investigating Photoisomerization Mechanisms in Ru(II) bis-Sulfoxides  
3:10 – 3:30 pm

Coffee Break  
3:30 – 3:50 pm

Session 5: Photochemistry and photophysics of molecules and materials  
Session Chair: Fred Lewis, Northwestern University  
3:50 – 5:05 pm

2013 I-APS Fellow Award  
14. Frank Quina, University of São Paulo  
Title: Photoprocesses of Natural Plant Pigments: The Anthocyanins  
3:55 – 4:35 pm

15. Elizabeth Harbron, College of William and Mary  
Title: Fluorescence Modulation in Conjugated Polymer Nanoparticles  
4:35 – 5:05 pm

Dinner  
5:05 – 7:30 pm

Session 6. Self-assembly and bio-applications of Light Initiated Processes  
Session Chair: James K. McCusker, Michigan State University  
7:30 – 9:10 pm

16. Bruce Armitage, Carnegie Mellon University  
Title: Enlightenment: Bright Fluorescent DNA Nanostructures for Bio-imaging and Detection  
7:30 – 8:00 pm

17. Steffen Jockusch, Columbia University  
Title: Photostabilization of Cyanine Dyes as Fluorophores for Single Molecule Spectroscopy  
8:05 – 8:35 pm

18. Belinda Heyne, University of Calgary  
Title: Directing the Self-Assembly of Cationic Dyes in Aqueous Solution  
8:40 – 9:10 pm

Poster Session, Sunset Lounge, Lido Beach Resort  
Full listing of poster abstracts available at http://i-aps.org  
9:10 – 11:30 pm
### Saturday, January 3, 2015

**Continental Breakfast, Lido Beach Grill and Lounge**  
7:30 – 8:30 am

**Session 7. Excited State Dynamics and Photochemistry**  
Session Chair: Felix Castellano, North Carolina State University  
8:30 – 10:10 am

**19. Gerald Meyer**, University of North Carolina at Chapel Hill  
*Title*: Do Atomistic Changes to Molecular Sensitizers Influence Interfacial Electron Transfer in Dye-Sensitized Solar Cells?  
8:30 – 9:00 am

**20. Jeffery Rack**, Ohio University  
*Title*: Dynamics and Isomerization in Photochromic Ruthenium Sulfoxide Complexes  
9:05 – 9:35 am

**21. Daniel E. Falvey**, University of Maryland  
*Title*: Applications of Photoinduced Electron Transfer to the Release of Stable Molecules  
9:40 – 10:10 am

**Coffee Break**  
10:10 – 10:30 am

**Session 8. Light Driven Processes at Interfaces**  
Session Chair: Felix Castellano, North Carolina State University  
10:30 – 12:15 pm

**The 2014 George S. Hammond Award**  
10:30 – 10:35 am

**22. Josef Michl**, University of Colorado  
*Title*: Singlet Fission: A Search for Chromophores and Their Optimal Coupling  
10:35 – 11:15 am

**23. Gregory Scholes**, Princeton University  
*Title*: Algae switch excitons on and off in light harvesting  
11:20 – 11:50 am

**24. 2014 Gerhard L. Closs Student Award: Elango Kumarasamy**,  
North Dakota State University, Supervisor: J. Sivaguru  
*Title*: Tale of Twisted Molecules: Stereospecific Phototransformations of Atropisomeric Maleimides  
11:55 -12:15 pm

**Lunch**  
12:20 – 2:00 pm

**Business Meeting**  
1:30 – 1:55 pm

**Session 9. Energy and Charge Transfer Phenomenon in Light Initiated Processes**  
Session Chair: Kirk Schanze, University of Florida  
2:00 – 3:35 pm

**2014 I-APS Award in Photochemistry**  
2:00 – 2:05 pm

**25. Claudia Turro**, Ohio State University  
*Title*: Excited States of Inorganic Complexes for Applications in Biology and Solar Energy  
2:05 – 2:45 pm
2014 I-APS Young Investigator Award
26. Joel Rosenthal, University of Delaware
   Title: Development and Spectroscopic Interrogation of New Catalyst
   Materials and Light Harvesting Assemblies for the Conversion of
   Carbon Dioxide to Solar Fuels

Coffee Break

Session 10. Emerging investigators award symposium
Session Chair: Kirk Schanze, University of Florida

2014 Giuseppe Cilento Award
27. Denis Fuentealba, University of Chile
   Title: Towards the Use of Biosupramolecular Assemblies as Carriers and
   Enhancers of Drug Photoactivity

Banquet at Tommy Bahama’s

The banquet site is located at 300 John Ringling Blvd. It is a fifteen-minute walk from the hotel,
adjacent to St. Armand’s Circle. A map to the restaurant is included at the back of the program.

The menu is Caribbean-style buffet and there will be vegetarian options. There will be an open
bar from 6:00-8:00 pm, and a cash bar thereafter.
**Sunday, January 4, 2015**

*Continental Breakfast, Lido Beach Grill and Lounge*  
7:30 – 8:30 am

**Session 11. Frontiers in Photochemical Research**  
*Session Chair: Clifford Kubiak, University of California San Diego.*  
8:30 – 10:10 am

28. **Mathias Weber**, University of Colorado  
*Title: Photodissociation of Mass-Selected Ions - Spectroscopy and Fragmentation Channels*  
8:30 – 9:00 am

29. **Elena Galoppini**, Rutgers University  
*Title: Tuning Energy Level Alignment At Organic/Semiconductor Interfaces Using A Built-In Dipole In Chromophore-Bridge-Anchor Compounds*  
9:05 – 9:35 am

30. **Ksenija Glusac**, Bowling Green State University  
*Title: In Search for Organic Catalytic Motifs for Solar Water Splitting*  
9:40 – 10:10 am

**Coffee Break**  
10:10 – 10:30 am

**Session 12. Young Investigators Symposium**  
*Session Chair: Clifford Kubiak, University of California San Diego.*  
10:00 – 11:45 am

31. **Luis Campos**, Columbia University  
*Title: Exciting Thiophene Rust*  
10:30 – 11:00 am

32. **Mahesh Pattabiraman**, University of Nebraska, Kearney.  
*Title: Cavitand mediated supramolecular control of bimolecular photochemical reactions*  
11:05 – 11:35 am

**Closing Remarks**  
11:35 – 11:45 am
The Role of Electron Transfer in the Oxidation of Thiols by Photoactivatable Atomic Oxygen Precursors

Author(s): Miao Zhang, Sara M. Baumann, and Ryan D. McCulla*, Dept. of Chemistry, St. Louis University

Abstract: The oxidation of the thiol group of cysteine is used by many redox-regulated proteins to respond to oxidative stress within cells. The oxidation of these proteins by reactive oxygen species initiates signaling cascades that lead to the regulation of metabolic processes. However, controlling the oxidation of state of specific proteins within a cell is a difficult challenge. Recently, we determined that the photodeoxygenation of an aqueous-soluble derivative of dibenzothiophene S-oxide (DBTO) was able to selectively oxidize the critical cysteine residue of the plant enzyme adenosine-5'-phosphosulfate (APS) kinase. This led us to investigate the mechanism of this oxidation. The photodeoxygenation of DBTO has been shown to occur by two distinct mechanisms. The first being a unimolecular deoxygenation leading to the corresponding sulfide and an oxidant posited as ground state atomic oxygen [O(3P)]. The second being a photoinduced electron transfer from a donor to DBTO leading to a hydroxysulfuranyl radical, which eventually results in the release of hydroxyl radical. Potentially, a thiol could be oxidized by either the release of O(3P) or by acting as an electron donor in the bimolecular photoreduction of DBTO. We have investigated the relative importance of both of these possible mechanisms for the oxidation of thiols.
Photophysical Studies on the Photoredox Catalysis of Alkene Anti-Markovnikov Hydrofunctionalization Reactions

Author(s): Nathan A. Romero and David A. Nicewicz

Department of Chemistry, University of North Carolina at Chapel Hill

Abstract: In the past several years, acridinium photooxidants have been employed in numerous valuable catalytic organic transformations. In particular, my laboratory has studied the use of these catalysts in anti-Markovnikov selective reactions of simple acids with alkenes. This lecture will discuss our efforts to understand the mechanism of this class of transformations using a variety of analytical techniques such as steady state and transient absorption and emission spectroscopies.
Strategies to Reduce the Rate of Charge Recombination

Author(s): Mahesh Hariharan*
Indian Institute of Science Education and Research Thiruvananthapuram, India.

Abstract: Long-lived charge separated states in crowded environment is vital for efficient artificial photosynthesis and photofunctional device applications. The hetero-junctions (HJs) in organic photovoltaics act as “transport highways” for the charge carriers to the respective electrodes. Careful organization of molecular architectures at the HJs in organic solar cells can dictate the lifetime of the excitons generated. Supramolecular organization relies on interplay between various inter/intra molecular interactions such as multipole electrostatic interactions, dispersion effects, p-p interactions, hydrogen bonding etc. that determines electronic and optical properties of the materials. Myriads of models are proposed to achieve better exciton diffusion lengths and charge carrier mobilities that govern the device efficiency. Mullen and co-workers demonstrated that compromise and dominance of various inter and intra molecular interactions operating in donor (D) - acceptor (A) self-assembled systems could generate segregated D-D/A-A stacks, D-A interdigitating stacks etc. Aida and co-workers demonstrated the photochemical generation of spatially separated charge carriers through co-axial nanotubular arrangement of D and A. Wasielewski et al. extended the survival time of charge separated states through self-assembled D-A tetramers, trefoils, dimers and hydrogen bonded foldamers. Recent report from our group demonstrated the importance of supramolecular vesicular scaffold in reducing the rate of charge recombination. Recently we were successful in synthesizing near-orthogonal D-A columnar stacks in CHCl3 to form spherical aggregates that show 10000-fold enhancement in the survival time of the charge transfer intermediates when compared to unstacked D-A system. The following scheme represents the different models of D-A self-assembled systems reported and under investigation.

References:
Photoinduced Electron transfer through Molecular-resolved Interfaces: Insight by ab-initio Modeling

Author(s): Barry D. Dunietz*
Department of Chemistry, Kent State University

Abstract: Photoinduced charge transfer processes through molecular interfaces are ubiquitous as they play a crucial role in determining functionality of biological systems and in enabling energy conversion applications. In this talk I will focus on our modeling of charge transfer processes between donor and acceptor organic semiconductors materials, where the electrostatic environment stabilizes charge separated states. We demonstrate our ability to provide insight to advance the design of the materials and the success in addressing relevant key challenges. Importantly I will introduce our parameter-free and fully quantum mechanical treatment of photo induced electron transfer kinetics in experimentally measured organic semi-conductor materials. The limitations of widely implemented alternative treatments that follow the semi-classical Marcus picture of charge transfer will be pointed out.
5 Alkyne photochemistry: from DNA cleavage to stereoelectronics

Author(s): Igor Alabugin*
Department of Chemistry, Florida State University

Abstract: Synthetic potential of alkynes, a spring-loaded combination of orthogonal functional groups, is amplified further by photochemical excitation. We will illustrate how alkyne photochemistry can be controlled by an interplay of aromaticity and antiaromaticity, gated by protonation, and fine-tuned by stereoelectronics. The implications range from light-activated DNA cleavage to incorporation of alkynes into useful cascade transformations.

6 Chemical Synthesis and Biological Studies of Antitumor Natural Products

Author(s): John A. Porco, Jr.*
Boston University

Abstract: We will describe development of a unified, biomimetic approach to the aglain-forbaglin-rocaaglamide classes of natural products. This approach involves photogeneration of oxidopyryliums via excited-state intramolecular proton transfer (ESIPT) of 3-hydroxyflavones followed by [3+2] dipolar cycloaddition to assemble the aglain core. An alpha-ketol rearrangement was employed to transform the aglain core to the cyclopenta[b,c]benzofuran (rocaglate) framework. Using ESIPT photocycloaddition, approaches will be outlined to synthesize the natural products methyl rocaglate, aglaiastatin, and silvestrol, a natural product derived from a plant found in Malaysia which is being developed as a treatment for acute lymphoblastic leukemia. Finally, the synthesis of the cyclopenta-[b,c]benzopyran natural products ponapensin and elliptifoline will be outlined. These studies determined that (+)-ponapensin and (-)-elliptifoline are enantiomeric to (-)-methyl rocaglate thereby suggesting a hypothesis for their biosyntheses.
Towards Understanding the Unique Reactivity of Triplet Vinylnitrenes

Author(s): Sujan Sarkar, Asako Sawai, Kousei Kanahara, Manabu Abe, Curt Wentrup, and Anna Gudmundsdottir*

School of Chemistry and Molecular Biosciences, The University of Queensland, Department of Chemistry, Hiroshima University, Department of Chemistry University of Cincinnati.

Abstract: Photolysis of 2-azido-1,4-naphthoquinone (1) in argon matrices at 8 K results in the corresponding triplet vinylnitrene 2 that was detected directly by IR spectroscopy. Vinylnitrene 2 is stable in argon matrices but upon further irradiation it forms 2-cyanonindane-1,3-dione (3). Similarly, irradiation of azide 1 in 2-methylietrahydrofuran matrices at 5 K resulted in the ESR spectrum of vinylnitrene 2, which is stable up to at least 100 K. The zero-field splitting parameters for nitrene 2, D/\hbar c = 0.7292 cm\(^{-1}\) and E/\hbar c = 0.0048 cm\(^{-1}\), verify that it has significant 1,3-biradical character. Vinylnitrene 2 is also observed directly in solution at ambient temperature with laser flash photolysis of 1. Density functional theory (DFT) calculations support the characterization of vinylnitrene 2 and the proposed mechanism for its formation. The reactivity of various other triplet vinylnitrenes will be discussed as well. Because vinylnitrene 2 is relatively stable, it has potential use as a building-block for high-spin assemblies.
8 Spatiotemporal Control of Biological Reactions: Applications of Excited State Chemistry

Author(s): Richard S. Givens*
Department of Chemistry, The University of Kansas

Abstract: Cages and Phototriggers are covalently attached substrates or reagents to photoremoveable chromophores thus rendering the substrate inactive. Termed photoremoveable protecting groups (PPGs), these chromophores have become the object of intense interest as initiators of complex biochemical and biological processes, e.g., enzyme catalysis, signal transmission, muscle contraction, and cell growth, a tool for probing the “triggering”, regulation, or arrest of a biological process at the molecular level. Significant advantages gained by photoinitiated processes are flexibility and precise control of three critical mechanistic parameters: temporal control – through design of ultra-fast ps to ns initiation rates; spatial control – through focused light sources to <25 mm; control of concentration – through manipulation of light intensity. Notwithstanding these advantages, the photochemical reactions of the protecting group bear significant consideration because fragmentation-release processes invariably complicate or compete with the reaction under study. The discharge of spent chromophore may be adversely influenced by solvent and pH, competing quenchers or O₂ and chromophores generated along with an array of interfering byproducts. The family of p-hydroxyphenacyl (pHP) protecting is largely devoid of, impervious to, or circumvents these limitations and therefore is especially well-suited for many biological applications. Advantages are accrued from the higher efficiencies, nearly quantitative chemical yields, rapid release rates, and 2PE capability. These features have led several other investigations and collaborations to probe mechanistic questions at the molecular level through determination of rate constants, activation parameters (Gap protein catalyzed GTP hydrolysis), neuronal transmission and neuron pruning (auditory signaling), and selective agonist-antagonist response (dopamine release). The chemistry, photoreactions and representative applications will be presented.

9 Biosensing with Charged Phenylene Ethynylene Oligomers

Author(s): David G. Whitten,* Eric H. Hill, Patrick Donabedian, Yue Zhang, Dominic Sanchez, Deborah G. Evans and Eva Y. Chi
Center for Biomedical Engineering
University of New Mexico Albuquerque, New Mexico, USA
Abstract: We have recently examined several complexes involving cationic or anionic \( \sigma \)-phenylene ethynylene oligomers (OPE) and oppositely charged molecules such as detergents, phospholipids, and choline esters of alkanolic acids. OPEs functionalized with carboxyl ester terminal groups render the oligomers non-fluorescent in aqueous solution but strongly fluorescent when self-assembled into a complex. UV-Vis Absorption and fluorescence spectroscopy is used to monitor enzyme activity through the photophysical changes that occur when the self-assembled complex is dissociated. Selectivity for specific enzymes is achieved by choosing targeted charged molecules that are complexed with the OPEs which act as substrates to the enzyme. Among those studied are various phospholipases and cholinesterases. We have also examined the sensitivity of the complex to agents which inhibit the activity of the enzymes and potential ways to utilize this for detection of toxins.
Phase Separation of Singlet Oxygen with Compartmented Sensitizers: Aspects Bordering on Photodynamic Therapy and Water Disinfection

Author(s): Niluksha Walalawela, David Aebisher, Dorota Bartusik, Yang Liu, Yuanyuan Zhao, Mark Barahman, QianFeng Xu, Alan M. Lyons, and Alexander Greer*

Department of Chemistry, Brooklyn College, City University of New York
Department of Chemistry, College of Staten Island, City University of New York.

Abstract: We have developed a phase-separated approach to photooxidations that employs a liquid at a solid/liquid or solid/gas/liquid interface using physical-organic techniques. These biphasic and triphasic photosensitizer systems contain regions that are controllably dry, partly wetted, and/or fully wetted. Part of the talk will be focused on a superhydrophobic surface synthesized by partially embedding silicon phthalocyanine sensitizing particles to specific locations on polydimethylsiloxane (PDMS) posts printed in a square array. In the presence of red light and oxygen, singlet oxygen is formed on the superhydrophobic surface and reacts with an anthracene compound within a freestanding water droplet to produce an endoperoxide. The results indicate that the superhydrophobic sensitizer surface offers a unique system to study singlet oxygen transfer routes where a balance of gas and liquid contributions of singlet oxygen is tunable within the same superhydrophobic surface. Two singlet oxygen microphotoreactor devices will also be described. In all, these systems physically isolate the photosensitizer from the solution which may be of practical importance for delivering singlet oxygen for water purification and medical devices.
11 Functional Materials from Self-Assembled Bis-Urea Macrocycles

Author(s): Linda S. Shimizu*
Department of Chemistry and Biochemistry, University of South Carolina

Abstract: Voids, cavities, pores or channels in molecular solids, porous materials or proteins can be used to encapsulate guests and modulate their reactivity. Our group has been utilizing the high fidelity self-assembly of bis-urea macrocycles to generate porous crystalline molecular hosts that contain homogeneous 1-dimensional channels. The size, shape and interior functionality of these channels are controlled by the simple macrocyclic building block. For example, phenylethynylene bis-urea macrocycle 1 assembles into columns with internal diameters of approximately 9 Å, while the smaller benzophenone derivative 2 has accessible channels with <6.5 Å diameters and displays a room temperature stable radical upon UV-irradiation. We investigated the uptake of guests such as coumarins, chromones, acenaphthylene, and stilbenes within the channels of assembled bis-urea macrocycles to afford crystalline inclusion complexes. We examine the structure of these complexes by solid-state methods and Grand Canonical Monte Carlo simulations to predict their reactivity and understand their selectivity. Upon UV-irradiation, we observed selective photodimerization reactions for those guests predicted by our simulations to be close paired within the columns. We our currently working to refine the simulations to be able to apply these methods more broadly to predict loading and reactivity within a broader range of hosts. Our goal is to understand the factors that control reactions and diffusion within channels of assembled bis-ureas to be able to understand reactivity and ultimately to design better catalysts.
Bile Salt Aggregates as Adaptable Host Systems

Author(s): Cornelia Bohne, Mehraveh Seyedalikhani, Denis Fuentealba, Satu Strandman and X.X. (Julian) Zhu

Abstract: Bile salts are amphiphilic molecules that form aggregates in solution. The size of the aggregates continuously increases as the bile salt concentration is raised and primary aggregates formed at low concentration are incorporated into larger secondary aggregates at high concentrations. Guest molecules bind to the different types of aggregates and the structure of the guest-aggregate system is adaptable. This adaptability is explored to achieve functional systems with molecules that are not soluble in water, such as photochromic compounds. In addition, the bile salt sodium deoxycholate forms gels that are thixotropic, providing an immobilized host system that can bind small molecules. Photophysical and rheological studies were performed to characterize the gels in the absence and presence of cucurbit[6]uril as an additive. Addition of the additive led to mechanically strengthened gels, which undergo hysteresis during heating and cooling cycles.
13 Investigating Photoisomerization Mechanisms in Ru(II) bis-Sulfoxides

Author(s): Albert W. King and Jeffrey J. Rack*
Ohio University

Abstract: Photoisomerizing ruthenium polypyridyl sulfoxide complexes combine the S→O linkage isomerization observed in electrochemical studies of Ru(II) amine complexes with the well-studied photophysics of ruthenium polypyridyl structures such that charge transfer excitation in heteroleptic polypyridine chelating sulfoxides leads to isomerization. The distinct S- and O-bonded isomers exhibit substantially different spectroscopic properties and thus afford a unique opportunity to observe the consequences of strong coupling of the electronic and nuclear wavefunctions during dynamic relaxation and isomerization processes. In order to develop our understanding of the excited state processes leading to isomerization in ruthenium sulfoxide complexes, we have focused on bis-sulfoxide complexes. Specifically, we have employed pump-repump-probe femtosecond time resolved spectroscopy to monitor isomerization in S,S-bonded [Ru(bpy)2(bpSO)]2+ (bpSO is 1,2-bis(phenylsulfinyl)ethane) to observe sequential isomerizations following sequential, single photon absorption events to produce the S,O- and O,O-bonded isomers. However, subsequent to minor modification of the bpSO ligand, as in F-bpSO (1,2-bis(2-fluorophenylsulfinyl)ethane), pump-probe transient absorption reveals both S,O- and O,O-bonded photoproducts following single photon excitation of the ground state S,S-isomer. This substitution modifies the coupling of the electronic and nuclear wavefunctions to facilitate a PES which accesses both photoproduct isomers and represents a current optimization of photochromic ruthenium sulfoxide complexes.

14 Photoprocesses of Natural Plant Pigments: The Anthocyanins

Author(s): Adilson A. Freitas, Antonio L. Maçanita and Frank H. Quina*
Centro de Química Estrutural, Instituto Superior Técnico, Lisbon, Portugal
Instituto de Química, Universidade de São Paulo, Brazil

Abstract: Anthocyanins are plant pigments responsible for the red and purple colors of the majority of fruits and flowers, as well as leaves. The basic chromophore of anthocyanins is a 7-hydroxyflavylium cation, substituted with several other hydroxyl and/or methoxy groups. The reddish colors are mainly due to the free flavylium cation form, while the bluish colors are normally associated with complexes with metal ions. In the ground state, the flavylium cation undergoes hydration in aqueous solution above about pH 3 to produce a colorless hemiacetal form, which can tautomerize to the colorless Z-chalcone
that then isomerizes to the E-chalcone. In nature, the color of anthocyanins is modulated and/or stabilized by complexation with metal ions or with colorless organic molecules (copigments). In the excited state, uncomplexed anthocyanins undergo ultrafast adiabatic deprotonation (<10 ps) in aqueous solution to give the short-lived (ca. 200 ps) excited quinonoidal base. The ultrafast deprotonation of anthocyanins in anionic sodium dodecylsulfate micelles provides information on the dynamics of protons at the micellar surface. Anthocyanins complexed with organic copigments undergo deactivation (ca. 240 fs) via a low-lying charge-transfer state that is even faster than deprotonation. The colorless hydration products are photoactive in the UV; thus, the hemiacetal form of anthocyanins exhibits photochemistry typical of a chromene, while the chalcones undergo E-Z photoisomerization. These photoprocesses can all potentially contribute to the photostability of anthocyanins in fruit and flowers and to the biological role of anthocyanins in protecting leaves from excess solar radiation.
15 Fluorescence Modulation in Conjugated Polymer Nanoparticles

Author(s): Elizabeth J. Harbron*
Department of Chemistry, College of William and Mary

Abstract: Conjugated polymer nanoparticles (CPNs or Pdots) hold exceptional promise as fluorophores for sensing and imaging applications due to their intense fluorescence brightness, high photostability, and colloidal stability in water. The possible applications of CPNs can be expanded by functionalizing them with dyes that can act as fluorescence resonance energy transfer (FRET) acceptors. We functionalize CPNs with stimulus-responsive dyes, which have two distinct molecular forms, only one of which can act as a FRET acceptor. Introduction of the stimulus induces transformation of the dye, activating or deactivating CPN-to-dye FRET. Depending on the photophysical characteristics of the dye, modulation of fluorescence intensity or color is observed. The modulation of CPN fluorescence in response to metal ion, pH, and light stimuli will be presented. The amplification of the FRET signal due to the light harvesting effect of the CPNs will also be described.

16 Enlightenment: Bright Fluorescent DNA Nanostructures for Bio-imaging and Detection

Author(s): Munira Fouz, Joanna Burdynska, Subha Das, Krzysztof Matyjaszewski, and Bruce A. Armitage*
Department of Chemistry, Carnegie Mellon University

Abstract: This presentation will focus on our efforts to create bright fluorescent labels for bio-imaging and detection. Our approach relies on the use of nanostructured DNA as a scaffold on which to assemble tens, hundreds or even thousands of fluorescent dye molecules. The resulting supramolecular fluorophores offer exceptional brightness due to their high molar extinction coefficients. The DNA scaffold allows the dyes to be packed into a dense array without self-quenching and standard synthetic modifications to the DNA permit tagging of other biorecognition components, such as antibodies. These DNA “nanotags” feature efficient FRET, allowing straightforward tuning of emission wavelengths from the blue to the near IR, high stability (thermal and enzymatic) and modular assembly from commercially available components. Recent work on hybrid materials involving DNA and synthetic polymers has led to antibody imaging agents that are at least 10-fold brighter than commercially available quantum dot- and organic dye-labeled analogues.
17 Photostabilization of Cyanine Dyes as Fluorophores for Single Molecule Spectroscopy

Author(s): Steffen Jockusch*, Qinsi Zheng, and Scott C. Blanchard  
Department of Chemistry, Columbia University New York; Department of Physiology and Biophysics, Weill Medical College of Cornell University in New York

Abstract: Small-molecule organic fluorophores, such as the cyanine dye Cy5, are widely used in single-molecule and super-resolution microscopy. Because organic fluorophores are significantly smaller in size than quantum dots or the green fluorescing protein, they are less perturbing to the biological system under interrogation. However, organic fluorophores are less photostable than quantum dots. In addition, stochastic blinking, which spans from microsecond to minute timescales, reduces the number of photons emitted. It is believed that triplet state population of the fluorophore is one of the main causes or bleaching and blinking. We showed that the popular red emitting fluorophore Cy5 exhibits greatly enhanced photostability when covalently linked to stabilizers, such as cyclooctatetraene (COT), nitrobenzyl alcohol, or Trolox. We showed that the triplet state lifetime of Cy5 is significantly reduced from ~ 60 µs for unmodified Cy5 to less than 1 µs for Cy5 with covalently linked triplet state quencher COT. The length of the carbon chain linker between Cy5 and COT appears to be critical. Reactive oxygen species, such as singlet oxygen and hydroxyl radicals, are probably generated from the triplet state of the fluorophore. We showed that the reduced triplet lifetimes in Cy5 with covalently linked COT correlate well with the reduced generation of singlet oxygen and higher photostability in single molecule fluorescence measurements.

18 Directing the Self-Assembly of Cationic Dyes in Aqueous Solution

Author(s): Sara M. Mooi, Samantha N. Keller, and Belinda Heyne*  
Department of Chemistry, University of Calgary

Abstract: Understanding the contribution of external factors on the organization of molecules is key in order to further research in supramolecular photochemistry.
Countless studies involve the association of organic molecules in environments rich in ionic species, yet their contribution in molecular organization is often disregarded. In order to advance the understanding of this topic, we investigated the organization of several cationic cyanine dyes in aqueous solution encouraged by various monovalent sodium salts. Cyanine dyes were chosen due to their propensity to undergo self-organization, leading to interesting photophysical properties resulting from the formation of their dimers and higher-ordered aggregates. Moreover, the study of their aggregation is in high demand due to their diverse application range including dye-sensitized solar cells. Our results indicate that a single monovalent salt can cause different aggregation responses depending on the cyanine dye. Experimental data coupled with computational calculations reveal that not only the geometry of the dye, but also its charge location play a role in the aggregate morphology. It is thought that contact ion pair formation and effective charge screening generated within that ion pair are responsible for self-assembly. For a contact ion pair to form, the dye and the counter ion must have similar free hydration energies, or water matching affinities. Therefore, it has become clear that it is not simply an increase in ionic strength that drives the aggregation of cyanine dyes in aqueous solution, but more specifically it is the size and property of the ion used to create the phenomenon.
**19** Do Atomistic Changes to Molecular Sensitizers Influence Interfacial Electron Transfer in Dye-Sensitized Solar Cells?

**Author(s):** Kiyoshi C.D. Robson,¹ Curtis P. Berlinguette¹, Ke Hu,² and Gerald J. Meyer²,*

¹Departments of Chemistry and Chemical & Biological Engineering, The University of British Columbia, 2036 Main Mall, Vancouver, British Columbia, Canada V6T1Z1
²Department of Chemistry, University of North Carolina at Chapel Hill, CB 3290, Chapel Hill, NC 27599

**Abstract:** A series of three bis(tridentate) cycloruthenated sensitizers and two organic sensitizers were designed to examine how chalcogen atoms influence interfacial electron transfer events that occur following light absorption by the sensitizers when attached to mesoporous TiO₂ thin films immersed in CH₃CN electrolytes. Spectroelectrochemistry was used to quantify the sensitizer $S^{+}/0$ reduction potentials and the density of TiO₂ acceptor states. Pulsed light excitation of the sensitized thin films resulted in rapid excited state injection, $k_{inj} > 10^{8}$ s⁻¹. Charge recombination ($S^{+}/TiO₂(e⁻) \rightarrow S/TiO₂$) rate constants were insensitive to the identity of the sensitizers, yet the open circuit photovoltages differed significantly. Mechanistic studies revealed that after excited state injection regeneration of the oxidized sensitizer by iodide (or Co(II) compounds), were often directly correlated with the open circuit photovoltages. In one case, Lewis acid-base adduct formation between oxidized iodide and a selenium heteroatom were specifically implicated to rationalize $S/TiO₂(e⁻) + I₃⁻ \rightarrow$ charge recombination. The data indicates that the location of the chalcogen atom on the sensitizers is critically important and that high short circuit photocurrents do not necessarily imply optimal regeneration efficiency as is often assumed.

**20** Dynamics and Isomerization in Photochromic Ruthenium Sulfoxide Complexes

**Author(s):** Jeffrey J. Rack*
Department of Chemistry and Biochemistry, Ohio University

**Abstract:** Photochromic compounds are light-activated molecular switches that convert photonic energy to potential energy for specific and selective excited state bond breaking and bond making reactions. Our examination of ruthenium and osmium polypryridine complexes containing sulfoxide ligands demonstrate that S-to-O isomerization is efficient, and can occur rapidly both in the solid state and solution. Picosecond transient absorption spectroscopic data show that S-to-O isomerization time constants may be as fast as 45 ps.
Recent studies of ruthenium polypyridine complexes containing chelating sulfoxides illustrate that two different colors of light may be used to trigger between the two ground states. These results and others will be presented and discussed.

21 Applications of Photoinduced Electron Transfer to the Release of Stable Molecules

Author(s): Daniel E. Falvey*
Department of Chemistry, University of Maryland

Abstract: One of the simplest bimolecular photochemical reactions is the transfer of a single electron from one molecule to another. Over the past several decades considerable experimental and theoretical work has been devoted to understanding the features that control the rates of these processes. This presentation will focus on the application of photochemical electron transfer reactions. Experiments aimed at developing photoreleasable protecting groups that can be activated with different wavelengths of light will be discussed as well as the photochemical reduction of CO$_2$. 
Singlet Fission: A Search for Chromophores and Their Optimal Coupling

Author(s): Jin Wen, Zdenek Havlas, and Josef Michl*
Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, Prague, Czech Republic, and University of Colorado, Boulder, CO, USA.

Abstract: Singlet fission is a process in which a singlet excited chromophore transfers some of its energy to a ground state neighbor and both end up in their respective triplet states, coupled into an overall singlet. Since it is spin-allowed, singlet fission can be extremely fast even though it produces triplets from singlets, and can outcompete all other excited state processes, resulting in a 200% yield of triplets. The process is of interest for photovoltaic solar cells, where its use would increase the maximum theoretical efficiency from the Shockley-Queisser limit of about 1/3 to nearly 1/2 without increasing significantly the complexity and cost of the cell. The problem with the practical utilization of singlet fission is that the number of materials in which it is known to occur efficiently is tiny. None of the half-dozen or so that are currently known appear to be very practical, although they are useful for fundamental studies of the mechanism, which is still only poorly understood. Most are large alternant hydrocarbons such as tetracene and pentacene, or their simple derivatives such as diphenyltetracene and rubrene. We shall describe our efforts to find additional classes of compounds that show promise as efficient singlet fission sensitizers, with two goals in mind: finding materials that are sturdy enough for practical use, and finding chromophores that are small enough for high-level theoretical treatment of their dimers. The search is based on the use of first principles both (i) to find chromophores in which singlet fission would be isoergic or slightly exoergic, $E(S1), E(T2) > 2E(T1)$, and (ii) to find an optimal way of coupling two or more chromophores together. The search for new chromophores is based on the strategy of partial stabilization of a biradical to a biradicaloid, taking advantage of the old concept of captodative stabilization of radicals for moving the first absorption band to an optimal spectral region. The search for optimal coupling motifs is based on a simple model for the description of diabatic states of a dimer in which only the highest occupied and lowest unoccupied molecular orbitals on each partner are considered.
Algae switch excitons on and off in light harvesting

Author(s): Gregory D. Scholes*
Department of Chemistry, Princeton University

Abstract: Recently a remarkable variation of photosynthetic light harvesting structures, and modification of the electronic Hamiltonian underpinning their function, has been discovered for the Cryptohyceae (cryptophyte algae) (1). This incredible family of structures provides the opportunity for femtosecond studies of the role excitons play in light harvesting. The electronic coupling is controlled between the pair of bilin chromophores at the center of the cryptophyte light harvesting complexes. The most common structure appears to be the ‘closed’ structure, where the protein subunits are sandwiched together so that the central chromophores approach to within a few Ångström of each other. A drastic modification is found in the genus Hemiselmis, where a single amino acid insertion in the small alpha-subunits leads to steric clash that rotates and separates the subunits, thereby rendering the electronic coupling between the central pair of bilins very small. I will report recent studies of these light harvesting complexes using 2D electronic spectroscopy and broadband pump-probe wavepacket spectroscopy.

24  Tale of Twisted Molecules: Stereospecific Phototransformations of Atropisomeric Maleimides

Author(s): Elango Kumarasamy and J. Sivaguru*
Department of Chemistry and Biochemistry, North Dakota State University

Abstract: Asymmetric phototransformation is a powerful methodology in synthetic chemistry that allows us to access new chemotypes that are structurally complex and enriched with stereogenic centers. However, the challenge associated with controlling the excited states presents significant obstacle in developing new methodologies that will useful to organic synthesis. Recent efforts from our research group introduced new organic scaffolds viz., atropisomeric chromophores that proved to be very efficient in undergoing stereospecific phototransformations to result in products that are enantiomerically pure. This methodology widely applies to several well-known photochemical transformations such as 4π and 6π-ring closure, Norrish-Yang reactions, [2+2]-photocycloaddition reactions etc. This talk will highlight recent advances in this methodology and present the chemistry of atropisomeric maleimides as a model system. Maleimides display rich and versatile photochemistry that are used in various synthetic manipulations. Atropisomeric maleimides displayed several interesting photochemical and photophysical properties that resulted in enantiomerically and regiochemically enriched products, which will be disclosed in this presentation.

25  Excited States of Inorganic Complexes for Applications in Biology and Solar Energy

Author(s): Claudia Turro*
Department of Chemistry and Biochemistry, The Ohio State University

Abstract: Excited state processes of transition metal complexes initiated by the absorption of light have potential applications in various fields, such as photochemotherapy (PCT) and solar energy conversion. These reactions include photoinduced ligand exchange, charge transfer, photoisomerization, and energy transfer to produce 1O2. In the case of Ru(II) and Rh2(II,II) complexes, the relative energies of the metal-to-ligand charge transfer (MLCT), ligand-field (LF, metal-centered), and ligand-centered (LC) excited states play a key role in the observed reactivity. In addition, the ability of many inorganic complexes to undergo ultrafast intersystem crossing (ISC), such that ISC is faster than internal conversion (IC) and vibrational cooling (VC), provides an additional platform for the exploration to tune the reactivity upon excitation with visible light. Ruthenium(II) and dirhodium(II,II) complexes with
lowest energy LC excited states character exhibit lifetimes in the microsecond timescale and produce singlet oxygen efficiently. In some cases, photoinduced ligand exchange is also observed in water, which generates bis-aqua metal-containing species that covalently binds to DNA. In addition, the photorelease of nitrile-containing drugs from transition metal complexes has also been explored. Ultrafast and steady-state experiments, together with calculations, were conducted to provide an understanding of the excited state manifold, electronic structure, and dynamics in these systems. Experiments designed to assay the biological activity of the complexes in vitro and in cell cultures will be presented. In addition to the use of nitriles for efficient photoinduced ligand exchange, new complexes with distorted geometry around the metal center were designed. These systems exhibit lower energy LF state(s), which provides a means to photorelease strong ligands, such as pyridine, with low energy light and relatively high quantum yields. Complexes that are able to undergo multiple processes upon excitation exhibit greater phototoxicity towards cancer cells compared to those that only produce singlet oxygen or only undergo ligand exchange. The enhanced activity is attributed to the multiple reactivity of these compounds, which represents a new class of potential PCT agents whose mode of action differs from those currently in use.

26 Development and Spectroscopic Interrogation of New Catalyst Materials and Light Harvesting Assemblies for the Conversion of Carbon Dioxide to Solar Fuels

Author(s): Joel Rosenthal*
Department of Chemistry and Biochemistry, University of Delaware

Abstract: The photoelectrochemical reduction of CO₂ to CO, generates an energy rich commodity chemical that can be coupled to liquid fuel production, however this transformation has historically been a major challenge in the field of molecular energy conversion. In response to this need, we have developed several inexpensive cathode materials for CO₂ reduction. These catalyst platforms can be used in conjunction with ionic liquids and other weak organic acids to effect the electrocatalytic conversion of CO₂ to CO with high current densities at low overpotentials. The systems we will describe are selective for production of CO, and display activity levels that have historically
only been observed using precious metal catalysts. Moreover, since coupling robust electrocatalysts for CO\textsubscript{2} reduction with renewable sources of electricity is an attractive route to sustainable fuel production, we have married our catalyst systems with photoelectrochemical (PEC) assemblies that facilitate the production of solar fuels. We will show that interfacing a triple-junction amorphous silicon photovoltaic with the inexpensive cathode materials developed in our lab, enables the storage of solar energy via the energetically uphill conversion of CO\textsubscript{2} to CO. In addition to developing new inexpensive platforms for CO\textsubscript{2} reduction and solar fuel production, we have also worked to elucidate the molecular design principles that are attendant to the energy efficient activation of CO\textsubscript{2} activation. Interrogation of the pathway by which our catalyst systems activate CO\textsubscript{2} using a suite of electrochemical and spectroscopic techniques, has revealed the primary factors that drive fuel generation. Implications for the future development of efficient architectures that can promote CO\textsubscript{2} reduction with high selectivity and efficiency will be discussed.
Towards the Use of Biosupramolecular Assemblies as Carriers and Enhancers of Drug Photoactivity

**Author(s):** Karina Scholtbach\(^a\), Ítalo Venegas\(^a\), Anita Tapia\(^a\), Hery Chung\(^a\), Javiera Cáceres\(^a\), Cornelia Bohne\(^b\) and Denis Fuentealba\(^a\)*

(a) Facultad de Química, Pontificia Universidad Católica de Chile; (b) Santiago, Chile

**Abstract:** Motivated by current promising research using cucurbit[n]urils (CB\(^n\), n = 5-10) macrocycles [1-2] in biological applications, we are investigating the use of these molecules to encapsulate, transport and improve the activity of photoactive drugs. Biosupramolecular assemblies involving both a macrocycle and a protein are interesting systems since they can provide further improvement of drug photoactivity by combining concepts as encapsulation, stabilization, specificity and biocompatibility. Following initial work by other authors [3-4], we studied the formation of ternary complexes between several well-known photoactive drugs such as riboflavin, methylene blue, acridine orange, safranin and tetra(N-methylpyridinium)porphyrin, using CB\(^7\) or CB\(^8\) and different proteins. Acridine orange and the cationic porphyrin showed selective formation of drug@CB\(^n\)-protein complexes with human or bovine serum albumin, respectively (scheme 1). The studies uncovered important aspects of the binding in these ternary systems such as the importance of the drug@CB\(^n\) complex conformation, the size of the drug and CB\(^n\), and their affinity. Once the complexes were formed, the photoactivity of the drugs were studied covering different aspects of their photochemistry. We show that photoactivity is enhanced in the ternary biosupramolecular assemblies due to CB\(^n\) stabilization of the excited state and the proximity of the protein, that doubles as a carrier and a target for reactive oxygen species and/or electron-transfer. Protein damage combines photo-oxidation, fragmentation and more importantly protein hydroperoxide formation. These latter species are long-lived and have the potential of inducing oxidative stress, and we are currently trying out these systems in cells to assess a potential enhancement of photoactivity in vivo. We are also developing strategies to tailor the formation of ternary complexes to other needs.

Acknowledgments D.F., I.V., K.S., J.C., A.T. and H.C. thank CONICYT (FONDECYT Grant N°11121223) and the Pontificia Universidad Católica de Chile (VRI and DIPOG) for the financial support. C.B. thanks NSERC for a Discovery grant.

Photodissociation of Mass-Selected Ions - Spectroscopy and Fragmentation Channels

Author(s): Sydney H. Kaufman, Shuang Xu and J. Mathias Weber*
JILA and Department of Chemistry & Biochemistry, University of Colorado at Boulder

Abstract: Although many photochemical processes occur in the condensed phase, the complexity of condensed-phase environments can make the study of photochemical processes in situ very difficult, particularly in solutions. One of the main problems on the road to understanding the mechanisms underlying photochemical processes and photophysical properties of molecules is the complexity of speciation in solutions, often rendering molecular level details of reaction mechanisms and intermediates inaccessible for study. Experimental techniques coupling mass spectrometric preparation of ionic species with laser spectroscopy allow experiments that can circumvent many of the complications of speciation in solutions. This is a powerful approach, since the species of interest can be selectively and cleanly prepared, and ionic complexes in vacuo can teach us much about their analogues in condensed-phase chemistry. We use a combination of electrospray ionization tandem mass spectrometry and photodissociation spectroscopy to study photophysical and photochemical properties of ionic molecules and complexes. Examples discussed in this presentation will be the photophysical and photochemical behavior of permanganate, chromate esters and copper-bipyridyl complexes.
Tuning Energy Level Alignment At Organic/Semiconductor Interfaces Using A Built-In Dipole In Chromophore-Bridge-Anchor Compounds

Author(s): Elena Galoppini*, Alberto Batarseh, Robert Allen Bartynski, Sylvie Rangan, and Lars Gundlach.
Department of Chemistry, Rutgers University-Newark; Department of Physics and Astronomy, Rutgers University-New Brunswick; Department of Physics, University of Delaware.

Abstract: Three Zn(II) tetraphenylporphyrins (ZnTPP) were synthesized to study the influence of a molecular dipole on the energy level alignment of a chromophore bound to a metal oxide semiconductor: ZnTPP-PE(DA)-IpaOMe (1), ZnTPP-PE-IpaOMe (2) and ZnTPP-PE(AD)-IpaOMe (3), each containing rigid-rod linker made of a p-phenylene ethynylene (PE) moiety terminated with the methyl ester of an isophthalic acid unit (Ipa). Porphyrins 1 and 3 contained an intramolecular dipole in the central phenyl ring, which was built by introducing electron donor (D, NMe2) and acceptor (A, NO2) substituents in para position to each other. In 1 the dipole was directed away from the Ipa group, and in 3 the relative position of the D and A substituents, and therefore the dipole direction, was reversed. UV-vis absorption and emission spectroscopies were used to probe the electronic structure of the compounds in solution, while UV photoemission spectroscopy was used to measure the relative position of the molecular levels of the chromophore with respect to the band edges of a ZnO single crystal substrate. The introduction of a molecular dipole did not alter the chromophore’s HOMO-LUMO gap, and the molecular level alignment of the compounds bound to the ZnO surface followed the behavior predicted by a simple parallel-plate capacitor model. Time-resolved electron transfer experiments of 1-3 bound to TiO2 nanoparticle films to determine the influence of the dipole on charge transfer kinetics are in progress and will be discussed in the talk.

In Search for Organic Catalytic Motifs for Solar Water Splitting

Author(s): Ksenija Glusac*
Department of Chemistry, Bowling Green State University, Bowling Green, OH 43403.
Abstract: This presentation will summarize our recent results from a study of catalytic water oxidation. To provide less expensive and more environmentally friendly alternatives for catalytic water splitting, the Glusac group studies earth-abundant catalytic motifs that utilize solely organic compounds made of C, H, N and O. In specific, the electrocatalytic water oxidation by flavinium and other iminium cations was investigated. Our preliminary results showed that a simple, flavin-based model compound catalyzes the water oxidation at large overpotentials and with the assistance of the working electrode’s surface. Since further mechanistic studies of this novel flavin-based system are complicated by the interfacial chemistry, we are searching for fully homogeneous analogs of the flavin-based catalyst. A series of either monomeric or covalently-linked iminium ions were investigated as model compounds for homogeneous catalysis. The conformational flexibility of model compounds was studied using NMR spectroscopy, while the oxidative behavior was investigated using electrochemical methods. The results of our study provide important information regarding the important structural motifs that are required for the catalysis.

31 Exciting Thiophene Rust

Author(s): Luis M. Campos*
Department of Chemistry, Columbia University

Abstract: The talk will discuss the oxidation chemistry of thiophenes and their role as singlet fission materials for next-generation solar cells.
Cavitand mediated supramolecular control of bimolecular photochemical reactions

Author(s): Mahesh Pattabiraman*
University of Nebraska

Abstract: Larger members of the cyclodextrin and cucurbituril macrocyclic cavitand families, cucurbit[8]uril and g-cyclodextrin, are capable of forming ternary inclusion complexes through encapsulation of two small organic molecules simultaneously. Photoexcitation of ternary inclusion complexes involving photoactive guests is an efficient approach for directing bimolecular photochemical reactions. For example, such an approach has been utilized in the past to steer alkene photochemistry towards the entropically less favorable photocycloaddition reaction. This presentation will feature our recent findings on the photocycloaddition reaction between non-identical photoactive alkenes (heterodimerization) achieved using a similar approach, in which reaction control was realized through host-guest and guest-guest supramolecular interactions. We have demonstrated that through an appropriate choice of non-identical reactant alkene pair with subtle, complementary electronic and steric characteristics, the inclusion process could be directed towards the hetero-complex predominantly, which upon irradiation yielded heterodimer as the major product. This approach was used to produce less symmetric, more complex cyclobutane containing structures than has been previously reported. Moreover, photochemical outcomes in conjunction with computational studies were used to predict the inclusion complex structure and the nature of supramolecular interactions between the components of the complex.
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32 Properties and Applications of Self-Assembled Benzophenone bis-urea Macrocycle
Arthur A. Korus* Linda S. Shimizu
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33 Heteroleptic Mixed-Metal Ru(II), Rh(III), Ru(II) Supramolecular Complexes as Photocatalysts for the Reduction of Water to Hydrogen Fuel
Department of Chemistry, Virginia Tech., Blacksburg, VA 24061-0212

34 The Photochemistry of N-Substituted Heteroaromatic Salts
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35 Photoinduced Mixed Valency.
Jane Henderson, Jonas Petersson, Allison Brown, Leif Hammarström, Clifford Kubiak*
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36 Design and Synthesis of Diruthenium(II, II) Complexes for Use Towards Photodynamic Therapy
Lauren M. Loftus*, Jessica D. Knoll, Claudia Turro
Department of Chemistry and Biochemistry, The Ohio State University

37 Singlet Oxygen Topology on the Nanoscale
Vanessa M. Dipasquale, David F. Zigler, Lauren E. Jarocha, Robert D. Schmidt, Cameron W. Pharr, Jackson Bloomfield, Ian MacKenzie*, Igor Kirilyuk, Anna Tora, Darrin Benjumea, and Malcolm D. E. Forbes
Department of Chemistry, University of North Carolina at Chapel Hill
38 Photophysics and Photochemistry of Hexabromoiridate Dianions in Various Solvents
Sergey M. Matveev*, Andrey S. Mereshchenko, Maxim S. Panov, Alexander N. Tarnovsky
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39 Ultrafast Femtosecond Transient Absorption and Time-Resolved Photoluminescence
Spectroscopy of CH$_3$NH$_3$PbI$_3$ Perovskite Films
Christopher McCleese*, Lili Wang, Anton Kovalsky, Yixin Zhao, and Clemens Burda
Department of Chemistry, Case Western Reserve University and School of Environ.
Science and Eng., Shanghai Jiao Tong University

40 Extending the Lifetime of Copper(I) Phenanthroline Complexes for Upconversion
Photochemistry
Catherine E. McCusker* and Felix N. Castellano
Department of Chemistry, North Carolina State University

41 Unusual Photophysics From Molecularly Derived, Self-Assembled Networks of Ir(III)
Photosensitizers in Water
Michelle M. McGoorty*, Rony S. Khnayzer, Rahkee Pani, Yaroslava Yingling, Felix N.
Castellano
Department of Chemistry and Department of Materials Science and Engineering, North Carolina State University

42 Photohydride Reactivity: From Thermochemical Cycles to Catalysis
Catherine L. Pitman, Seth M. Barrett, Kelsey R. Brereton, Sam A. Slattery, Becca L.
McCoy, Alexander J. M. Miller*
Department of Chemistry, University of North Carolina at Chapel Hill

43 Enhanced Dynamics of Charge Transport for DNA-Lipid Complexes in an Organic
Solvent
Ashutosh Kumar Mishra,* Ryan M. Young, Michael R. Wasielewski and Frederick D.
Lewis
Department of Chemistry and Argonne-Northwestern Solar Energy Research (ANSER)
Center, Northwestern University

44 The Twisted Tale of Ethylene: Photochemical Transformation of Enynes to Fulvenes via
a Cyclization-Fragmentation Cascade.
Rana K. Mohamed‡‡, Gabriel dos Passos Gomes‡, Thais De Faria‡, Kjell Jorner§, Henrik
Ottosson§, Igor V. Alabugin‡
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Chemistry - BMC, Uppsala University, Uppsala, Sweden.

45 Ultrafast Dynamics in Multifunctional Polymers for Solar Energy Conversion
Zachary A. Morseth,* Li Wang, Toan V. Pho, Gyu Leem, Egle Puodziukynaite, Alexander T. Gilligan, Kirk S. Schanze, John. R. Reynolds, and John M. Papanikolas
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Chemistry and Biochemistry, Georgia Institute of Technology, and Department of
Chemistry, University of Florida
Analysis of the DNA-Cleaving Efficiencies of Bifunctional Heteroaromatic Salts
Courtney B. Mullins*, Lauren M. Hoth, Gurjit Kaur, B. Woods Curry, Emily H. Stewart,
Jonathan P. Giurintano, Wolfgang H. Kramer
Department of Chemistry and Biochemistry, Millsaps College, Jackson, MS, USA 39210

Synthesis and characterization of novel carboxifталocianinas with potential
application in Photodynamic Therapy
Francisco B. Nascimento* and Anderson O. Ribeiro
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Near-Infrared Fluorescent "Core-Shell" Conjugated Polymer Nanoparticles
Carlos A. Chavez and Evgeni E. Nesterov*
Department of Chemistry, Louisiana State University

Photoresponsive Metal-coordination Materials for Biological Applications
Giuseppe E. Giammanco; Anton O. Razgoniaev; Dayana A. Muizzi; Christopher T.
Sosnofsky; Jonathan D. Mase; Alexs D. Ostrowski*
Department of Chemistry and Center for Photochemical Sciences, Bowling Green
State University

Controllable Energy Transfer in Light-Harvesting Metal-Organic Frameworks
Derek E. Williams,* Ekaterina A. Dolgopolova, Andrei V. Palukoshka, Natalia B.
Shustova
Department of Chemistry, University of South Carolina

Investigation of the Photodimerization of 1,2-Dialkoxy-9,10-Anthraquinones
Jason Pifer*, Paul B. Jones
Department of Chemistry, Wake Forest University

Modifying the Photophysical Properties of ReI Tricarbonyl Complexes by Using
Different P,N-Bidentate Ligands
Pablo Mella, Juan C. Palma, Marjorie Cepeda, German Gunther, Pedro Aguirre,
Nancy Pizarro* and Andres Vega.
Departamento de Ciencias Quimicas, Universidad Andres Bello. Depto. de Quimica
Organica y Fisicoquimica, Facultad de Ciencias Quimicas y Farm., Universidad de
Chile. Depto. de Quimica Inorganica y Analitica, Facultad de Ciencias Quimicas y
Farm., Universidad de Chile. Centro para el Desarrollo de la Nanociencia y la
Nanotecnologia, CEDENNA.

Cellular and Biophysical Studies on Plant Flavonoids as Antioxidants
Ka’Bresha Potts2*, Donald Davis1, Ming Shenwu2, Irene Arguello2 and Bidisha
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1Chemistry Department, 2Biology Department, Tougaloo College, Tougaloo, MS
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Progressive Acylation of Pyrene Engineers Solid State Packing and Colour via C–
H•••H–C, C–H•••O and π–π Interactions
Shinaj K. Rajagopal*, Abbey M. Philip, Kalaivanan Nagarajan and Mahesh Hariharan
School of Chemistry, Indian Institute of Science Education and Research Thiruvananthapuram

55 Synthesis, Shine light and Recycle: Photodegradation of Polymer/Oligomer Derived from Renewable Bioresources.
Ramya Raghunathan,* Saravanakumar Rajendran, Retheesh Krishnan, Mukund. P. Sibi, Dean Webster, J. Sivaguru
Department of Chemistry and Biochemistry, North Dakota State University, Fargo, ND.

Elamparuthi Ramasamy*, Ashwini B. Danao, Barnali Mondal, and V. Ramamurthy
Department of Chemistry, University of Miami

57 Excited state behavior of benzoxazole derivatives in a confined medium
Fabiano S. Santos,1,2 Elamparuthi Ramasamy,2,* V. Ramamurthy,2 Fabiano S. Rodembusch1
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58 Synthesis, photochemistry and photophysics characterization for new optically active phthalocyanine with potential application in photodynamic therapy
Aline A. Ramos* and Anderson O. Ribeiro
Centro de Ciências Naturais e Humanas, Universidade Federal do ABC

59 Solution and Solid State Photodimerization of Cyclopentenones: Key Correlations to the Bond Formation during Dimerization with Kinetics, Crystal Lattice and DFT Calculations
R. A. A. Upul Ranaweera*, Geethika K. Weragoda, Kelsey M. Griffin, Rachel M. Robinson, Jennifer A. Coffman, Jeanette A. Krause, and Anna D. Gudmundsdottir*
Department of Chemistry, University of Cincinnati, Cincinnati OH 45221-0172, USA.

60 Photoisomerization of and Photoaddition to the 1,4-Diphenyl-1,3-butadienes in Ethanol. Trapping Conical Intersections
Christopher E. Redwood,*, Jack Saltiel
Department of Chemistry, Florida State University, Tallahassee, FL 32306-4390

61 Transition Metal Complexes used for the Detection of Mismatched DNA Base Pairs
Thomas N. Rohrbaugh Jr*, and Claudia Turro
Department of Chemistry and Biochemistry, The Ohio State University

62 Mechanistic Investigations on Acridinium-Mediated Photoredox Catalysis
Nathan A. Romero*, David A. Nicewicz
Department of Chemistry, University of North Carolina - Chapel Hill
63 Photodimerization of Chromone in the Presence of Assembled Phenylethynylene Bis-urea Macrocycles
Sahan R. Salpage*, Logan S. Donevant, Mark D. Smith, and Linda S. Shimizu
Department of Chemistry and Biochemistry, University of South Carolina

64 NIR emissive silver nanoclusters as biolabels
Chirantan Sen-Mukherjee,1,2,∗ Tony Saracino,1 Faren White,1 Bidisha Sengupta1
1Department of Chemistry, Tougaloo College, MS 39174 2Madison Central High School, Madison, MS 39110

65 Excited State Proton Transfer of Fisetin, Quercetin and their Chromophores in Duplex and Quadruplex DNA ligands: A Biophysical Study
Kabresha Potts1, Donald Davis2 and Bidisha Sengupta2∗
Department of Biology1, Department of Chemistry2, Tougaloo College, Tougaloo, MS 39174

66 Development of Ruthenium Complexes as Photocaging Groups
Rajgopal Sharma,* Jessica Knoll, Izabela Podgorski, Claudia Turro and Jeremy J. Kodanko
1) Department of Chemistry, Wayne State University 2) Department of Pharmacology, Wayne State University and 3) Department of Chemistry and Biochemistry, The Ohio State University

67 Photoinduced Charge Transport in DNA-based Three-Way Junctions
Arunoday P Singh*, Ryan M. Young, Michael R. Wasielewski, Frederick D. Lewis
Department of Chemistry, Northwestern University, Argonne-Northwestern Solar Energy Research (ANSER) Center, Northwestern University.

68 Photodegradation of Cochineal in Solution and Paints
Leah M. Bowers, Sarah J. Schmidtke Sobeck*
Department of Chemistry, The College of Wooster

69 Endo/Exo Complexation of Bipyridine Bis-urea Macrocycle with Ruthenium
Bozumeh Som*, Sahan R. Salpage and Linda S. Shimizu
Department of Chemistry and Biochemistry, University of South Carolina

70 Study of cell viability of a phthalocyanine derivative on breast cancer cells.
Thaiza F. M. Souza*, Anderson O. Ribeiro and Giselle Cerchiaro
Centro de Ciências Naturais e Humanas, Universidade Federal do ABC, Brazil.

71 A comparison of the aggregation behaviour and photoproperties of phthalocyanines and naphthalocyanines derivatives
Thalita F. M. de Souza* and Anderson O. Ribeiro
Centro de Ciências Naturais e Humanas, Universidade Federal do ABC, Brazil

72 Steric Hindrance Dependence on the Photophysical Properties of a Donor-π-Acceptor Organic Nonlinear Absorbing Chromophore
Air Force Research Laboratory, Materials and Manufacturing Directorate General Dynamics Information Technology Southwestern Ohio Council for Higher Education

73 Photophysics and Reverse Saturable Absorption of Ir(III) Complexes
Wenfang Sun,* Yuhao Li, Rui Liu, Zhongjing Li, Naveen Dandu, Peng Cui, Jinquan Chen, Chengzhe Wang, Svetlana Kilina, Bern Kohler
Department of Chemistry and Biochemistry, North Dakota State University and Department of Chemistry and Biochemistry, Montana State University

74 Novel chiral thioureas as efficient organo-photocatalysts to mediate [2+2]-photocycloaddition of coumarin derivatives
Nandini Vallavoj*, Selvakumar Serradurai, Mukund Sibi and J. Sivaguru
Department of Chemistry and Biochemistry, North Dakota State University, Fargo ND.

75 The photophysical behavior of a ReI complex-embedded-polymeric sisqueloxane film: fac-[(phen)Re(CO)3Br]
Ramiro Spada, Marjorie Cepeda-Plaza, Germán Günther, Nancy Pizarro, Rodrigo Palacios, María L. Gómez, Andrés Vega*
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76 Stability of Ru(II), Ru(II),Pt(II) and Ru(II),Rh(III),Ru(II) Supramolecular Complexes Containing Enantiomerically Pure Light Absorbing Subunits
Alec T. Wagner* and Karen J. Brewer
Department of Chemistry, Virginia Tech

77 Modulating Electron Transfer Dynamics at Dye-Semiconductor Interfaces via Self-Assembled Bilayers
Jamie Wang*, Ian Murphy, Kenneth Hanson
Department of Chemistry and Biochemistry, Florida State University

78 Towards the Design of Rh(II)-Rh(III) Dimers that Function as Single-Component Proton Reduction Photocatalysts
Travis A. White*, Suzanne E. Witt, Zhanyong Li, Kim R. Dunbar, and Claudia Turro.
Department of Chemistry, Texas A&M University and Department of Chemistry and Biochemistry, The Ohio State University

79 Light-Activated Drug Release using Heterobimetallic Ruthenium and Cobalt Complexes
Rachel Whitman, Claudia Turro*
Department of Chemistry and Biochemistry
80 Controllable Energy Transfer in Light-Harvesting Metal-Organic Frameworks.
Derek E. Williams,* Ekaterina A. Dolgopolova, Andrei V. Palukoshka, Natalia B. Shustova
Department of Chemistry, University of South Carolina

81 Dipyridinium Dihydrodioxin: DNA Duplex Clamp and Autocatalytic DNA Cleaving Agent
Center for Photochemical Sciences, Bowling Green State University

82 Formamidinate Bridged Dirhodium Complexes for Electrocatalytic Proton Reduction
Suzanne E. Witt*, Travis A. White, Zhanyong Li, Kim R. Dunbar, and Claudia Turro
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83 Injection Dynamics of Thermally Equilibrated Chromophores on TiO2: Origin of the Biexponential Kinetics From 1 to 1500 ps
David F. Zigler*, Dennis L. Ashford, Li Wang, Erik M. Grumstrup, Robert J. Brown, Zachary A. Morseth, Melissa K. Gish, Stephanie E. Bettis, Robert J. Dillion, Michael R. Norris, Leila Alibabaei, M. Kyle Brenneman, David W. Thompson, Thomas J. Meyer, John M. Papanikolas
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84 Solution and Solid State Photodimerization of Cyclopentenones: Key Correlations to the Bond Formation during Dimerization with Kinetics, Crystal Lattice and DFT Calculations.
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85 Photoactive Teflon Surfaces that Release Sensitizer Drug Molecules
Goutam Ghosh†, Mihaela Minnii†, Ashwini A. Ghogare†, Inna Abramova†, Keith Cenge†, Theresa M. Busch‡, and Alexander Greer‡,*
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86 A Preliminary Mechanistic Study of Photoinduced 18O-Atom Exchange in Nitrosamines: Dependence on Nitrosamine Substituents
Marilene Silva Oliveira†‡, Ashwini A. Ghogare‡, Inna Abramova‡, Edyta M. Greer,§ and Fernanda Manso Prado‡, Paolo Di Mascio‡, and Alexander Greer‡,*
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Benzylic Bond Formation and Cleavage
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Map to Banquet Location (Tommy Bahama’s Restaurant)

Banquet will take place on the 2nd floor from 6:00-9:00 pm
Saturday, January 3, 2015