INTER-AMERICAN PHOTOCHEMICAL SOCIETY

22nd Winter Inter-American Photochemical Society Meeting

January 2-5, 2013, Sarasota, Florida

Ultrafast SYSTEMS

22nd Winter Inter-American Photochemical Society Meeting

Wednesday, January 2, 2013

Registration 4:00 – 7:00 pm

Dinner 5:00 – 7:00 pm

Opening Comments, Igor Alabugin & Jeffrey Rack 7:00 – 7:05 pm

Session 1, Inorganic Photochemistry

Session Moderator, Gerald (Jerry) Meyer, Johns Hopkins University

Thomas Meyer, University of North Carolina, *2012 Porter Medal* 7:05 – 7:35 pm

What do we know about MLCT excited states?

Russell Schmehl, Tulane University 7:35 – 8:05 pm

Another lap for $[Ru(bpy)_3]^{2+}$ derivatives: reversible energy transfer, oxygen sensing and reporting reactions of singlet oxygen with substrates

Karen Brewer, Virginia Tech 8:05 – 8:35 pm

Intricate Balance of Steric and Electronic Factors with Reactivity to allow Directed Charge Transfer, Photoinitiated Electron Collection and Development of Molecular Devices as Single Component Photocatalysts for Hydrogen Production

Felix Castellano, Bowling Green State University 8:35 – 9:05 pm

Photochemical Upconversion: Sensitized Triplet Fusion

Reception, Sunset Lounge, Lido Beach Resort 9:05 – 11:00 pm

Thursday, January 3, 2013

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

Session 2, Polymers and Biological Photochemistry

Session Moderator, Tom Meyer, UNC

Kirk Schanze, University of Florida, *2011 I-APS award* 8:30 – 9:00 am

Photonic Polymers: Properties and Applications

David Whitten, University of New Mexico 9:00 – 9:30 am

Photochemistry and Photophysical Studies of

Phenyleneethynylene Oligomers in Aqueous and Non-Aqueous Solutions

Jack Saltiel, Florida State University 9:30 – 10:00 am

Photoisomerization of Pre- and Provitamin D_3 in EPA at 77 K: One-Bond-Twist not Hula-Twist

Coffee Break 10:00 – 10:15 am

Session Moderator, Jim McCusker, Michigan State University

Elizabeth Gaillard, Northern Illinois University 10:15 – 10:45 am

Age related changes to the transmission properties of the human eye; implications for retinal disease

Mauricio Baptista, Universidade de São Paulo 10:45 – 11:15 am

Controlling cell death pathways by photosensization reactions

Sherri McFarland, Acadia University 11:15 – 11:45 am

Exploitation of Long-lived ^{3}IL Excited States for Inorganic PDT: Verification in a Metastatic Melanoma Model

Roberto da Silva, Universidade de São Paulo 11:45 – 12:15 pm

Therapeutic potential of photochemically active nitrosyl ruthenium complexes as nitric oxide and singlet oxygen producers

Lunch 12:15 – 2:00 pm

Session 3, Zimmerman Symposium

Session Moderator, Igor Alabugin, Florida State University

Words in Memory of Howard Zimmerman, David Schuster, NYU 2:00 – 2:20 pm

Josef Michl, University of Colorado 2:20 – 2:50 pm

How does a saturated molecule accommodate electronic excitation?

Pengfei Wang, University of Alabama at Birmingham 2:50 – 3:20 pm

Development of a new photolabile protecting group toolbox

Coffee Break 3:20 – 3:35 pm

Andrei Kutateladze, University of Denver 3:35 – 4:05 pm

Photoassisted Synthetic Chemistry: Rapid Access to Novel Polyheterocyclic Scaffolds

Frederick D. Lewis, Northwestern University 4:05 – 4:35 pm

Thymine-Thymine Photodimerization Revisited

Evgueni Nesterov, Louisiana State University 4:35 – 5:05 pm

Exciton Delocalization in Monolayers of Conjugated Oligomers: Design of Self-Amplifying Fluorescent Sensors

Dinner 5:05 – 7:00 pm

Session 4, Zimmerman Symposium

Session Moderator, David Schuster, NYU

Robert McMahon, University of Wisconsin 7:00 – 7:30 pm

Photochemistry and Spectroscopy of Thiophene Carbenes

Laren Tolbert, Georgia Tech 7:30 – 8:00 pm

The versatile photochemistry and molecular biology of the GFP chromophore

Miguel Garcia-Garibay, UCLA *2012 I-APS award* 8:00 – 8:30 pm

Photochemical Kinetics and Mechanisms in the Solid State

Poster Session, Sunset Lounge, Lido Beach Resort 8:30 – 11:00 pm

Friday, January 4, 2013

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

Session 5, Inorganic Photochemistry

Session Moderator, Edith (Phoebe) Glazer, University of Kentucky

David McMillin, Purdue University, *2011 I-APS Fellow* 8:30 – 9:00 am

Radiationless Decay in Platinum(II) Polypyridines with a Bound Phenyl

Wenfang Sun, North Dakota State University 9:00 – 9:30 am

Photophysics and nonlinear absorption of platinum diimine complexes

Nancy Pizarro, Universidad Nacional Andrés Bello 9:30 – 10:00 am

Synthesis and photophysical properties of Re(I) tricarbonyl complexes with bidentate phosphine-imine ligands

Coffee Break 10:00 – 10:15 am

Joseph Hupp, Northwestern University 10:15 – 10:45 am

Designing Interfaces for Photoelectrochemical Energy Conversion.

Heinz Frei, Lawrence Berkeley National Laboratory 10:45 – 11:15 am

Nanoscale Cobalt Oxide Core - Silica Shell Units for Artificial Photosynthesis

Ken Knappenberger, Florida State University, *2012 Young Investigator* 11:15 – 11:45 am

Nanoparticle Optical Properties and Relaxation Dynamics Studied by Single-Particle Spectroscopy

Lunch 11:45 – 1:25 pm

I-APS Business Meeting - Everyone Welcome 1:00 - 1:30 pm

Session 6, Ultrafast Spectroscopy

Session Moderator, Clemens Burda, Case Western Reserve University

Igor Rubtsov, Tulane University 1:30 – 2:00 pm

Ballistic energy transport in molecules

David McCamant, University of Rochester 2:00 – 2:30 pm

Ultrafast charge and energy transfer probed by femtosecond electronic and vibrational spectroscopy

John Papanikolas, University of North Carolina 2:30 – 3:00 pm

Ultrafast Energy and Electron Transfer in Light Harvesting Polymers

Coffee Break 3:00 – 3:15 pm

Niels Damrauer, University of Colorado 3:15 – 3:45 pm

Manipulating nuclear motions to control excited state energy conversion

Terry Gustafson, The Ohio State University 3:45 – 4:15 pm

Structure and Dynamics in M_2 δ-Conjugated π-Systems

Pedro Aramendia 4:15 – 4:45 pm

In cage mobility in thin polymer films probed by single molecule spectral and orientational fluctuations

Transportation (10-min interval bus service) to Banquet 5:00 – 5:50 pm

Banquet, Mote Marine Laboratory 6:00 – 9:00 pm

Saturday, January 5, 2013

Continental Breakfast, Lido Beach Grill and Lounge	7:30 – 8:30 am
Session 7	
Session Moderator, Bruce Armitage, Carnegie Mellon University	
Hammond Award presented by Bruce Armitage; words in memory of George Hammond and recipient of the award, Nicholas J. Turro	8:30 – 9:00 am
J. Sivaguru, North Dakota State University *2011 Young Investigator*	9:00 – 9:30 am
Atropisomeric Molecular Templates for Asymmetric Photoreactions	
Sergei Tretiak, Los Alamos National Laboratory	9:30 – 10:00 am
Modeling of Energy and Charge Transfer in Organic Conjugated Materials	
Coffee Break	10:00 – 10:15 am
Paul Kropp, University of North Carolina, *2012 IAPS Fellow*	10:15 – 10:45 am
A Fifty-Year Love Affair with Photochemistry: Shining Light Among Giants	
Natalia Pacioni, Universidad Nacional de Cordoba, *2012 Cilento Award*	10:45 – 11:10 am
Photophysics and Photochemistry to Differentiate between Metal Nanoparticles in Mixtures: an Analytical Strategy	
Mintu Porel, University of Miami *2012 Closs Award*	11:10 – 11:35 am
Water Soluble Organic Hosts as Modulators of the Photophysical Processes of Organic Guests	
Lunch	11:35 – 1:25 pm
Travel to Ultrafast Systems, LLC (See page 113)	1:30 – 2:00 pm
Ultrafast Systems Open House (See page 113 for details)	2:00 – 5:00 pm

Oral Presentations

Abstracts

2012 Porter Medal Lecture

1 What do we know about MLCT excited states?

Author(s): David W. Thompson and Thomas J. Meyer*

Department of Chemistry, University of North Carolina

Abstract: The Metal-to-Ligand Charge Transfer (MLCT) excited states of $Ru(bpy)_3^{2+}$ and related polypyridyl complexes have a notable history and outsized impact in photochemistry and photophysics. Impact is evidenced by 10,000's of publications to date and applications that range from sensing to Artificial Photosynthesis. A combination of transient and steady state measurements, combined with synthesis and theory, have given deep insight into electronic and molecular structure. Synthesis, dating back to the 1950's and Dwyer and Gyarfas and their co-workers, has been exploited to modify and control light absorption and excited state properties and, with them, excited state electron and energy transfer reactivity. Ligand-based synthesis has opened doors to linkage strategies and routes for incorporating MLCT excited states into molecular assemblies, polymers, peptides, and interfaces for energy conversion in dye sensitized solar cells (DSSC) and dye sensitized Photoelectrosynthesis cells (DSPEC).

2 Intramolecular energy transfer, oxygen quenching and singlet oxygen reactivity in Ru(II) diimine - pyrene systems

Author(s): T.A. Grusenmeyer, J. Chen, Y. Jin, J.J. Rack, R. Williams, W. Zipfel and R. H. Schmehl*

Department of Chemistry, Tulane University and Department of Chemistry, Ohio University and Department of Biomedical Engineering, Cornell University

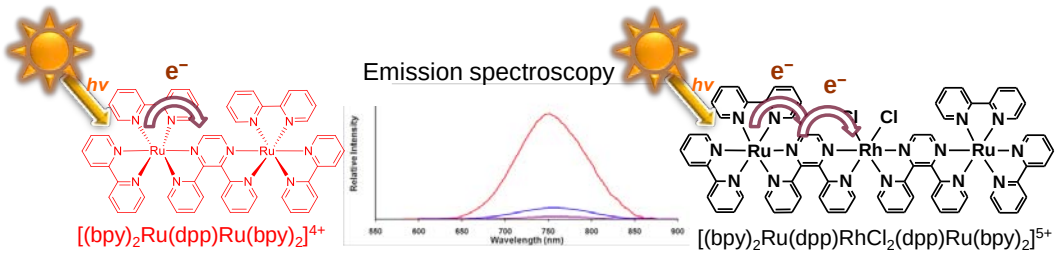
Abstract: Reversible intramolecular energy transfer has been studied in a wide variety of bichromophoric systems over the years. In this example, one of the chromophores, a Ru(II) diimine complex, has four carboxylate substituents and the excited state energy of the chromophore depends on the degree of protonation. The luminescence spectral data can be fit by assuming two, two proton, acid dissociation processes (one proton on each of two bipyridyl ligands that have two carboxylate substituents). When this complex is covalently linked to pyrene, reversible energy transfer between the MLCT state of the Ru(II) diimine complex and the pyrene is observed in the excited state. At high pH (above pH 7), the equilibrium favors a largely pyrene localized excited state and the excited state is efficiently quenched by oxygen. In neutral or higher pH solutions, the system makes an excellent oxygen sensor, especially in relatively hypoxic conditions. Singlet oxygen generated by this bichromophoric system reacts with a variety of substrates in aqueous solution and results in interesting luminescence behavior from the bichromophoric singlet oxygen sensitizer.

3 Intricate Balance of Steric and Electronic Factors with Reactivity to Allow Directed Charge Transfer, Photoinitiated Electron Collection and Development of Molecular Devices as Single Component Photocatalysts for Hydrogen Production

Author(s): Gerald Manbeck, Travis White, Jessica Knoll, Rongwei Zhou, Hannah Mallalieu, Skye King, Brittany Whitaker, Karen J. Brewer.*

Department of Chemistry , Virginia Tech, Blacksburg, VA 24061-0212

Abstract: Mixed-metal supramolecular complexes composed of sub-units with complex redox and excited state properties function as single component photocatalysts for hydrogen production. Energetically very close Rh(dσ*) and BL(π*) orbitals and reactivity at the Rh site requite careful tuning of sterics and electronics to provide catalytic activity in solar energy photocatalysis. Probing and understanding the interplay of sub-units and perturbation of component properties is a major focus. Ru,Rh supramolecules absorb UV and visible light throughout much of the solar spectrum, use this light to generate charge separation on a molecular scale, move the excited electron to a remote acceptor to allow subsequent excitation and ultimately electron collection, and deliver electrons H_2O to produce H_2. The number of events and complexity of these processes occurring in concert requires significant control at the molecular level to provide for sufficient overall light to fuel production efficiency. Structurally diverse supramolecules with multiple metal centers, different polyazine bridging ligands (BL) and varied terminal ligands (TL) are provided by newly developed synthetic methodologies and molecular architectures, allowing exploration of the factors impacting single component photocatalysis. Molecular architectures will include several classes: $[\{(TL)_2Ru^{II}(BL)\}_2Rh^{III}X_2]^{n+}$, $[\{\{(TL)_2Ru^{II}(BL)\}_2Ru^{II}(BL')\}_2Rh^{III}X_2]^{n+}$, $[(TL)_2Ru^{II}(BL)Rh^{III}X_2(TL')]^{n+}$, $[\{(TL)_2Ru^{II}(BL)\}_2Ru^{II}(BL')PtX_2]^{n+}$, $[(TL)_2Ru^{II}(BL)Ru^{II}(TL')(BL')PtX_2]^{n+}$, $[(TL)_2Ru^{II}(BL)Rh^{I}(TL')]^{n+}$. Acknowledgement is made to BES, U.S. DOE DEFG02-05ER15751 for their generous financial support.



4 Photochemical Upconversion

Author(s): Felix N. Castellano

Department of Chemistry & Center for Photochemical Sciences, Bowling Green State University

Abstract: One focus of our research program involves the study of sensitized triplet-triplet annihilation (TTA) or triplet fusion (TF) in solution using highly photostable metal-organic chromophores in conjunction with energetically appropriate organic molecules with large singlet-triplet gaps. Selective excitation of the long-wavelength absorbing sensitizer efficiently generates long-lived triplet states that serve as energy transfer donors. In the presence of appropriate molecular acceptors, diffusion controlled triplet-triplet energy transfer takes place, producing the excited triplet state of the acceptor while regenerating the ground state of the sensitizer. When sufficient numbers of the sensitized triplets are produced, TTA takes place which results in either frequency upconverted light or the formation of desired chemical products. Various combinations of donor and acceptor have been explored and data will be presented on a number of these systems spanning light conversions ranging from the near-visible to the near-IR. This presentation will also describe many examples of upconversion phenomena realized in solid-state polymeric materials along with emerging classes of acceptor/annihilator chromophores. TF processes will be shown to operate at high efficiencies with concomitant linear incident power density response, demonstrated in both theory and experiment using non-coherent photons. Finally, upconversion-based photoaction observed in water splitting photoelectrochemical cells and operational photovoltaics will be discussed.

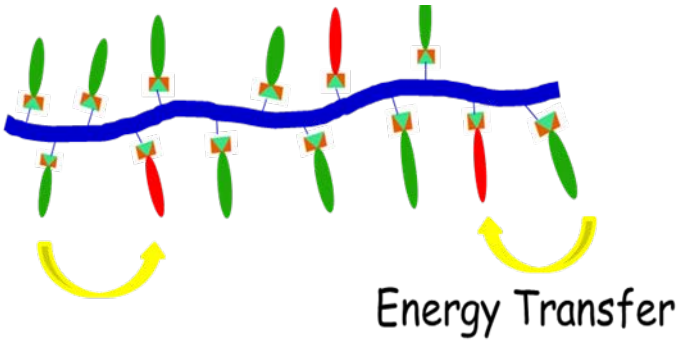
2011 I-APS Award Lecture

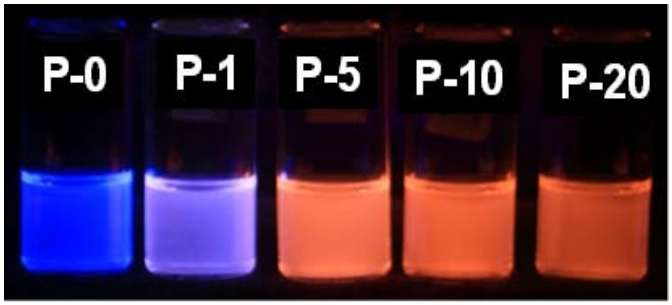
5 Photonic Polymers: Properties and Applications

Author(s): Kirk S. Schanze

Department of Chemistry and Center for Macromolecular Science and Engineering, University of Florida, Gainesville, FL 32611-7200

Abstract: Polymeric chromophore arrays have been investigated to provide an understanding of the mechanism and dynamics of energy transport and for application in fluorescent sensors and photoelectrochemical cells. At one extreme are conjugated polymers and polyelectrolytes consisting of an array of strongly coupled (π-conjugated) chromophores. These systems exhibit highly efficient light absorption and ultrafast energy transfer. Another class of polymeric chromophores consists of a non-conjugated backbone (e.g., polystyrene) functionalized with pendant chromophoric units. Here we will describe polystyrenes that are funcationalized with transition metal chromophores such as $Ru(bpy)_3^{2+}$ and π-conjugated oligomer chromophores, as well as "hybrid systems" that feature both a π-conjugated backbone functionalized with pendant chromophores. Photophysical and photoelectrochemical studies provide evidence for exciton transport by various mechanisms including Förster dipole-dipole and Dexter exchange.





6 Photochemistry and Photophysical Studies of Phenyleneethynylene Oligomers in Aqueous and Non-Aqueous Solutions

Author(s): David G. Whitten,* Eric H. Hil

Nanoscience and Microsystems Program, University of New Mexico
Center for Biomedical Engineering, University of New Mexico

Abstract: Cationic oligo *p*-phenylene-ethynylenes have been shown to be useful as sensors and powerful light-activated antimicrobials, making knowledge of their photochemistry essential for development of potential applications which may involve exposure to light, moisture and air. In this study, two different classes of these compounds are irradiated in water and methanol both in the presence and absence of oxygen, and the photolysis is monitored by absorbance and fluorescence spectroscopy. Product characterization by mass spectrometry revealed three major reaction pathways; addition of water across the triple bond of the ethynyl group, the addition of singlet-oxygen across the triple-bond in the presence of oxygen, and the cleavage of the alkoxy side chains leaving phenols in the series of compounds with charged side-chains.

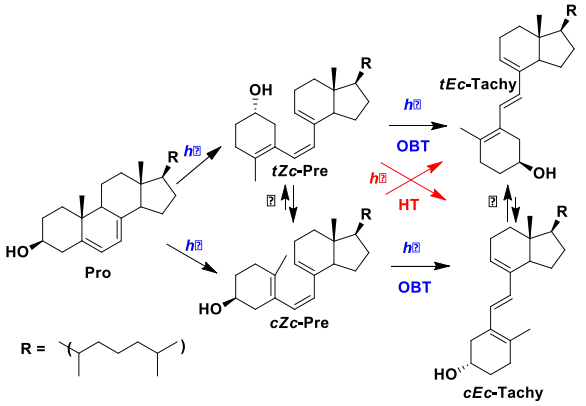
7 Photoisomerization of Pre- and Provitamin D_3 in EPA at 77 K: One-Bond-Twist not Hula-Twist

Author(s): Jack Saltiel,* Christopher Redwood, Malgorzata Bayda

Department of Chemistry and Biochemistry, Florida State University

Abstract: Fuß and co-workers studied the photoisomerization of previtamin D_3 (Pre) in EPA (5:5:2) glass at 90 K starting from Pre, prepared in situ via the photochemical ring opening of provitamin D_3 (Pro).[1] The UV spectrum of the tachysterol photoproduct (Tachy) matched the spectrum of thermally equilibrated Tachy. Assuming that Pro opens up to the *s-cis,s-cis*-conformer of Pre (*cZc*-Pre) which, retaining its conformation in the glassy medium, gives the stable *s-trans,s-cis*-conformer of Tachy (*tEc*-Tachy), they concluded that in the glassy medium Pre photoisomerization occurs via the Hula-twist mechanism. Widely accepted as the most definitive experimental demonstration of the HT mechanism in free volume confining media, this proposal led to a flurry of activity and many claims of HT photoproducts.

Because UV spectra reveal little concerning conformer distributions, we investigated the photoisomerization of Pre in EPA at 77 K using fluorescence spectroscopy. Our results show that equilibrated Tachy exists as a mixture of three conformers, the major of which we assign to *tEc*- and *cEc*-Tachy. Irradiation of equilibrated Pre reveals that it exists as a single conformer which gives a single Tachy conformer. In contrast, irradiation of Pro leads to three Pre and three Tachy conformers. Curve resolution based on singular value decompo-sition yielded the fluorescence and fluorescence excitation spectra of the conformers. Their structures were assigned based on the expectation that *cEc*- and *cZc*-conformers absorb to the red of *tEc*- and *tZc*-conformers, respectively. Our conclusion is that, remarkably, the major Pre conformer formed from Pro is *tZc*-Pre and not the expected *cZc*-Pre. *tZc*- and *cZc*-Pre photoisomerizations in EPA proceed by the conventional one-bond-twist photoisomerization mechanism to give *tEc*- and *cEc*-Tachy, respectively. Work on the photoisomerization of lumisterol is in progress.



References: 1. A. M. Müller, S. Lochbrunner, W. E. Schmid, W. Fuß, *Angew. Chem.* 1998, *110*, 520-522; *Angew. Chem. Int. Ed.* 1998, *37*, 505-507

Acknowledgment. The National Science Foundation, most recently by Grant CHE-0846636, supported this research.

8 Age related changes to the transmission properties of the human eye; implications for retinal disease

Author(s): Elizabeth R. Gaillard,* James P. Dillon, John C. Merriam, Gopala Krishnamurthy

Dept. of Chemistry and Biochemistry, Northern Illinois University

Abstract: The visible light absorbing pigment mixture, lipofuscin, accumulates in the human retina with age. The pattern of accumulation is interesting in that the amount of pigment increases rapidly in the first decade of life and then levels off until ca. 50 years of age. The transmission of the young primate anterior segment also undergoes changes in the first decade. It has a maximum absorption at 365 nm due to the presence of the O-glucoside of 3-hydroxykynurenine (3-HKG) in the lens. This is synthesized in the last trimester of gestation. Although this compound filters out most of the ultraviolet light from reaching the retina, there is a small window of transmission centered on an absorption minimum at 320 nm. This closes by the second decade of life. The window of transmission of ultraviolet light to the primate retina may explain the initial accelerated formation of lipofuscin in the young human retina by photoreduction of the initially formed retinal-ethanolamine Schiff base. The resulting amine appears to accelerate the formation of blue light absorbing products.

9 Controlling cell death pathways by photosensization reactions

Author(s): Mauricio S. Baptista

Instituto de Química, Universidade de São Paulo

Abstract: Learning to control the fate of cells by light may change the way we treat several human diseases. In this seminar I will initially present data showing how the structure of natural or synthetic photosensitizers (present as soluble molecules or dispersed nanoparticles), are related to the efficiency and mechanism of cell death. I aim to discuss two recent findings: 1. photoinduced generation of ROS can be used to trigger specific mechanisms of cell death, lowering by several orders the amount of ROS necessary to drive tumorous cells to death. 2. Visible light cause damage in skin cells by photosensitization of melanins and flavins.

10 Exploitation of Long-lived ^{3}IL Excited States for Inorganic PDT: Verification in a Metastatic Melanoma Model

Author(s): Susan M. A. Monro, Richard Lincoln, Ruifa Zong, Lars Kohler, Randolph P. Thummel, and Sherri A. McFarland*

Acadia University (S. Monro, R. Lincoln, S. McFarland); University of Houston (R. Zong, L. Kohler, and R. Thummel)

Abstract: Clinical photodynamic therapy, or PDT, is a strategy for treating cancer that relies on the use of a relatively nontoxic organic photosensitizer (PS) that generates cytotoxic singlet oxygen upon activation with red light. PDT has the potential to offer significant advantages over traditional approaches to cancer therapy (e.g., chemotherapy, immunotherapy, surgery, and radiation) due to its low systemic toxicity, non-invasive delivery, and its ability to be repeated many times alone or in combination with other treatment modalities. In practice functional PDT is narrow in scope because the method requires a very precise interaction between the PS, light, oxygen, and the target tissue. Simultaneous optimization of all variables presents a challenge, and, as a consequence, PDT is not widely known nor generally accepted as a powerful alternative in mainstream oncology. To address this very real problem, we believe that PDT research must shift from a PS-centered approach to one that offers a complete package, including PS, light source, and protocol, for a specific type of cancer. Toward this end, we have chosen inorganic PDT, exploiting long-lived ^{3}IL excited states in Ru(II) dyads, to target metastatic melanoma using an in vitro model. The reason behind the approach, the cancer target, and preliminary results will be highlighted.

11 Therapeutic potential of photochemically active nitrosyl ruthenium complexes as nitric oxide and singlet oxygen producers

Author(s): Lilian Franco; Tassiele Heinrich; Loyanne Ramos; Juliana Biazzotto and Roberto S. da Silva*

Pharmacy School, University of Sao Paulo

Abstract: This work describes synthesis, kinetic, photochemical and photobiological studies of some nitrosyl ruthenium complex type $[RuL_5NO]_n^+$ and $[RuL_5NO]$—antibody used as nitric oxide (NO) deliver system. Cell viability was studied under light irradiation effect of $[RuL_5NO]$ complex. One of this complex is $[\{(Ru(bpy_2)NO)\}_2(pz)Ru(Pc)pz)]$ (I) (where pc = phthalocyanine, bpy = 2,2'-bipyridine and pz = pyrazine ligand) as putative system to improve photodynamic therapy (PDT). Once phthalocyanine compounds are widely used in PDT due to their capacity of singlet oxygen generation, cytotoxicity assays against murine melanoma cell line B16F10 were evaluated as well. The compound was able to inhibit cellular viability when irradiated at 660 nm, compared with the treatment without photo stimulus. Similar studies was also conduced with Quantum dot coupled to nitrosyl ruthenium (QD-Ru) system. The generated QD-Ru was able to produce NO by photoinduced eletron transfer as well singlet oxygen by energy transfer. The cell viability were found between 10-25 % with 5 J/cm of potency in ligh irradiation. The cell death is mainly attributed to the apoptosis mechanism.

Acknowledgements: FAPESP, CNPq, NAP photochemical

12 Howard E. Zimmerman

Author(s): David I. Schuster

Department of Chemistry, New York University

Abstract: A brief introduction to the special memorial symposium in honor of the late Howard Zimmerman will emphasize the seminal role he played in the development of organic photochemistry as a major area of fundamental research.

13 How Does a Saturated Molecule Accommodate Electronic Excitation?

Author(s): Matthew K. MacLeod and Josef Michl*

Department of Chemistry and Biochemistry, University of Colorado, Boulder,CO, USA, and Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, Prague, Czech Republic

Abstract: A hole in the HOMO and an electron in the LUMO usually characterize vertical excitation to a molecular S_1 state. Relaxation on S_1 surface in a thermal bath determines its further fate. Often, the molecule first reaches thermal equilibrium in an S_1 minimum. If S_1 excitation resides in π and/or *n* electrons, the σ bonds present guarantee some structural resemblance to the S_0 structure, although bonds may be extended, shortened, bent and twisted. Fluorescence is somewhat Stokes-shifted.

What happens in saturated molecules such as alkanes or silanes that contain no valence electrons other those of σ bonds, needed to hold the molecule together? Relaxation into an S_1 minimum may still occur and fluorescence is hugely Stokes shifted by up to 3 - 4 eV.[1] What are the geometrical distortions? In H_2, the S_1 bond length is nearly double and the state resembles a tight ion pair ($H^+H^- \longleftrightarrow H^-H^+$). In larger molecules, the structures of relaxed S_1 states are unknown.

We used ab initio and DFT methods to find them for peralkylated oligosilanes *n*-Si_nR_{2n+2}.[2] Their blue and green emissions are due to structures with highly localized electronic excitation. The hole and the electron are located on a single trigonally bipyramidalized (TBP) Si atom or on two Si atoms intermediate between tetrahedral and TBP. The hole is in σ_{SiSi} bonds and the electron is shared between σ^*_{SiSi} or σ^*_{CSi} antibonds and a non-bonding fifth valence orbital on the Si atom, constructed from its 4s, 4p, and some 3d atomic orbitals. Such valence shell expansion also occurs in certain conformers in the S_0 state of radical anions.

Acknowledgement. We thank the NSF for support (CHE-0848477).

References:

1. Hirayama, F.; Lipsky, S. *J. Chem. Phys.* 1969, *51*, 3616.
2. MacLeod, M.; Michl, J. *Collect. Czech. Chem. Commun.* 2011, *76*, 2085, MacLeod, M. K.; Kobr, L.; Michl, J. *J. Phys. Chem. A.* 2012, *116*, 10507, MacLeod, M. K., *Ph. D. Dissertation*, *University of Colorado at Boulder*, 2012, and unpublished results.

14 Pursuit of the Mechanism for the photo-Favorskii Rearrangement: Application of the Zimmerman Paradigm

Author(s): Richard S. Givens

The University of Kansas

Abstract: Photoactivation of masked or protected functional groups are among the important applications of organic photochemistry. Many of light activated processes' attributes that power functional group exposure offer several major advantages over other chemical or physical methods including better control of temporal, spatial, and concentration variables of the protecting group release. Notwithstanding these advantages, the photochemistry of the protecting group itself bears equal consideration because fragmentation-release processes are invariably influenced by solvent and pH effects, the presence of competing quenchers and chromophores including the spent protecting group, and an array of interfering chemical byproducts. The family of *p*-hydroxyphenacyl (pHP) protecting groups is largely devoid of or imperious to most of these limiting factors and thus is especially well-suited for biological applications. Advantages accrue from the higher efficiencies (ϕ's range from 0.05 to 1.0), from quantitative chemical yields and from rapid release rates (10^8 – 10^9 s^{-1}). These features have led to pHP applications by others for the determination of individual rate constants for GTP hydrolysis by GTPase in G-protein regulation of cell growth and for selective agonist-antagonist responses at auditory neural receptors.

The virtue of pHP photochemistry rests on the fast release and rearrangement from the excited triplet state of the chromophore. The hydrophilically driven photo-Favorskii rearrangement begins with a fast (fs) heterolytic disconnection of the leaving group, a process that also initiates the chromophore's rearrangement. The subsequent molecular transformation, which defies the imagination, results in the formation of *p*-hydroxyphenylacetic acid. The entire release and rearrangement sequence is completed within a few ns. A stepwise rationale has been developed by application of the exemplary four step models employing the 'Zimmerman paradigm' of excitation, bond alteration, demotion followed by further ground state bond alteration for photochemical reactions. Evidence for the contributions of the excited state and ground state bond alterations will also be presented.

15 Development of a photolabile protecting group toolbox

Author(s): Pengfei Wang

Department of Chemistry, University of Alabama at Birmingham

Abstract: We have recently developed a series of photocleavable protecting groups (PPGs) for protection of carbonyl and hydroxyl groups. These new PPGs are structurally simple, easy to prepare, to install and to remove. They are remarkably stable toward various chemical treatments. In particular, their unique structural features led to new protecting protocols, and for the first time both protection and deprotection reactions can be conducted under neutral and mild conditions without using any other chemical reagents. For carbonyl protection, we have achieved selective removal of different carbonyl PPGs by changing irradiation wavelength. We have also demonstrated that deprotection of both carbonyl and hydroxyl PPGs can be successfully carried out with irradiation of sunlight without requirement of photochemical devices. Most recent advance expands the scope of the new PPGs for applications in aqueous environments.

16 Photoassisted Synthetic Chemistry: Rapid Access to Novel Polyheterocyclic Scaffolds

Author(s): Andrei G Kutateladze,* Olga A. Mukhina, and N.N. Bhuvan Kumar

Department of Chemistry and Biochemistry, University of Denver

Abstract: Photochemical reactions hold unparalleled promise for building novel carbo- and heterocyclic scaffolds, offering expeditious access to difficult synthetic targets, otherwise not accessible via the ground state chemistry. Yet, photochemistry is underutilized by the synthetic community, which is true for Diversity Oriented Synthesis (DOS) and especially for solid-supported split-and-pool combinatorial synthesis. We have been filling this gaping hole in the combinatorial chemistry toolbox by developing a new methodology of photoassisted DOS for rapid access to topologically diverse polyheterocyclic core scaffolds possessing unique topology and decorated by peripheral functional groups and carbo/heterocyclic pendants rigidly or semi-rigidly held in a unique spatial configuration by these novel core heterocyclic frameworks. Rapid access to such topologically diverse scaffolds is realized via key photochemical steps and their combination with ground state reactions, most prominently the new unprecedented excited state cycloaddition of photogenerated azaxylylenes. Azaxylylenes photogenerated from modular photoprecursors, which contain tethered furan, pyrrol, or thiophene pendants, undergo intramolecular [4+4] or [4+2] cycloadditions with considerable selectivity. This photoassisted synthetic strategy allows for modular design of the photoactive precursors based on simple click-like chemical reactions completed with a high-yielding intramolecular photocyclization to assemble polyheterocycles possessing pyrroloquinolinol, quinolizinol, azacane, and related cores.

17 Thymine-Thymine Photodimerization Revisited

Author(s): Frederick D. Lewis

Department of Chemistry, Northwestern University

Abstract: The absorption of ultraviolet light by DNA results in the formation of a variety of pyrimidine dimers, the most prevalent of which is the cis-syn thymine-thymine dimer formed via the (2 + 2) cycloaddition reaction of adjacent thymines. Low quantum yields for TT dimerization have been variously attributed to ultrafast excited state decay channels, the low probability of adjacent thymines adopting reactive ground state geometries (ground state conformational control), and charge transfer quenching of excited thymines by ground state purines. We have investigated the context dependence of the TT dimerization efficiency in single strand and hairpin duplex sequences possessing a single TT or TTT step with a small number of flanking bases. Our experimental results for simple sequences containing A and T bases and either natural or locked nucleic acids are in good agreement with a computational model for ground state conformational control developed by McCullagh and Schatz. We also find that both ground and excited state electron donor-acceptor interactions with flanking purines influence the efficiency of TT dimerization.

18 Exciton Delocalization in Monolayers of Conjugated Oligomers: Design of Self-Amplifying Fluorescent Sensors

Author(s): Brian G. Imsick, Jiba Raj Acharya, and Evgueni E. Nesterov*

Department of Chemistry, Louisiana State University

Abstract: Extended π-electron conjugated systems display strong fluorescence which makes them a valuable platform for numerous applications in optoelectronic and sensing devices. These applications can further benefit from ratiometric behavior of their fluorescent emission, i.e. emission color change upon analyte recognition. This behavior can, in principle, be achieved if a π-conjugated system possesses two weakly coupled fluorophores, each of them emitting at markedly different wavelengths. When the efficiency of intramolecular photoexcitation energy migration from the higher to the lower energy gap fluorophore is attenuated, the relative intensities of these two emission bands will change. Such modulation of photoexcitation energy transfer can be achieved by analyte binding to a terminal receptor in a specially designed end-functionalized oligo(p-phenylene ethynylene)s. Surface-immobilized monolayers of these molecular sensors are characterized by increased molecular order and display significant signal amplification due to enhanced intermolecular energy transfer within the monolayer. This general phenomenon offers a superior platform for designing ratiometric fluorescent sensors. Examples of recently developed fluorescent sensors utilizing this approach will be described in this presentation.

19 Photochemistry and Spectroscopy of Thiophene Carbenes

Author(s): Caroline R. Pharr, Laura A. Kopff, and Robert J. McMahon*

Department of Chemistry, University of Wisconsin-Madison, Madison, WI; United States

Abstract: Our research group maintains a long-standing interest in the structure and reactivity of aryl carbenes. Our interest in these reactive intermediates stems from their fundamentally interesting photochemistry and spectroscopy, as well as their relevance to chemical processes occurring in interstellar space or other harsh reaction environments. We recently undertook a comprehensive study to generate and characterize thienylcarbenes – species that formally represent products derived from the addition of atomic carbon to thiophene – as well as their benzo analogs. Despite considerable interest in these species over many years, evidence for their intermediacy is either indirect or nonexistent. A notable finding involves the detection and characterization of a variety of triplet thienyl carbene derivatives. These carbenes exhibit a remarkable diversity of photochemical rearrangement pathways.

20 The versatile photochemistry and molecular biology of the GFP chromophore.

Author(s): Laren M Tolbert

School of Chemistry and Biochemistry, Georgia Institute of Technology

Abstract: Encapsulation of rationally designed fluorescent protein chromophores within certain cavitands, in liquid crystals, in polymers, and in protein binding sites results in a remarkable fluorescence enhancement. These molecules serve as sensitive probes for the environment of the host, particularly proteins involved in signaling. Potential applications as sensors, in Förster resonance energy transfer (FRET), and in activation of nuclear receptors will be presented.

2012 I-APS Award Lecture

21 Reaction Mechanisms and Absolute Kinetics in Solid State Photoreactions

Author(s): Miguel A. Garcia-Garibay

Department of Chemistry & Biochemistry, University of California, Los Angeles

Abstract: Photochemical reactions and photophysical processes in crystalline solids tend to occur with a high level of control and have a great potential for applications in materials science and in solvent-free, green chemical synthesis. While it is true that their rigid environments prevent many chemical transformations, we have been able to "engineer" a number of solid state reactions in a reliable manner by taking advantage of suitable crystalline precursors of highly reactive intermediates. The next set of developments in this field will rely on mechanistic insights analogous to those available for photochemical reactions in the gas phase and in solution. In this context, the use of optical methods to detect and determine the kinetics of excited states and reactive intermediates would be ideal. However, studies in large single crystals and bulk powders are hampered by their high optical densities, strong light scattering, and multiphotonic processes. To address these limitations, we have shown that nanocrystals in the 100-300 nm range, with sizes that are smaller than the wavelength of light used for excitation, are amenable to pump-probe optical and magnetic resonance methods when suspended in water in a flow system. The material in this presentation will include general aspects of photochemical reactions in crystals and examples of detailed reaction mechanism based on absolute rate constants measured in the solid state.

2011 I-APS Fellow Lecture

22 Radiationless Decay in Platinum(II) Polypyridines with a Bound Phenyl

Author(s): Daniel P. Lazzaro and David R. McMillin*

Department of Chemistry, Purdue University

Abstract: Certain platinum(II) polypyridine complexes are excellent luminophores suitable for many potential applications, but the majority of systems are non-emissive in fluid solution. Ligand design is important, and incorporating strong-field ligands generally promotes emission, an enigmatic exception being Pt(trpy)Ph$^+$, where trpy denotes 2,2':6',2"-terpyridine. An energy-based analysis suggests the complex is non-emissive due to ^{3}SBLCT (sigma-bond-to-ligand charge transfer) character in the lowest energy excited state. The bases for two distinct strategies for inducing emission from aryl derivatives then become clear. The established approach involves incorporating the phenyl group into a (N^N^C) cyclometalating ligand, but it now appears that the rigidity of the ligand framework is decisive. The alternative strategy presened, which involves expanding the chromophore and altering the orbital parentage of the emitting state, is capable of suppressing radiationless decay even further. Thus, the Pt(4'-pyren-1-yl-trpy)Ph$^+$ system emits from a substituent-based triplet excited state that has a lifetime of 45 microseconds in fluid solution.

23 Platinum diimine complexes as broadband nonlinear absorbing materials

Author(s): Wenfang Sun,* Rui Liu, Yuhao Li, Bingguang Zhang, Xuguang Liu, Alexander Azenkeng, Naveen Dandu, Dapeng Zhou, Timothy M. Pritchett, Joy E. Haley, Ksenija Glusac, Svetlana Kilina

Department of Chemistry and Biochemistry, North Dakota State University; Energy and Environmental Research Center, University of North Dakota; Department of Chemistry, Bowling Green State University; Army Research Laboratory; and Air Force Research Laboratory

Abstract: Organic materials with broadband nonlinear absorption in the visible to the near-IR region are desired for a variety of photonic device applications. Platinum diimine complexes are promising broadband excited-state absorbers in the visible to the near-IR region. However, due to the very weak ground-state absorption of many reported Pt(II) diimine complexes in the near-IR region, it is not possible to populate the excited state via one-photon absorption in this region. To overcome this disadvantage, we designed and synthesized several series of Pt(II) diimine complexes containing fluorenyl component either on the acetylide ligands or on the diimine ligand to increase the two-photon absorption of these complexes in the near-IR region. In such a case, we can access the excited state via two-photon absorption. Combination of two-photon absorption and excited-state absorption not only expands the nonlinear absorption spectral region but also enhances the nonlinear transmission performance in the near-IR region.

24 Synthesis and Photophysical Properties of Re(I) Tricarbonyl Complexes with Bidentate Phosphine-Imine Ligands

Author(s): Nancy Pizarro*, Hector Gallardo, Felipe Venegas, Eduardo Chamorro, Germán Günther and Andrés Vega

Departamento de Ciencias Químicas, Universidad Andres Bello; Centro para el Desarrollo de la Nanociencia y la Nanotecnología, CEDENNA, and Departamento de Química Orgánica y Fisicoquímica, Universidad de Chile

Abstract: Because of their remarkable luminescent properties at room-temperature, Rhenium(I) tricarbonyl complexes have increasingly become very valuable molecular fragments to be inserted into molecules designed for technological applications. In contrast to the widely studied N,N-bidentate Rhenium(I) tricarbonyl complexes, relatively much less attention has been paid to their P,N-bidentate ReI tricarbonyl analogues. Phosphine-type ligands having a second kind of coordinating atom or function have demonstrated indeed a great impact in many areas of chemistry. In the present work, we want to show the photophysical behaviour of a recently prepared mononuclear ReI complex: [P,N-{$(C_6H_5)_2(C_5H_4N)P$}$Re(CO)_3Br$], including rationalization by means of modern DFT computational tools. In addition, with the aim to investigate and modulate its optical properties, this complex has been used as precursor to prepare the derivatives [P,N-{$(C_6H_5)_2(C_5H_4N)P$}$Re(CO)_3L$], by removal of the bromide ion with a silver salt followed by the subsequent addition of a ligand, like a vinyl anchored molecule (L: 4-vinylpyridine). The results show that the presence of the ligand 4-vinylpyridine modifies completely the photophysical properties of the precursor complex. The synthesis of the mononuclear complex [(phen)$Re(CO)_3(Br)$] (phen: 1,10-phenantroline), was made in order to be used as comparison point for P,N-complexes. Unexpectedly, we also obtained the complex [$(CO)_3$(phen)Re(μ-Br)Re(phen)$(CO)_3$] [$(CO)_3Re(\mu\text{-}Br)_3Re(CO)_3$], which has been isolated and characterized by single crystal x-rays diffraction. Their main photophysical properties will be also shown.

25 Designing Interfaces for Photoelectrochemical Energy Conversion

Author(s): Joseph Hupp

Northwestern University and Argonne National Laboratory

Abstract: My lab has found atomic layer deposition (ALD) to be an extraordinarily versatile tool for synthesizing materials for photoelectrochemical energy conversion. While much of our focus is on dye-sensitized solar cells for light-to-electrical energy conversion, this presentation will focus on water splitting, and in particular the water-to-dioxygen half reaction. A seemingly ideal photo-electrode material for this reaction is α-Fe_2O_3 – essentially rust in dehydrated form.* This material is inexpensive, highly photo-oxidizing, and capable of absorbing light to wavelengths as long as 600 nm. Despite hundreds of studies, however, it has failed to perform at anywhere near hoped-for efficiencies. Nevertheless, it does indeed photo-catalytically oxidize water to O_2. This talk will focus on efforts, using ALD-fabricated structures, to identify and understand mechanistic bottlenecks, and on synthesis-driven approaches for circumventing them.

*For a recent critical review, see: "Toward Solar Fuels: Water Splitting with Sunlight and Rust?" M. J. Katz, et al. *Coord. Chem. Rev.* 2012, *21-22*, 2521-2529.

26 Cobalt Oxide Core – Silica Shell Units for Artificial Photosynthesis

Author(s): Heinz Frei

Physical Biosciences Division, Lawrence Berkeley National Laboratory, University of California, Berkeley, CA 94720

Abstract: The long term goal of our research is the direct conversion of carbon dioxide and water with visible light to a liquid fuel in a nanoscale assembly. Focusing on robust inorganic molecular light absorbers and metal oxide nanocatalysts, geometries are explored that afford the coupling of the components across a proton transmitting nanoscale silica layer under separation of the water oxidation catalysis from all other photosynthetic processes. Using recently developed heterobinuclear charge-transfer units as visible light chromophores, Co_3O_4 as multi-electron catalyst for water oxidation, and core-shell nanotube geometry for separating the O_2 evolution from light absorber and reduction chemistry, we are developing an assembly for closing the photosynthetic cycle on the nanoscale. Molecular wires of type oligo(paraphenylene vinylene) embedded into the silica shell afford controlled hole transport from the visible light sensitizer on the outside to the Co_3O_4 catalyst on the inside of the nanotube assembly. Vibrational, optical and X-ray spectroscopic characterization of structure and function of charge transfer units and catalysts play an essential role in our effort to assemble the nanoscale photosynthetic unit.

2012 I-APS Young Investigator Award Lecture

27 Nanoparticle Optical Properties and Relaxation Dynamics Studied by Single-particle Spectroscopy

Author(s): Kenneth L. Knappenberger, Jr.

Department of Chemistry and Biochemistry, Florida State University

Abstract: Accurate descriptions of nanoparticle surface plasmon fields are critical for developing a predictive understanding of the many photochemical processes that they mediate. I will present results obtained from nonlinear optical (NLO) spectroscopy experiments carried out at the single-particle level to probe nanoparticle electromagnetic surface fields. As one example, we report the observation of magnetic dipolar contributions to the NLO response of colloidal solid gold nanosphere (SGN) dimers, using single-particle polarization-resolved second harmonic generation (SHG) spectroscopy. Unambiguous circular dichroism in the SHG signal was observed for many of the structures, indicating the presence of a chiral plasmon field within the interparticle gap. Detailed analysis of the polarization line shapes of the SHG intensities obtained by continuous polarization variation suggested that the effect resulted from strong magnetic dipolar contributions to the nanostructure's optical properties. The relative magnetic-dipolar and electric-dipolar contributions to the NLO response were structure dependent, an effect that would have been obscured for ensemble measurements. I will also present femtosecond time-resolved pump –surface plasmon probe results obtained from hollow gold nanospheres dispersed in a range of fluids, which were used to determine mechanisms of energy transfer from the nanoparticles to the surroundings. These findings may be significant for applications using the plasmonic nanostructure platform including nanoantennas, biosensing and field-mediated photochemistry, including solar-energy conversion.

28 Ballistic energy transport in molecules

Author(s): Natalia I. Rubtsova, Zhiwei Lin, Igor V. Rubtsov*

Department of Chemistry, Tulane University

Abstract: Energy transport in a variety of molecules is experimentally assessed using a relaxation-assisted two-dimensional infrared (RA 2DIR) spectroscopy method. The amplitude of the cross peak between the tag (initially excited) and reporter vibrational modes, measured as a function of the time delay between the tag excitation and reporter probing, convey the energy transport dynamics in the molecule between the tag and the reporter. Compounds featuring polyethylene glycol (PEG) and perfluoroalkane oligomeric linkers were studied. Energy transport between the terminal azido and carbonyl groups of the azido-PEG-succinimide ester compounds with a number of repeating PEG units of 0, 4, 8, and 12 was investigated and the transport speed of ca. 500 m/s was found. The transport efficiency, taken as the cross-peak amplitude at the maximum, decays exponentially with the chain length with a characteristic decay distance of 15.7 +/- 1 Å. A constant speed transport was also found in perfluoroalkane oligomers with various chain lengths of 3, 5, 7, 9, and 11 carbon atoms terminated by a carboxylic acid moiety at one end and $–CF_2H$ group at another end. Substantial mode delocalization across the oligomeric units is found, which supports the energy propagation as a wavepacket. Factors influencing the transport efficiency and the propagation speed are discussed.

29 Ultrafast Charge and Energy Transfer Probed by Femtosecond Electronic and Vibrational Spectroscopy

Author(s): David W. McCamant

Department of Chemistry, University of Rochester

Abstract: This talk will present our recent results probing the ultrafast charge-transfer events in dimethylaminobenzonitrile (DMABN, "Lippert's molecule") and the energy transfer processes that occur in dye-sensitized Pt(diimine)(dithiolate) compounds used for solar hydrogen production. In DMABN, we have utilized femtosecond stimulated Raman spectroscopy to reveal the dynamics of individual vibrational modes during and immediately following photoinduced charge-transfer. By combining time-resolved vibrational spectroscopy with quantum chemical calculations of molecular anharmonicity it is possible to test current theoretical models of DMABN's ultrafast excited state dynamics. Dye sensitized platinum compounds have interesting capabilities for light harvesting in solar fuel cells and photovoltaics. Our work has shown that the energies of intermediate charge-separated electronic states modulate the speed of both singlet and triplet energy transfer in these molecular dyads. Our recent work has probed the solvent dependence of these energy transfer processes and the dynamics of electron injection from the Pt-bpy to TiO_2 semiconductor particles.

30 Ultrafast Energy and Electron Transfer in Ru(II) Loaded Light Harvesting Polymers

Author(s): John M. Papanikolas

Department of Chemistry, University of North Carolina at Chapel Hill

Abstract: The excited state energy migration dynamics in a polymeric light harvesting assemblies consisting of multiple polypyridyl Ru(II) coordination complexes linked together through a polymer backbone have been studied using ultrafast laser techniques. Both inert polymers that function only as a scaffold (e.g. polystyrene), and polymers capable of light-harvesting (e.g. polyfluorene and polythiophene) have been investigated. In the former case, photoexcitation of the Ru(II) sites leads to site-to-site energy transport with remarkable efficiency, that stems from the long excited state lifetime of the Ru(II) complex. With the incorporation of conjugated polymers, photoexcitation of the backbone is also possible, resulting in competitive charge separation and energy transfer processes, in addition to site-to-site hopping. Transient absorption measurements follow the excited state dynamics on time scales ranging from femtoseconds to microseconds, capturing energy transfer, back triplet transfer, and charge-recombination events. Our results demonstrate the ability of these hybrid assemblies to combine the large extinction coefficients of conjugated polymers with the long-lived excited states of Ru(II) polypyridyl complexes.

31 Manipulating nuclear motions to control excited state energy conversion

Author(s): Niels H. Damrauer

University of Colorado at Boulder

Abstract: The Damrauer group is broadly interested in controlling photochemical transformations by exploiting nuclear degrees of freedom to alter electronic coupling and reorganization energy between reactants and products. We approach this in our efforts to manipulate excited-state dynamics using adaptively and rationally phase-shaped broadband laser fields as well as in our design of chromophores for visible-light driven electron transfer photochemistry. In this talk I will highlight efforts to interrogate and control photochemical pathways in coordination complexes wherein internal proton or halogen motions modulate rates of charge-transfer-derived non-radiative decay.

32 Structure and Dynamics in $M_2\delta$-Conjugated π-Systems

Author(s): Samantha E. Brown-Xu, Malcolm H. Chisholm, Christopher B. Durr, Terry L. Gustafson,* Thomas F. Spilker

Department of Chemistry and Biochemistry, The Ohio State University

Abstract: We are studying a class of metal-metal quadruply bonded compounds for use in a variety of molecular electronics, including photosensitization of solar cells. The compounds studied have the general molecular formula trans-$M_2(X_2C\text{-}L)_2(X_2CL')_2$, where M = Mo or W, X = NiPr or O, and L and L' represent organic groups. Compounds of this type are known to possess low energy states that can be described as metal-to-ligand charge transfer (MLCT) or metal-centered ($\delta\delta^*$) in both the singlet and triplet manifolds where the ordering of these states depends strongly on the nature of the chosen metal and the ligand organic π-conjugation. We are using steady-state and time-resolved electronic and vibrational spectroscopy to investigate the photophysical and photochemical properties of this class of molecules. Femtosecond time-resolved infrared spectroscopy (fsTRIR) has been used to verify the assignments of the lowest energy singlet and triplet states and also to elucidate the extent of charge delocalization within these states. In particular, the fsTRIR experiments have utilized probe regions characteristic of both L-bound IR reporter groups as well as the CN_2 or CO_2 vibrations inherent to the ligands to make these assignments. Furthermore, DFT calculations of neutral and singly reduced model systems have been used to simulate the vibrational spectra of the ground and excited state compounds, respectively, and support the results.

33 In Cage Mobility in Thin Polymer Films Probed by Single Molecule Spectral and Orientational Fluctuations

Author(s): Pedro F. Aramendía

INQUIMAE and Dept. Química Inorgánica. FCEN. Universidad de Buenos Aires and CIBION-CONICET. Ciudad de Buenos Aires. Argentina

Abstract: The in cage mobility of Nile Red embedded in nanometric thin films of poly(alkylmethacrylates) was studied by single molecule fluorescence microscopy. Fluorescence emission spectra were recorded as a function of time in different locations of the polymer film by confocal microscopy, in the 278–323 K temperature range. Three types of emission spectra were identified. The spectra with the highest emission energy spectra show small amplitude fluctuations. The other two types of emission profiles exchange more frequently. The fluctuations are analyzed by the complementary cumulative distribution function of spectral emission energy difference between successive spectra in a time trace. The fluctuations show three components: two of them with zero mean average and distinctly different standard deviations and a third component with much lower probability and an amplitude of 0.13–0.15 eV. The behavior of the spectral fluctuations is very similar in all conditions, pointing to a common feature of the probe–polymer cage as responsible for their presence.

Orientational rearrangements of the fluorophores were monitored by polarized wide field emission of single molecules, as well as by polarized emission of bulk samples under polarized irradiation with photobleaching. in the same systems. We observe neat changes in the mobility behavior between polymer films and within the same polymer matrix with the film thickness that parallel the expected change in the glass transition temperature of the sample. The difference in behavior between the spectral and orientational fluctuations with the environment can be explained by the different space requirements of both types of variations.

2011 I-APS Young Investigator Award Lecture

34 Atropisomeric Molecular Templates for Asymmetric Photoreactions

Author(s): J. Sivaguru

Department of Chemistry and Biochemistry, North Dakota State University, Fargo, ND 58108-6050.

Abstract: The presentation will highlight a new methodology to enhance enantioselectivity during asymmetric phototransformations in solution, where axial chirality in the reactant is transformed to point chirality in the product. Conventional chiral auxiliaries employed in ground state thermal reactions are not effective for asymmetric photochemical transformations. Our approach to the problem is to use atropisomeric chromophores that introduce a chiral bias to the reaction pathway, leading to high selectivity in the photoproduct. We have shown that the chiral bias can be manipulated by both sterics and H-bonding interactions. The presentation will highlight our ongoing investigations where we have achieved >90% enantiomeric excess in the product at ambient conditions in various light induced transformations in solution using atropisomeric photochromophores. As representative example to generalize our methodology four different photochemical transformations will be highlighted viz., a) 6π-photocyclization b) hydrogen-abstraction, c) 4π-photocyclization and d) [2+2]-photocycloaddition.

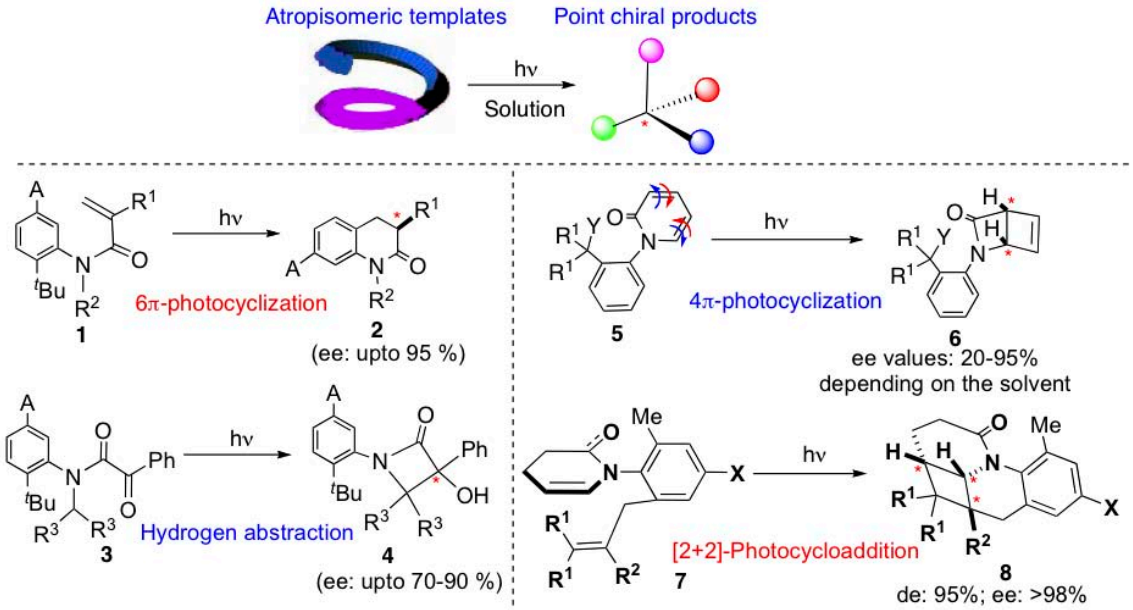


Figure 1: Enantiospecific photochemical transformations with atropisomeric templates.

35 Modeling of Energy and Charge Transfer in Organic Conjugated Materials

Author(s): Sergei Tretiak

Los Alamos National Laboratory.

Abstract: We use recently developed Non-Adiabatic Excited State Molecular Dynamics (NA-ESMD) framework incorporating non-adiabatic quantum transitions to study ultrafast dynamics and exciton transport in several large molecular systems. Our analysis shows intricate details of photoinduced vibronic relaxation and identifies the conformational degrees of freedom leading to ultrafast dynamics and energy transfer. This theoretical modeling allows us to understand and to potentially manipulate excited state dynamics and energy transfer pathways in a number of organic molecular materials suitable for a variety of technological applications. Finally, I will discuss comprehensive theoretical/experimental characterization of the molecular donor in a highly efficient solution processed small molecule bulk-heterojunction photovoltaic device. Our results show that the investigated molecule, showing record-breaking power conversion efficiency, does not have any "special" feature. It is a combination of multiple properties, including broad uv/vis light absorption, combination of several donor- and acceptor-rich regions on a single molecule, high crystallization potential, the chemical purity and optimized morphology of the active layer - all being responsible for the exceptional device performance

INTER-AMERICAN PHOTOCHEMICAL SOCIETY

36 Shining Light—Among Giants

Author(s): Paul J. Kropp

Department of Chemistry, University of North Carolina at Chapel Hill

Abstract: The highlights of a fifty-year love affair with photochemistry will be discussed—including elopement from industry to academia and forays with cross-conjugated cyclohexa-dienones, alkenes, and alkyl halides. All done in the midst of giants in the field.

2012 Cilento Award Lecture

37 Photophysics and Photochemistry to Differentiate between Metal Nanoparticles in Mixtures: an Analytical Strategy

Author(s): Natalia L. Pacioni,* Santiago D. Salas, and Alicia V. Veglia

INFIQC, Departamento de Quimica Organica, Facultad de Ciencias Quimicas, Universidad Nacional de Cordoba

Abstract: Research on environmental and health consequences that could be produced by the increasing use of nanomaterials (eg. metal nanoparticles, NM) is still in their infancy. The success of these research fields as well as the establishment of new regulations for these emerging pollutants is closely related to the availability of reliable analytical methods that permit to distinguish and quantify different NM. Nevertheless, there is still a lack of standarized analytical methods to detect and evaluate NM in environmental samples. Regarding to this, one of the main challenges we currently are facing is the development of strategies that allow us to detect these nanoparticles and to facilitate their quantification in environmental studies.[1]

Among their unique properties, NM like gold and silver have a characteristic extinction in the UV-visible region named as Surface Plasmon Resonance Band (SPB) that is sensitive to several factors such as size, shape, coverage and interparticle distance; and that has been proved to produce interesting light-induced phenomena on molecules in the vicinity of the metal surface.[2]

Presented here are some examples of developing analytical strategies in our group to distinguish between different gold and silver nanoparticles in mixtures. These methods are based on the specific and/or selective interaction between the NM and, molecular and supramolecular switches that induces variations on the photophysics or photochemistry of the interacting systems. For example, these modifications are reflected by changes either on the nanoparticle SPB or on the spectroscopic properties such as absorption, fluorescence, induced circular dichroism of the interacting species observed as a shift in the position of the signals and either enhancement or decrease of their intensity.

References
[1] Ferreira da Silva, B. et al. *TrAC Trends in Anal. Chem.* 2011, *30*, 528. Weinberg, H. et al. *TrAC Trends in Anal. Chem.* 2011, *30*, 72; H Zänker et al. *Annu. Rev. Anal. Chem.* 2012, *5*, 107.
[2] Anger, P et al. *Phys. Rev. Lett.* 2006, *94*,4; Pacioni, N. L. et al, *J. Am. Chem. Soc.* 2010, *132*, 6298; Stamplecoskie, K.G. et al *J. Am. Chem. Soc.* 2011, *133*, 9160; Stamplecoskie, K.G. et al, *J. Phys. Chem. C*, 2011, *115*, 1403.

2012 Closs Award Lecture

38 Water Soluble Organic Hosts as Modulators of the Photophysical Processes of Organic Guests

Author(s): Mintu Porel* and V. Ramamurthy

Department of Chemistry, University of Miami, Coral Gables, FL-33146

Abstract: The importance of supramolecular assemblies to control the excited and ground-state processes of organic molecules has received continued interest during the last few decades. The investigation on the contribution of a water soluble organic host molecule namely octa acid (OA, Figure 1(i)) as reaction cavity for manipulating the photo-chemical and photophysical properties of organic molecules will be highlighted in this presentation. Two molecules of OA cavitand form a capsuleplex (represented as OA_2) in presence of organic guest molecules in water as shown in Figure 1(i). The interior of OA_2 capsuleplex is nonpolar and does not contain water molecules despite the complex being present in water.[1] Photoinduced electron transfer from a coumarin dye incarcerated within OA_2 nanocapsule to the acceptor methylviologen free in solution was studied (Figure 1(ii)). Comparison to the electron transfer in free solution showed significantly accelerated dynamics and essentially no solvent relaxation when the donor was encapsulated into the host molecule.[2,3] This led to the study of electron transfer from an OA encapsulated coumarin dye molecule to the semiconductor TiO_2 film (Figure 1(ii)).[4] Occurrence of electron transfer was demonstrated through steady state emission measurements.

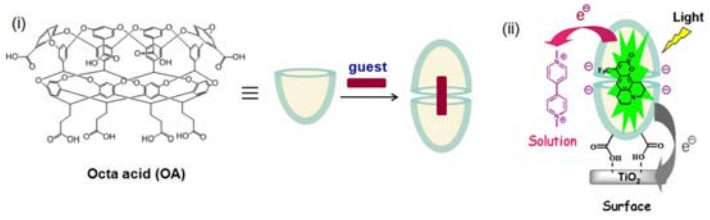


Figure 1 (i) Structure of water soluble organic host octa acid and the formation of its complex with the guest and (ii) electron transfer from encapsulated dye to the acceptor in solution and to semiconductor

Spin communication between two molecules, one confined and excited (triplet or singlet) and the other one free and paramagnetic was demonstrated through quenching of fluorescence and/or phosphorescence by nitroxides as paramagnetic radical species. Transfer of spin polarization from incarcerated triplet molecules to a nitroxide free in solution was investigated through time resolved chemically induced dynamic electron polarization (CIDEP). The presentation will include details of the experimental studies carried out in collaboration with Professors Turro, Gallopini and Burda's groups on electron and spin transfer between an OA incarcerated molecule and another present outside but close to the capsule in water.

We are grateful to Prof. N. J. Turro, Prof. E. Galoppini, Prof. C. Burda, Prof. M. F. Ottaviani, Dr. S. Jockusch, Dr. M. Freitag, Ms. A. Klimczak, Mr. C. –H. Chuang for their instrumental facilities, data collection and valuable discussion. We thank the National Science Foundation for generous financial support.

(1) Mintu Porel; Nithyanandhan Jayaraj; Lakshmi S. Kaanumalle; Murthy V. S. N. Maddipatla; Anand Parthasarathy; V. Ramamurthy, Langmuir, 2009, 25, 3473-3481. (2) Mintu Porel; Chi-Hung Chuang; Clemens Burda; V. Ramamurthy, J. Am. Chem. Soc., 2012, 134, 14718-14721. (3) Mintu Porel; Steffen Jockusch; Anand Parthasarathy; Jayathirtha V. Rao; Nicholas J. Turro.; V. Ramamurthy, Chem. Commun., 2012, 48, 2710-2712. (4) Mintu Porel; Agnieszka Klimczak; Marina Freitag; Elena Galoppini; V.Ramamurthy Langmuir, 2012, 28, 3355-3359.

Poster Presentations Abstracts

1 Investigation of the Photosubstitution of Octahedral Ruthenium Compounds

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Abstract: The emission of *cis*-$[Ru(bpy)_3]^{2+}$ (bpy = 2,2'-bipyridine) has been well studied and is believed to take place from a triplet metal to ligand charge transfer state (^{3}MLCT) with a temperature dependence resulting from a thermally accessible non-emissive triplet ligand field state (^{3}LF) higher in energy then the ^{3}MLCT state. The ^{3}LF state is generally known as the state from which photosubstitution arises. *Cis*-$[Ru(bpy)_3]^{2+}$ was found to have a decrease in quantum yield of emission with a comparative increase in quantum yield of photosubsitution upon increasing temperature, leading to the conclusion that the ^{3}LF is populated from the ^{3}MLCT state. The temperature dependence of the emission of the related complexes *cis*-$[Ru(bpy)_2L_2]^{2+,}$ where L is a photo-labile ligand such as pyridine or acetonitrile, was found to fit the same model, but the of photosubstitution of such complexes shows a smaller increase with temperature than expected. Ultrafast transient absorption spectra show the formation of the photoproduct within the laser pulse of the experiment. The lifetime of the decay of the ^{3}MLCT state remains the same before and after the decay associated spectra of the photo product is subtracted, indicating that the photo product does not come from the ^{3}MLCT state. This implies that the photo product is formed on the fs to ps time scale in competition with the ^{3}MLCT state. The great majority of the ligand subsitution is believed to arise from the ^{3}LF state that is populated directly from the initially excited state and not from its thermal population from the ^{3}MLCT state.

2 pH-Gated Light-Activated Alkyne Conjugates for Double-Strand DNA Cleavage

Author(s): Kemal Kaya,* Juan Rojas, Z. Sokolikj, W.-Y. Yong, S. Roy, and Igor V. Alabugin

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Abstract: We describe a family of hybrid compounds for the most efficient light-activated double-strand (ds) DNA cleavage known to date. This family represents the second generation of "switchable" molecular systems for pH-gated ds DNA-cleavage which combine a potent DNA-photocleaver and a pH-regulated part derived from a dipeptide. Design of the pH-switchable part utilizes amino groups of different basicity. Whereas the basic amino groups are protonated throughout the biologically relevant pH range, the pH-gating amines undergo protonation at the pH threshold which separates cancer and normal cells. Control over the reactivity and selectivity is achieved via transformation of the initial protonation state (a monocation or a dication) into a trication at the acidic pH. This change leads to an extraordinary increase in the efficiency of ds DNA cleavage leading to the ds:ss ratios comparable with the most efficient nonenzymatic ds DNA cleavers. Statistical analysis reveals that these high ds:ss ratios result from the combination of several factors: (a) true double-stranded cleavage, and (b) conversion of single-stranded (ss)-scission into ds cleavage.

Reference

Breiner, B.; Kaya, K.; Roy, S.; Yang, W.-Y.; Alabugin, I. V. Hybrids of Amino Acids and Acetylenic DNA-Photocleavers: Optimizing Efficiency and Selectivity for Cancer Phototherapy. *Org. Biomol. Chem*. 2012, *10*, 3974-3987. Yang, W.-Y.; Roy, S.; A. R.; Phrathep, B.; Rengert, Z.; Alabugin, I. V. Engineering Multiple pH-Gated Transitions for Selective and Efficient Double Strand DNA Photocleavage in Hypoxic Tumors. *J. Med. Chem.*, 2011, *54*, 8501 8516. Yang, W.-Y.; Marrone, S. A.; Minors, N.; Zorio, D. A. R.; Alabugin, I. V. Fine-tuning alkyne cycloadditions: Insights into photochemistry responsible for the double-strand DNA-cleavage via structural perturbations in diaryl alkyne conjugates. *Beilst. J. Org. Chem.*, 2011, *7*, 813–823. Yang, W.-Y.; Cao, Q.; Callahan, C.; Galvis, C.; Sang, A. Q.-X.; Alabugin, I. V. Intracellular DNA Damage by Lysine-Acetylene Conjugates. *Journal of Nucleic Acids* 2010, doi:10.4061/2010/931394. Yang, W.-Y.; Breiner, B.; Kovalenko, S. V.; Ben, C.; Singh, M.; LeGrand, S. N.; Sang, A. Q.-X.; Strouse, G. F., Copland, J. A.; Alabugin I. V. C-Lysine Conjugates: pH-Controlled Light-Activated Reagents for Efficient Double Stranded DNA Cleavage with Implications for Cancer Therapy, *J. Am. Chem. Soc.*, 2009, *131*, 11458–11470.

3 Water Structuration in the Aqueous Pool of Sucrose Monoesters Reversed Micelles

Author(s): Anakenna Ortega and Germán Günther*

Laboratorio de Cinética y Fotoquímica, Facultad de Ciencias Químicas y Farmacéuticas, Universidad de Chile.

Abstract: In this work the structuration of water promoted by the presence of sucrose moieties in the aqueous pool of reversed micelles was studied. Also, we investigated the effect of water structuration on the generation and reactivity of singlet molecular oxygen.

The structuration of water molecules inside the aqueous pools of sucrose monoester reversed micelles formed in chloroform was examined in terms of the behavior of the acid-base equilibrium of pyranine (a known pH fluorescent probe). At high contents of water (large values of R, $[H_2O]$/[surfactant]), the water inside the pool behaves like pure water, and pyranine emission involves protonated and de-protonated excited states. While at low water content (values of R lower than 10), water molecules are less available, because their intense interaction with hydroxyl groups of sucrose. Pyranine equilibrium is almost completely displaced to the protonated form, and only one emission band is observed. This behavior has been reported for other systems of reversed micelles. For example in AOT reversed micelles, the structuration has been observed until R equals 5, however for all sucrose monoesters the structuration is maintained until R 10. [1,2]

The effect of water structuration and the concomitant change in viscosity was analyzed in terms of generation and reactivity of singlet molecular oxygen, $O_2(^1\Sigma_g)$. By using steady state measurements the rate constant of 1,3-diphenylisobenzofuran (DPBF) consumption (or singlet oxygen generation rate constant) was determined to be higher in reverse micelles of sucrose esters when compared with neat chloroform. Additionally, the total quenching rate constant of $O_2(^1\Sigma_g)$ by the carotenoid astaxanthin (ASTA) and DPBF were evaluated. The results obtained as a function of R, show a different behavior for both quenchers, consequence of their different localization in the micelar interface. The substituted furan, DPBF, has a lower total quenching rate constant in sucrose monoester reversed micelles than in homogeneous solvent.

Finally, time resolved singlet oxygen emission allowed us, from the time emission profile, to determine Rose Bengal triplet state lifetime. Values evaluated in reversed micelles at different R values show a decrease from 4.0 to 1.5 microseconds (the triplet lifetime determined in water was 2.9 microseconds). This behavior can be explained in terms of media viscosity and oxygen concentration in the micelar system.

Acknowledgements: The authors thank financial support of grant Fondecyt 1080412 and 1120196.

Bibliography

[1] Montenegro, M. A.; Nazareno, M. A.; Durantini, E. N.; Borsarelli, C. D., Photochemistry and Photobiology 2002, 75, (4), 353-361.
[2] Borsarelli, C.; Braslavsky, S., Journal of Physical Chemistry B 1997, 101, (31),6036-6042.

4 Photodimerization of HCl Salt of trans Azastilbenes in the Solid State in Presence and Absence of H_2O

Author(s): Barnali Mondal,* Burjor Captain and V. Ramamurthy

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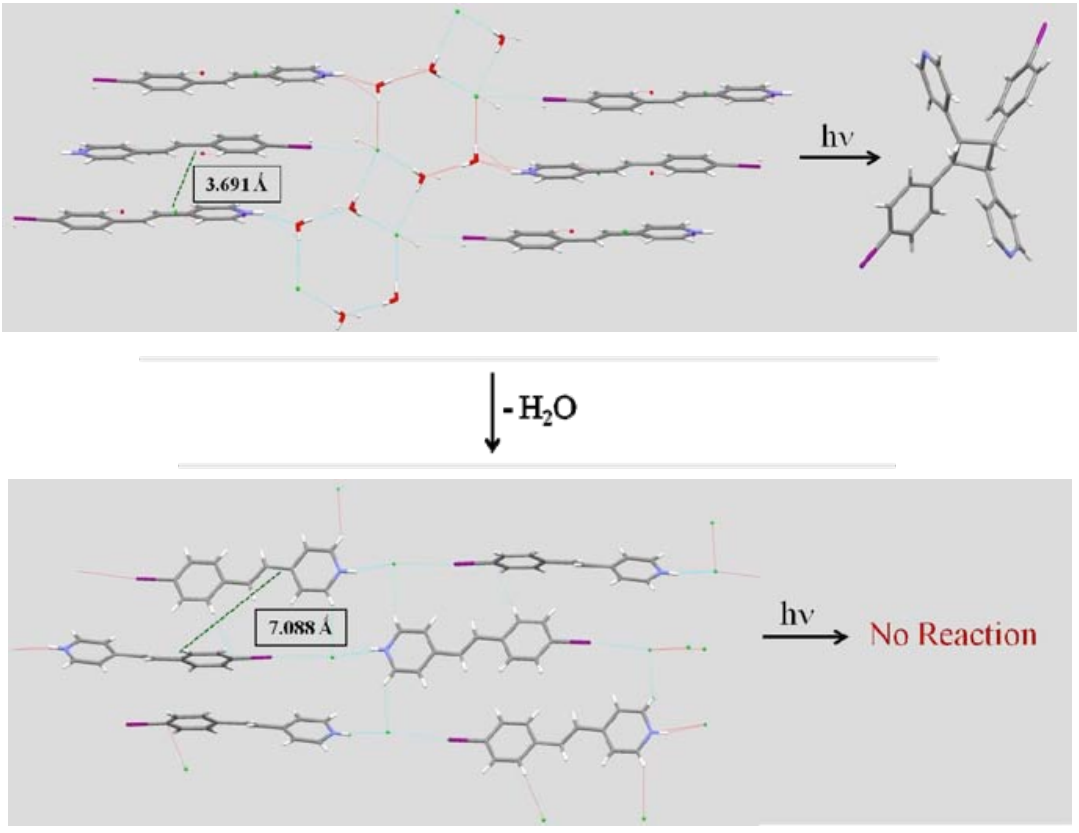
Abstract: Protonation of an electron rich pyridyl to an electron-deficient pyridinium ion results in orientation of olefin molecules towards a single dimer in the crystalline state. The weak intercation between the Cl^- counterion, H_2O, electron deficient pyridinium ring and electron rich phenyl ring leads to crystal packing where the reactant olefin molecules are held together at a distance < 4.2 Å as measured between two alkene units. On the contrary the anhydrous HCl salt of the trans azastilbenes align in a different manner, where the distance between two alkene units is > 4.2 Å. The orientations in the crystal unit play an important role in their photochemical reactivity.



5 Understanding the spore photoproduct (SP) formation and enzymatic repair

Author(s): Gengjie Lin, Linlin Yang, Renae Nelson, David Ames, and Lei Li*

Department of Chemistry & Chemical Biology, Indiana University-Purdue University Indianapolis (IUPUI)

Abstract: The only DNA photo-damage product detected in bacterial endospores is a special thymine dimer 5-thyminyl-5,6-dihydrothymine, also called spore photoproduct or SP. In contrast, thymine photo-dimerization in normal cells results in the cyclobutane dimer and the (6-4) photoproduct. SP accumulates in spores during the sporulation phase and is repaired by enzyme spore photoproduct lyase (SPL) at the early germination phase. SPL utilizes a unique [4Fe-4S] cluster coupled by S-adenosylmethionine (SAM) to generate a 5 -deoxyadenosyl radical to repair SP and belongs to the radical SAM superfamily. Despite the fact that SP was discovered nearly half a century ago and the strong interest of the scientific community to understand its formation and repair, neither process is mechanistically well understood.

Our laboratory is interested in understanding both aspects of the SP biochemistry; our studies to date have made significant progress in these two closely related fields. By employing deuterium labeled dinucleotide TpT, we demonstrated that SP is formed via an intramolecular H atom transfer process between the two thymine residues, answering a key question in SP photo-formation. By using a neutral formacetal linker instead of a phosphate between the two thymine residues, we successfully obtained the first crystal structure of SP 50 years after its discovery. By utilizing the deuterium labeled SP substrates, we proved that the previous SPL mechanism is oversimplified. Our latest data suggest that SPL utilizes a novel radical transfer pathway with one cysteine and two tyrosines as the essential elements for catalysis.

6 Photochemistry of para-Aminobenzoic acid Derivatives as a Function Electron-Accepting Moiety and Solvent Environment

Author(s): Sarah J. Schmidtke Sobeck

Department of Chemistry, The College of Wooster

Abstract: The physicochemical properties of a series of para-aminobenzoic acid (PABA) compounds with variations at the electron-accepting moiety are being studied. Following photoexcitation PABA derivatives may undergo an intramolecular charge transfer (ICT) resulting in the formation of a zwitterionic species. The present study compares the photochemistry of the parent acid relative to ester and thionoester derivatives. The thermodynamics and kinetics of photo-induced processes are measured using temperature- and time-dependent spectroscopy. The measurements are carried out in a range of solvents, with varying intermolecular interactions, to assess the impact of solvent-solute interactions on the photochemistry. Quantum calculations complement experimental work by allowing visualization of electron density changes upon photoexcitation and structural differences between derivatives. The reaction is observed to be the least favorable for the thionoester derivative, and the thermodynamic driving forces for the ICT varies depending upon the solvent and electron-accepting moiety. Time-resolved spectra reveal different excited state dynamics in those solvents, such as methanol, that have the ability to form strong specific solvent-solute interactions relative to those with weaker intermolecular interactions. The studies provide a richer understanding of the role of molecular substituents and solvent upon the reactivity of small organic molecules, providing a stepping-stone to understanding the chemistry of more complex biological and materials systems.

7 Thermolysis and Photolysis of 2-Ethyl-4-nitro-1(2H)-isoquinolinium Hydroperoxide

Author(s): Renat Khatmullin, Dapeng Zhou, Ekaterina Mirzakulova and Ksenija D. Glusac

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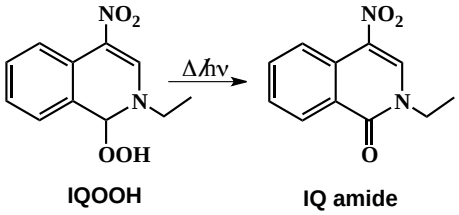
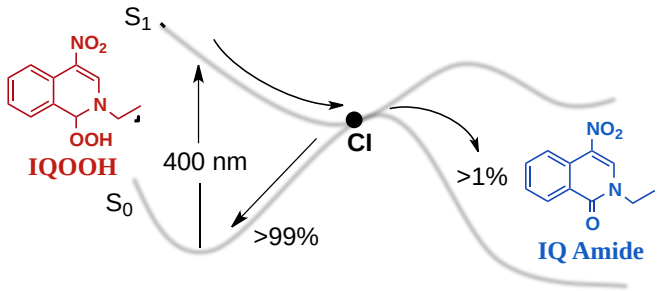
Abstract: The thermal and light induced O-O bond breaking of 2-ethyl-4-nitro-1(2H)-isoquinolinium hydroperoxide (IQOOH) were studied using 1H NMR, steady state UV/vis spectroscopy, femtosecond UV/vis transient absorption and time-dependent density functional theory (TD DFT) calculations. Thermal O-O bond breaking occurs at room temperature to generate water and the corresponding amide (Scheme 1).



Scheme 1: Formation of IQ amide upon thermolysis of IQOOH.

Interestingly, the stability of IQOOH is significantly increased in the presence of small amounts of methanolThe photochemical process yields the same products, as confirmed using NMR and UV/vis spectroscopy. Femtosecond transient absorption studies provide additional detail of the photochemical process and suggest that the S1 state of IQOOH undergoes fast internal conversion to the vibrationally excited ground state, from which the O-O bond breaking occurs (Scheme 2). This result was supported by the fact that the model compound IQOH exhibits similar excited-state decay lifetimes as IQOOH, which is assigned to the S1 → S0 internal conversion.



Scheme 2: Illustration of the proposed mechanism of IQOOH excited-state deactivation.

8 Oxidation of Biological Thiols by Photoactivatable Atomic Oxygen Precursors

Author(s): Miao Zhang, Sara Baumann and Ryan D. McCulla*

Department of Chemistry, Saint Louis University

Abstract: Judicious application of reactive oxygen species (ROS), such as hydroxyl radical and singlet oxygen , has been used therapeutically and to gain information about the functions, interactions, and structures of biological macromolecules. Atomic oxygen is the putative oxidant generated during the photodeoxygenation of various aromatic heterocyclic oxides and is surprisingly selectively for such a small oxidant. Our efforts have focused on examining the reactivity of atomic oxygen with a range of biomolecules. Initial studies indicated that atomic oxygen is thiophilic and reacts selectivity with thiols over other susceptible functional groups such as alkenes. A particularly interesting potential application of this reactivity is exquisite control over the function of redox-regulated proteins. For example, recent work proposed that the plant enzyme adenosine-5'-phosphosulfate (APS) kinase regulates the formation 3'-phospho-adenosine-5'-phosphosulfate (PAPS), which is the sulfate donor for the modification of multiple natural products. The primary regulation mechanism for APS kinase is the formation of an intersubunit disulfide between Cys86 and Cys119 in the N-terminal loop. We have studied the oxidation of APS kinase by photochemically released atomic oxygen and found near quantitative control over the oxidation state of the critical cysteine residues of APS kinase.

9 Novel Spectroscopic Probes for Detecting UV-Induced DNA Damage

Author(s): Amira F. El-Yazbi* and Glen R. Loppnow

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Abstract: The goal of this work is to design probes that are superior to conventional molecular beacons (MBs) (Figure 1) in detecting UV-induced DNA damage. The first approach was to design MBs with modified DNA backbones. So we tried the locked nucleic acid (LNA) MBs and the chimeric RNA-DNA MB (chMB) (Figure 1).

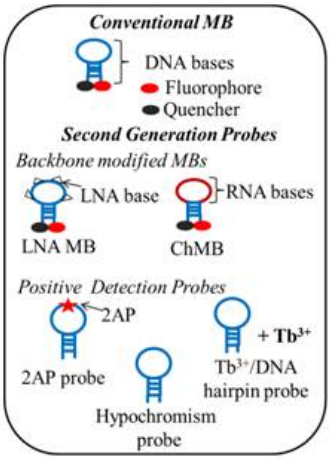

Figure 1. Schematic diagram of the probes used in this work.

Our results show that chMBs are more sensitive and selective for DNA damage than LNA MBs that have comparable selectivity to conventional MBs. However, these probes all show signals that are inversely proportional to the amount of damage. Therefore, we designed probes that give signals directly proportional to damage. Probes with 2-aminopurine (2AP) (Figure 1) as a fluorescent base show no fluorescence for undamaged DNA and fluorescence for damaged DNA. 2AP probes offer high sensitivity and selectivity comparable to MBs, but are expensive, especially with an increasing number of 2APs in the probe. Thus, a hypochromism probe (Figure 1) was designed. The hypochromic effect arises from the formation of a double-stranded target-hairpin hybrid. With accumulated UV exposure, the target-hairpin hybrid concentration decreases and the absorbance increases. This probe is more selective and is more than ten times cheaper than MBs but is less sensitive. The need for a sensitive, selective and inexpensive probe was the motivation to design a Tb^{3+}/hairpin probe (Figure 1). Single-stranded DNA greatly enhances the Tb^{3+} emission, but duplex DNA does not. The Tb^{3+}/hairpin probe proves to be the most sensitive and selective probe for the quantification of DNA damage of all probes presented here. In addition it is considered to be the cheapest probe of all the fluorescent probes discussed. This talk will discuss the design and applications of such probes.

10 Light Activation of Enzyme Inhibition

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Department of Chemistry and Biochemistry, The Ohio State University
Department of Pharmacology, Wayne State University

Abstract: Metal complexes are important tools for chemical biology and have proven applications as diagnostics and therapeutics. Research in the Kodanko laboratory focuses on the development of novel metal complexes for biological applications, in particular for targeting enzymes. A method was developed for caging cysteine protease inhibitors with ruthenium complexes. Inhibitors are released by light, leading to high levels of selectivity for enzyme inhibition under light vs. dark conditions. This method provides a novel way to achieve great spatial and kinetic control over protease activity that may be useful for chemical biology and anticancer applications.

11 Detecting Trace Amounts of Environmental Pollutants by Fluorescence Spectroscopy

Author(s): Olga Rinco,* Andrew Knight, Valarie Fyfe

Department of Chemistry, Luther College

Abstract: Furans and polychlorinated biphenyls (PCBs) are two classes of environmental pollutants that scientists are interested in due to their toxicity and abundance. Due to industrial production, these compounds readily containminate the enivorment as well as cause harm to humans and animals. The primary goal of this research is to develop a method of detecting trace amounts of furans and PCBs by various fluorescence techniques as well as to determine the detection limit of pollutants in water. A variety of furans, PCBs, and other common photophysical molecules were used as probes, with α and β cyclodextrin present as host macromolecules. Homogenous fluorescence, Stern-Volmer quenching, and fluorescence binding studies were preformed on the pollutants along with the supramolecule containing the host-guest complex. Other experiments performed included absorbance studies and quantitative analysis of the detection limits of the pollutants by fluorescence. The common photophysical probes employed were naphthalene and xylene, and were used to develop and understand the methodology being employed for the pollutants within the cyclbodextrin cavity. The pollutants which were found to bind strongest to β-cyclodextrin were dibenzofuran-4-carboxylic acid, dibenzofuran-4-carboxaldehyde, PCB 77 and PCB 1. It was determined using a binding study analysis that dibenzofuran-4-carboxaldehyde was bound inside the -cyclodextrin cavity with a 1:1 ratio. The other pollutants are still under investigation.

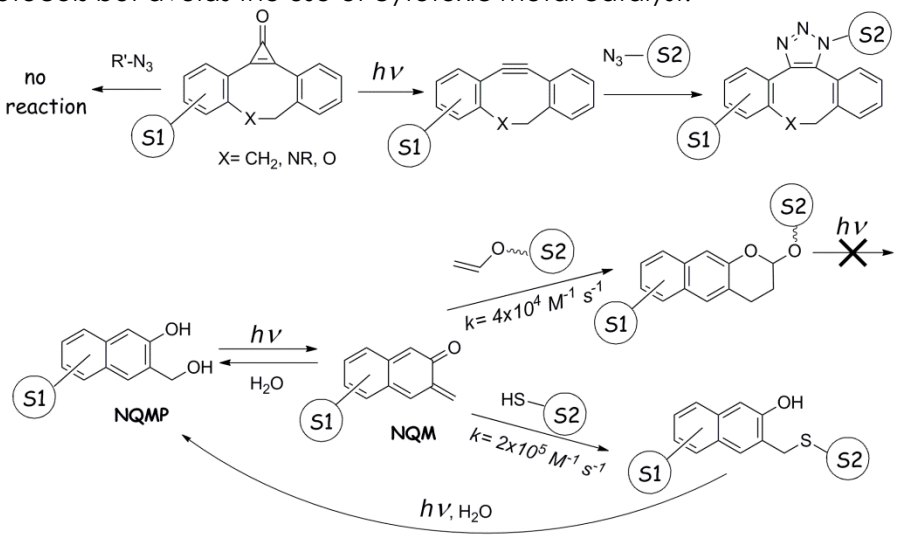
12 Photo-Click Chemistry Tools for Biology and Material Sciences

Author(s): Selvanatan Arumugam, Emmanuel Nekongo, Vladimir Popik*

Department of Chemistry, University of Georgia

Abstract: Photo-triggering expands the utility of the widely used "click-chemistry" by allowing for the spatial and temporal control of the process. The absence of potentially detrimental catalysts and/or activating reagents is another beneficial feature of this approach. Three novel photo-click ligation strategies have been recently developed in our laboratory.

The first method relies on the photo-decarbonylation of cyclopropenone moiety incorporated into an 8-membered ring. Such cyclopropenones do not react with azides in the dark but produce azide-reactive cyclooctynes upon irradiation. This method has the advantage of being compatible with well-developed azide bioorthogonal reporter protocols but avoids the use of cytotoxic metal catalyst.



The second approach is based on a very rapid hetero Diels-Alder addition of photogenerated o-naphthoquinone methides (NQMs) to vinyl ethers producing photostable benzochroman derivatives. The unreacted oNQM is rapidly hydrated to regenerate the starting 3-(hydroxymethyl)-2-naphthol. This competition between hydration and cycloaddition makes oNQMs highly selective, since only vinyl ethers are reactive enough to form the Diels-Alder adduct in an aqueous solution. This method is orthogonal to the acetylene-azide click chemistry.

The third method permits selective and reversible modification of free cysteine residues of proteins or thiol group in other substrates, as well as reversible immobilization and surface patterning. This method makes use of a very facile reaction between NQM and thiols to give hydrolytically stable thioether.

13 Excited State Dynamics and Photoinduced Charge Separation in Polyazine-Bridged Ru(II),Pt(II) Trimetallic Complexes

Author(s): Jessica D. Knoll,*† M. Kyle Brennaman,‡ Thomas J. Meyer,‡ Karen J. Brewer†

†Department of Chemistry, Virginia Tech
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Abstract: Supramolecular complexes coupling a light absorber (LA) to a reactive metal (RM) through a bridging ligand (BL) are attractive photocatalysts for H2O reduction. A series of supramolecules $[(Ph_2phen)_2Ru(dpp)Ru(bpy)(BL)PtCl_2](PF_6)_4$, ($Ph_2phen$ = 4,7-diphenyl-1,10-phenanthroline, dpp = 2,3-bis(2-pyridyl)pyrazine, bpy = 2,2´-bipyridine, BL = dpp or dpq = 2,3-bis(2-pyridyl)quinoxaline) were constructed to exhibit less complicated spectroscopy compared to the previously studied tetrametallic analogues $[\{(Ph_2phen)_2Ru(dpp)\}_2-Ru(BL)PtCl_2](PF_6)_6$. The trimetallic complexes feature a spatially separated outer Ru HOMO and remote BL LUMO. The complexes are efficient light absorbers with ligand ππ* transitions and many overlapping Ru(dπ)-ligand(π*) CT transitions dominating the UV region and visible regions, respectively, resulting in complicated spectroscopy. The lowest-lying optically accessible transition is outer Ru(dπ)-dpp(π*) ^{1}CT in nature, despite the lower-lying BL acceptor orbitals. The bimetallic analogues $[(Ph_2phen)_2Ru(dpp)-Ru(bpy)(BL)](PF_6)_4$ serve as photophysical models for the trimetallic complexes as they possess an emissive excited state of the same nature (outer Ru(dπ)-dpp(π*) ^{3}CT), energy and similar coordination environment. Excitation of the bimetallic models populates the emissive ^{3}MLCT state with unit efficiency independent of excitation wavelength; however, coordination of cis-$PtCl_2$ to form the trimetallic complex results in non-unity population of the emissive state, evidenced by unusual excitation wavelength dependence in emission and transient absorption spectroscopy. Competitive population of a non-emissive, low-lying ^{3}CS (charge separated) excited state with oxidized outer Ru and reduced remote BL occurs. The unusual photophysics, with attention to transient absorption spectroscopy, is reported herein.

14 Highly Fluorescent Push-Pull Bithiophenes: A Solvatochromic Investigation.

Author(s): Andréanne Bolduc,* Yanmei Dong, W.G. Skene

Department of Chemistry, University of Montreal, Pavillon J.A. Bombardier C.P.6128, succ. Centre-Ville, Montreal, Qc, H3C 1J7

Abstract: Conjugated materials have received much attention lately because of their opto-electronic properties that make them suitable for use in plastic electronic. Thiophene derivatives have been widely used because of their high stability and their low oxidation potentials. The properties of conjugated thiophenes have resulted in their use in a wide range of applications, from organic photovoltaïcs to anti-static packaging. One of the interesting properties of thiophenes is their fluorescence. However, high fluorescence quantum yields Φ_{fl} can only be obtained with thiophenes having a degree of oligomerization higher than 6. This limits their use in emitting-related applications due to solubility problems. It is therefore of interest to be able to obtain bithiophenes to with Φ_{fl}.

The major fluorescence deactivation pathway for small oligothiophenes is intersystem crossing (ISC) to the triplet state. A good strategy to suppress this inherent deactivation is to introduce electronic groups that modifiy the energy gap. Adding electron withdrawing and electron donating groups can dramatically increase the fluorescence of bithiophenes. It is also of interest to make push-pull systems with aminothiophene derivatives, due to their potential use as fluorescent probes.

Herein, we present the synthesis and photophysical characterization of a series of bithiophenes illustrated in Figure 1. The effect of the electron withdrawing group's nature as well as its position was investigated. The push-pull character of the molecules was responsible for the high Φ_{fl} that were obtained: 83, 76 and 74% for compounds 2, 3 and 6, respectively. Since 1, 4 and 5 did not exhibit high fluorescence; multiple characterizations were made to investigate the deactivation pathways. It was found that the fluorescence of 1is deactivated because of the rotation between the thiophenes, while 4 and 5 are quenched by photoinduced electron transfer involving the nitro group in the 4' position.

One interesting feature of the aminothiophenes is their fluorosolvatochromism. Compounds 2, 3 and 6 all exhibited strong fluorosolvatochromism when going from apolar ether to polar acetonitrile. Interestingly, the fluorescence is quenched in protic solvents such as ethanol and methanol due to hydrogen abstraction.

References
Roncali, J.; Chem. Rev., 1992, 711-738.
Becker, R.S.; Seixas de Melo, J.; Maçanita, L.; Elisei, F.; J. Phys. Chem., 1996, 100, 18683-18695.
Seixas de Melo, J.; Elisei, F.; Gartner, C.; Aloisi, G.G.; Becker, R.S.; J. Phys. Chem. A., 2000, 104, 6907-6911.
Demchenko, A.P.; Mély, Y.; Duportail, G.; Klymchenko, A.S.; Biophys. J., 2009, 96, 3461-3470.
Dong, Y.; Bolduc, A.; McGregor, N.; Skene, W.G.; Org. Lett., 2011, 13, 1844-1847.
Bolduc, A.; Dong, Y.; Guérin, A.; Skene, W.G.; Phys. Chem. Chem. Phys., 2012, 14, 6946-6956.

15 Multiplex Platforms for DNA and RNA damage

Author(s): Christine Pinnock, Swaroop Sasidharanpillai, Sindhu Nair, and Glen R. Loppnow*

Department of Chemistry, University of Alberta

Abstract: DNA damage is the first step in cancer, cellular aging and other inheritable diseases. Existing methods for detecting such damage include polymerase chain reaction (PCR), HPLC/MS-MS, GC-MS, gel electrophoresis, ^{32}P-postlabeling-HPLC assays and various immunoassays. These methods provide accurate measurement of some types of damage, but are typically complex and may introduce additional lesions. Also, they are useful for single samples, but are difficult to multiplex. In this poster, I will present two multiplex methods for detecting ssDNA and ssRNA damage, using microplates and microarrays.

One assay for UVC-induced DNA damage in multiple oligonucleotides simultaneously is to use a 96-well microplate and smart probes to detect the UVC-induced DNA damage. Our results show that the oligonucleotide damage constants obtained with this method are reproducible and similar to those obtained in cuvettes. The results show that the damage kinetics upon irradiation is sensitive to the different types of photoproducts formed in the different sequences used; i.e. poly-A oligonucleotides containing guanine are damaged at a faster rate than poly-A oligonucleotides containing either thymine or cytosine.

We also printed three different ssDNA target sequences on a microarray slide and measured their UVC damage constants using fluorescent hairpin probes. First-order exponential decay curves demonstrate that the damage for poly-dA ssDNA is less with small amounts of thymine nucleobases. Similar experimental results will be discussed for selected miRNA targets on microarray slides.

16 Differential Photochromic vs. Electrochromic Ring Opening of Quinazolinespirohexadienones

Author(s): Jonathan P. Moerdyk, Kyndra B. Sluiter, Amy L. Speelman, Benjamin J. Pollock, Eugene J. Lynch, William F. Polik, and Jason G. Gillmore*

Department of Chemistry, Hope College, Holland, MI

Abstract: We are working to develop a new class of photooxidants based on organic photochromes that would add an additional level of gating to the process of photoinduced charge transfer (PICT) initiation of cation radical reactions with relevance to a variety of materials applications. Photochromes with long wavelength isomers (LW) capable of acting as photooxidants but with short wavelength isomers (SW) less capable of doing so are sought. This necessitates photochromes that revert only thermally and that have excited state reduction potentials that are more positive for LW than for SW. (As the difference in excitation energies is in the opposite direction, this requires a very large difference in ground state reduction potentials!)

The parent perimidinespirohexadienone (PSHD) photochrome meets these basic requirements, but with a very modest difference in excited state reduction potential between SW and LW, thus with minimal capacity for gating and modest photooxidizing power. In attempting to tune the redox properties of these photochromes, we have recently studied quinazolinespirohexadienones (QSHDs), asymmetric analogs of the parent. These QSHDs are predicted (on basis of our recently reported correlation of DFT calculations with experimental electrochemical data) to be more reducible in their LW than the parent PSHDs. We have recently reported the synthesis of these QSHDs and have proven by NOE experiments the direction of their photochromic ring opening. We now report on the basis of NMR and CV results that electrochromic ring and thermal ring opening proceed in the opposite direction. Recent electrochemical, photochemical and photophysical measurements will be presented, and the results rationalized with the help of DFT calculations.

17 Dynamics and mechanism of damaged DNA repair by photolyase

Author(s): Zheyun Liu,* Chuang Tan, Xunmin Guo, Ya-Ting Kao, Jiang Li, Lijuan Wang, Aziz Sancar[2] and Dongping Zhong

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Abstract: One of the major UV-induced DNA damage products is cyclobutane pyrimidine dimer (CPD) photolesion, which has covalent bonds connecting two adjacent bases and causes DNA mutagenesis or even skin cancer. In all plants and some animals except mammals, CPD can be completely repaired by a kind of enzyme, photolyase, with presence of visible light. Photolyase utilizes an electron to restore the normal DNA. However, the questions still remain: how photolyase delivers an electron into damaged DNA and what is the detailed molecular mechanism of DNA restoration after electron transfer. In our recent study, we used state-of-the-art femtosecond-resolved method accompanied by techniques of molecular biology and solved the entire molecular mechanism of CPD repair. There are two possible pathways for the electron transfer toward damaged DNA from theoretical calculation and crystal structure views: the first one has a smaller distance gap without any intervening molecule in between; the later one has a longer tunneling distance while the process is mediated a part of the enzyme. Using the ultrafast detection method, we observed the dynamics of photolyase donating one electron into CPD. Strikingly, we found that the electron would rather travel through a longer distance in this case. The distinctive structure of the enzyme confines the tunneling pathway of electron and determines the transfer dynamics. After the initial charge transfer, we also solved that the anionic CPD follows a splitting mechanism in which both bonds connecting two bases breaks sequentially within ninety picoseconds, which is less than one-to-ten-billionth of a second and is much faster than the accompanying side reactions. Finally, we answered how photolyase acquires a close-to-unity repair efficiency. With a series of single-point mutations of amino acids at the active site in photolyase, the CPD repair efficiency can drop by more than fifty percent. Using the obtained repair efficiencies, we solved dynamics of all elementary steps in photolyase mutants with femtosecond method. All these mutations change the electron transfer rates between enzyme and DNA significantly which finally leads to a decrease of the total repair efficiency. It appears that the microenvironment of this enzyme has been optimized while all steps in this process reach a delicate balance with maximized efficiency. In summary, we solved the complete temporal-evolution of CPD repair for the first time and elucidated how photolyase restores normal DNA efficiently.

18 Mechanistic Diversity in the Binding Dynamics of Guests with Curbit[n]urils

Author(s): Cornelia Bohne

Department of Chemistry, University of Victoria

Abstract: Cucurbit[n]urils (CB[n]s) form host-guest complexes, which can have very high binding constants. These host systems are formed from glycouril units and the entrances to the cavities are lined with carbonyl groups. Cations can be bound to the portals of CB[n]s. We recently showed that the 2-naphthyl-1-ethylammonium cation (NpH^+) only binds to CB[7] without any bound Na^+ cations. The association rate constant is high and similar to those observed for guest binding to cyclodextrins. In contrast, the dissociation rate constant for NpH^+ from CB[7] is much slower leading to the high equilibrium constant observed. Studies for the binding dynamics of different guests with different CB[n]s showed that the mechanism for NpH^+ with CB[7] is not general. The binding dynamics of trans-1,4-diaminocyclohexane dication with CB[7] occurs with CB[7]•Na^+ in an exchange mechanism and the dissociation rate of the guest can be modulated with the concentration of sodium cations. Only the trans-isomer of l-methyl-4-(4-hydroxystyryl)pyridinium betaine binds to CB[6] and the binding occurs with CB[6]•Na^+. Binding to CB[6] inhibits the trans-to-cis photoisomerization of l-methyl-4-(4-hydroxystyryl)pyridinium betaine which occurs in the aqueous phase. These examples show that kinetic studies can be employed to uncover the mechanistic diversity of guest binding to CB[n]s.

19 Photoresponsive Lipid-based Nanoparticles: Towards On-demand Drug Delivery

Author(s): Yamuma Kandasamy, Jianxin Cai, Alisha Beler, Patrick D. Andrews, and R. Scott Murphy*

Department of Chemistry and Biochemistry, University of Regina

Abstract: We are developing photochromic molecules that will be integrated with lipid-based supramolecular assemblies such as micelles and lipid vesicles to form photoresponsive nanoparticles. These biocompatible nanoparticles will have potential application in 'on-demand' drug delivery where the delivered dose will be regulated with light. We have synthesized amphiphilic dithienylethene derivatives and characterized their photochromic properties. We have also examined their inclusion in micelles and lipid vesicles. Our most recent developments regarding the functionality of these photoresponsive nanoparticles will be presented.

20 Time-Resolved Spectroscopic Study of the Photochemistry of Tiaprofenic Acid in a Neutral Phosphate Buffered Aqueous Solution From Femtoseconds to Final Products

Author(s): Tao Su, Jiani Ma, Ming-De Li, Xiangguo Guan, Lihong Yu and David Lee Phillips*

The University of Hong Kong, Department of Chemistry

Abstract: The photo-decarboxylation mechanism of tiaprofenic acid (TPA) was investigated by femtosecond transient absorption (fs-TA), nanosecond transient absorption (ns-TA) and nanosecond time-resolved resonance Raman (ns-TR^3) spectroscopic experiments in a neutral phosphate buffered solution (PBS). In addition, density functional theory (DFT) calculations were presented to help interpret the experimental results. Resonance Raman and DFT calculation results revealed that the deprotonated tiaprofenic acid (TPA^-) form was the primary species that is photo-excited in a neutral PBS aqueous solution. The fs-TA experimental data indicated that the lowest lying excited singlet state S1 underwent an efficient intersystem crossing process (ISC) to quickly transform into the lowest lying excited triplet state T1 that then undergoes decarboxylation to generate a triplet biradical species (TB^3). Ns-TA and ns-TR^3 results observed a protonation process for TB^3 to produce a neutral species (TBP^3) that then decayed via ISC to produce a singlet TBP species that further reacted to make the final product (DTPA).

21 How and When Does an Unusual and Efficient Photoredox Reaction of 2-(1-Hydroxyethyl) 9, 10-Anthraquinone Occur? A Combined Time-Resolved Spectroscopic and DFT Study

Author(s): Jiani Ma, Tao Su and David Lee Phillips*

Department of Chemistry, The University of Hong Kong

Abstract: The photophysics and photochemical reactions of 2-(1-hydroxyethyl) 9,10-anthroquinone (2-HEAQ) were studied using femtosecond transient absorption (fs-TA), nanosecond transient absorption (ns-TA) and nanosecond time-resolved resonance Raman (ns-TR^3) spectroscopy techniques and density functional theory (DFT) calculations. In acetonitrile 2-HEAQ underwent efficient intersystem crossing to triplet excited state ((2-HEAQ)^3). A typical photoreduction reaction for aromatic ketones took place via production of ketyl radical intermediate for 2-HEAQ in isopropanol. In water-containing solutions with pH values between 2 to 10, an unusual photoredox reaction reported by Wan and coworkers was detected and characterized. The observation of the protonated species in neutral and acidic aqueous solutions by fs-TA spectra indicated the carbonyl oxygen of (2-HEAQ)^3 was protonated initially and acted as precursor of the photoredox reaction. Preference of the photoredox reaction under moderate acidic conditions compared to neutral condition observed using ns-TR3 spectroscopy was consistent with results from DFT calculations, which suggested the protonation of the carbonyl group was the rate-determining step. Under stronger acidic conditions (pH 0), although the protonated (2-HEAQ)^3 was formed, the predominant reaction was the photohydration reaction instead of the photoredox reaction. In stronger basic solutions (pH 12), (2-HEAQ)^3 decayed with no obvious photochemical reactions detected by the time-resolved spectroscopic experiments. The reaction mechanisms and key reactive intermediates for the unusual photoredox reaction were elucidated from the time-resolved spectroscopy and DFT results. A brief discussion is given of when photoredox reactions may likely take place in the photochemistry of aromatic carbonyl-containing compounds and possible implications for using BP and AQ scaffolds for phototrigger compounds.

22 Fluorescence Photoactivation by Intermolecular Proton Transfer

Author(s): Subramani Swaminathan,* Marco Petriella, Erhan Deniz, Janet Cusido, James D. Baker, Mariano L. Bossi and Françisco M. Raymo

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Department of Biology,University of Miami, Coral Gables, Florida.
INQUIMAE, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Pabellón 2, Ciudad Universitaria, 1428 - Buenos Aires, Argentina

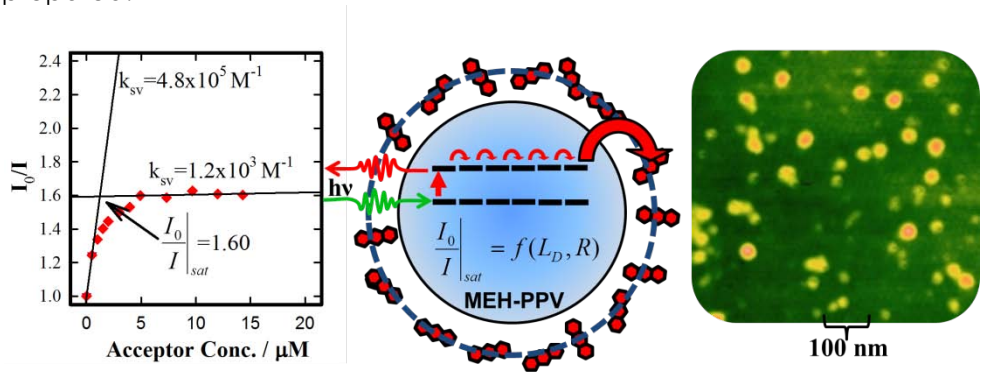
Abstract: We designed a strategy to activate fluorescence under the influence of optical stimulations based on the intermolecular transfer of protons. Specifically, the illumination of a 2-nitrobenzyl derivative at an activating wavelength is accompanied by the release of hydrogen bromide. In turn, the photogenerated acid encourages the opening of an oxazine ring embedded within a halochromic compound. This structural transformation extends the conjugation of an adjacent coumarin fluorophore and enables its absorption at an appropriate excitation wavelength. Indeed, this bimolecular system offers the opportunity to activate fluorescence in liquid solutions, within rigid matrixes and inside micellar assemblies, relying on the interplay of activating and exciting beams. Furthermore, this strategy permits the permanent imprinting of fluorescent patterns on polymer films, the monitoring of proton diffusion within such materials in real time on a millisecond time scale, and the acquisition of images with spatial resolution at the nanometer level. Thus, our operating principles for fluorescence activation can eventually lead to the development of valuable photoswitchable probes for imaging applications and versatile mechanisms for the investigation of proton transport.

23 Amplified Quenching of Conjugated Polymer Nanoparticle Emission for Exciton Diffusion Length Measurement

Author(s): Josiah A. Bjorgaard* and Muhammet E. Köse

Department of Chemistry and Biochemisty, North Dakota State University

Abstract: A novel method for measuring exciton diffusion length in nanoparticles (NPs) of conjugated materials is presented. Using NPs of the prototypical conjugated polymer MEH-PPV, titrations with cationic acceptor dyes in an aqueous environment display amplified emission quenching with a Stern-Volmer constant in excess of 105 M^{-1}. At acceptor concentrations above 3-5 μM, the Stern-Volmer constant is drastically reduced, indicating saturation of NP surfaces with acceptor molecules. Various exciton diffusion models are examined to explain the observed amplified emission quenching. Explicit calculation of Förster resonance energy transfer rates fails to provide reasonable results, most likely due to difficulty in accurately determining Förster radii, local acceptor concentration, and average donor-acceptor distance. A model describing boundary quenching with variable efficiency provides the best estimation of exciton diffusion length. For NPs with mean radius of 28 nm, the three dimensional exciton diffusion length is measured as 12±2 nm, assuming quenching efficiency above 80%. This result is comparable to the lower region of reported values in thin films ranging from 10-25 nm. Both the derived model and the experimental methodology allow robust measurement of exciton diffusion length for any luminescent conjugated material from which NPs can be prepared.



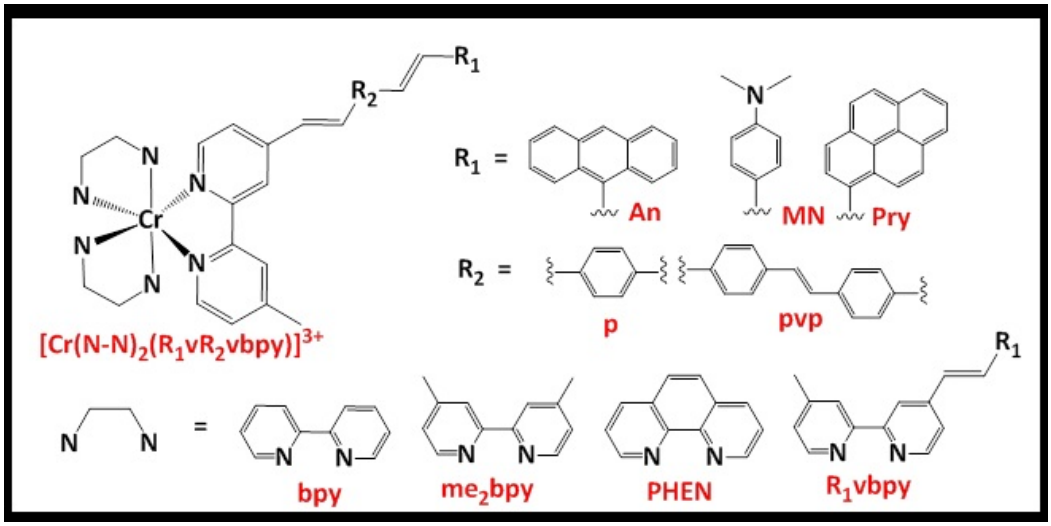
24 Chromium Complexes Containing Aryl-phenylene-vinylene Bipyridine Ligands for Reverse Saturable Absorbers

Author(s): Gilbert K. Kosgei,* and Russell H. Schmehl

Department of Chemistry, Tulane University

Abstract: We have synthesized new metal complexes which will be good candidates for reverse saturable absorbers and to study excited state energy transfer (Figure 1).

They are coordinated to mono-functionalized bipyridyl ligands attached to various aryls (R_1) synthesized by utilizing multi-step Wittig-Horner reactions procedures. The ligands are linked by extended π-conjugated phenylenevinylene backbones (R_2) which serves to lower the energy of the triplet excited state of the ligand. The photophysical properties of the ligands and Cr^{3+} complexes have been studied and reported.



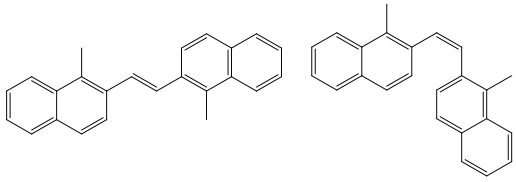
25 Adiabatic Cis→Trans Photoisomerization of 1,2-di(1-Methyl-2-naphthyl)ethene in S1

Author(s): V. K. Ratheesh Kumar,* Frank B. Mallory, Clelia W. Mallory and Jack Saltiel

Departments of Chemistry, Florida State University, Bryn Mawr College and University of Pennsylvania

Abstract: Olson first proposed olefin photoisomerization through an adiabatic path in S_1 leading to the formation of excited isomer.[1] Experimental evidence for this mechanism was obtained in the cis→trans direction for 9-styrylanthracene.[2] We showed that the cis → trans adiabatic contribution gains in importance as the size of the aryl substituent on the double bond increases. It is very small in *cis*-stilbene (0.2%),[3a] ten times more efficient in the 2-naphthyl/phenyl analog[3b] and 100% efficient in the 2-anthryl/phenyl analog.[3c] Furthermore, in the latter two cases, cis→trans adiabatic photoisomerization is conformer specific, being observed only in the more extended conformers.[3b,c]

To better define the scope of the adiabatic pathway, we are studying the *cis* → *trans* photoisomerization of *cis*-1,2-di(1-methyl-2-naphthyl)ethene (*c*-D-1-MNE) which is expected to exist primarily as the extended conformer in solution. The adiabatic pathway is immediately revealed by the fact that *c*-D-1-MNE and *t*-D-1-MNE have identical, λ_{exc}-independent fluorescence spectra in methylcyclohexane (MCH) and the same τ_f.



They feature the expected[3d] vibronic bands of the *t*-D-1-MNE fluorescence spectrum but the excitation spectrum of *t*-D-1-MNE fluorescence from *c*-D-1-MNE follows the *c*-D-1-MNE absorption spectrum. The quantum yield of adiabatic *cis*→*trans* photoisomerization, $\phi_{c\to t}^{ad}$ = 0.26, was calculated from the ratio of the fluorescence quantum yields, ϕ_f^c = 0.17 and ϕ_f^t = 0.64. It is somewhat lower than the overall quantum yield, $\phi_{c\to t}$ = 0.35, indicating that most *c*-D-1-MNE photoisomerization in MCH follows the adiabatic pathway. On increasing *T*, ϕ_f^c increases and ϕ_f^t decreases. The quantum yield of the adiabatic pathway drops from 0.26 in MCH to 0.17 and 0.10 in toluene and acetonitrile, respectively, whereas the overall quantum yield, $\phi_{c\to t}$, increases from 0.35 to 0.44 and 0.47 in the same order. Solvent polarizability and polarity stabilization of a zwitterionic intermediate, $^1\pi^*$, could account for this result.

Acknowledgment. The National Science Foundation, most recently by Grant CHE-0846636, supported this research.

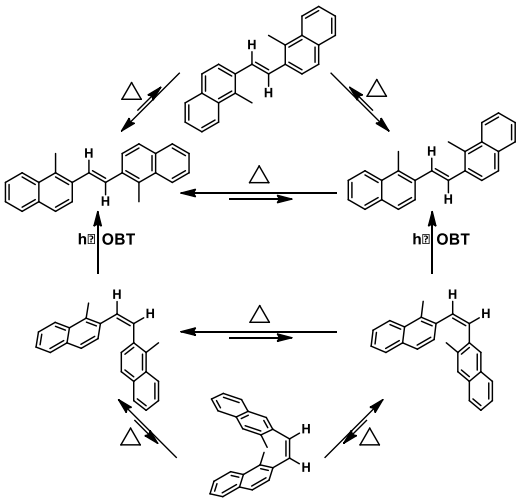
Refrences
1. Olson, A. R. Trans. Faraday Soc. 1931, 27, 69-76.
2. Sandros, K.; Becker, H.-D. J. Photochem. 1987, 39, 301-315.
3. Saltiel, J.; Waller, A. S.; Sears, Jr., D. F. J. Am. Chem. Soc. 1993, 115, 2453-2465.
4. Saltiel, J.; Tarkalanov, N.; Sears, D. F., Jr. J. Am. Chem. Soc. 1995, 117, 5586-5587.
5. Saltiel, J.; Zhang, Y.; Sears, D. F., Jr. J. Am. Chem. Soc. 1996, 118, 2811-2817.
6. Sun, Y.-P.; Sears, D. F., Jr.; Saltiel, J.; Mallory, F. B.; Mallory, C. W.; Buser, C. A. J. Am. Chem. Soc. 1988, 110, 6974-6984.

26 Photoisomerization of cis-1,2-Di(1-methyl-2-naphthyl)ethene in Glassy Media at 77 K: Effects of the Rate of Cooling. No Hula-twist.

Author(s): Christopher Redwood,* Ratheesh Kumar V. K., Stuart Hutchinson, Frank B. Mallory, Clelia W. Mallory, Ronald J. Clark, Olga Dmitrenko and Jack Saltiel

Departments of Chemistry, Florida State University, Bryn Mawr College, University of Pennsylvania, University of Delaware

Abstract: The claim that *cis*-1-(2-naphthyl)-2-phenylethene (*c*-NPE) undergoes one bond twist (OBT) *cis-trans* photoisomerization in methylcyclohexane (MCH) glass at 77 K was based on direct formation of the stable conformer of the *t*-NPE product.[1] That conclusion was disputed because Hula-twist (HT) photoisomerization about the benzylic CH would lead to the same result.[2] To settle the issue, the photoisomerization of *cis*-1,2-Di(1-methyl-2-napthyl)ethene (*c*-DMNE) is studied by fluorescence spectroscopy at 77 K in organic glasses. Steric requirements of the methyl groups restrict the isomers to a narrow distribution of conformer structures, as shown in the Scheme. Nonplanarity in the geometry of each *t*-DMNE conformer causes each to relax into two distinct geometries differing in the relative direction of dihedral angles with respect to the central alkene plane. The conformer duality is predicted by theory and confirmed by the resolution of geometrically distinct conformer specific fluorescence spectra.



Self-modeling curve-resolution is used to decompose the multivariate system into conformer specific emission spectra, which are then applied to determine the mechanism of *cis-trans* photoisomerization. Rapid cooling of the *c*-DMNE solution gives a mixture of two conformers, each of which undergoes one bond twist photoisomerization to the corresponding *t*-DMNE conformer. Slow cooling allows trapping of the most enthalpically favored *c*-DMNE conformer which undergoes one bond twist photoisomerization to the enthalpically favored conformer of *t*-DMNE.

Acknowledgment. The National Science Foundation, most recently by Grant CHE-0846636, supported this research.

References

1. Saltiel, J.; Krishna, T. S. R.; Turek, A. M. *J. Am. Chem. Soc.* 2005, *127*, 6938-6939.
2. Yang, L.-Y.; Liu, R. S. H. *Photochem. Photobiol.* 2007, *83*, 1436-1440.

27 Tuning Excited State and Ground State Dynamics in Photochromic Ruthenium and Osmium Complexes with Chelating Sulfoxides

Author(s): Komal Garg,* James T. Engle, Christopher J. Ziegler and Jeffrey J. Rack

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2. Department of Chemistry, Knight Chemical Laboratory, University of Akron, Akron, 44325

Abstract: The photochemistry and photophysics of polypyridine metal transition complexes is a continuing area of interest in inorganic photochemistry. Ruthenium sulfoxide complexes, a class of such chromophores, may be used in solar cells, or as molecular switches in a variety information storage devices. Herein, we report the synthesis and spectroscopic properties of $[Ru(bpy)_2(py\text{-}et\text{-}SO)]^{2+}$ and $[Os(bpy)_2(py\text{-}et\text{-}SO)]^{2+}$, where bpy is 2,2´-bipyridine, py-et-SO is 2-(propane-2-sulfinylethyl)-pyridine. We found that by simply increasing the chelate ring size from 5 to 6 leads to dramatic photoreactivity changes in these complexes. There is a striking increase in the quantum yields of isomerization ($\Phi_{S\text{-}O}$) for complexes with a six-membered chelate ring relative to a five-membered chelate ring. For the osmium compound, we report that isomerization may only be triggered by electrochemical oxidation. The compounds have been analyzed by X-ray crystallography, ^{1}H-NMR, UV-Visible absorption and ultrafast transient absorption spectroscopy. Analysis of data reveals quite important features in the electronic structure of these complexes. These data and other details for both complexes will be discussed.

28 Investigating Sequential Isomerizations in a Photochromic Ruthenium Sulfoxide Complex via 2-Color Pump-Repump-Probe Spectroscopy

Author(s): Albert W. King,* Yuhuan Jin, James T. Engle, Christopher J. Ziegler and Jeffrey J. Rack

Department of Chemistry and Biochemistry, Ohio University, Athens, OH
Department of Chemistry, University of Akron, Akron, OH

Abstract: Photochromic compounds have been employed to effect technologies ranging from optical data storage and manipulation to controlling biological activity. Notably, photoisomerizing ruthenium sulfoxides promise diverse applications, especially acting as attractive candidates for the development of novel energy storage methodologies and having been demonstrated to impart photomechanical functionality in polymer films through covalent incorporation in the polymer. Investigation of the photochemistry of relevant isomerizing complexes is critical to the further development of functional and practical materials. Ultrafast 3-color pump-pump-probe spectroscopy has recently been developed and utilized to investigate the metastable ground states accessible in promising photoisomerizing ruthenium sulfoxide complexes. The observed photochemistry of the model complex, $[Ru(bpy)_2(bpSO)]^{2+}$, where bpy is 2,2'-bipyridine and bpSO is 1,2-bis(phenylsulfinyl)ethane, is reported here. The observed time constants for the respective [S,S] →[S,O] and [S,O] → [O,O] isomerizations are ~ 60 ps and ground state formation is complete within ~ 150 ps, representing the fastest observed isomerization of a metal sulfoxide.

29 Photo-mechanical Effects of Amorphous Polymers with Photochromic Ruthenium Complexes

Author(s): Yuhuan Jin,* and Jeffrey J. Rack

Department of Chemistry and Biochemistry, Ohio University

Abstract: Photochromic molecules undergo an isomerization upon irradiation with light of a specific wavelength. The isomerization yields a photoproduct different from the ground state isomer in molecular structure and potential energy, which gives the possibility to convert light energy into mechanical energy. Much of the research in this area has been performed on azobenzene liquid crystal network polymers and diarylethene single crystals. Here, we demonstrate that amorphous polymers comprising photochromic Ruthenium sulfoxide monomers show reversible macroscopic photo-mechanical effects at room temperature. The phototriggered action is due to an excited isomerization of the sulfoxide from S to O bonding and from O to S bonding. This polymer thin film (5.0 mm X 1.0 mm) bends reversibly under irradiation of low intensity 370nm and 472nm laser light. Nanoindentation studies shows that the Youngs' modulus increased about 30% after irradiation. Detailed results will be presented, as well as a model to explain the observed behavior.

30 Excited State Deactivation Pathways of Ruthenium Polypyridyl Compounds Relevant to Dye-Sensitized Solar Cells

Author(s): Ryan M. O'Donnell,* Patrik G. Johansson, Maria Abrahamsson, and Gerald J. Meyer

Department of Chemistry, Johns Hopkins University and Department of Chemistry, Chalmers University of Technology

Abstract: Although thermal degradation studies of dye sensitized solar cells (DSSCs) can be found in the literature, few reports detail deactivation pathways for the metal-to-ligand charge transfer (MLCT) excited state of ruthenium polypyridyl compounds commonly employed in DSSCs. Variable temperature photoluminescence studies were performed on DSSC-relevant compounds of the general type cis-$Ru(LL)_2(X)_2$, where LL is a bipyridyl ligand and X is CN^- or NCS^-, and contrasted with the well-known $Ru(bpy)_3^{2+}$ and $Os(bpy)_3^{2+}$, where bpy is 2,2'-bipyridine, to identify deactivation pathways. A modified Arrhenius analysis revealed internal conversion to two different states, assigned to an upper MLCT excited state and a ligand field (LF) excited state. Deactivation through the upper MLCT excited state typically displayed pre-exponential factors of 107 – 108 s^{-1} with activation energies of 400 to 900 cm-1, whereas relaxation rates through LF states occurred with 1014 - 1015 s-1 and activation energies of 4000 to 5000 cm-1. Excited state deactivation of cis-$Ru(dcbH_2)_2(NCS)_2$, where $dcbH_2$ is 4,4'-$(CO_2H)_2$-2,2'-bipyridine, also called N3, anchored to mesoporous TiO_2 or ZrO_2 thin films immersed in CH_3CN occurred through the upper MLCT excited state with activational parameters in good agreement with those abstracted from fluid solution data. An intriguing finding of these studies is that the LF excited states appeared to be at higher energy than one would anticipate for a weak field ligand like isothiocyanate. Therefore, ligand loss photochemistry of DSSCs through the population of dissociative LF excited states was unlikely to occur at room temperature for cis-$Ru(LL)_2(NCS)_2$ type compounds.

31 Exploring the Photochemistry and Photophysical Properties of Cationic Oligo-p-Phenylene Ethynylenes

Author(s): Eric H. Hill,* Kirk S. Schanze, David G. Whitten

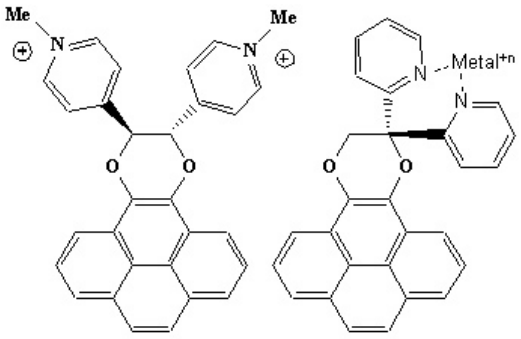
Nanoscience and Microsystems Program, University of New Mexico
Department of Chemistry, University of Florida
Center for Biomedical Engineering, University of New Mexico

Abstract: Previous studies by the Whitten and Schanze groups have explored the sensing capabilities and antimicrobial properties of a class of cationic compounds based on the p-Phenylene-ethynylene backbone. In this work, I discuss the photochemistry and photophysical properties of these compounds, and how small changes in the structure of the different compounds in the series can lead to very large changes in the photochemistry. The progress of the photoreactions are followed by UV-Visible and fluorescence spectroscopy and the products are characterized by high-resolution mass spectrometry. Through this research, we have been able to determine which compounds are more likely to react in environmental conditions, and the implications of the photoreactivity on the compounds ability to kill bacteria. Our conclusions have allowed us to better understand the structure-reactivity relationships of this unique class of compounds.

32 DNA Binding Requirement for Photochemical Cleavage of DNA Oligomers with Dihydrodioxins.

Author(s): A. E. Shamaev, K. E. Karabaeva, A. S. Mereshchenko, E. F. Khisamutdinov, N. B. Leontis, M. S. Panov, A. N. Tarnovsky and R. M. Wilson*
Center for Photochemical Sciences and Department of Chemistry
Bowling Green State University

Abstract: Pyrene dihydrodioxins (PDHDs) release ortho-quinones upon irradiation. Some PDHDs are also excellent DNA cleaving agents. It had been assumed that the mechanism for DNA cleavage stemmed from its reactions with the released quinone. In order to better understand the mechanism of DNA cleavage and damage, two families of DHD's have been prepared and studied, the symmetrical 1,2-dipyridininium PDHD **1** and metal-binding 1,1-dipyridinium PDHD **2**. The former, **1**, binds strongly to DNA and cleaves it efficiently. However, it has a low quantum yield for quinone release. The latter, **2**, does not bind to DNA and does not cleave DNA. However, it has a relatively high quantum yield for quinone release. Ultrafast transient absorption spectroscopy indicates that both classes of DHDs undergo efficient electron transfer from the pyrene to a pyridine moiety as their primary photochemical event. Therefore, it is now proposed that the species required for DNA cleavage is the intercalated pyrene radical cation and not the quinone that is release at a later stage in the photochemical cascade. The mechanism of this DNA cleavage process is currently under investigation using high resolution ESI-FT mass spectrometry where the DNA/DHD complexes and their photoproducts can be observed directly. The progress in this area of research will be described in this presentation.



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33 Synthesis and Characterization of Doped Iron-Oxide Nanostructured Electrodes for Use in Solar Energy Conversion Devices

Author(s): Jordan E. Katz*

Department of Chemistry and Biochemistry, Denison University

Abstract: To address the growing need to produce carbon-free energy on a global scale, we have synthesized and characterized arrays of doped iron-oxide nanostructures for use as photoelectrodes to directly convert sunlight to chemical fuels. Using an iterative and systematic approach to synthesis, we seek to establish new methods to produce iron-based mixed-metal oxides with unique chemical compositions and nanometer-scale architectures. We use one-pot, inexpensive synthetic methods, including microwave-assisted and conventional hydrothermal synthesis, and electrodeposition, to grow self-assembled nanorod arrays to directly form low-cost photoelectrodes composed of elements that are abundant and non-toxic.

We have successfully made doped iron-oxide nanorod electrodes in one-step syntheses that show increased photocurrent at the oxygen reduction potential under simulated solar illumination in 1 M NaOH. Scanning electron microscopy shows formation of large-area arrays of nanorods ~50 nm in diameter composed of the hematite phase (alpha-Fe_2O_3), as confirmed by powder X-ray diffraction. Investigation by energy dispersive spectroscopy does not indicate segregation of dopant atoms in the structure. High light intensity open-circuit voltage measurements provide a convenient measure of approximate band edge positions as a function of electrode composition and morphology. Our ongoing work to aims to correlate the structure of these novel materials with their photoelectrochemical properties to better understand how compositional variations, in tandem with electrode morphology, can be used to optimize performance of working solar cells.

34 Light Induced Stereospecific [2+2]-Photocycloaddition of Atropisomeric 3,4-Dihydro-2-pyridones

Author(s): Elango Kumarasamy* and J. Sivaguru

Department of chemistry and Biochemistry
North Dakota State University

Abstract: Light induced asymmetric [2+2]-photocycloaddition of dihydro-2-pyridones proceeds through triplet pathway leading to high enantio- and diastereoselectivity in the photoproduct. This methodology gives us an avenue to synthesize highly complex polycyclic ring systems with control over stereochemistry in the photoproduct. The presentation will highlight the mechanistic details and the role of axial chirality in which the traditional bulky group responsible for atropisomeric nature of the substrate(s) was replaced by a small shielding group to control the stereochemical course of the photochemical transformation.

35 Light Induced stereospecific intramolecular hydrogen abstraction of axially chiral enones

Author(s): Nandini Vallavoju,* J. Sivaguru

Department of Chemistry & Biochemistry, North Dakota State University

Abstract: Accessing chirally enriched molecular architectures through photochemical transformations demands the use of photo-candidates with built-in molecular restrictions. Employing molecularly chiral photochromophores is a viable methodology to achieve high selectivity in asymmetric photochemical transformations. The poster will present preliminary results from our lab where atropisomeric enones undergo enantiospecific H-abstraction leading to spiro-lactam photoproduct. Anomeric effect and steric hindrance likely play a key role in determining the selectivity (enantio- and diastereo- selectivity) in the photoproduct. The poster will detail the origin of these effects and provide a mechanistic rationale.

36 Light induced enantiospecific photocycloaddition of maleimides

Author(s): Ramya Raghunathan*, Elango Kumarasamy, and J. Sivaguru

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Abstract: Maleimides are known to undergo versatile photochemistry depending on the choice of wavelength, substituent(s) and concentration. But there are very few reports that details stereospecific reactions of maleimides. Recent methodology developed in our lab allowed us to successfully perform stereospecific photochemical reactions on these systems. The presentation will highlight preliminary results of this endeavor and the mechanistic insights into the intramolecular photocycloaddition of maleimides leading to high ee values in the photoproduct.

37 Investigation of the Triplet Energy and Electron Transfer Capability of Octa acid Host using Benzonorbornadiene, Dibenzobarrelene and N-methylacridinium Probes

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Abstract: The photochemistry and photophysics of many water insoluble organic molecules encapsulated inside the octa acid (OA) capsule have been studied extensively in the past. These previous studies demonstrate that the cavity of OA, a host molecule, acts as an inert medium for any photophysical/photochemical studies. The reported results so far indicate that under UV irradiation of a guest@(OA)2 capsular assembly, either electron transfer or energy transfer process occurs only between two molecules separated by the walls of the OA which clearly shows the innocent nature of OA during this processes. Photochemistry of benzonorbornadiene (1, figure1) and dibenzobarrelene (2, figure1) in solution were well studied and known to be multiplicity (singlet or triplet) dependent. Photolysis of 1 and 2 gives different products in the presence and absence of a triplet sensitzer respectively. Observation of only triplet sensitized products upon irradiation of (2)2@(OA)2 and (3)2@(OA) indicates that the OA molecule can act as a triplet sensitizer. Further photophysical studies with N-methylacridinium salt shows that the OA molecule also has the ability to transfer electron to an acceptor molecule.

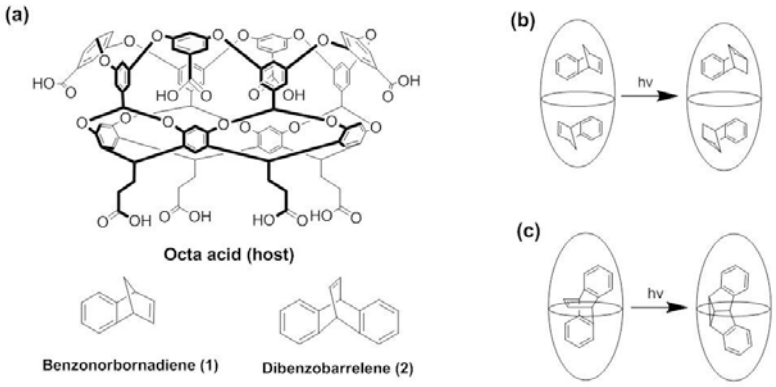

Figure 1. (a) Structure of deep-cavity cavitand octa acid (**OA**), benzonorbornadiene (**1**) and dibenzobarrelene (**2**). (b) and (c) represents the photochemistry of benzonorbornadiene and dibenzobarrelene inside the octa acid capsule respectively.

38 Crystalline Phenylethynylene bis-urea Nanotubes as Molecular Scale Reaction Vessels

Author(s): Sahan R. Salpage,* Sandipan Dawn, Linda S. Shimizu

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Abstract: Crystalline materials with well define and robust nanocavities can use as molecular scale reaction vessels [1]. Our group specialize in design and synthesis of bis-urea macrocycles that can self-assemble into tubular structures through urea-urea bifurcated hydrogen bonding to yield well define porous nanotubes [2]. These nanotube confinements serve as the "host" for specific "guest" molecules. Compared to solution sate, inclusion solid state reactions favor a particular reaction pathway which give more control over the reactivity and reaction products due to restricted molecular motion of guest molecules inside host cavities [3]. Herein we report the influence of self-assembled phenylethynylene bis-urea macrocycle on facilitating [2+2] photodimerization reactions of acenphthylene, coumarin [4] and quinolone derivatives.

References

[1] Inokuma, Y.; Kawano, M.; Fujita, M. Nat. Chem. 2011, 3, 349-358.

[2] Dewal, M. B.; Lufaso, M. W.; Hughes, A. D.; Samuel, S. A.; Pellechia, P. J.; Shimizu, L. S. Chem. Mater. 2006, 18, 4855-4864.

[3] Ramamurthy, V.; Parthasarathy. A. Isr. J. Chem. 2011, 51, 817 – 829.

[4] Dawn, S.; Dewal, M. B.; Sobransingh, D.; Paderes, M. C.; Wibowo, A. C.; Smith, M. D.; Krause, J. A.; Pellechia, P. J.; Shimizu, L. S. J. Am. Chem. Soc. 2011, 133, 7025–7032.

39 Exciplex and Excimer Formation in Blended Films of Dyes and Bisphthalimide Quenchers

Author(s): David J. Stewart,* Matthew J. Dalton, Rachel N. Swiger, Thomas M. Cooper, Joy E. Haley, and Loon-Seng Tan

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Abstract: Spin-cast and melted films of three different dyes blended with nonconjugated bisphthalimides were prepared. The dyes are D-π-D, A- -A, and D- π -A type, where π is a fluorene core, D is an electron donating diphenylamino group, and A is an electron accepting benzothiazole group. Upon visible-light excitation of the dyes, quenching of the excited state occurs via exciplex formation between dye and bisphthalimide molecules, or in some cases excimer formation between two dye molecules. The extent of exciplex formation is dependent on the driving force, which can be calculated using the energy difference between the lowest unoccupied molecular orbitals (LUMOs) of the dyes and bisphthalimides. The exciplex emission energies can also be predicted by calculating the difference between the LUMO level of the bisphthalimide and the highest occupied molecular orbital (HOMO) of the dye. These calculated values show good agreement with experiment. The exciplex lifetimes are significantly longer than the lone dyes, and could be exploited for potential uses in solar energy conversion and storage or nonlinear photonics. The morphology of the films is also important as the exciplex lifetimes in the melted films are much longer than in the spin-cast films.

40 Photoinduced Ligand Loss in Ruthenium(II) Complexes

Author(s): Bryan Albani,* Christopher B. Durr, and Claudia Turro

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Abstract: Understanding the photochemistry of transition metal complexes is essential for the advancement of many research areas including photovoltaic devices, energy storage, biomolecular sensing, and therapeutics. The concept of photoinduced ligand loss from a metal center has been investigated for some of these applications. Our lab has shown the complex $[Ru(bpy)_2(MeCN)_2]^{2+}$ (bpy = 2,2'-bipyridine, MeCN = acetonitrile), upon irradiation (≥ 450 nm), exchanges the monodentate MeCN ligands for coordinating solvents such as H_2O or DMSO. To study the effect of altering the bidentate ligands around the ruthenium core have on ligand loss, the complexes $[Ru(phen)_2(MeCN)_2]^{2+}$ (phen = 1,10-phenathroline), $[Ru(biq)(phen)(MeCN)_2]^{2+}$ (biq = 2,2'-biquinoline), and $[Ru(biq)_2(MeCN)_2]^{2+}$ were synthesized and characterized. As expected, the addition of the biq ligand red shifts the metal-to-ligand charge transfer (MLCT) and all complexes undergo ligand loss when irradiated with light corresponding to the tail end of the MLCT peak. The photoinduced ligand loss of the complexes was monitored by UV-Vis spectroscopy and 1H NMR spectroscopy. Interestingly the asymmetric complex, $Ru(biq)(phen)(MeCN)_2]^{2+}$, reveals a much more defined intermediate upon irradiation in H_2O relative to the other two complexes, indicating one MeCN ligand is more photolabile than the other in this complex. Moreover, altering the energy and intensity of irradiation can enhance this selectivity. The asymmetric complex was irradiated with low energy light (≥ 550 nm) in a pyridine/MeCN mixture and the intermediate was isolated and characterized by X-ray crystallography. The MeCN trans to the phen ligand was replaced with pyridine indicating it is the more photolabile ligand. This photoinduced ligand exchange could potentially serve as a selective drug delivery agent or an inorganic synthetic tool.

41 Enantiospecific Photochemical Transformations Under Elevated Pressure

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Abstract: Atropisomeric compounds have attracted the interest of chemists due to their unique properties in biologically relevant molecules. These molecules are often prone to racemization at elevated temperatures. To control the racemization process at elevated temperatures and to understand the molecular dynamics of such systems, we have investigated the effect of elevated pressure on atropisomeric acrylanilides, -oxoamides and pyridones. The poster presentation will detail the role of elevated pressures in the stabilizing these atropisomeric substrates leading to slow racemization as well as the effect of elevated pressures in facilitating axial chiral transfer during photochemical transformations.

42 Photochemical Generation of Singlet Oxygen by Benzophenone bis-Urea Macrocycle

Author(s): Michael F. Geer* and Linda Shimizu

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Abstract: Oxidation of small molecules is widely used as feedstock in the polymer industry and the research of pharmaceuticals.[1] One of the simplest oxidants is molecular oxygen, but because of its size and reactivity it is difficult to control the selectivity of these reactions. A promising method for control has been in the development of molecular containers that can restrict the conformations and availability of the reactive species.[2] Our group has been exploring the scope of the bis-urea macrocyclic assembly motif and the use of resulting porous crystals as extended molecular containers for control of photo-chemical reactions such as the [2+2] photo-dimerization of unsaturated ketones and coumarin species. These macrocycles form robust columnar structures through the urea-urea three centered hydrogen bonding to afford crystals that can uptake guest molecules.[3] Here, we report the use of a benzophenone bis-urea macrocycle to generate singlet oxygen and facilitate the oxidation of 2-methyl-2-butene to produce 3-methyl-2-butene-1-ol, a product previously only observed with the selenium catalyzed oxidations.

References

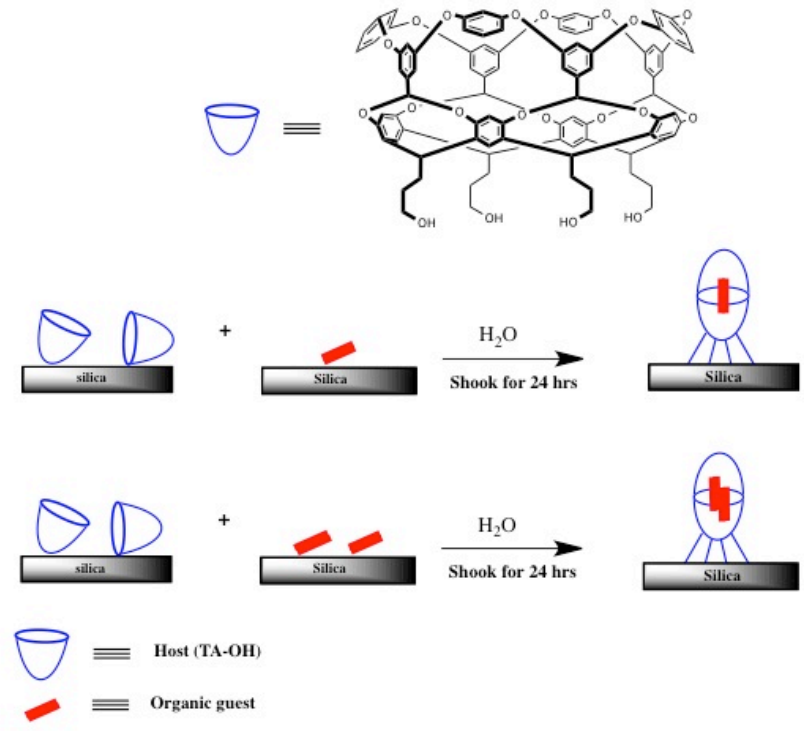
1. (a) Bregeault, J. M., Dalton Transactions 2003, (17), 3289-3302; (b) Chow, T. W. S.; Chen, G. Q.; Liu, Y. G.; Zhou, C. Y.; Che, C. M., Pure Appl Chem 2012, 84 (8), 1685-1704; (c) Kessel, D.; Reiners, J., Israel Journal of Chemistry 2012, 52 (8-9), 674-680.
2. (a) Inokuma, Y.; Kawano, M.; Fujita, M., Nature Chemistry 2011, 3 (5), 349-358; (b) Ramamurthy, V.; Parthasarathy, A., Israel Journal of Chemistry 2011, 51 (7), 817-829; (c) Sivaguru, J.; Poon, T.; Franz, R.; Jockusch, S.; Adam, W.; Turro, N. J., J. Am. Chem. Soc. 2004, 126 (35), 10816-10817.
3. Yang, J.; Dewal, M. B.; Profeta, S.; Smith, M. D.; Li, Y. Y.; Shimizu, L. S., J. Am. Chem. Soc. 2008, 130 (2), 612-621.

43 Host-Guest Capsular Assembly Formation on Silica Surface

Author(s): Elamparuthi Ramasamy,* Ramamurthy Vaidhyanathan

University of Miami

Abstract: Formation of a capsular assembly of water-insoluble host Tetrol (TA-OH) was achieved by adding water to silica gel. Depending upon the organic guest molecules, either 1:2 (guest : host) or 2:2 capsular assemblies were formed. The excited state properties of the guest molecule that was encapsulated within the host on the silica surface was different from that observed alone on the silica surface. This was evident by observing the phosphorescence and excimer emission. The high cage effect was observed upon photolysis of 1-phenyl-3-tolyl 2-propanone included within the host TA-OH on silica surfaces, which supported the formation of capsular assembly on silica surface.



44 Materials Incorporating Antimicrobial Polymers and Oligomers: Design, Characterization and Biocidal Studies

Author(s): Anand Parthasarathy,* Thomas Corbitt, Dimitri Dascier, Eunkyung Ji, Linnea Ista, Lance Edens, David J. Keller, David G. Whitten and Kirk S. Schanze

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Abstract: Conjugated polyelectrolytes (CPEs) are conjugated polymers with ionic side chains which make them soluble in water. We have previously shown that direct photoexcitation of these polymers produces the polymer triplet which is capable of sensitizing the formation of singlet oxygen. Our studies have clearly proved that CPEs with cationic side chains are capable of killing pathogenic bacteria upon exposure to light. The overall effect is attributed to both the ability of the cationic CPEs to interact with the bacterial membrane and the damage caused to the bacteria by the CPE generated reactive oxygen species (ROS). Recently, we have also established cationic oligo (phenylene ethynylene) derivatives (OPEs) to possess light activated biocidal properties. To probe the utility of the antimicrobial CPEs and OPEs, we have devised strategies to incorporate them into fiber samples such as cotton, filter paper, fabric pieces and glass substrates. The modified surfaces are characterized by several analytical techniques and found to possess efficient biocidal properties. Our current focus is on developing smart surfaces that can capture, kill and release bacteria in a controllable fashion. This work is highlighted in this presentation.

References

1. Ji, E.; Corbitt, T.; Parthasarathy, A.; Schazne, K. S.; Whitten, D. G, Light- and Dark Activated Biocidal Action of Conjugated Polyelectrolytes, *ACS Appl. Mater. Interfaces*, 2011, *3*, 2820.
2. Ista, L.; Dascier, D; Ji, E.; Parthasarathy, A.; Corbitt, T.; Schanze, K. S.; Whitten, D. G., Conjugated polyelectrolyte grafted cotton fibers act as 'micro flypaper' for the removal and destruction of bacteria , *ACS Appl. Mater. Interfaces*, 2011, *3*, 2932.
3. Zhou, Z.; Corbitt, T.; Parthasarathy, A.; Tang, Y.; Ista, L.; Schanze, K.S.; Whitten, D.G., ""End-only" Functionalized Oligo Phenylene Ethynylenes: Synthesis, Photophysical and Biocidal Activity. *J. Phys. Chem. Lett.*, 2010, *1* (21), 3207–3212.

45 Non-Aggregating, Conjugated Polyelectrolytes

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Abstract: Conjugated polyelectrolytes (CPEs) are π-conjugated polymers featuring ionic solubilizing groups (i. e. $-NR_3^+$, COO^-, SO_3^-) that make them soluble in water and other polar solvents. In the group of CPEs, especially poly(phenylene ethynylene)s (PPEs) received considerable attention as materials for ultrasensitive chemo- and biosensors. The optical properties PPEs in different solvents have been well documented. While in methanol, the fluorescence of the PPEs consists of a distinct band with a clear vibronic structure, a broad and red-shifted fluorescence with significantly lower quantum yield can observed in aqueous solutions. This effect was attributed to the formation of aggregates in water.

The current work focuses on a new type of PPEs that contains the same electronic structure but a different linker between the backbone and the solubilizing ionic side chains (i.e., $-CH_2-$ vs. $-OCH_2-$). Interestingly, the emission of these polymers is very similar both in methanol and in water. In addition, the fluorescence quantum yield of these polymers remains high in water. The photophysical results suggest that the PPEs with CH_2-linker are less aggregated in water, in contrast to PPEs with OCH_2-linker. Further, the fluorescence quenching of these polymers with opposite charged quenchers (methylviologene (MV), 3,3'-diethyloxacarbocyanine (DOC)) indicates amplified quenching effects.

46 Phenylene Vinylene Platinum(II) Acetylides with Prodigious Two-Photon Absorption in solution and solid polymer matrix

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Abstract: Organometallic complexes comprising platinum (II) acetylide core linked with different pi-conjugated chromophores are promising materials for applications requiring strong nonlinear-optical response. In the dual-mode optical power limiting, the chromophore first undergoes ultrafast two-photon absorption (2PA) in singlet manifold, followed by rapid intersystem crossing promoted by the heavy atom effect to afford the triplet state, which can subsequently absorb via the T1-Tn transition. Here we present a series of linear- and cross-conjugated p-phenylene vinylene platinum (II) acetylides (TPV1-Ph, TP01-TPV2, crossTPV1, crossTPV3) with extended pi-conjugated chains and discuss their linear- and nonlinear photophysical properties, including comparison to the properties of the constituting ligand chromophores. Remarkably high femtosecond 2PA cross-section values (up to 10,000 GM) were obtained for several of the new complexes by both nonlinear transmission (NLT) and two-photon excited fluorescence (2PEF) method. The large 2PA values, especially in crossTPV1 and crossTPV3, span broad range of wavelengths, 570 – 810 nm, which overlaps with maximum wavelength of strong T-T excited state absorption measured by nanosecond transient absorption method. This combination of properties is rendering these compounds efficient dual-mode nonlinear absorbers in the visible to near-IR. For practical OPL applications platinum complexes have been incorporated into PMMA monoliths, which showed comparable to the solution photophysical properties but much higher stability to air and photo degradation.

47 Photo-induced Interactions of Dirhodium Complexes with DNA

Author(s): Alycia M. Palmer,* Claudia Turro

Department of Chemistry and Biochemistry, The Ohio State University

Abstract: The DNA interactions of Cisplatin have been well-studied, and it is widely accepted that the chemotherapy drug covalently binds purine bases after activation by thermal hydrolysis. This DNA adduct is thought to disrupt transcription and lead to apoptosis. However, thermal activation of the complex limits its specificity, and healthy cells are also affected. Several complexes exist that can be photo-activated, rather than thermally activated, to produce the DNA-reactive species, and these are promising to reduce global toxicity during treatment. Complexes of the type *cis*-$Rh_2(CH_3COOH)_2(CH_3CN)_6]^{2+}$ and *cis-HH*-$[Rh_2(HNOCCH_3)_2(CH_3CN)_6]^{2+}$ exhibit photoinduced ligand exchange of CH_3CN for H_2O solvent molecules to yield the DNA-reactive bis-aqua products. Additionally, in the dark these complexes are inert. In this work, the interactions of a series of dirhodium complexes with oligonucleotides have been assessed through ESI mass spectrometry. The results provide insight into the binding selectivity of dirhodium complexes for DNA and highlight the potential of these complexes as agents for photodynamic therapy.

48 Sn(IV) Schiff Base Complexes: a New Class of Photosensitizer for Photoredox Reactions

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Abstract: This work illustrates the synthesis and characterization of a series of four fluorescent Sn(IV) schiff base complexes, which also access long-lived triplet excited states. The complexes absorb visible light (λ_{max} = 420 to 462 nm) and the optical properties are easily tunable without laborious synthetic manipulations. Phosphorescence is not observed in these molecules; however, the triplet excited states are easy to monitor using nanosecond transient absorption spectroscopy. The lifetimes of the triplet excited states are on the order of 10^{-5} - 10^{-6} s. The triplet state energies were determined via energy transfer reactions with a series of organic triplet acceptors. Two derivatives have triplet energies higher than trans-stilbene (ET = 17500 cm^{-1}). The complexes are quenched effectively by electron donors (i.e. 10-methyphenothiazine (Eo ($mPTZ^{*+}$)/V vs SCE = +0.79V)). These results demonstrate the potential for the development of novel photosensitizers based on main group elements with high spin orbit coupling constants. Recently, we have expanded our search for suitable photosensitizers by exploring Sn complexes containing salen ligands as well as examining other N^N^O derivatives.

49 Steady-State and Time-Resolved EPR Investigation of Nanostructures in Catanionic Mixtures of SDS/DTAC

Author(s): Lauren E. Jarocha* and Malcolm D.E. Forbes
The University of North Carolina at Chapel Hill

Abstract: The physical properties of nanostructures formed from a mixture of two common, oppositely charged surfactants, dodecyltrimethyl ammonium chloride (DTAC) and sodium dodecyl sulfate (SDS), is examined by X-band (9.5 GHz) steady-state (SSEPR) and time-resolved electron paramagnetic resonance spectroscopy (TREPR). A micelle to vesicle transition occurs as the mixing ratio approaches equimolar. SSEPR is sensitive to the diffusional motion of a stable spin probe, 5-doxyl-stearic acid, incorporated inside surfactant nanostructures. Changes to the spectral line shape and decreasing rotational correlation times reflect the slowed rotational tumbling of larger nanostructures, the increased viscosity inside the nanostructure, and the increased ordering of the surfactant tails at mixing ratios near equimolar. TREPR is sensitive to the diffusional motion of photochemically generated radical pairs inside the nanostructures. Following a 308nm excimer laser flash, the excited triplet state of benzophenone is formed and then quenched by hydrogen atom abstraction from the alkyl tail of a surfactant molecule. This creates a radical pair confined to the interior of the micelle or vesicle structure. As the mixing ratio of SDS and DTAC approaches equimolar, the observation of the alkyl-based radical and the contribution to the TREPR spectra from the spin-correlated radical pair mechanism (SCRPM) of chemically induced dynamic electron polarization (CIDEP) changes substantially. These observations can be understood in relation to increased packing of surfactant alkyl chains and an increase in size during the micelle to vesicle transition, both of which affect the diffusional motion of the radical pair. Because both techniques are sensitive to different motional behavior within the surfactant based nanostructures, SSEPR and TREPR provide complementary information in the observation of phase changes in catanionic surfactant mixtures.

50 Ultrafast Microscopy of Quantum Dot Films

Author(s): David F. Zigler,[1,2]* Michelle M. Gabriel,[2] Erik M. Grumstrup,[2] Emma Brown Cating,[2] Justin R. Kirshbrown,[2] James K. Parker,[1] John. M. Papanikolas[2]

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Abstract: Quantum dot solar cells (QDSCs) are an attractive alternative to single crystalline photovoltaics due to their inexpensive fabrication and high theoretical solar conversion efficiency. The experimental efficiency of these devices, while steadily improving, is still far below the theoretical limit. New iterations of QDSCs would benefit from a better understanding of photoinduced charge carrier dynamics on microscopic dimensions and ultrafast timescales. With this in mind, we used ultrafast far-field microscopy to study the spatially resolved electronic properties of quantum dot films. These were compared to ensemble measurements of the films using femtosecond transient absorption spectroscopy and photoluminescence spectroscopy.

51 A P-type NiO dye-sensitized photosynthetic cell (DSPEC) for H_2 production from water consisting of cyclometalated ruthenium sensitizers and cobaloxime catalysts.

Author(s): Zhiqiang ji,* Yiying Wu

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Abstract: We present a photocathode which can split water to generate hydrogen under illumination with applied bias. The electrode comprises a mesoporous NiO film loaded with a single layer of cyclometalated ruthenium sensitizers (O22). The appended pyridine ring on O22 can coordinate to cobalt metal center in cobaloxime, hydrogen production catalyst through self-assemble process. The PEC test was carried out in a homemade cell using our photocathode as a working electrode, Ag/AgCl aq. as a reference electrode, and a pt wire as a counter electrode. To enhance the performance, a single layer of $Al_2O_x(OH)_y$ is coated on NiO film by ALD method. The photocatalytic activity of the photocathode was evaluated by the linear sweep voltammogram under chopped light. Under illumination, a cathodic photocurrent of ~ 20 $\mu A/cm^2$ is observed, which is nearly independent of the applied voltage. The onset potential of photocurrent is around 0.25 V vs. Ref., which is very close to valence band of NiO (0.5 V vs. NHE). In addition, without surface loaded catalysts, the cathodic photocurrent is diminished. A chrono-amperogram of the illuminated photocathode at an applied bias of -0.4 V vs. Ref. showed very stable photocurrent within 2.5 hours. The hydrogen produced during the experiment was confirmed by gas chromatography measurement.

52 Radical-Triplet Pair Interactions as Probes of Long-Range Polymer Motion in Solution

Author(s): Soo-Yeon Sim,* Malcolm D. E. Forbes

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Abstract: Electron spin exchange interactions between stable nitroxide free radicals and photoexcited triplet states of the ester side chains in acrylate polymers lead to electron spin polarization in the nitroxide radical. This emissive radical-triplet pair mechanism (RTPM) polarization is observed on the sub-microsecond time scale using time-resolved electron paramagnetic resonance (TREPR) spectroscopy. Random incorporation of nitroxide side chains into poly(methyl methacrylate) varies the probability of contact between radicals and ester triplet states. The magnitude of the RTPM polarization is reflected by the probability of such encounters. Competing Norrish I cleavage of the ester side chain dominates the TREPR spectrum if the probability of radical-triplet encounters is low. The phenomenon has been studied as a function of mole percent of incorporated nitroxide, temperature, solvent, and ester side chain structure. The utility of such systems for the study of long–range motions of polymer chains in solution is discussed.

53 Exploration of a novel ligand to ligand charge transfer in dirhodium paddlewheel complexes

Author(s): Nicholas A. Leed,* Zhayong Li, Nicole Dickson, Kim R. Dunbar, and Claudia Turro

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Abstract: While organic photochemistry can provide some useful analogues for inorganic photochemistry, many of the typical organic paradigms do not follow leaving much to be discovered. Exploration of the photophysical properties of various dirhodium paddlewheel complexes with formamidinate bridging ligands yielded unusual and unexpected results. Further analysis by ultrafast transient absorbance and DFT calculations suggest a new ligand to ligand charge transfer (LLCT) excited state, where the hole and electron are positioned across the metal and are localized on the ligands.

54 Polymerization of a Columnar Assembled Diacetylene Macrocycle

Author(s): Weiwei Xu,* Yuewen Xu, Pravin Paudel, Andrew B. Greytak, and Linda S. Shimizu

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Abstract: Due to the extended π electron delocalization along their backbones, conjugated polymers exhibit interesting electric and optical properties for applications including light emitting diodes (LEDs),[1] photovoltaic cells,[2] and sensors.[3] Our group developed a polymerizable macrocycle which contains two diacetylene units, that are rigidly separated. These macrocycles self-assemble into columnar structures and can be polymerized under thermal or UV-light irradiation conditions to afford porous polydiacetylene macrocycle (PDM) fibers.[4] The channels are accessible to guests and can take up dopants such as I2. Herein we report investigation of the assembly of the macrocycles under different conditions to give micro fibers and crystals, and study their subsequent polymerization. We examine the absorption of iodine into the fiber and use micro organic field-effect transistor (micro-OFET) devices to characterize the conductivity of iodine treated PDM (PDM-I2) fibers. The roughly linear I-V curve indicates essentially ohmic conduction of PDM-I2 fiber which possesses a conductivity of about 10^{-5}-10^{-4} S/cm.

References

(1) Moerner, W. E.; Silence, S. M. *Chem Rev* 1994, *94*, 127.

(2) Bundgaard, E.; Krebs, F. C. *Sol Energ Mat Sol C* 2007, *91*, 954.

(3) Thomas, S. W.; Joly, G. D.; Swager, T. M. *Chem Rev* 2007, *107*, 1339.

(4) Xu, Y.W.; Smith, M.D.; Geer, M.F.; Pellechia, P.J.; Brown, J.C.; Wibowo, A.C; Shimizu, L.S. *J. Am. Chem. Soc.* 2010, *132*, 5334.

55 Quinoxaline Based Semiconducting Polymers: Effect of Fluorination on Optoelectronic and Physical Properties

Author(s): Akila Iyer, M. Erkan Köse*

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Abstract: The present work is focused on the synthesis of a novel fluorinated quinoxaline based semiconducting polymer. The acceptor unit has been copolymerized with an electron-rich benzodithiophene based donor system to yield a low band gap polymer (PBDT-QxF). Two different routes have been followed to synthesize 5,8-Dibromo-2,3-diethyl-6,7-difluoroquinoxaline (QxF) as the new acceptor system. For the donor monomer, (4,8-bis(octyloxy)benzo[1,2-b:4,5-b´]dithiophene-2,6-diyl)bis-(trimethylstannane) (BDT) was chosen and synthesized using the reported literature.[1] A non-fluorinated analogue of the same polymer (PBDT-Qx) has also been synthesized to disclose the effects of fluorination on the physical properties of the polymer. PBDT-QxF exhibits both lower optical band gap and better thermal and oxidative stability when compared to non-fluorinated analogue.

References

[1] Huo, L. J.; Hou, J. H.; Chen, H. Y.; Zhang, S. Q.; Jiang, Y.; Chen, T. L.; Yang, Y. *Macromolecules* 2009, *42*, 6564.

56 Alkyl Radical Generation via Sequential Photoreactions

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Abstract: Anaerobic photolysis of 1,2-didodecyloxy-9,10-anthraquinone with visible light produced an anthraquinoyl dimer and an alkyl radical corresponding to the 1-alkyl group minus one methylene. This reaction pattern was consistent across a wide range of 1,2-dialkoxy-9,10-anthraquinones. However, 1-methyl, 1-ethyl, and 1-benzyl quinones did not produce dimer; instead these analogs produced the corresponding 1-keto derivative.

When the nucleophiles were added to the reaction mixture prior to introduction of oxygen, dimer formation was prevented. In its place was obtained a 1-carboxyl derivative. When triflic anhydride was introduced prior to oxygen, an anthracene lactone with a 10-triflate substituent was obtained.

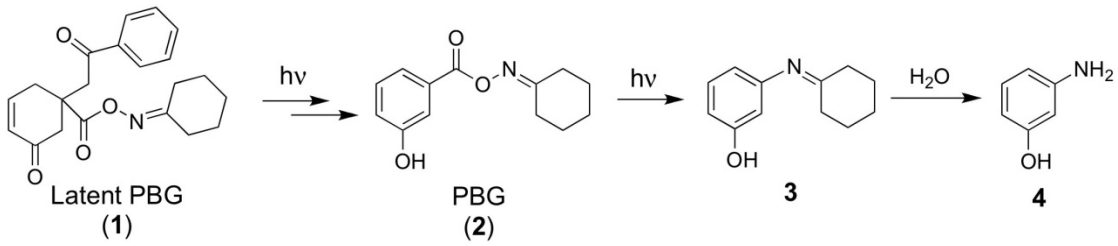
The radical could be trapped to give either alkane or alkyl halide. We propose a mechanism in which products are obtained via three sequential photoreactions and provide a means for converting primary alcohols or halides to an alkane or alkyl halide with one less carbon.

57 Photochemistry of Two Stage Photobase Generator for Optical Microlithography

Author(s): Yongjun Li,* Yuji Hagiwara, Steffen Jockusch, David I. Schuster, C. Grant Willson, and Nicholas J. Turro

Department of Chemistry, Columbia University and Department of Chemical Engineering, University of Texas at Austin

Abstract: Optical microlithography is a technique that produces integrated circuits and other micro- and nanoscale devices. To extend the resolution limit, two–stage photobase generator (PBG) has been designed, the one that requires two sequential photochemical reactions to generate a base. Two-stage PBG with a delay in the onset of base generation as dose would increase the fidelity of the printed image. As shown in the figure below, a latent PBG that incorporates benzophenone, cyclohexenone and oxime ester moieties was synthesized. Upon photoexcitation, the latent PBG (1) produces PBG (2) via Norrish Type II reaction. Upon absorbing the second photon, the PBG (2) forms the imine (3) via decarboxylation. Finally, the imine (3) is hydrolyzed in water to produce the amine base (4). We characterized photoproducts of each step and measured the quantum efficiencies. The results show that the designed compound behaves as a two-stage photobase generator with a delay in the onset of base generation upon photolysis.



58 Photo-ligation and Phase Transfer of Inorganic Nanocrystals to Hydrophilic Media

Author(s): Naiqian Zhan,* Goutam Palui, Tommaso Avellini and Hedi Mattoussi

Department of Chemistry and Biochemistry, Florida State University

Abstract: Colloidal semiconducting nanocrystals (quantum dots, QDs) exhibit several unique photophysical properties, including tunable narrow emission and remarkable photo- and chemical stability. These properties combined have generated tremendous interest to use them as fluorescent platforms to improve our understanding of a variety of biological process. Because high quality nanocrystals are usually prepared in hydrophobic, a great effort has centered on developing straightforward and reproducible schemes to promote their transfer to buffer media and to endow them with biocompatibility.

Here, we describe a novel, photo-mediated strategy to promote the transfer of QDs to polar and buffer media using lipoic acid (LA)-based ligand, where reduction of dithiolane ring using 350 nm UV irradiation and cap exchange takes place in-situ in the presence of TOP/TOPO-QDs. This strategy is complementary to previous phase transfer methods by eliminating $NaBH_4$ reduction step and is adapted to modify QDs surface with diverse functionalities (e.g. carboxy, amine, aldehyde and azide. This effective strategy is simple to implement and fully compatible with an array of ligands including pure LA, LA-PEG and more compact LA-appended zwitterion, with the final QD materials maintaining their optical and spectroscopic characteristics. In addition to providing QDs with great colloidal stability, this strategy is gentle towards sensitive groups such as azide and aldehyde. Furthermore, we found that QDs stabilized with compact DHLA-zw are fully compatible with metal-affinity self-assembly with polyhistidine-appended proteins.

59 Using Coordination Chemistry for the Development of Novel Anti-cancer Agents

Author(s): David K. Heidary, Ph.D., Brock S. Howerton, Erin Wachter, Yang Sun and Edith C. Glazer*

Department of Chemistry, University of Kentucky

Abstract: Cisplatin remains one of the most widely used anti-cancer treatments in the world, despite its systemic toxicity and debilitating side effects. Light-activated ruthenium agents offer an alternative approach to kill cells in a spatially defined area, reducing damage to healthy tissues. A family of ruthenium compounds were designed to be inert in the dark, but activated by visible light to become cytotoxic. The coordination compounds produce extensive DNA damage and exhibited excellent light-induced toxicity in a variety of cancer cell lines. The intrinsic tunability of the design scheme allows for rational modulation of photophysical and photochemical features, with resulting biological implications.

60 New Ru(II),Rh(III) Bimetallic Motif with Tridentate Ligand on the Rh(III) Center

Author(s): Rongwei Zhou, Dexter G. Wimer, Gerald F. Manbeck, Travis A. White, Jing Wang, Karen J. Brewer*

Department of chemistry, Virginia Tech

Abstract: A new Ru(II), Rh(III) bimetallic motif has been designed by coupling a light absorber unit $[Ru(bpy)_2(dpp)]^{2+}$ (bpy = 2,2'-bipyridine and dpp = 2,3-bis(pyridyl)pyrazine) to a Rh(III) center where a tridentate ligand is attached. This new motif $[Ru(bpy)_2(dpp)RhCl(TL)](PF_6)_4$ (TL = tpy = 2,2':6,2''-terpyridine or tpm = tris(pyrazol-1-yl) methane) offers a new forum to investigate the effect the Rh(III) terminal ligand has on the electrochemical and photophysical properties in comparison with $[Ru(bpy)_2(dpp)RhCl_2(bpy)](PF_6)_3$. These complexes display different reductive electrochemical behaviors. The tpy analogue shows an overlapping RhIII/II/I reduction couples while in other complexes RhIII/II and RhII/I are separated. A Rh($d\sigma^*$)-based LUMO (lowest unoccupied molecular orbit) and a Ru($d\pi$)-based HOMO (highest occupied molecular orbit) were found in all complexes, enabling these complexes to be photoinduced electron collectors. The presence of this low-lying ^{3}MMCT state (metal-to-metal charge transfer) can lead to electron transfer from ^{3}MLCT to ^{3}MMCT, which accounts for the lower quantum yields of these complexes compared to a model complex $[\{Ru(bpy)_2\}_2(dpp)]^{4+}$.

Acknowledgment is made to the Chemical Sciences, Office of Basic Energy Sciences, Office of Sciences, U.S. Department of Energy DE FG02-05-ER15751 for generous financial support.

61 Platinum(II) Complexes Based on 6-Fluorenyl-2,2'-bipyridyl Ligands: Synthesis, Photophysics, and Nonlinear Transmission

Author(s): Zhongjing Li,* Wenfang Sun

Department of Chemistry and Biochemistry, North Dakota State University

Abstract: The photophysical properties of platinum(II) complexes have been intensely investigated because they are closely related to the application of these complexes in OLEDs, dye-sensitized solar cells, photodynamic therapy, and nonlinear transmissions. Platinum complexes with nonlinear absorption are of particular interest to us because of their potential application in nonlinear optics.In this study, 7-substituted fluorene was incorporated onto the 6-position of the 2,2'-bipyridine to facilitate two-photon absorption and reverse saturable absorption. The structure-property relationship was investigated in three series of related Pt(II) complexes: 1) attaching the electron-donating or withdrawing substituent directly at the 7-position of fluorene; 2) extenting the π-conjugation of the C^N^N ligand by incorporating 4-substituted phenyl acetylene on the 7-position of fluorene; 3) varying the linkage between the fluorene and benzothiazole components. These modifications induce intriguing effects in the photophysics of the platinum complexes, which were studied in detail by UV-Vis, emission, transient absorption spectroscopy, and via DFT calculations. The results showed that the ground and excited states of the complexes were effectively modified by our structure variation. Meanwhile, all the complexes exhibit considerable broadband transient absorption and their nonlinear transmission performances were evaluated by ns laser at 532 nm.

62 The Photochemistry of Bifunctional Nitrogen Onium Salts

Author(s): Wolfgang H. Kramer*, Anna K. Allred, Irene S. Corrao, Melinda K. Solomon, James P. McVaugh, Emily H. Stewart, B. Woods Curry

Department of Chemistry and Biochemistry, Millsaps College, Jackson, Mississippi
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Abstract: Combining 1,8-naphthalimides with nitrogen onium salt moieties yields a class of bifunctional compounds with interesting photochemistry. The nitrogen onium salt can easily be synthesized by oxidation of an aromatic heterocycle and subsequent alkylation of the resulting N-oxide. 1,8-naphthalimide fluorescence is influenced by the heterocyclic part of the compound. Oxidation state, substitution pattern and protonation have an effect on the fluorescence properties and Stern-Volmer analysis suggests different modes of quenching. While the absorption spectrum suggests clean separation of the chromophors, irradiation of the 1,8-naphthalimide leads to onium salt photochemistry. Analysis of the photoinduced homolytic N-O bond cleavage indicates a 0.6 quantum yield of transient species, a heteroaromatic radical cation and an oxygen centered radical. The energy wasting step appears to be geminate ion pair recombination to yield alkoxy substituted aromatic heterocycles. A proton is produced in this reaction and several methods have been investigated to monitor this side reaction by focusing on analysis of proton concentration. Titration with p-nitro phenolate yields the results that best correlate with the time resolved studies. This allows us to quantify the side reaction for several novel onium salts.

Novel syntheses combine separate building blocks by ester or amide linkages, leading to a greater variety of structures. The bifunctional compounds are tested as DNA cleavers and structural elements that enhance cleaving are integrated in future syntheses. Analysis of ground state association led to the conclusion that a DNA binding moiety (thus the attachment of 1,8-naphthalimide) is required for the simple nitrogen onium salts based on quinoline, isoquinoline or phenanthridine. DNA binding is measured by spectroscopic techniques. DNA cleaving is observed by simple gel electrophoresis. CD analysis of the cleavage assays indicates a change in structure which might be due to dissociation based on the reduced affinity of the photoproducts. Comparison with binding experiments with just the photoproducts indicates a more complex relationship.

63 Synthesis of Dirhodium Complexes for Potential Use in Photodynamic Therapy

Author(s): Kyle A. Vasquez,* Scott J. Burya, and Claudia Turro

Department of Chemistry and Biochemistry, The Ohio State University

Abstract: Dirhodium complexes derived from the parent paddlewheel complex $Rh_2(O_2CCH_3)_4$ were synthesized in order to provide specific interactions with double-stranded DNA upon irradiation with low energy light. In particular, complexes possessing ligands with an extended -system for DNA intercalation were investigated. These series include ***cis***-$[Rh_2(O_2CCH_3)_2(L)(CH_3CN)_2]^{2+}$, where L represents bpy (2,2´-bipyridine), phen (1,10-phenanthroline), dpq (dipyrido[3,2-f:2',3'-h]quinoxaline), dppz (dipyrido[3,2-***a***:2',3'-***c***]phenazine), and dppn (benzo[*i*]dipyrido[3,2-***a***:2',3'-***c***]phenazine). In addition to possible intercalation, upon irradiation with visible light, these complexes undergo ligand exchange, such that covalent metal-DNA interactions are also possible. The photochemistry and DNA binding of the complexes will be presented.

64 Magnetic Field Effects on Phosphorescence: Spin Dynamics in Triplet-born Radical Pairs

Author(s): Tomoyasu Mani,* Elizabeth M. Higbee, and Sergei A. Vinogradov

Department of Biochemistry and Biophysics, University of Pennsylvania

Abstract: Control over dynamics of excited states of molecules is of fundamental importance to for utilization of these states in all areas of technology. We are exploring the possibility of imposing magnetic control over formation of phosphorescent triplet states by influencing spin dynamics in radical pairs, formed as a result of photoinduced electron transfer (PET). Here, we demonstrate that visible phosphorescence, can be modulated by weak magnetic fields (<1T) in bichromophoric donor-acceptor systems containing phosphorescent chromophores. Studies of electron and energy transfer dynamics in a series of dyads comprising platinum (II) porphyrins (PtP) and complementary electron acceptors (rhodamine derivatives and methyl viologens) are presented. A model explaining magnetic modulation is proposed, which is based on reversible electron transfer between the initially formed local triplet state of PtP and a long-lived RP. External magnetic field modulates spin dynamics in the RP, affecting contribution of the singlet RP recombination channel and thereby influencing the phosphorescence. This demonstration may open up new possibilities for utilization of emissive triplet states in imaging and phototherapy.

65 Experimental Excited-State Dipole Moments of Organic Compounds

Author(s): Cyril Parkanyi

Department of Chemistry and Biochemistry, Florida Atlantic University, Boca Raton, FL 33431-0991

Abstract: Electric dipole moments represent an important physical property of organic molecules that can be applied to various structural problems. Theoretical ground-state and excited-state dipole moments can be computed by a number of various methods, from simple empirical calculations to ab initio methods. Experimental ground-state dipole moments can be obtained by using the dielectric constants, microvawe spectroscopy, and molecular beams. Similarly as the ground-state dipole moments, experimental excited-state dipole moments are based on ground-state moments and a change of a spectral band in an electronic spectrum caused by an electric field - external (electrochromism) or internal (solvatochromism). The solvatochromic methods (solvent-shift methods) are experimentally much simpler because they to not use any external field. However, they are less accurate and reliable than the electrochromic methods. There are various methods available with solvatochromic equations used for this purpose. For emitting (fluorescent and phosphorescent) compounds, the Kawski-Chamma-Viallet and Bakhshiev equations and our recently developed Mulder-Parkanyi equations are available.

Simpler McRae and Suppan equations have to be used for nonemitting compounds. Electrooptical methods (electrochromism) are experimentally much more difficult and include electric polarization of fluorescence and phosphorescence, electric dichroism, and absorption spectra in the vapor phase in an electric field (Stark effect). All these approaches will be discussed and compared.

66 Electrode-Assisted Catalytic Water Oxidation By N(5)-Ethyl Flavinium Ion

Author(s): Ekaterina Mirzakulova,* Renat Khatmullin,* Janitha Walpitha, Thomas Corrigan, and Ksenija D. Glusac

Department of Chemistry, Bowling Green State University, Bowling Green, OH 43403

Abstract: The amount of energy consumed today is greater than it has been in the past century due to the population and economic growth. Electrocatalytic water oxidation is one of the promising ways to store solar energy in the form of chemical fuels. For the past few decades, this process has been driven by various transition metal complexes. This is the first report of a fully organic, flavin-based compound, N(5)-ethylflavinium ion, Et-Fl$^+$ that can perform catalytic water oxidation. During the bulk electrolysis of aqueous Et-Fl$^+$ solutions at several potentials above +1.9 V the evolution of oxygen was detected. Although the catalysis was observed on glassy carbon and platinum working electrodes, no catalysis was found on fluoride-doped tin oxide (FTO) electrode. Density functional theory calculations were conducted to investigate the possible mechanism of carbon electrode mediated water oxidation catalysis by Et-Fl$^+$. Based on the calculated thermodynamic values, a mechanism is proposed in which the oxygen evolution occurs from a peroxide intermediate formed between the oxidized flavin pseudobase and the oxidized carbon electrode.

67 Deactivation Dynamics through Photoisomerization Quantum Yield Analyses for fac-[Re(CO)$_3$(phen)(trans-L)]$^+$ Complexes

Author(s): Kassio P.S. Zanoni* and Neyde Y. Murakami Iha

Instituto de Química – USP – SP, Brazil

Abstract: The *trans*-to-*cis* photoisomerization quantum yields (Φ) for ***fac***-[Re(CO)$_3$(phen)(***trans***-stpyOMe)]$^+$ were determined in acetonitrile and the true values, corrected by NMR signals of *trans*- and *cis*-isomer complexes[1], were compared to other [Re(CO)$_3$(phen)(*trans*-L)]$^+$ photoreactions. For complexes ***1*** to ***3***, see table, the lowest energy band extends to the visible region and is assigned[2] to ^{1}MLCT$_{Re\rightarrow Phen}$ with contribution of higher energy ^{1}IL$_{trans\text{-}L}$. Since the ligands themselves do not absorb at 404 nm, the occurrence of photoreaction to yield *cis*-photoproduct at this wavelength is ascribed to the MLCT$_{Re\rightarrow Phen}$ sensitization of the reactive ^{3}IL$_{trans\text{-}L}$ state. On the other hand, the protonated uncoordinated *trans*-stpyOMe absorbs at 404 nm, indicating a more stabilized π-π* excited state when compared to the others and does photoreact efficiently. Its coordination to Re(I), complex ***4***, maintains the IL$_{trans\text{-}L}$ excited state as the lowest one. Thus, the photoisomerization occurs only through IL$_{trans\text{-}L}$ states with no contribution of sensitization by metal complex. Unlike the other three complexes, the matching Φ for ***4*** in all irradiation wavelengths and the similar values when compared to the protonated *trans*-stpyOMe demonstrate the importance of the metal complex sensitization for organic substrates that do not absorb in the visible region.

Compound	$\Phi_{313\ nm}$	$\Phi_{334\ nm}$	$\Phi_{365\ nm}$	$\Phi_{404\ nm}$	Reference
Protonated ***trans*-bpe**, *trans*-1,2-bis(4-pyridyl)ethylene [a]	0.19 ± 0.02 [b]	0.15 ± 0.01 [b]	NLA [c]	NLA	[2]
complex 1, *fac*-[Re(CO)$_3$(phen)(***trans*-bpe**)]$^+$	0.81 ± 0.07	---	0.80 ± 0.07	0.77 ± 0.09	[1]
Protonated ***trans*-stpy,** *trans*-4-styrylpyridine [a]	0.54 ± 0.01	---	0.58 ± 0.04	NLA	[2]
complex 2, *fac*-[Re(CO)$_3$(phen)(***trans*-stpy**)]$^+$	0.59 ± 0.05	---	0.60 ± 0.06	0.43 ± 0.02	[1]
Protonated ***trans*-stpyCN,** *trans*-4-(4-cyano)-styrylpyridine [a]	0.47 ± 0.05	0.49 ± 0.05	0.52 ± 0.05	NLA	[3]
complex 3, *fac*-[Re(CO)$_3$(phen)(***trans*-stpyCN**)]$^+$	0.58 ± 0.02	0.58 ± 0.03	0.61 ± 0.06	0.42 ± 0.02	[3]
Protonated ***trans*-stpyOMe,** *trans*-4-(4-methoxy)-styrylpyridine [a]	0.61 ± 0.04	---	0.67 ± 0.04	0.68 ± 0.07	
complex 4, *fac*-[Re(CO)$_3$(phen)(***trans*-stpyOMe**)]$^+$	0.54 ± 0.05	---	0.62 ± 0.04	0.59 ± 0.04	

[a] Ligand protonation simulates coordination effect
[b] Methanolic solutiion
[c] NLA: No light absorption

References: [1] Inorg. Chim. Acta 363 (2010) 294; [2] Coord. Chem. Rev. 250 (2006) 1669; [3] Inorg. Chem. Commun. 20 (2012) 105. Acknowledgments: FAPESP and CNPq.

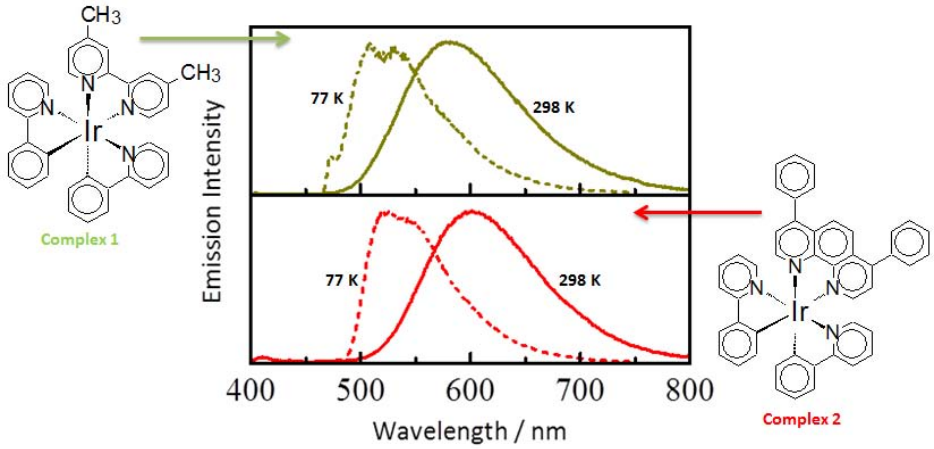
68 Detailed Elucidation of Photophysical Characteristics of Heteroleptic Cyclometalated Ir(III) Complexes

Author(s): Kassio P. S. Zanoni,[1,2]* Bruna K. Kariazaki,[1] Neyde Y. Murakami Iha,[1] Akitaka Ito,[2] and Thomas J. Meyer[2]

[1]Instituto de Química - USP – SP, Brazil
[2]Department of Chemistry – UNC at Chapel Hill – NC, USA.

Abstract: Few works tried to further explain the absorption and emission spectra of Ir(III) complexes since the strong spin-orbit coupling effect exerted by the metal core has heavy impacts on their photophysical properties.

Detailed photophysical behaviors of $[Ir(ppy)_2(dmb)](PF_6)$, **1**, and $[Ir(ppy)_2(Ph_2phen)](PF_6)$, **2**, were evaluated based on TD-DFT calculations[1,2] and Franck-Condon emission spectral fittings[3]. At 298 K, they exhibit broad and structureless emission spectra in acetonitrile, which follows a first order exponential decay. Emission energy of **2** was lower due to the presence of electron-withdrawing phenyl groups in the NN ligand, than that of **1**, with electron-donating methyl groups. TD-DFT calculations suggest that the lowest-energy transitions of the complexes are best characterized by MLCT. The HOMO is Ir(III) t_{2g} and ppy π mixed orbitals and the LUMO consists of NN π^* orbital. Detailed Franck-Condon band shape analysis of their emission reveals one vibrational fitting mode at 298 K, in contrast with the emission at 77 K, which spectra are narrowed and split into two vibrational modes of ^{3}MLCT.



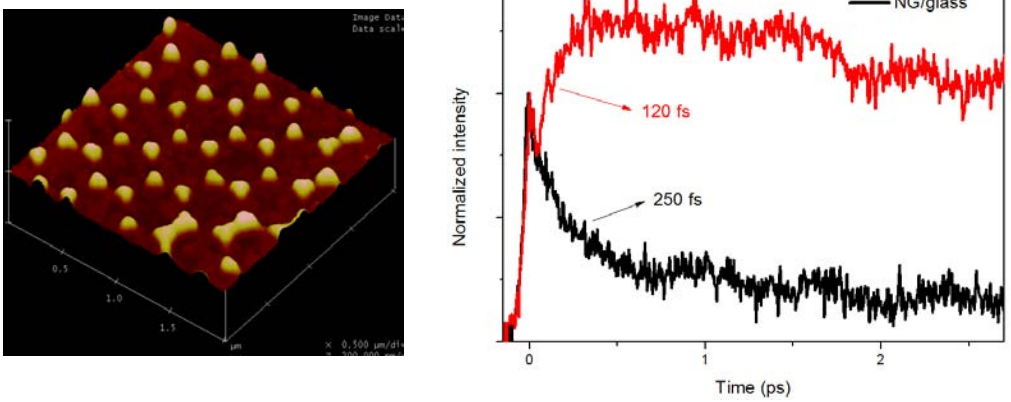
References: [1] Inorg. Chem. 46 (2007) 8533; [2] Inorg. Chem. 51 (2012) 7722; [3] Phys. Chem. Chem. Phys. 14 (2012) 13731. Acknowledgments: FAPESP and CNPq.

69 Femtosecond dynamics in gold nanopyramid/ITO hybrids

Author(s): Guilherme F. Ferbonink,[1] Edna Spada,[1] Cristiano M.B. Cordeiro,[1] Teresa D.Z. Atvars,[2] Carlos H.B. Cruz,[2] and Rene A. Nome[2]*

[1]Instituto de Química, [2]Instituto de Física Gleb Wataghin, State University of Campinas

Abstract: The present work explores the use of a 50 fs home-built ultrafast pump-probe spectroscopy apparatus to measure the ultrafast dynamics of plasmons in gold nanopyramids prepared by nanosphere lithography over two substrates: (i) glass and (ii) 190 nm indium tin oxide (ITO) film over glass. AFM and SEM images show uniform array of Au islands with a 45 +/- 5 nm height, and 220 nm base width. Initially, 50-fs time-resolution pump-probe measurements on Au islands deposited over glass (NG/glass: black curve in the above figure, right) were performed. The results are similar to data previously reported in the literature. Afterwards, we performed pump-probe measurements on Au islands deposited over ITO substrate (NG/ITO/glass: red curve in the above figure, right). The initial rise/decay dynamics are similar to Au islands on glass, suggesting similar plasmon dynamics. However, the time-scales associated with electron-phonon coupling are qualitatively different in the two systems: whereas an ultrafast decay is observed for the NG/glass system, we observe an ultrafast rise for the NG/ITO/glass system. Interestingly, the longer picosecond time response (lattice relaxation and coherent oscillations) are similar in magnitude and sign for both systems, further indicating that the electron-phonon dynamics differs in both systems.



(a) (b)

Figure: (a) SEM micrograph of Au nanopyramids over ITO/glass prepared by nanosphere lithography; (b) ultrafast pump-probe measurements of Au/glass and Au/ITO/glass.

70 Femtosecond Time-Resolved Electron Transfer Studies across the Interfaces of Nano-and Macromolecular Structures

Author(s): Chi-Hung Chuang

Department of Chemistry, Case Western Reserve University, 10900 Euclid Avenue, Cleveland, Ohio 44106, United States

Abstract: My interest in the photoscience has been focused on the photoinduced electron transfer (ET) dynamics in nanomaterials and macromolecular systems. Femtosecond laser spectroscopy has become a powerful technique to investigate charge transfer dynamics in nano- and macromolecular systems with a time resolution of 100 fs (10-13 s) and better. Using femtosecond transient (TA) absorption and time-resolved photoluminescence spectroscopy, we have studied the electron versus the hole dynamics in quasi-type-II hetero-nanomaterials. By choosing the pump wavelength in resonance with the respective core and shell transitions, we were able to measure the excited electron and hole dynamics selectively. Both charge carriers transfer through the interface within one picosecond, but the subsequent relaxation of the electron and hole is very distinguishable. On the basis of our TA measurements and analysis from the steady-state spectra, we find the mixed core - charge transfer states and the ET occurs in the Marcus inverted region. We are also interested in the ET across a molecular interface, such as the organic capsule named octa acid by the Ramamurthy group, underlying very similar photophysical principles. These studies on organic macromolecular systems, we have recently started to publish. We believe that understanding the charge carrier dynamics in nano- and supramolecular systems will pave the way to emergent optoelectronic and photovoltaic applications based on the design of functional nanoarchitectures. Moreover, exploring novel combinations of materials, which are earth-abundant and environmentally benign, will make photovoltaics more applicable for broader use. Heterostructured assemblies (organic and inorganic) are pivotal materials in this context and I will report on my discoveries during my Ph.D. time.

References

1. Chuang, C.-H.; Burda, C. *J. Phys. Chem. Lett.* 2012, *3*, 1921-1927. 2. Porel, M.; Chuang, C.-H.; Burda, C.; Ramamurthy, V. *J. Am. Chem. Soc.* 2012, *134*, 14718-14721. 3. Chuang, C.-H.; Chen, X.; Burda, C. *Ann. Phys.*2012, accepted (DOI: 10.1002/andp.201200129). 4. Chuang, C.-H.; Doane, T. L.; Lo, S. S.; Scholes, G. D.; Burda, C. *ACS Nano* 2011, *5*, 6016-6024. 5. Chuang, C.-H.; Lo, S. S.; Scholes, G. D.; Burda, C. *J. Phys. Chem. Lett.*2 010, *1*, 2530-2535.

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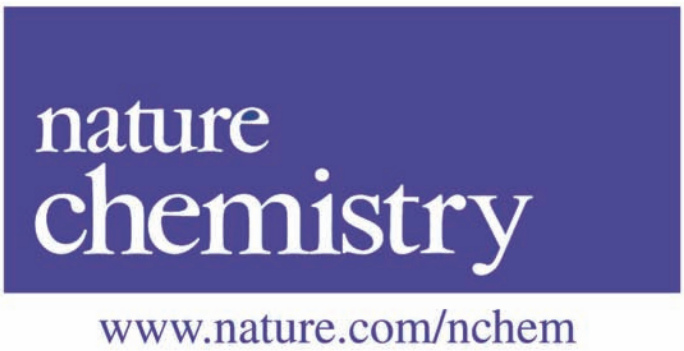

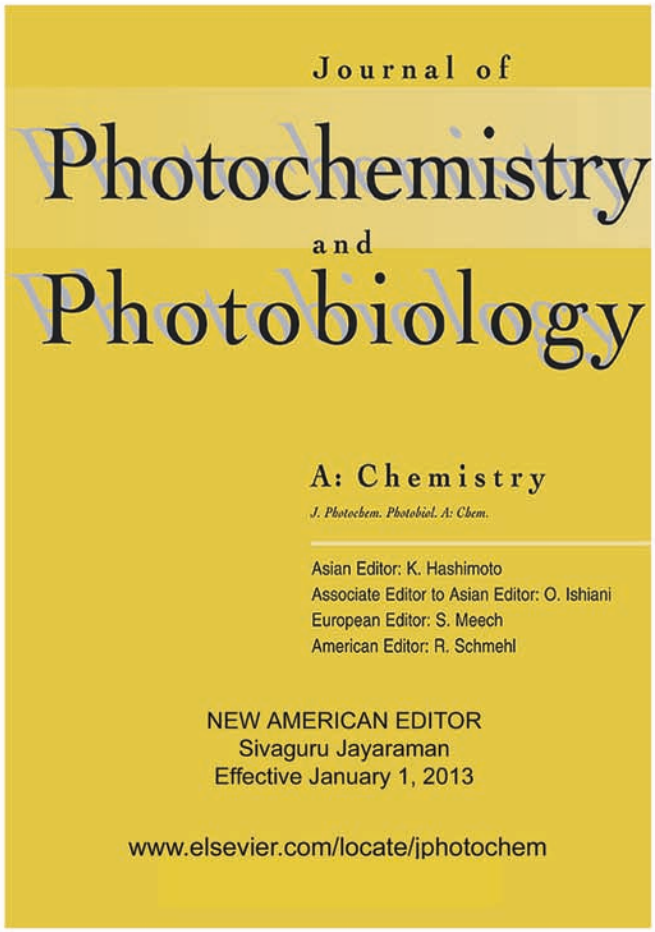

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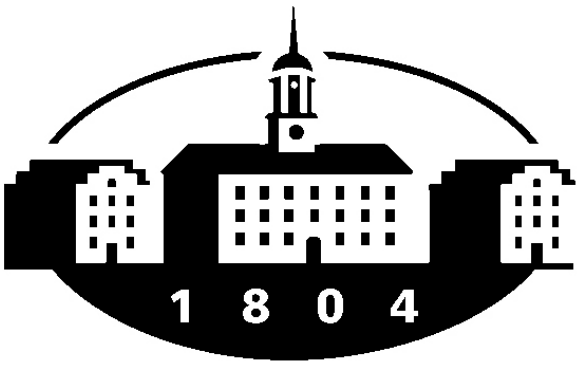

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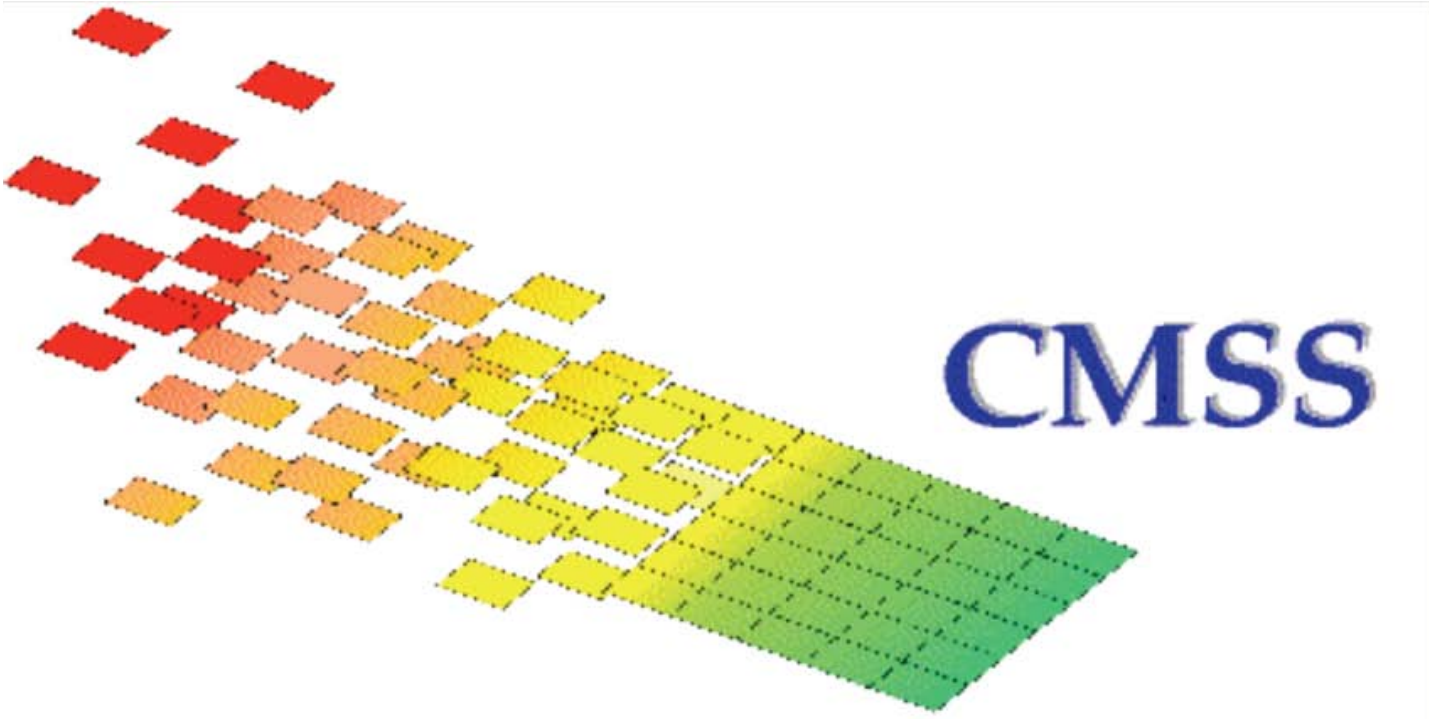

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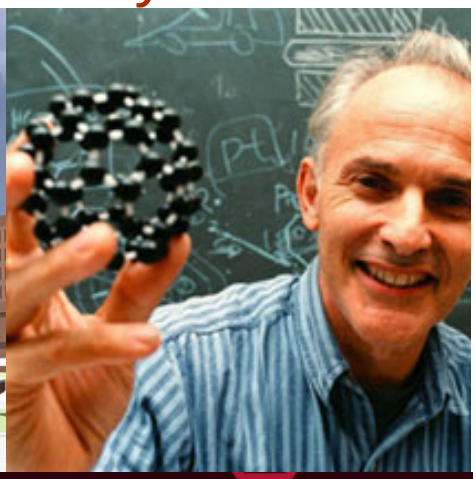

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