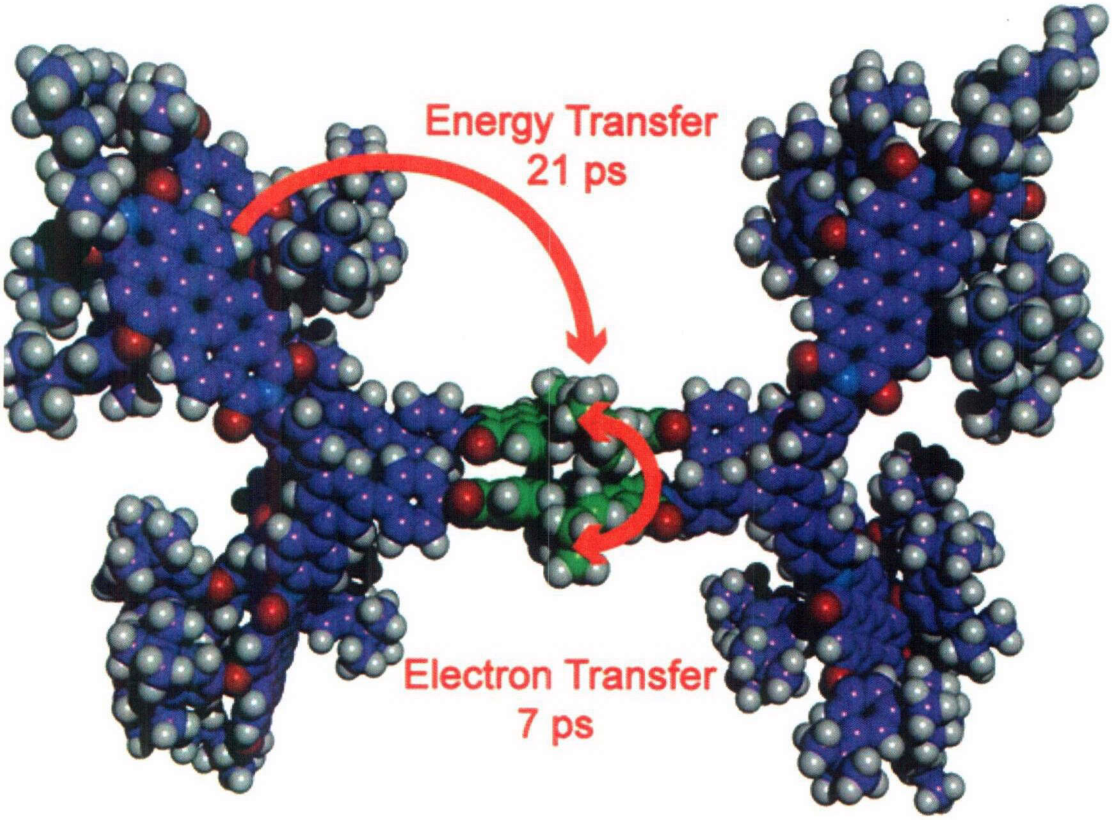
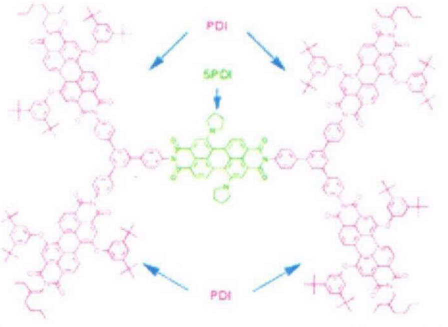
Proceedings of the

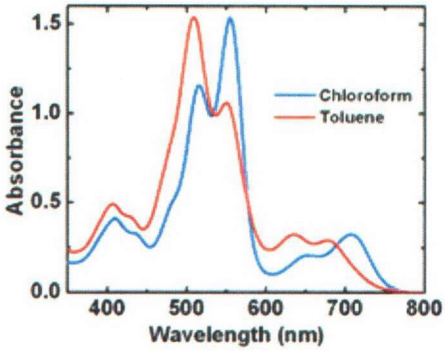
Twenty-Eighth DOE Solar Photochemistry Research Conference



Sponsored by:
Chemical Sciences, Geosciences and Biosciences Division
Office of Basic Energy Sciences
U.S. Department of Energy

Held at:
Airlie Conference Center
Warrenton, Virginia
June 4-7, 2006





Cover Graphics

An important bioinspired approach to achieving artificial photosynthesis is the development of synthetically accessible building blocks capable of self-assembly into a functional system. The space-filling structure in the center of the page is the self-assembled dimer of the covalent chemical structure shown at the bottom center of the page. The structure of the dimer was determined using small-angle X-ray scattering in solution at the Advanced Photon Source (Argonne National Laboratory). The monomer consists of four robust perylenediimide (PDI) chromophores (in purple) that funnel excitation energy to a covalently linked 5PDI chromophore (in green). Dimerization of this light-harvesting antenna structure results in self-assembly of a functional special pair of 5PDI (green) chromophores. The electronic absorption spectra of these arrays (lower right) are consistent with the presence of dimers in toluene and monomers in chloroform, and show that these structures provide excellent solar spectra coverage. Photoexcitation of PDI is followed by rapid energy transfer from PDI to $(5PDI)_2$ and ultrafast, quantitative formation of $5PDI^{+\bullet}$-$5PDI^{-\bullet}$. The charge separation observed in the self-assembled dimer is an example of emergent behavior that is not present when the monomer is photoexcited. (Michael Wasielewski, Northwestern University)

FOREWORD

The 28th Department of Energy Solar Photochemistry Research Conference is being held June 4-7, 2006, at the Airlie Conference Center in Warrenton, Virginia. The purpose of the meeting is to foster collaboration, cooperation, and the exchange of new information and ideas among grantees and contractors of the Chemical Sciences, Geosciences and Biosciences Division of the Office of Basic Energy Sciences.

Solar photochemical energy conversion is an important long-range option for meeting our future energy needs. It is becoming increasingly apparent that worldwide demands for increased energy consumption will need to be met with carbon-dioxide neutral energy technologies such as solar photoconversion. The attraction of solar photochemical and photoelectrochemical conversion is that fuels, chemicals, and electricity can be produced with minimal environmental pollution and with closed renewable energy cycles. The DOE solar photochemistry research program emphasizes fundamental processes aimed at the capture and conversion of solar energy to chemical or electrical energy. The program sponsors basic research in organic and inorganic photochemistry, electron and energy transfer in homogeneous and heterogeneous media, photocatalysis, and photoelectrochemistry. The photosynthetic reaction center and antenna systems are studied as models for design of efficient photoinduced charge separation in biomimetic/photocatalytic assemblies.

The conference agenda features topical sessions on photoinduced charge separation by transition metal complexes and molecular assemblies; light harvesting and charge separation in natural photosynthesis; solid-state organic photosystems; charge transfer at interfaces; dye-sensitized solar cells; and nanohybrid assemblies for solar photoconversion. Our special guest plenary lecturer is Professor Leif Hammarström of Uppsala University, who will discuss coupled electron transfer reactions in biomimetic assemblies. Among the poster abstracts may be found a number of new projects in solar hydrogen production, resulting from the FY 2005 DOE solicitation for proposals on Basic Research for the Hydrogen Fuel Initiative. In this volume may be found the agenda for the meeting, abstracts of the 26 formal presentations, 49 poster abstracts, and an address list for the 93 participants.

I would like to express my sincere appreciation to Lydia Ferguson and the staff of the Airlie Conference Center for their gracious hospitality. Special thanks are due to Sophia Kitts of the Oak Ridge Institute of Science and Technology for logistical support and for preparation of this volume. The success of the conference will be due to all of the participants for their generous sharing of knowledge, experience, and enthusiasm in this important endeavor of solar photoconversion.

Mary E. Gress
Chemical Sciences, Geosciences
and Biosciences Division
Office of Basic Energy Sciences

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Session VI—Interfacial Charge Transfer

Session VII—Dye-Sensitized Solar Cells

Session VIII—Quantum Dots and Hybrid Assemblies for Solar Photoconversion

Poster Abstracts

Program

28th DOE SOLAR PHOTOCHEMISTRY RESEARCH CONFERENCE

June 4-7, 2006

Airlie Conference Center
Warrenton, Virginia

PROGRAM

Sunday, June 4

5:00 - 11:00 p.m. Reception and Registration, Roof Terrace
6:30 - 8:00 p.m. Buffet Dinner, Airlie Dining Room

Monday Morning, June 5

SESSION I
Plenary Session
Mary E. Gress, Chairman

7:30 a.m. Breakfast, Airlie Dining Room

8:30 a.m. Opening Remarks
Mary E. Gress, U.S. Department of Energy

8:45 a.m. **Plenary Lecture.** Biomimetic Approaches to Artificial Photosynthesis
Leif Hammarström, Uppsala University

9:45 a.m. Coffee Break

SESSION II
Charge Separation by Transition Metal Complexes
Russell H. Schmehl, Chair

10:15 a.m. Platinum Diimine Bis(acetylide) Complexes for Photoinduced Charge Separation
Richard Eisenberg, University of Rochester

10:45 a.m. Molecular Structural Dynamics of Photoactive Transition Metal Complexes in Solar Energy Conversion
Lin X. Chen, Argonne National Laboratory

11:15 a.m. Electron-Transfer and Spectroscopic Behavior of Multi-Transition Metal Donor-Acceptor Complexes
John F. Endicott, Wayne State University

11:50 a.m. Lunch, Airlie Dining Room

Monday Afternoon, June 5

SESSION III
Molecular Assemblies for Charge Separation
Marye Anne Fox, Chair

1:00 p.m. Charge and Spin Transport Dynamics in Molecules and Self-Assembled Nanostructures Inspired by Photosynthesis
Michael R. Wasielewski, Northwestern University

1:30 p.m. Fundamental Studies of Charge Migration and Delocalization Relevant to Solar Energy Conversion
Michael J. Therien, University of Pennsylvania

2:00 p.m. DNA Photonics
Frederick D. Lewis, Northwestern University

Monday Evening, June 5

SESSION IV
Photoinduced Charge Separation and Light Harvesting in Natural Photosynthesis
David F. Bocian, Chair

5:30 p.m. Direct Evidence for Bidirectional Electron Transfer in Photosystem I
Oleg G. Poluektov, Argonne National Laboratory

6:00 p.m. Electron Transport Involving Carotenoid and Chlorophyll Molecules in Photosystem II
Gary W. Brudwig, Yale University

6:30 p.m. Dinner, Airlie Dining Room

7:30 p.m. Posters (Odd numbers), Jefferson Room
Light Refreshments on Roof Terrace

Tuesday Morning, June 6

7:30 a.m. Breakfast

8:30 a.m. Exploring Electron Transfer in Light-Harvesting Arrays
James R. Norris, University of Chicago

9:00 a.m. Primary Processes in Photosynthesis: Light Harvesting and Its Regulation
Graham R. Fleming, Lawrence Berkeley National Laboratory

SESSION V

Excited-State Charge Transport in π-Conjugated Molecular Wires and Films

Garry Rumbles, Chair

9:30 a.m. Nanoscale Assemblies of Conjugated Polyelectrolytes. Energy Transport, Energy Transduction and Photovoltaic Cells

Kirk S. Schanze, Valeria D. Kleiman, John R. Reynolds, University of Florida

10:15 a.m. Coffee Break

10:45 a.m. Molecular Wires for Energy Conversion

John R. Miller, Brookhaven National Laboratory

11:15 a.m. Excited Electronic States in Carbon Nanotubes

Louis Brus, Columbia University

11:45 a.m. Novel Solar Photon Conversion Processes Investigated by Terahertz Spectroscopy

Matthew C. Beard, National Renewable Energy Laboratory

Tuesday Afternoon, June 6

12:15 p.m. Lunch
1:30 p.m. Depart for Luray Caverns and Monticello

Tuesday Evening, June 6

SESSION VI

Interfacial Charge Transfer

Thomas J. Meyer, Chair

5:30 p.m. Ground- and Excited-State Charge Transfer in Molecular- and Nano-scale Systems

Carol Creutz, Brookhaven National Laboratory

6:00 p.m. Electron Transfer at ZnO/Liquid Contacts: Elucidation of the Rate Constant at Optimal Exoergicity, Direct Observation of the Marcus Inverted Region, Evaluation of Reorganization Energies at a Semiconductor Electrode, and Direct Measurement of Driving Force and Electronic Coupling Effects on Interfacial Charge Transfer

Nathan S. Lewis, California Institute of Technology

6:30 p.m. Social Hour, Pavilion
7:30 p.m. Cookout, Pavilion

8:30 p.m. Posters (Even numbers)
Light Refreshments on Roof Terrace

Wednesday Morning, June 7

7:30 a.m. Breakfast

SESSION VII
Dye-Sensitized Solar Cells
Joseph T. Hupp, Chair

8:30 a.m. Electron Transfer Dynamics in Efficient Molecular Solar Cells
Gerald J. Meyer, Johns Hopkins University

9:00 a.m. Linkers for Semiconductor Nanoparticle Sensitization: Models for Electron Transfer and Solar Cell Applications
Elena Galoppini, Rutgers University

9:30 a.m. Coffee Break

10:00 a.m. Ultrafast Electron Injection from Adsorbates to Nanocrystalline Semiconductor Thin Films: pH and Semiconductor Dependence
Tim Lian, Emory University

10:30 a.m. Interfacial Photochemical Processes in Sensitized Nanostructured Electrodes
Arthur J. Frank, National Renewable Energy Laboratory

11:00 a.m. Ultrafast Dynamics and Chromophore Design in Dye-Sensitized TiO_2-Based Solar Cells
James K. McCusker, Michigan State University

11:40 a.m. Lunch, Airlie Dining Room

Wednesday Afternoon, June 7

SESSION VIII
Quantum Dots and Hybrid Assemblies for Solar Photoconversion
Mark T. Spitler, Chair

12:45 p.m. Molecularly Wired Hybrid Assemblies for Photoelectrochemical Conversion of Light Energy
Prashant V. Kamat, Radiation Laboratory, University of Notre Dame

1:15 p.m.	Coupling of TiO_2 Nanocrystallites to Proteins **Nada M. Dimitrijevic**, Argonne National Laboratory
1:45 p.m.	Electrosynthesized Oxide Semiconductors for Photoelectrochemical Applications **Krishnan Rajeshwar**, The University of Texas at Arlington
2:15 p.m.	Ultra-Efficient and Ultra-Fast Multiple Exciton Generation from Single Photons Absorbed in Semiconductor Quantum Dots and Its Impact on High Efficiency Solar Photon Conversion **Arthur J. Nozik**, National Renewable Energy Laboratory
2:45 p.m.	Closing Remarks **Mary E. Gress**, U.S. Department of Energy

Session I

Plenary Session

BIOMIMETIC APPROACHES TO ARTIFICIAL PHOTOSYNTHESIS

Leif Hammarström, Magnus Anderlund, Olof Johansson, Reiner Lomoth, Ann Magnuson, Sascha Ott, Stenbjörn Styring

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In our work towards artificial photosynthesis, we build on principles from the natural enzymes Photosystem II and Fe-hydrogenases. An important theme in this biomimetic effort is that of coupled electron transfer reactions, which have so far received only little attention: (1) each absorbed photon leads to charge separation on a single-electron level only, while catalytic water splitting and hydrogen production are multi-electron processes. There is thus the need for controlling accumulative electron transfer on molecular components; (2) water splitting and proton reduction at the potential catalysts necessarily requires the management of proton release and/or uptake. Far from being just a stoichiometric requirement this controls the electron transfer processes by proton-coupled electron transfer (PCET); (3) redox-active links between the photosensitizers and the catalysts are required to rectify the accumulative electron transfer reactions, and will often be the starting points of PCET.

In Photosystem II, light-induced water oxidation is catalyzed by a manganese cluster. Using ruthenium(II)-polypyridine complexes as light-absorbing pigments we made the first Ru-Mn and Ru-Mn_2 complexes and demonstrated light-induced manganese oxidation[1] The coupling of single-electron light reactions to accumulation of redox equivalents on a potentially catalytic complex is very rarely mimicked, but an obvious necessity for a light-driven water-splitting system. Thus, we have achieved at least three light-driven oxidation steps of a manganese dimer[2] process accompanied by ligand exchange reactions that compensated for the accumulated charge and made continued oxidation possible. These reactions were investigated in some detail by EPR, FTIR-spectroelectrochemistry and on-line ESI-MS/electrochemistry techniques.[2b] At high H_2O:CH_3CN solvent ratios, water was bound to the manganese already in the reduced state. The oxidation was then coupled to a proton release in each step, similar to the case in Photosystem II, leading to a high-valent di-μ-oxo complex.

We prepared and studied the first Mn_2-containing donor-acceptor triad (Mn_2-$Ru(bpy)_3$-acceptor). Thus, we demonstrated a surprisingly long-lived, light-induced charge separation. The half-life of 200 μs is more than two orders of magnitude better than for previously reported Ru-based triads. In a 140 K fluid solvent, this half-life was dramatically increased to c.a. 0.5 s, which is comparable to the long-lived states observed in natural reaction centers. We showed that the manganese complex imposes a high reorganization energy for electron transfer.[3]

A tyrosine residue, Tyr_Z, close to the manganese cluster in Photosystem II is the site where the coupling of electron and proton transfer on the donor side starts. Detailed mechanistic studies of Ru-Tyr and Ru-Trp complexes revealed that the corresponding reaction is in most cases a concerted PCET, but can be switched the between concerted and step-wise. Within a new mechanistic model we proposed, we obtained quantitative data for the parameters that govern the competition between these mechanisms.[4] Furthermore, we have earlier shown that the concerted PCET from tyrosine and tryptophan gives a pH-dependent rate, and that the rate dependence on pH follows a Marcus' free energy dependence.[4b] At high pH, the rate of pure ET from the tyrosinate form is hundred-fold higher than for the concerted PCET, due to a higher reorganization energy for the latter. Oxidation of a hydrogen-bonded $tyrosine_Z$ in Photosystem II at pH>7 shows a kinetically intermediate behavior, and we have proposed a "rate ladder" for tyrosine oxidation (see Figure 1). Work in progress on Ru-Tyr with internal hydrogen bonds systems supports our proposal.

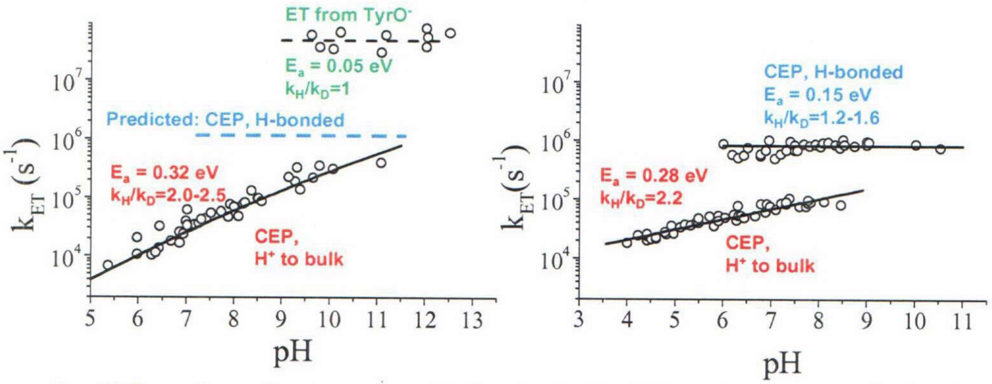

Figure 1: *pH-dependence for tyrosine oxidation in Ru-Tyr(left) and manganese-depleted Photosystem II (right). While the kinetics at low pH is very similar, the reaction at pH>10 in Ru-Tyr it is for a tyrosinate, but at pH>7 in PSII it is for a hydrogen-bonded tyrosine. We propose that the latter reaction also is concerted (CEP) with kinetics parameters intermediate between a non-bonded tyrosine and a tyrosinate, i.e. a "rate ladder" where the tyrosine with an internal hydrogen bond is the intermediate "step" of the ladder.*

We have recently made mimics for the Fe-hydrogenase active sites, which catalyze the reduction of protons to H_2. We have demonstrated electrocatalytic hydrogen production with the mildest overpotential so far reported.[6a] Our ongoing studies have suggested different patterns of proton-electron transfer steps in the catalytic mechanism, depending on the potential applied. Importantly, we have shown that the formation of a hydride intermediate can be very slow and thus rate limiting. This is in contrast to previous beliefs that the H-H bond formation was always the limiting step. Furthermore, we have been able to synthesize a biomimetic Fe_2 complex with both a proton and a bridging hydride, a state which may be a snap-shot of the precursor structure to the H-H bond forming step (Figure 2).[6b]

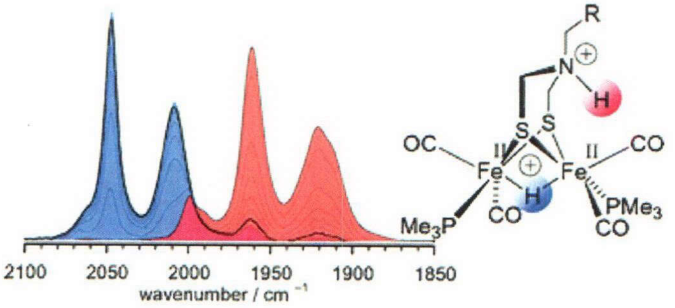

Figure 2: *A biomimetic Fe_2 complex with both a bridging hydride and a proton – a possible analog of the critical intermediate in the catalytic H_2-formation cycle. Surprisingly, the complex could be prepared in four different protonation states, including those with either a hydride or a proton. [ref. 5b]*

Acknowledgements: This work is performed in the Swedish Consortium for Artificial Photosynthesis. Financial support comes from The Swedish Energy Agency, the European Commission (NEST-STRP "SOLAR-H"), The Swedish Research Council, The K&A Wallenberg Foundation and the Royal Swedish Academy of Sciences.

References:

(1) L. Hammarström *Curr. Opinion. Chem. Biol.* **2003**, *7*, 666; L. Sun et al. *Chem. Soc. Rev.* **2001**, *30*, 36.
(2) a) P. Huang et al. *J. Inorg. Biochem.* **2002**, *91*, 159; b) G. Eilers et al. *Dalton Trans* **2005**, 1033.
(3) M. Borgström et al. *J. Am. Chem. Soc.* **2005**, *125*, 17504.
(4) a) M. Sjödin et al. *J. Am. Chem. Soc.* **2005**, *127*, 3855; b) M. Sjödin et al. *J. Am. Chem. Soc.* **2000**, *122*, 3932.
(5) a) S. Ott et al. *Angew. Chem., Int. Ed. Engl.* **2004**, *43*, 1006; b) L Schwartz et al. *Chem. Commun.* **2006**, 520.

Session II

Charge Separation by Transition Metal Complexes

PLATINUM DIIMINE BIS(ACETYLIDE) COMPLEXES FOR PHOTOINDUCED CHARGE SEPARATION

Soma Chakraborty, Jacob Schneider, Paul Jarosz, Pingwu Du and
Richard Eisenberg

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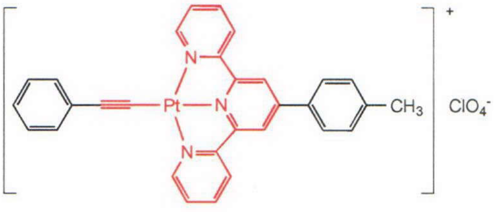
Photoinduced charge separation is one of the critical initial steps in light-to-chemical energy conversion. In this project, the approach to study this process involves the synthesis of dyad and triad systems in which electron transfer donors and acceptors are attached to a chromophore in spatially specific locations, followed by examination of the spectroscopy and photophysics of these systems. The chromophores employed in these studies are platinum(II) complexes containing aryl acetylide and di- or triimine ligands. During the current contract, efforts have focussed on cationic terpyridyl complexes exemplified by **1** as the chromophore of choice. We have also begun to explore the viability of **1** and related systems as chromophores for the direct production of hydrogen from aqueous protons and a sacrificial electron donor, following much earlier work done with Ru(II) tris diimine systems. These results, obtained from multiple component solutions with viologen or diquat electron transfer agents and colloidal Pt catalysts, are encouraging and indicate that the Pt complexes are competent as photosensitizers for the reductive side of the water splitting reaction.

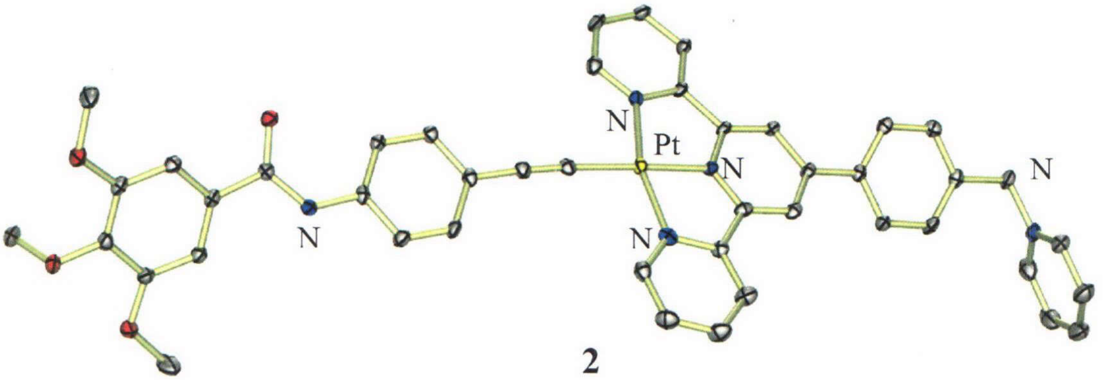


1

Dyads and Triads for Photoinduced Charge Separation and Electron Transfer. The syntheses of dyads and triads for photoinduced charge separation involve multistep procedures that have often proved challenging for the facile preparation and isolation of pure systems. A number of factors other than the redox properties and quenching ability of donors and acceptors, such as the solubility of intermediates and products, the availability of precursors, the sequence of coupling reactions and protection-deprotection strategies for synthesis, have entered into the execution of our efforts. Predictive capability regarding the effectiveness of different components and bridges has also shown itself to be difficult as well.

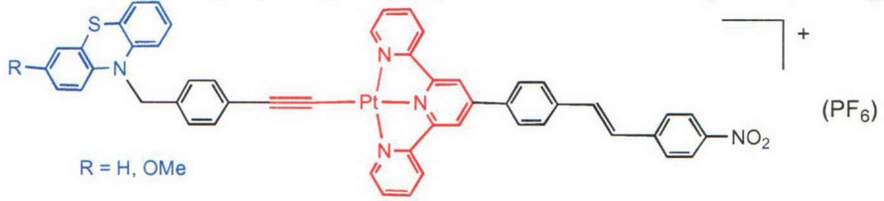
During the last three years, the donor-chromophore-acceptor (D-C-A) triad featuring a trimethoxybenzamide donor and a pyridinium acceptor (**2**) has been synthesized and structurally characterized. This represents the first time that such a triad has been crystallographically studied. The structure of **2**, which exhibits a donor···acceptor separation of nearly 29 Å, is shown below. Transient absorption (TA) experiments performed in collaboration with Prof. Russell Schmehl of Tulane University on **2** and the associated D-C and C-A dyads as well as the chromophore reveal that while reductive quenching proceeds efficiently, charge separation by electron transfer into the pyridinium acceptor does not occur. Further studies also show that the attachment of pyridinium and related acceptors such as nicotinamide and N-methyl-4,4'-bipyridinium through the benzylic carbon of the tolylterpyridyl ligand is not sufficiently stable to base so as to render this attachment unsuitable for further development.

A different triad shown as **3** and associated D-C and C-A dyads have also been prepared and examined by transient absorption spectroscopy that gives evidence of a charge separated state



2

with a lifetime of 230 ns. This value compares well to a 70 ns lifetime found for a D-C-A triad with similar donor and acceptor but containing a Pt diimine bis(acetylide) chromophore. However, analysis of the TA results also indicates that the CS state in **3** is formed inefficiently, underscoring yet another consideration in constructing such systems. Recent efforts in the synthesis of new triads have concentrated on preparing suitably functionalized components using Kröhnke cyclizations such that these components can be linked together using Suzuki and/or Stille couplings while having the ability to bind to the dark catalyst needed for H_2 generation.



3

Hydrogen Production Based on the Platinum Terpyridyl Acetylide Chromophore. Complex **1** exhibits a strong photoluminescence in solution with λ_{max}^{em} at 605 nm corresponding to the ^{3}MLCT dπ(Pt)–π*(terpy) excited state. The luminescence is readily quenched by either triethanolamine (TEOA) as an electron donor or by methyl viologen (MV^{2+}) as an electron acceptor. Both quenching processes exhibit Stern-Volmer behavior with k_q values for TEOA and MV^{2+} being 1.4×10^9 and 3.3×10^9 $M^{-1}s^{-1}$, respectively, consistent with dynamic quenching.

We have found that **1** serves as a photosensitizer for the reduction of aqueous protons to H_2. In the hydrogen generating system, triethanolamine (TEOA) acts as the sacrificial electron donor, methyl viologen (MV^{2+}) functions as an electron transfer agent and colloidal Pt stabilized by polyacrylate serves as the catalyst for H_2 formation. While the Pt(II) chromophore undergoes both oxidative and reductive quenching, H_2 is only seen when *both* TEOA and MV^{2+} are present. Irradiation of the reaction solution for 10 hours with $\lambda > 410$ nm leads to 85 turnovers and an overall yield of 34% based on TEOA. While H_2 evolution is maximized for the system at pH 7, it is also seen at pH 5 and 9, in contrast with earlier reports using $Ru(bpy)_3^{2+}$ as the photosensitizer. This is the first time that a Pt diimine or terpyridyl complex has been used as the photosensitizer for H_2 generation from aqueous protons. While optimization of the system is ongoing, we have found that polyvinyl alcohol (PVA) and citrate stabilized colloids also function well and that various diquaternized 2,2' bipyridines (diquats) can be used in place of MV^{2+}. In fact when the diquat 2,12-dimethyl-7,8-dihydro-6H-dipyrido[1,2-a :2',1'-c]-[1,4]diazepinium dibromide is employed, over 300 turnovers of H_2 are achieved. Additional new results will be discussed.

DOE-SUPPORTED PUBLICATIONS (2004-2006)

Vapochromism and Its Structural Basis in a Luminescent Pt(II) Terpyridine–Nicotinamide Complex, Wadas, T. J.; Wang, Q. -M.; Kim, Y. -J.; Flaschenreim, C.; Blanton, T. N.; Eisenberg, R. *J. Am. Chem. Soc.* **2004**, *126*, 16841-16849.

Facile Synthesis, Structure, and Luminescence Properties of Pt(diimine)bis(arylacetylide) Chromophore-Donor Dyads, Wadas, T. J.; Chakraborty, S.; Lachicotte, R. J.; Wang, Q. -M.; Eisenberg, R. *Inorg. Chem.* **2005**, *44*, 2628-2638.

Synthesis, Structure, Characterization, and Photophysical Studies of a New Platinum Terpyridyl-Based Triad with Covalently Linked Donor and Acceptor Groups, Chakraborty, S.; Wadas, T. J.; Hester, H.; Flaschenreim, C.; Schmehl, R.; Eisenberg, R. *Inorg. Chem.* **2005**, *44*, 6284-6293.

Preface: Overview of the Forum on Solar and Renewable Energy, Eisenberg, R.; Nocera, D. G. *Inorg. Chem.* **2005**, *44*, 6799-6801.

Platinum Chromophore-Based Systems for Photoinduced Charge Separation: A Molecular Design Approach for Artificial Photosynthesis, Chakraborty, S.; Wadas, T. J.; Hester, H.; Schmehl, R.; Eisenberg, R. *Inorg. Chem.* **2005**, *44*, 6865-6878.

Photocatalytic Generation of Hydrogen from Water Using a Platinum(II) Terpyridyl Acetylide Chromophore, Du, P. -W.; Schneider, J.; Jarosz, P.; Eisenberg R. . *J. Am. Chem. Soc.* **2006**, in press.

Molecular Assemblies Based on the Platinum Terpyridyl Acetylide Chromophore. Towards Long-lived Charge Separation, Jarosz, P.; Du, P. -W.; Schneider, J.; Eisenberg R. Manuscript in preparation.

Attachment of Platinum Terpyridyl Acetylides to Mesoporous TiO_2. Photochemical Processes toward Proton Reduction, Schneider, J.; Jarosz, P.; Du, P. -W.; Eisenberg R. Manuscript in preparation.

MOLECULAR STRUCTURAL DYNAMICS OF PHOTOACTIVE TRANSITION METAL COMPLEXES IN SOLAR ENERGY CONVERSION

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C. D. Grant[c], E. W. Castner[c], J. Rosenthal[d], D. G. Nocera[d]

Chemistry Division[a] and Advanced Photon Source[b], Argonne National Laboratory
Department of Chemistry, Rutgers University[c]
Department of Chemistry, Massachusetts Institute of Technology[d]

Transition metal complexes play important roles in solar energy conversion due to their intense absorption within the solar spectrum, their capability of transferring electron and energy through the metal to ligand charge transfer (MLCT) or ligand to metal charge transfer (LMCT) excited state, and their capability of binding substrates through coordination geometry changes. Hence, structural dynamics of these complexes in their excited states need to be understood in order to gain the knowledge of controlling solar energy conversion processes. We will present our recent studies on structural dynamics of two metal complexes using both ultrafast optical spectroscopy and laser initiated time-resolved x-ray absorption spectroscopy (LITR-XAS). In order to fully understand the roles of transition metal complexes in solar energy conversion, structural dynamics of these molecules in their excited states on ultrafast time scales are needed.

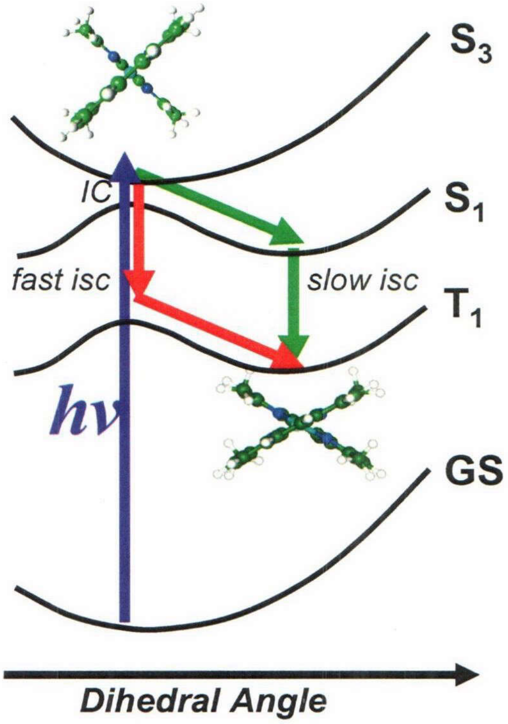

Fig. 1 The MLCT Excited state pathways of $[Cu(I)(dmp)_2]^+$.

Ultrafast structural dynamics of $[Cu(I)(dmp)_2]^+$ in different solvents In recent years, we have studied the excited MLCT state structures of $[Cu(I)(dmp)_2]^+$ in coordinating and non-coordinating solvents, acetonitrile and toluene, respectively, using LITR-XAS as well as ultrafast transient absorption spectroscopy. Our results revealed the MLCT state dynamics of this complex with three distinguishable time constants, 0.5-0.7 ps, 10-20 ps, and 2-100 ns. The LITR-XAS method on time scales of 100 ps and longer established the formation of the solvent-MLCT state complexes in both solvents with different Cu-to-ligand distances, despite of previously recognized exciplex in acetonitrile only. However, the structural information on faster time scales was not resolved due to the mismatch of the x-ray pulse duration from the synchrotron source. The initial optical transient absorption results suggested that a molecular flattening of the excited state from a tetrahedral geometry took place on 10-ps time scale, whose structural changes could be resolved by 2-ps or shorter x-ray pulses after a future renovation of the synchrotron. However, our recent ultrafast fluorescence up-conversion measurements in collaboration with Castner Group revealed complicated and much faster excited

MLCT state flattening process whose rate could not be measured directly, but could be extrapolated by the rates of other decay processes (Fig. 1). Meanwhile, ultrafast excited state transient absorption spectra of the complex in a series of solvents with different viscosities have been measured, showing no dependency on the solvent viscosity in the two fast rate constants. The results suggest an inner-shell large amplitude movement of the excited state complex, map out complicated excited state decay pathways along the reaction coordinates, and show structure-dependent rate constants for intersystem crossing and internal conversion processes. The structure-dependent energy levels of molecular orbitals are also discussed. The ultrafast mechanistic movements of the excited state are unexpected and their association with variation of the rate constants provides new insights into the excited state pathways that have not been recognized before.

Excited state structural dynamics of metalloporphyrins Metalloporphyrin excited states frequently act as electron donor/acceptor or light harvesting antenna in solar fuel/electric production processes due to their analogous structure and properties in natural photosynthesis. In addition, the versatility of the central metal in metalloporphyrins creates various possibility of using these compounds in photochemical reactions to induce bond formation or cleavage. Using LITR-XAS method, the transient ligation species as well as transient oxidation changes of the metal in metalloporphyrins can be studied with 100-ps time resolution. Recently, we carried out studies on the singlet and triplet excited state structures of zinc tetraphenylporphyrin (ZnTPP) with and without the axial ligation. The results indicated the significant structural changes in the singlet state, but only minor changes were observed in the triplet state. The observed differences in these two states will be discussed in the context with their electronic structures. Moreover, we started to measure the transient structure after the photocleavage in a bis-Fe(III)porphyrin system in collaboration with Nocera Group (Fig. 2). The LMCT state of the molecule can be induced via UV excitation which eventually triggers the Fe-O bond cleavage producing one high valence Fe(IV) and one low valence Fe(II). The electronic structural difference between the closed configuration of the ground state and the open configuration of the excited state are reflected in the LITR-XAS spectra collected within 200 ps after the LMCT transition. The direct structural information of the excited state metalloporphyrins obtained in our experiment provides for the first time the possibility of mapping out the structure and reactivity correlation in photochemical reactions.

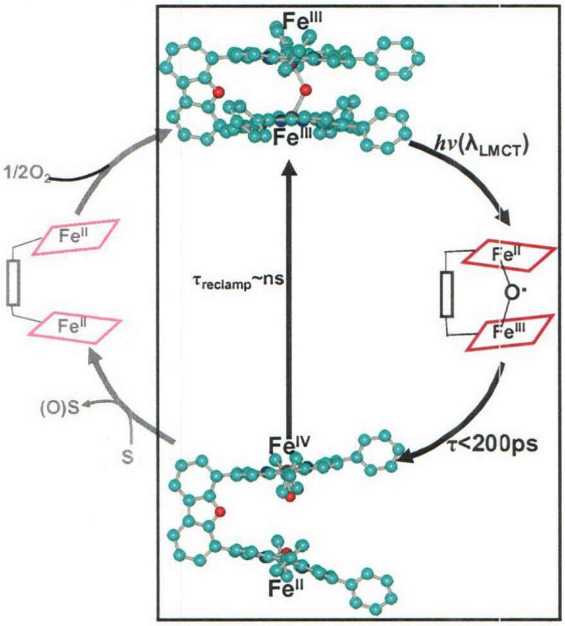

Fig. 2 Photoinduced opening and reclamping of bis-Fe(III) porphyrin.

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ELECTRON-TRANSFER AND SPECTROSCOPIC BEHAVIOR OF MULTI-TRANSITION METAL DONOR-ACCEPTOR COMPLEXES

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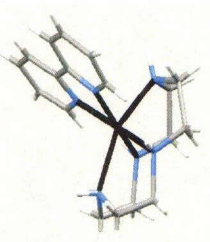
Summary. The major goals of this research project are to experimentally probe fundamental aspects of center-to-center, photoinduced electron and energy transfer processes in complexes containing two or more metal centers, and, ultimately, to use the principles inferred in the design of new systems useful in energy conversion applications. Pursuit of these goals has resulted in the study of some very fundamental issues of photoinduced charge transfer and the work during this period has focused largely on two general areas: (a) the use of emission spectral band shapes to probe the properties of charge transfer excited states; and (b) the examination of metal-metal interactions in halide-bridged, face-to-face di-nickel, $[L^{(2)}(Ni^{II})_2X_nY]^{(3-n)+}$ complexes where $L^{(2)}$ contains two aliphatic-tetraaza-macrocyclic ligands are linked by xylene.

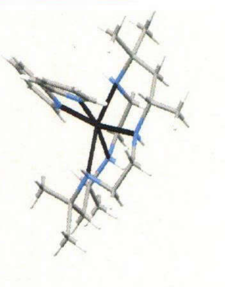
Synthesis and characterization of model compounds. The design, synthesis and characterization of a related a series of metal complexes is necessary for each physical property probed. Some of the complexes have been previously reported and some have not; all were fully characterized. Among the complexes used: (a) $[Ru(L)_4bpy]^{2+}$ complexes for $(L)_4$ = combinations of bpy and am(m)ine ligands; (b) $[Ru(bpy)_4PP]^{2+}$ and $[Ru(NH_3)_4PP]^{2+}$ complexes for PP = tetraaza-polypyridyl ligands; (c) $[\{Ru(L)_4\}_2PP]^{4+}$ complexes; (d) bimetallic and trimetallic complexes with CN^- bridging ligands; (e) bimetallic, macrocyclic ligand complexes with xylene linkers.

Areas of research during this period. **1.** Emission band shapes as probes of CT excited state properties. The vibronic side band contributions to Ru/bpy and Ru/PP emission spectra in 77 K frozen solutions vary over a considerable range. A systematic approach to examining these variations is based on the assumptions that these contributions arise from progressions in the vibrational modes (k) that characterize the excited state distortions, that these vibronic contributions have Gaussian band shapes and that the intensities of the first order vibronic components can be represented by $I_{max(k)} = \left(\frac{\lambda_k}{h\nu_k}\right) I_{max(f)}$. The fundamental component, $I_{max(f)}$ corresponding to the $\{e,0'\} \rightarrow \{g,0\}$ transition, obtained from the Gaussian deconvolution of the experimental spectrum, is subtracted from the original spectrum and the resulting difference spectrum is multiplied by the difference between the emission energy, $h\nu_m$, and the maximum of the fundamental to give a reorganizational energy profile (emrep), Λ_x. The procedure has been modeled[1] with respect to resonance-Raman data (from other laboratories) for $(L)_4 = (bpy)_2$ [2] and $(NH_3)_4$.[3] The variations of Λ_x are proportional to variations in the reorganizational energy contributions of the distortion modes, and the differences in these can be related to differences in the extents of configurational mixing among the electronic states of the complexes. This approach has been applied to several problems: (a) Effects of ground state-excited state configurational mixing. The Λ_x amplitudes decrease strongly with decreases in MLCT excited state energies for most series of related complexes;[1,4,5] e.g.,

$\Lambda_{x(max)}$ for $[Ru(bpy)_3]^{2+}$ is about twice that for $[Ru(NH_3)_4bpy]^{2+}$, and this is consistent with the differences in MLCT excited state energies and the very large electronic matrix elements (~ 7,000 cm^{-1}) for MLCT/ground state mixing.[1] (b) Possible ^{3}LF/^{3}MLCT configurational mixing.[5,6] A comparison of the isotopic shifts in zpes and emreps, supplemented by the X-ray structures of several $[Ru(L)_4bpy]^{2+}$, complexes suggests some configurational mixing between the MLCT excited states of most complexes with relatively low energy ligand field excited states. (c) Electronic coupling in mixed valence excited states.[4] The CT emission maxima for the bimetallic Ru^{II}-PP-Ru^{II} complexes are at much lower energies than those of the monometallic Ru^{II}-PP analogs, and the vibronic contributions far more intense than expected when the excited state energy differences are taken into account. This suggests that the bridging ligand mediated superexchange coupling of the degenerate mixed valence MLCT excited states, *{Ru^{III}-(PP$^-$)-Ru^{II}}, is smaller than for the {Ru^{III}-PP-Ru^{II}} ground states.



$[Ru([12]aneN_4)bpy]^{2+}$



$[Ru(r\text{-}Me_6[14]aneN_4)bpy]^{2+}$

2. *Detection of high frequency vibronic contributions.* By means of the comparison of emission spectra and emreps of proteo (CH or NH) and deutereo (CD or ND) isotopomers, we have been able to identify and/or set limits on the amplitudes of the vibrational reorganizational energies for the very weak vibronic contributions of the high frequency C-H and N-H stretching vibrations in several $[Ru(L)_4bpy]^{2+}$ and $[(Am)Cr^{III}(CN^-)Ru^{II}(NH_3)_5]^{n+}$ complexes.[1,5-8]

3. *Ligand mediated interchanges of triplet and singlet state electronic configurations in halide-bridged di-nickel(II) complexes.*[9] The comparison of 100 K and 300 K X-ray crystal structures of $\{[L^{(2)}Ni_2Br_2]^{2+}\}_n$ (an infinite chain of pairs of complexes at 77K, identical complexes at 300 K) and $[L^{(2)}Ni_2Br_3]^+$ (a single molecule) have unsymmetrical Ni(II) coordination sites at 100 K: one site has the relatively long equatorial Ni-N bond distances and the relatively short axial Ni-Br bond distances typical of the triplet electronic configuration and the other with the shorter Ni-N and longer Ni-Br bond distances typical of the singlet state. At 300 K the coordination sites of both centers in both complexes are identical, with Ni-ligand bond lengths that are the average of those of the low temperature singlet and triplet sites, and with very large thermal ellipsoids only for the bridging bromides. The magnetic moments are the same for both complexes at both temperatures (one triplet and one singlet center): it appears that activation of the low frequency axial vibrational motion couples with the interchange of the electronic configurations between the Ni(II) centers, so that at at 100 K the electronic configurations of Ni are "localized" while configurational interchange at room temperature appears to be more rapid than Ni-N vibrational relaxation.

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Session III

Molecular Assemblies for Charge Separation

CHARGE AND SPIN TRANSPORT DYNAMICS IN MOLECULES AND SELF-ASSEMBLED NANOSTRUCTURES INSPIRED BY PHOTOSYNTHESIS

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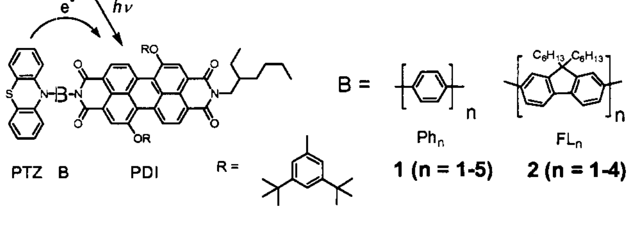
Bridge Dynamics Control Wire-like Charge Transport. The effectiveness of long-distance charge transport in molecules is dictated by whether strongly distance-dependent superexchange or weakly distance-dependent charge hopping mechanisms dominate. These mechanisms in turn depend on the dynamics of the bridge molecule (B) linking the donor (D) to the acceptor (A) in a D-B-A system. We have used a series of *p*-phenylene (Ph_n), **1**, and fluorenyl (FL_n) oligomers, **2**, where n=1-5, to link a phenothiazine (PTZ) electron donor to a perylene-3,4:9,10-bis(dicarboximide) (PDI) electron acceptor. Selective photoexcitation of PDI within PTZ-Ph_n-PDI results in charge separation to produce $^1(PTZ^{+\bullet}\text{-}Ph_n\text{-}PDI^{-\bullet})$, which undergoes radical pair (RP) intersystem crossing to yield $^3(PTZ^{+\bullet}\text{-}Ph_n\text{-}PDI^{-\bullet})$. The triplet RP then recombines to give ^{3*}PDI. The ^{3*}PDI yield exhibits distinct resonances as a function of applied magnetic field, yielding the magnetic exchange coupling *2J*, which directly monitors the superexchange contribution to the electron transfer reaction. We recently observed well-defined regions of superexchange and thermally-activated hopping in the temperature dependence of charge recombination. A fit to the thermally activated charge recombination rates of the Ph_3 and Ph_4 bridges yields activation barriers of 1290 cm^{-1} and 2030 cm^{-1}, which match closely with experimentally observed barriers for the planarization of terphenyl and quaterphenyl. The temperature dependence of the donor-acceptor superexchange coupling, V_{DA}, measured using magnetic field effects on the yield of ^{3*}PDI shows that charge recombination depends strongly on changes in bridge conformations, which translate into changes in bridge energetics, and result in conformational gating of the charge recombination process.



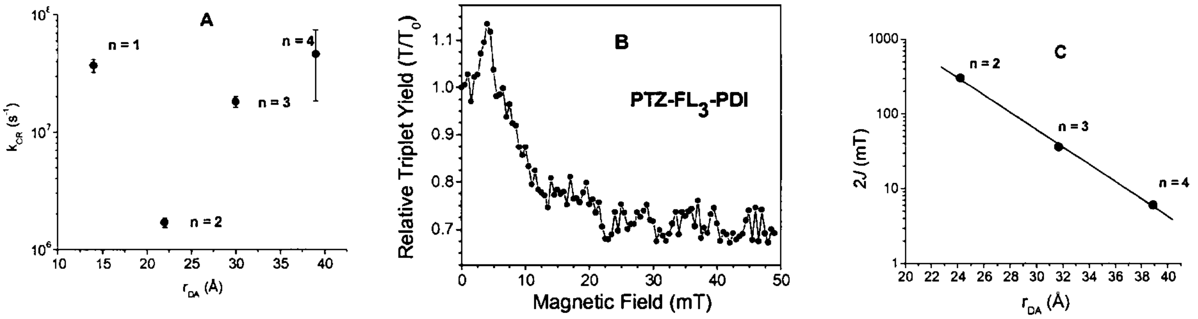


Figure 1. A) Plot of charge recombination rate constant vs. distance for $PTZ^{+\bullet}\text{-}FL_n\text{-}PDI^{-\bullet}$. B) Plot of relative yield of PTZ-FL_3-^{3*}PDI vs. magnetic field. C) Plot of ln(*2J*) vs. distance for $PTZ^{+\bullet}\text{-}FL_n\text{-}PDI^{-\bullet}$.

Using D-B-A molecules having FL_n bridges, **2**, we have shown that the D-A distance can be varied *without significantly changing the energies of the relevant bridge states*. In toluene, the rate constants for charge recombination, Figure 1A, as well as the energy levels of the relevant $PTZ\text{-}FL_n^{+\bullet}\text{-}PDI^{-\bullet}$ bridge states for n = 1-4 are only weakly distance dependent, where the transition between the superexchange and hopping mechanisms occurs at $n = 2$. Measurements of $2J$, Figure 1B, and therefore the superexchange interaction, diminish exponentially with distance, Figure 1C, while the overall charge recombination rates through FL_n for $n = 3, 4$ are dominated by charge hopping. It is clear from these studies that both bridge energetics and molecular motions within D-B-A molecules are critically important for accessing efficient mechanisms of charge transport over long distances.

Self-Assembly Strategies for Integrated Photofunctional Nanostructures. Achieving a functional integrated artificial photosynthetic system requires hierarchical organization at both the molecular and supramolecular level. Covalent synthesis provides functional building blocks with well-defined molecular geometries and donor-acceptor distances, while self-assembly provides a facile way to assemble large numbers of molecules into structures that can bridge length scales from nanometers to macroscopic dimensions. It can also lead to synergistic and *emergent* properties that are not intrinsic to the building blocks themselves. Our strategy uses covalent building blocks with particular shapes, sizes, and intermolecular interactions to direct the formation of supramolecular structures having enhanced charge transport properties.

We have used the well known aggregation properties of PDI chromophores to carry out the function of bringing two green 5PDI molecules close to one another as well as provide a light-harvesting antenna array, molecule **3**, which self-assembles into stacked dimers $(\mathbf{3})_2$ in solution as revealed by SAXS, Figure 2. This dimeric array demonstrates that self-assembly of a robust PDI-based artificial light-harvesting antenna structure induces self-assembly of a functional special pair of 5PDI molecules that undergoes ultrafast, quantitative charge separation. The structure consists of four PDI molecules attached to a single 5PDI core, which self-assembles to form $(\mathbf{3})_2$ in toluene. Femtosecond transient absorption spectroscopy shows that energy transfer from $(PDI)_2$ to $(5PDI)_2$ occurs with $\tau = 21$ ps, followed by excited state symmetry breaking of $^{1*}(5PDI)_2$ to produce $5PDI^{+\bullet}\text{-}5PDI^{-\bullet}$ quantitatively with $\tau_{CS} = 7$ ps. The ion pair recombines with $\tau_{CR} = 420$ ps. Electron transfer occurs only in the dimeric system, and does not occur in the disassembled monomer, thus mimicking both antenna and special pair function in photosynthesis. The charge separation observed in $(\mathbf{3})_2$ is an example of emergent behavior that is not present when monomeric **3** is photoexcited.

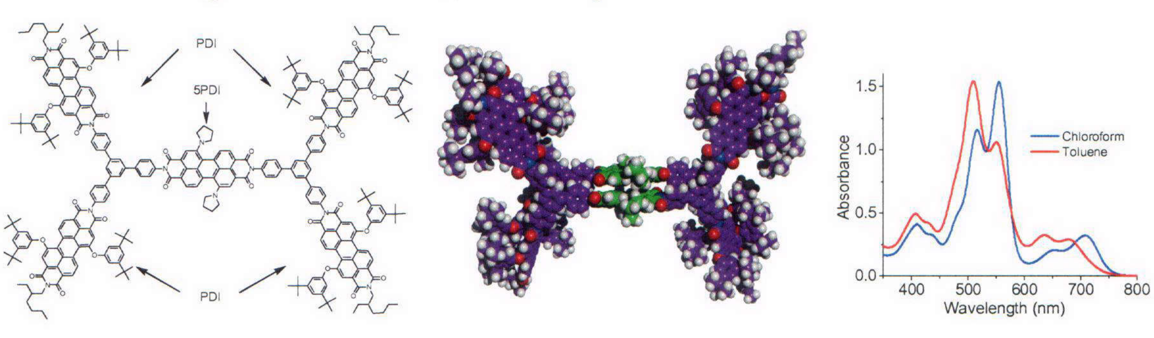


Figure 2. Chemical structure of **3** (left), the best fit structure of $(\mathbf{3})_2$ from modeling the SAXS data (center), and the UV-VIS spectra showing dimerization in toluene (monomers in $CHCl_3$) (right).

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FUNDAMENTAL STUDIES OF CHARGE MIGRATION AND DELOCALIZATION RELEVANT TO SOLAR ENERGY CONVERSION

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This program seeks to understand the molecular-level principles by which complex chemical systems carry out photochemical charge separation, transport, and storage, and how these insights will impact the design of practical solar energy conversion and storage devices. Towards these goals, this program focuses on: (1) carrying out fundamental mechanistic and transient dynamical studies of proton-coupled electron-transfer (PCET) reactions; (2) characterizing and interrogating via electron paramagnetic resonance (EPR) spectroscopic methods novel conjugated materials that feature large charge delocalization lengths; and (3) exploring excitation delocalization and migration, as well as polaron transport properties of meso-scale (nano-to-micron-sized) assemblies that are capable of segregating light-harvesting antennae, nanoscale wire-like conduction elements, and distinct oxidizing and reducing environments. Examples of projects carried out over the past two years include:

Conjugated Chromophore Arrays with Unusually Large Polaron Delocalization Lengths. Variable temperature X-band EPR spectroscopic data for the cation radical states of *meso*-to-*meso* ethyne-bridged (porphinato)zinc(II) oligomers (PZn_n species) $[\mathbf{PZn_2\text{-}PZn_7}]^+$, which span an ~18-75 Å length scale, evince peak-to-peak EPR line widths (ΔB_{p-p}) that diminish with conjugation length. Analysis of these EPR data show that $\mathbf{PZn_n}^+$ structures possess the largest hole polaron delocalization lengths yet measured; experiments carried out over a 4-298 K temperature domain show remarkably that the charge delocalization length remains invariant with temperature. These cation radical EPR data are well described by a stochastic, near barrierless, one dimensional charge hopping model developed by Norris for N equivalent sites on a polymer chain where the theoretical EPR line width is given by: $\Delta B_{p-p}(\text{N-mer}) = (1/N^{1/2})\Delta B_{p-p}(\text{monomer})$; $\mathbf{PZn_n}^+$ oligomers are the first such systems to verify a Norris-type hole delocalization mechanism over a substantial (~75 Å) length scale. This study demonstrates that polymeric building blocks having low magnitude inner sphere reorganization energies enable the development of electronic materials having long polaron delocalization length.

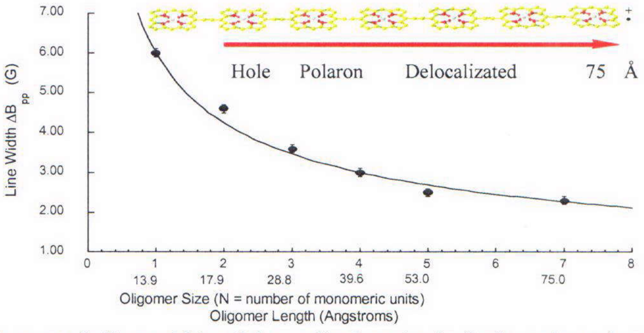

Figure 1. Plot of EPR peak-to-peak line width of the radical cationic (hole-polaron) states of $\mathbf{PZn_1\text{-}PZn_7}$ at 298 K. The abscissa is gives oligomer size represented by number of monomeric PZn units N and oligomer length in Å. The solid line is a fit to $6.0/(N^{1/2})$ (G).

Orientational Dependence of Cofacial Porphyrin-Quinone Electronic Interactions within the Strong Coupling Regime. The relative magnitudes of the electronic coupling matrix element (H_{DA}) in two electronically excited face-to-face (porphinato)zinc(II)-quinone (PZn-Q) assemblies ($^{1}1\beta$-ZnA* and $^{1}1\beta$-ZnB*) that feature a sub-van der Waals donor-acceptor (D-A) interplanar separation, and differ only with respect to the quinonyl orientation relative to the porphyrin plane, were evaluated. Experiment and theory indicate that the extent to which ([P-Q]*, ψ_{e}) and CT ([P^{+}-Q^{-}], ψ_{CT}) configurations are mixed in $^{1}1\beta$-ZnA* greatly exceeds that for the $^{1}1\beta$-ZnB* structure. Orbital overlap analysis shows that the weaker coupling in $^{1}1\beta$-ZnB* relative to $^{1}1\beta$-ZnA* arises from orientation-driven overlap cancellations, and differences in the extent to which the Q O atoms contribute to D-A mixing. Of the handful of studies that probe the dependence of D-A orientation upon ET, few, if any, have probed its impact in the limit of strong D-A electronic interaction. This study demonstrates the sensitivity of CT transition moments to D-A orientation at contact, and underscores the strong dependence of D-A coupling upon the nature of π-stacking.

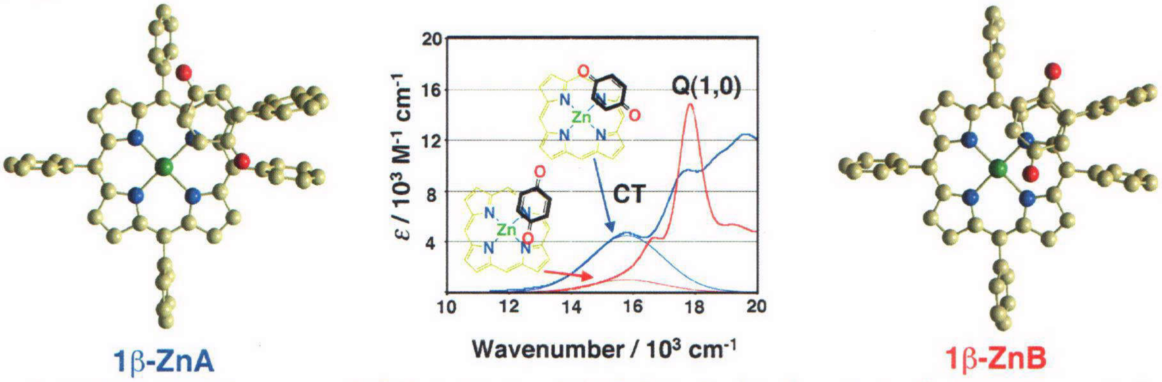

Figure 2. (a) Linear visible spectra of 1β-ZnA (blue) and 1β-ZnB (red); thin lines depict Gaussian deconvolutions of the CT bands.

Revealing the Degree of Charge Transfer in Ground and Charge-Separated States via Ultrafast Visible Pump / Mid IR Probe Spectroscopy. We have demonstrated a new fs visible pump/mid-IR probe spectroscopic approach to assess directly the ground and excited state degrees of charge transfer (CT) in donor-spacer-acceptor (D-Sp-A) structures. Two classes of (porphinato)zinc(II) (PZn)-based D-Sp-A compounds with either quinonyl (Q) or *N*-(*N*'-octyl)pyromellitic diimide (PI) electron acceptors were interrogated. These data show that the acceptor mode frequency shift, $\Delta\nu_{A}$, determined by this method provides a more accurate measure of the degree of CT in ground and charge-separated states relative to other techniques which rely on the ground-state frequency shift alone; this added accuracy, coupled with the ability of this method to interrogate the electronic interaction matrix element between ground and CS states, enable determination of new experimental benchmarks to test the power of complimentary computational methods, and provides a means to probe the degree of CT in transitions that either overlap strongly with other bands or possess low oscillator strength.

DOE-Supported Publications (2004-2006)

(1) The Degree of Charge Transfer in Ground and Charge-Separated States Revealed by Ultrafast Visible Pump / Mid IR Probe Spectroscopy, I. V. Rubtsov, Y. K. Kang, N. P. Redmore, R. M. Allen, J. Zheng, D. N. Beratan, and M. J. Therien, *J. Am. Chem. Soc.* **2004**, *126*, 5022-5023.

(2) Impact of Electronic Asymmetry on Photoexcited Triplet-State Spin Distributions in Conjugated Porphyrin Oligomers Probed via EPR Spectroscopy, P. J. Angiolillo, H. T Uyeda, T. V. Duncan, and M. J. Therien, *J. Phys. Chem. B.* **2004**, *108*, 11893-11903.

(3) Generalized Mulliken-Hush Analysis of Electronic Coupling in Compressed π-Stacked Porphyrin-Bridge-Quinone Systems, J. Zheng, Y. K. Kang, M. J. Therien, and D. N. Beratan, *J. Am. Chem. Soc.* **2005**, *127*, 11303-11310.

(4) Conjugated Chromophore Arrays with Unusually Large Polaron Delocalization Lengths, K. Susumu, P. R. Frail, P. J. Angiolillo, and M. J. Therien, *J. Am. Chem. Soc.* Accepted for publication.

(5) Orientational Dependence of Cofacial Porphyrin-Quinone Electronic Interactions within the Strong Coupling Regime, Y. K. Kang, J. Zheng, I. V. Rubtsov, D. N. Beratan, and M. J. Therien, *J. Am. Chem. Soc.* Submitted.

DNA PHOTONICS

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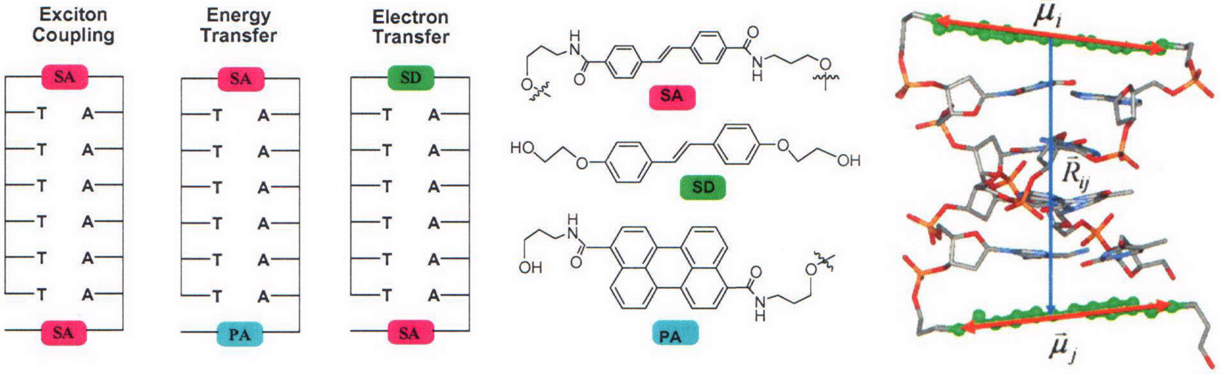
The objective of this project is to investigate photoinduced charge separation in supramolecular systems which possess an electron donor and acceptor separated by aromatic spacers having a face-to-face or π-stacked geometric relationship. The π-stacked base pairs in duplex DNA possess such a geometry and have been proposed to function as a "molecular wire." Our approach to the study of electronic interactions in DNA is based on the use of hairpin-forming bis(oligonucleotide) conjugates in which a chromophore serves as a linker connecting two complementary oligonucleotide arms. Second generation systems contain an additional chromophore at the opposite end of the duplex from the hairpin linker (Scheme 1). Appropriate selection of the two chromophores makes possible the investigation of several different types of electronic interactions, including exciton coupling, energy transfer, and electron transfer.



Scheme 1. Structures of capped hairpins, chromophores, and a vector model of the interaction between chromophores separated by four base pairs.

Capped hairpins possessing two SA chromophores separated by 1 to 11 A:T base pairs have been used to investigate the distance and angle dependence of exciton coupling. Exciton coupling between two identical chromophores results in CD spectra for the individual chromophores having opposite signs and equal intensity. Thus even very weak coupling can result in a bisignate spectrum (Cotton effect). The rotational strength of an isolated CD transition is determined by the imaginary part of the dot product between the electronic and magnetic transition dipoles. In the case of small Davydov splitting between chromophores whose transition dipoles μ_i are perpendicular to the distance vector R_{ij} (Scheme 1), the complex expression for the rotational strength $\Delta\varepsilon$ can be simplified to provide eq 1.

$$\Delta\varepsilon \approx \pm\frac{\pi}{4\lambda}\mu_i^2\mu_j^2R_{ij}^{-2}\sin(2\theta) \qquad (1)$$

According to eq. 1 , the CD intensity should display a R_{ij}^{-2} dependence and have maximum intensity when the dihedral angle θ between the chromophore transition dipoles is 45° or

135° (with an inversion in sign) but zero intensity when they are parallel or perpendicular. The sign and relative intensities for the experimental CD spectra are in excellent agreement with spectra calculated using the vector model of Scheme 1.

Electronic excitation of the SA-SA capped hairpins results in electron transfer to form long-lived charged separated states in which the SA chromophores serve as both acceptor and donor. Investigation of the mechanism and dynamics of charge separation and charge recombination by means of fs pump-probe spectroscopy indicates that charge separation occurs via hole injection into the A:T bridge rather than a single step superexchange mechanism.

Capped hairpins possessing SA and PA chromophores have been used to investigate the distance and angle dependence of fluorescence resonance energy transfer (FRET). According to the semiclassical vector model proposed by Förster, the efficiency of energy transfer is dependent several factors, including a geometric factor κ, which is described by eq 2, where e_1, e_2, and e_{12} are the unit vectors of the donor and acceptor transition dipoles and distance between their centers. In cases where the dipoles are randomly aligned, a constant value of $\kappa^2 = 2/3$ is normally assumed.

$$\kappa = \bar{e}_1 \cdot \bar{e}_2 - 3(\bar{e}_1 \cdot \bar{e}_{12})(\bar{e}_{12} \cdot \bar{e}_2) \qquad (2)$$

Experimental values for the SA fluorescence quantum yield are in good agreement with the values obtained using the oriented dipole model (Scheme 1), but not with those provided by the averaged dipole model. The discrepancy between the experimental data and averaged dipole model is particularly noticeable for capped hairpins with 7 to 9 intervening base pairs, the observed SA fluorescence quantum yield being as much as five times larger than the value predicted by the averaged dipole model.

The mechanism and dynamics of photoinduced charge separation and charge recombination has been investigated in synthetic DNA hairpins possessing donor (SE) and acceptor (SA) stilbenes separated by a one to seven A:T base pairs. The application of femtosecond broadband pump-probe spectroscopy, nanosecond transient absorption spectroscopy, and picosecond fluorescence decay measurements permits detailed analysis of the formation and decay of the stilbene acceptor singlet state and of the charge separated intermediates. When the donor and acceptor are separated by a single A:T base pair charge separation occurs via a single step superexchange mechanism. However when the donor and acceptor are separated by two or more A:T base pairs charge separation occurs via a multistep process consisting of charge injection, charge migration, and charge trapping. Rate constants for charge separation and charge recombination are dependent upon the donor-acceptor distance, however the rate constant for charge injection is independent of the donor-acceptor distance. Previous results from our laboratory provide examples of electron transfer which occurs exclusively via hole injection and exclusively via superexchange. The observation of crossover from a superexchange to a hopping mechanism provides a “missing link” in the analysis of DNA electron transfer and requires reevaluation of the existing literature for photoinduced electron transfer in DNA.

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Session IV

Photoinduced Charge Separation and Light Harvesting in Natural Photosynthesis

DIRECT EVIDENCE FOR BIDIRECTIONAL ELECTRON TRANSFER IN PHOTOSYSTEM I

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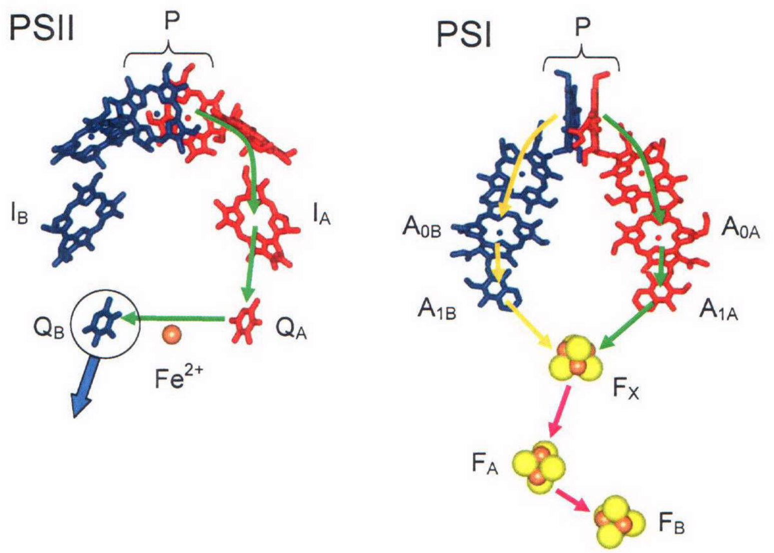
Natural photosynthesis remains a paradigm for defining the fundamental mechanisms of efficient photochemical energy conversion in molecular-based systems. This process occurs by photoinitiated electron transfer reactions between cofactors embedded in integral membrane reaction center (RC) proteins. Although structures for several photosynthetic RC proteins have been determined and the key features of photosynthetic electron transfer are broadly understood, important details of how the synergy between the cofactors and the surrounding protein optimizes electron transfer reactions have yet to be resolved. Therefore, our research is focused on the discovery of fundamental physical-chemical mechanisms responsible for highly efficient photochemical energy conversion in natural photosynthesis. Central problems addressed in our program are the following: what is the protein's role in controlling and defining optimal pathways for electron transfer reactions; what is the response of the protein to rapid charge transfer and what is the mechanism of efficient charge stabilization; how are conformational protein dynamics link to RC function? We anticipate that the fundamental understanding of structure-function relationships in biological electron transfer can be extended to provide a benchmark for controlling electron transfer in biomimetic systems. To tackle these problems in both natural and artificial photosynthetic systems, we have developed advanced, pulsed high-field EPR techniques that allow us to directly inspect the details of unpaired electron-matrix interactions. Here I will present our results on the application of these techniques for the problem of directionality of electron transfer in Photosystem I.

The efficient charge separation that occurs within RC proteins is the most important step of photosynthetic solar energy conversion. Although classified into two types, Type I and Type II, all RCs consist of a dimeric core, where each polypeptide binds a branch of cofactors (see Figure). From the primary electron donor, P, which is a dimer of chlorophyll molecules, these two nearly symmetrical potential electron acceptor chains (branches A and B) extend across the membrane. Anoxygenic photosynthesis of photosynthetic bacteria occurs in both Type I and II RCs; whereas, oxygenic photosynthesis of higher plants, cyanobacteria, and algae require the symbiotic linking of Type II and I RCs (Photosystem II and Photosystem I, respectively).

Determining the functional roles for the pairs of cofactor branches is fundamental for understanding both the evolution of photosynthesis and the mechanisms of photosynthetic charge separation. In Type II RCs, e.g., Photosystem II (PSII), light-driven primary electron transfer (ET) reactions take place exclusively through the A branch of redox-active components (unidirectional ET) resulting in the charge separated state, $P^+Q_A^-$, where Q_A^- is the reduced quinone cofactor in the A branch. Subsequently, ET proceeds from Q_A^- to the terminal quinone electron acceptor, Q_B, the quinone cofactor in the B branch. Q_B is a mobile electron carrier.

Following two proton-coupled electron transfer events, Q_B is reduced to a hydroquinone and leaves the RC.



In Photosystem I (PSI) photoexcitation of P initiates sequential ET through two spectroscopically identified electron acceptors, A_0, a chlorophyll molecule, and A_1, a phylloquinone. From A_1^- the electron is transferred to the [4Fe–4S] cluster F_X, and further to F_A and F_B, two iron-sulfur clusters held within an extrinsic protein subunit (see Figure) Thus, unlike Type II RCs, ET in PSI does not terminate at two functionally distinct quinines. Is ET in Type I RCs likewise functionally asymmetric? Resolution of this basic, yet important, issue of ET directionality (uni *vs.* bi) in PSI has remained an experimental challenge.

Experimental reports that address the directionality of ET in PSI are based on optical and time-resolved (TR) EPR studies of ET in wild-type and site-directed mutants. Observation of biphasic ET rates from A_1^- to F_X, 5-10 ns and 150-200 ns, has been discussed as an indication of bidirectional ET in PSI. However, without concomitant structural evidence, kinetic data is open to multiple interpretations.

We observed two distinct transient spectra of $P^+A_1^-$ radical pair from the PSI RC proteins of the cyanobacterium *Synechococcus lividus* using high-field (HF) TR-EPR methods. The application of advanced HF EPR techniques, with superior spectral resolution, allows us to distinguish the different geometries of these two transient radical pairs and correlate their structures with kinetic data and the X-ray crystal structures of PSI. The opportunity to unravel the geometry of the radical pairs derives from the sensitivity of the well-resolved lineshapes of the HF TR-EPR spectra of the spin-correlated radical pairs to the magnetic interactions within these photochemically generated donor/acceptor pairs as well as to their relative orientations. We demonstrated that the geometries of the two distinct donor/acceptor pairs correspond to the charge separated states along the A and B branches, and that our assignments of radical pair geometries are in excellent agreement with the X-ray crystal structure of PSI. Together with previously reported data, the concomitant structural and kinetic information obtained with HF EPR provide unambiguous evidence of bidirectional ET in PSI. Thus, unidirectionality of ET is not a general property that is optimized for efficiency of photochemical solar energy conversion. More generally, these results point to a role for the protein in ultimately controlling the directionality of ET pathways. The heterodimeric structure of the core in PSI proteins allows independent fine tuning of the redox properties of the cofactors in ET branches, thus allowing PSI to be more robust and less susceptible to local damage compared to Type I RCs that have homodimer structure.

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ELECTRON TRANSPORT INVOLVING CAROTENOID AND CHLOROPHYLL MOLECULES IN PHOTOSYSTEM II

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Carotenoids have long been known to function in photosynthetic systems as light-harvesting pigments, as photoprotective molecules in triplet energy-transfer processes, as singlet O_2 scavengers and as components that stabilize pigment-protein structures. Recently, photosystem II (PS II) has been found to utilize β-carotene as a redox center whereby the carotenoid acts as a molecular wire to facilitate long-range electron transfer. The aim of this research program is to understand how the functions of carotenoid molecules are tuned in natural photosynthetic systems. Our recent work has focussed on characterizing the electron-transfer function of carotenoids in cyanobacterial PS II core complexes (cofactors shown in Figure 1).

The primary photochemical reactions of PS II lead to the oxidation of water and involve the electron donors in the O_2-evolving complex. PS II is unique among photosynthetic reaction centers in having β-carotene (Car) and chlorophyll (Chl) secondary electron donors. Car and Chl are photooxidized in high yield under conditions, such as low temperature, in which electron donation from the O_2-evolving complex is inhibited. Although near-IR absorbance and EPR spectroscopic signatures of the Car^+ and Chl^+ radicals have been identified,[1-2] the number of redox-active Chl and Car molecules, their locations within the PS II complex, the electron-transfer sequence(s) involving them and their function(s) are still uncertain.

We have characterized the photooxidation and decay of the redox-active accessory chlorophylls (Chl) and β-carotenes (Car) in oxygen-evolving PS II core complexes from *Synechocystis* PCC 6803 by near-IR absorbance and EPR spectroscopies over a range of cryogenic temperatures from 20 to 160 K. In contrast to previous results for Mn-depleted PS II, a number of near-IR absorption bands are resolved in the light-minus-dark difference spectra. Gaussian deconvolution of the near-IR absorption spectra was used to identify absorption maxima at 745 nm, 750 nm, 792 nm, 808 nm, 814 nm, 825 nm, and 840 nm that are attributed to chlorophyll radical cations (Figure 2). The kinetics of formation of these Chl^+ species using laser pulses and continuous illumination

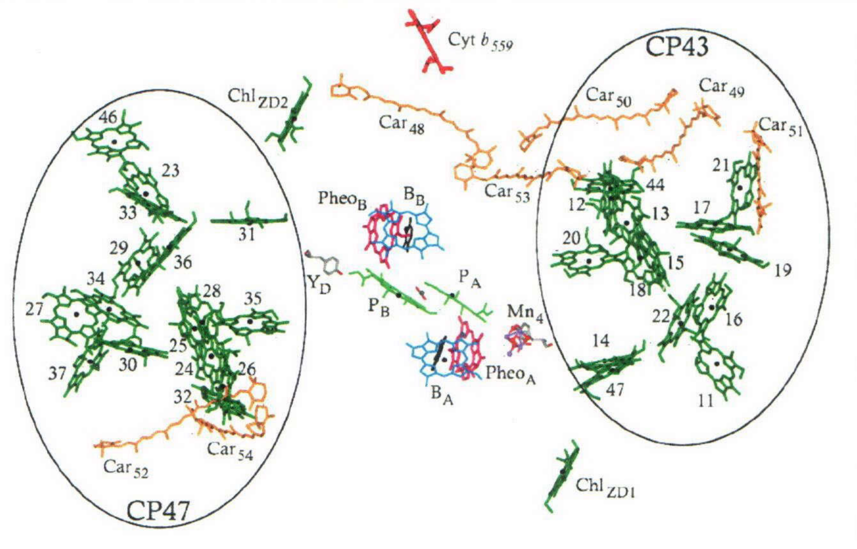

Figure 1: PS II cofactors shown perpendicular to the membrane (PDB code 1S5L).

with white light (0.01 ms – 30 min) and their subsequent decay in the dark was measured. Some of the Chl$^+$ species form and decay rapidly, whereas additional Chl$^+$ species were observed to form after extended illumination up to 30 min. The fast decaying absorption bands observed after illumination at 20 K could be generated again by re-illuminating the sample. Quantitation by EPR spectroscopy gives a yield of 0.85 radicals per PS II, and the yield of oxidized cytochrome b$_{559}$ by optical difference spectroscopy is 0.15 per PS II. The yield of Q_A^- reaches a maximum of 1.0 per PS II after 100 sec of illumination. These results confirm that low-temperature illumination gives a single stable charge separation per PS II, as expected. Potential locations of Chl$^+$ and Car$^+$ species, and the pathways for their formation, are analyzed based on the rates of their formation and decay by using Marcus theory together with the recent X-ray crystal structure of PS II. These results provide new insight into the alternate electron-donation pathways to P680$^+$.

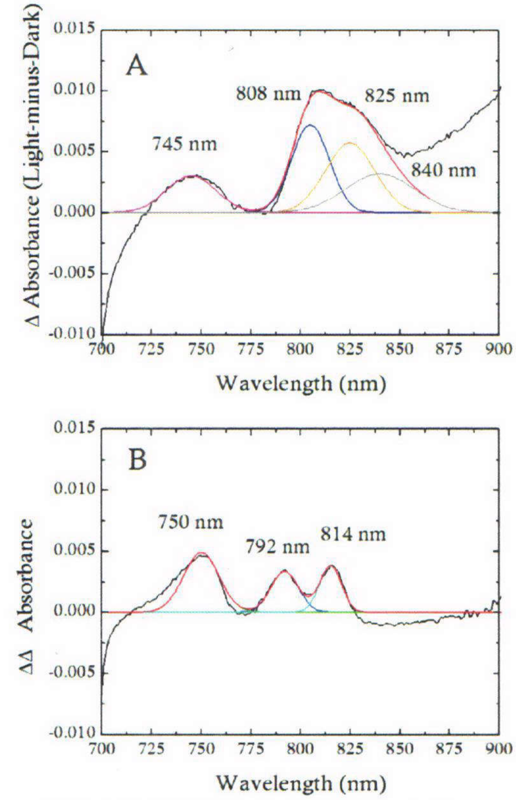

Figure 2: Gaussian deconvolutions of: (A) slow decaying Chl$^+$ species and (B) fast decaying Chl$^+$ species.

Future work is aimed at determining the rates and yields of the secondary electron transfer reactions in PS II reaction centers in which the redox properties of the cofactors are systematically modulated by changing the carotenoid cofactors or by altering the electrostatic interactions with cytochrome b$_{559}$ or the Mn complex in the oxygen-evolving complex. In collaboration with Bruce Diner at DuPont, we are investigating carotenoid photooxidation in cyanobacterial mutants with altered carotenoid composition. Studies of these samples, in which the secondary electron transfer pathways in PS II have been modified, will provide new information of the sequence of secondary electron transfers and on their function. These data can then be correlated with the emerging structural information for PS II in order to understand the factors that tune the redox role of β-carotene in PS II and to determine the electron- vs. energy-transfer roles of carotenoids in photosynthetic reaction centers.

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EXPLORING ELECTRON TRANSFER IN LIGHT HARVESTING ARRAYS

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Molecular devices proposed for the utilization of solar energy depend on electron transfer in supermolecular assemblies. This project seeks to elucidate the role of the matrix in electron transfer reactions by exploring electron transfer in natural and artificial reaction centers and light harvesting complexes in the liquid and solid state.

Chemically induced dynamic electron polarization (CIDEP) is a tool for investigating photoinduced radical pairs and electron transfer. We have used CIDEP to explore artificial reaction centers and other systems. Some artificial reaction centers intrinsically exhibit CIDEP while other systems require addition of exogenous reagents to photoinduce radical pairs observable by CIDEP. Unusual CIDEP has been observed with time resolved EPR in the conducting biopolymer melanin and suggests a novel means to explore the conduction process in polymers.

A major difference exists between the CIDEP of radical pairs in normal solutions and the radical pairs associated with supermolecular arrays and conducting polymers. Radical pairs of simple molecules in liquids experience normal three–dimensional diffusion while they undergo electron transfer, recombination and termination reactions. For example, after creation, the acceptor molecules frequently undergo diffusion away from the donor molecules and encounter unreduced acceptor molecules. If these encounters result in electron transfer reactions with other unreduced acceptor molecules, then the electron spin polarization (ESP) associated with the hyperfine structure is lost. The loss of ESP results because multiple electron transfers in liquid solutions are not likely to return the electron spins back to their original molecules and consequently hyperfine induced ESP is destroyed

Radical pairs in supermolecular arrays and conducting polymers also experience similar factors. However, because their electron spins are confined to the same supermolecular array or polymer, both forward and backward electron transfer is also confined. Assuming no interchain hopping, backward electron transfer in a supermolecular array returns the electron to the same previous molecule and as a result revives hyperfine driven ESP. If electron transfer is confined within a supermolecular array, then forward electron transfer results in loss of the hyperfine driven ESP while backward electron transfer replenishes the ESP. The result is that an ESP "memory" effect can occur that is effectively impossible without a supermolecular array or polymer.

This difference in CIDEP between normal solution and supermolecular arrays should provide a new tool for characterizing electron transfer reactions involved in solar energy transduction. A more complete explanation of this "memory" effect of CIDEP in supermolecular arrays and polymers will be presented. Such CIDEP studies should be especially applicable to the artificial reaction centers that have attached molecular wires.

The LH1 complex can be considered to be a biopolymer of interacting bacteriochlorophyll molecules. The bacteriochlorophyll molecules are organized into a polymeric structure by means of membrane spanning, polypeptide helical units. The means by which this helical protein matrix enhances electron transfer at cryogenic temperatures and in the rigid medium is particularly poorly understood. Using time resolved EPR and pulsed EPR this work has found that electron transfer continues to occur at 4K in oxidized LH1 indicating that the interaction between at least some of the chromophores is larger than the relevant heterogeneity, including that of the matrix. To characterize the role of the matrix in determining heterogeneity and electron transfer rates as the medium becomes rigid, light harvesting model systems are being explored in organic glasses for comparison to the natural LH1 protein complex solubilized in aqueous buffer. A variety of time resolved and pulsed EPR techniques are being exploited to follow electron transfer as the solvent becomes rigid.

The role of the matrix in electron transfer in light harvesting arrays and reaction centers will be investigated by new techniques to be available after arrival of a new pulsed EPR. Additionally, future studies will employ time domain and pulsed EPR to record CIDEP effects for the exploration of supermolecular assemblies involved in light harvesting and photoinduced charge separation.

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PRIMARY PROCESSES IN PHOTOSYNTHESIS: LIGHT HARVESTING AND ITS REGULATION

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New multidimensional optical spectroscopies hold great promise for elucidating the design principles of natural photosynthetic light harvesting. We developed two-dimensional Fourier transform photon echo spectroscopy in the visible wavelength range to reveal the electronic couplings, the spatial arrangement of the exciton states, and the pathways of energy flow in pigment-protein complexes. Our first application was to the FMO protein of green sulfur bacteria. It was also necessary to develop the method of analysis of the 2D spectra and this was done in collaboration with Professor Minhaeng Cho of Korea University. We found that the spatial arrangement of the exciton states enables large jumps in energy such that the lowest exciton state is reached from any starting point in two or three steps. This picture of energy flow contrasts with what might be expected from a simple downhill/stepladder model. We found oscillations in the amplitudes of diagonal peaks in the spectrum which we believe represent electronic coherences between the exciton levels. The FMO complex is a particularly suitable system to study electronic coherence since the energy gaps correspond to accessible frequencies and the dephasing times are relatively long.

We have recently completed a study of the 2D spectrum of the purple bacterial LH3 protein. This is a significantly more complex system than FMO since it contains two sets of bacteriochlorophyll molecules, one set weakly coupled, one set strongly coupled, along with interactions between the two sets. Our analysis show that the B800 molecules must be modeled as an excitonic system at 77K. It also shows that B800 to B820 energy transfer occurs preferentially to higher, dark levels of the B820 manifold. This confirms the conclusion of Scholes and Fleming, and Sumi (and later Silbey) that a generalized version of Forster theory is not based directly on the overlap of emission and absorption spectra is needed to describe this system.

We also developed two-color photon echo peak shift spectroscopy as a complementary method to the 2D approach. We have applied this technique to Photosystem I and to purple bacterial reaction centers, and if time permits our results and conclusions will be described.

The regulation of light harvesting in Photosystem II by the process known as nonphotochemical quenching (NPQ) is not well understood at the molecular level ultrafast spectroscopy using transgenic plants lacking the PsbS gene led us to propose that a zeaxanthin-chorophyll complex was responsible for the major component of NPQ known as qE. We found a strong signal at 1000nm consistent with the spectrum of the zeaxanthin radical cation only under conditions of high light levels when PsbS is active. The strength of this signal correlated with the amount of qE, being twice as large as in the plant with twice the usual number of copies of the PsbS gene. This leads us to propose that electron transfer (from zeaxanthin to chlorophyll) is the quenching mechanism of qE. Where in the PSII super complex it occurs and how the quenching center is formed is still not known.

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Session V

Excited-State Charge Transport in π-Conjugated Molecular Wires and Films

NANOSCALE ASSEMBLIES OF CONJUGATED POLYELECTROLYTES. ENERGY TRANSPORT, ENERGY TRANSDUCTION AND PHOTOVOLTAIC CELLS

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Conjugated polyelectrolytes (CPEs) are polymers that feature a π-conjugated backbone substituted with ionic solubilizing groups such as sulfonate, ammonium, carboxylate, or phosphonate ($-SO_3^-$, $-NR_3^+$, $-CO_2^-$, $-PO_3^{2-}$, respectively, example structures are shown in Figure 1). Conjugated polyelectrolytes are soluble in and processable from water, and they retain the favorable optoelectronic properties characteristic of the conjugated backbone (e.g., strong optical absorption and fluorescence, semiconductor properties). In addition, CPEs are amphiphilic with a strong propensity to self-assemble in solution and into nanostructured, layer-by-layer (LbL) films. This program is investigating the properties of CPEs, with emphasis placed on studies of the mechanism of "amplified quenching", intra- and interchain excited state energy transport, self-assembly into nanoscale CPE assemblies (films and colloids) and solar cells constructed using CPEs as the active material. In order to address the program objectives, the effort combines synthetic monomer and polymer chemistry, steady-state and time-resolved photophysics, along with thin-film and solar cell fabrication and characterization.

Synthetic organic/polymer chemistry plays a key role in this work. As part of this effort, efficient synthetic methods have been developed allowing "direct" synthesis of CPEs from ionic monomers, as well as "indirect" methods in which organic-soluble precursor polymers are first synthesized and characterized, and subsequently the ionic side groups are unmasked in a post-polymerization step. Both of these approaches afford pure polymers with relatively high molecular weights in quantities sufficient to allow physical chemical studies, layer-by-layer film preparation, and photovoltaic cell work to be accomplished. Recent synthetic efforts have led to the preparation of a homologous series of polymers in which the HOMO-LUMO band gap is systematically varied, giving rise to a family of materials that absorb throughout the visible spectrum (Figure 1).

We have demonstrated that charged quenchers such as methyl viologen and cyanine dyes quench the luminescence from oppositely charged CPEs with extremely high efficiency. Stern-Volmer constants as large as 10^8 M^{-1} have been observed in specific systems. Investigations of CPEs in a variety of solvents show that interchain (polymer-polymer) aggregation plays an important role in determining their photophysics and the efficiency of amplified quenching by oppositely charged ionic quenchers. Aggregation is especially important in water, and interchain singlet exciton diffusion is believed to be a dominant pathway giving rise to highly efficient quenching by ionic quenchers. Aggregation induced quenching of the singlet exciton is also significant, especially in the lower

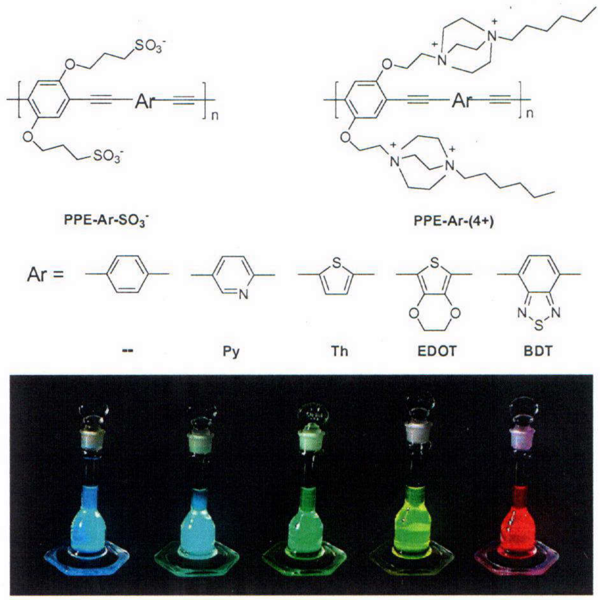

Figure 1. Top: Structures of variable HOMO-LUMO gap CPEs. Bottom: Color photograph of methanol solutions of CPEs under illumination with near-UV light.

band gap (red emitting) CPEs that have been prepared to date.

Fluorescence upconversion and transient absorption spectroscopy have been applied to CPE-quencher ion systems in solution, and the results demonstrate that the dynamics of exciton transport and quenching are very rapid. In many cases, quenching is dominated by an ultrafast component due to rapid interchain exciton diffusion in the CPE aggregates. We have also been successful in applying transient absorption spectroscopy to nanostructured layer-by-layer films consisting of CPEs. These studies provide evidence for ultrafast charge and energy transport taking place in the assemblies.

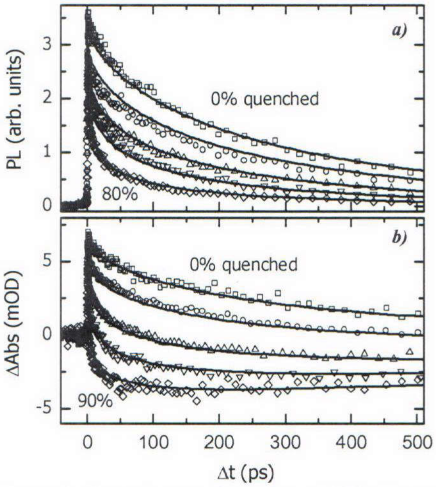

Figure 2. Excited state dynamics of PPE-SO_3^- in CH_3OH for different concentrations of added cyanine dye quencher. a) Up-conversion signal of fluorescence detected at 450 nm for and b) transient absorption at a probe wavelength of 680 nm.

Fabrication of LbL films consisting of CPEs has been developed with a robotic system to the point where it is now routine to construct films with 30 or more polyelectrolyte bilayers. Characterization of the resulting films by optical, epifluorescence, electron and atomic force microscopy reveals that the films are smooth (RMS roughness < 5 nm) and uniform over large areas (1 x 1 cm). Multilayer, nanostructured films consisting of CPEs with different band gaps have been fabricated; however, strong interchain interactions (aggregation) which lead to fluorescence quenching have made time-resolved studies of vectorial exciton transport through the multilayer films difficult.

Finally, we have considerable success in demonstrating the capability of using LbL CPE films as the active medium in polymer photovoltaic cells as illustrated by the structures, concepts and results of Figure 3. Although the overall optical-to-electrical power conversion efficiency of the cells is comparatively low (likely due to poor carrier transport in the films), the cells provide a platform for fundamental research concerning the relationship between the nanostructure of the active layer and overall cell performance. We have demonstrated the capability of adsorbing the CPEs onto nanostructured TiO_2, and using the resulting films in relatively efficient polymer-TiO_2 hybrid regenerative solar cells. The finding that the CPEs can be efficiently adsorbed onto metal oxide surfaces and they undergo efficient charge injection into the semiconductor opens up the opportunity to use this combination of materials as a new platform to study exciton and charge transport in multilayer CPE films constructed atop wide band gap semiconductors.

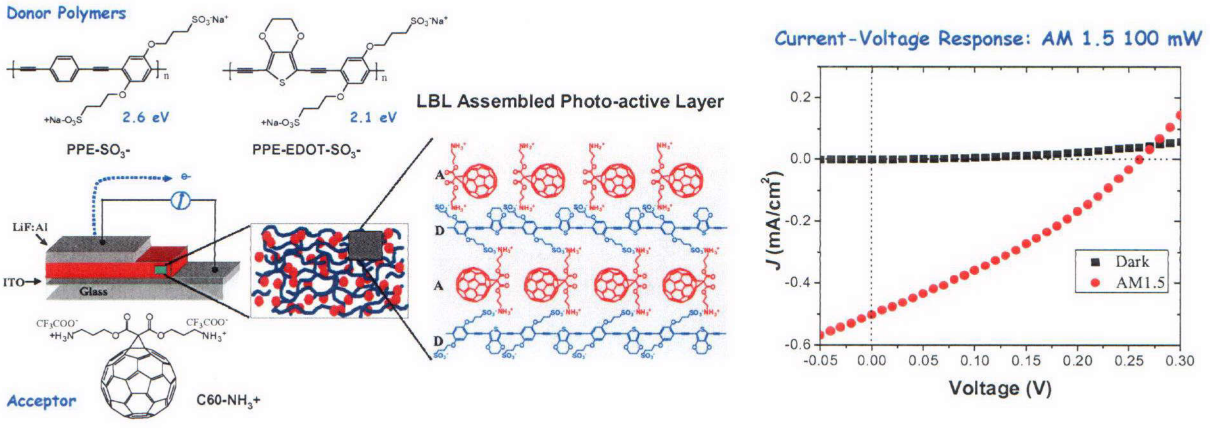

Figure 3. Schematic diagram demonstrating LbL construction of multi-anionic CPEs with a dicationic C60 derivative for inclusion in a photovoltaic cell and demonstration of the obserbed AM 1.5 photovoltaic efficiency.

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MOLECULAR WIRES FOR ENERGY CONVERSION

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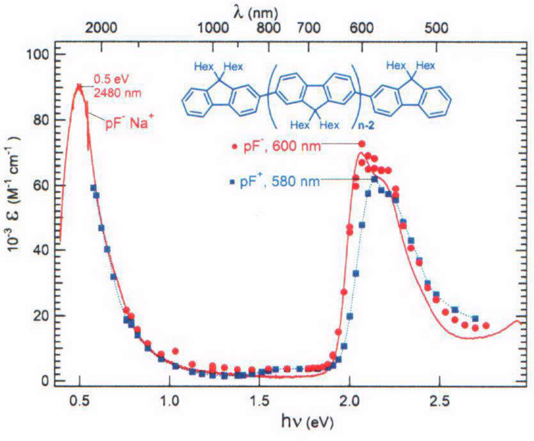
The BES Solar Photochemistry program has a rich history in the investigation of tunneling through bridges, and a recent interest in injection of charges to give them a real (thermal) existence. This work investigate injection of charges into long, conjugated molecules, which alone, attached to surfaces or in concert with nanoparticles, appear to have enormous potential to capture solar energy for conversion to electrical energy (photovoltaics) or chemical energy (fuels). This potential stems from the possibility that these "wires" could be fashioned into molecular materials for solar conversion that might function with high efficiency but be produced cheaply. A field called "plastic solar"[1] has created solar cells having efficiencies that started low; rose rapidly with subsequent research, but may now be growing more slowly, while they are still well below those of silicon. There is substantial reason to believe that solar photoconversion based on these conjugated polymers can achieve very high efficiencies since they can be elaborated based on principles learned in natural and artificial[2] photosynthesis.

That goal will require knowledge of fundamental principles, and essential properties governing the behavior of charges and excitations in molecular wires, including basic considerations of the natures of "excitonic materials." Of special importance are aspects of charges in conjugated polymers that control their rapid transport over long distances and knowledge of energy levels so they may be tuned for performance. At present the energy levels are often inadequately known and not easily measured for most of these materials. This program seeks to determine natures and energies of charges in conjugated polymers and their transport. The principal tool is pulse radiolysis at BNL's Laser Electron Accelerator Facility (LEAF).

Optical spectra for electrons or holes in wires typically contain low-energy near infrared (NIR) absorption bands as seen in Figure 1 for polyfluorene (pF) anions and cations. A simple MO argument supports the notion that low-energy bands are diagnostic of delocalized charges and may predict transport. Studies proposed below will examine this question further. NIR bands similar to those in Figure 1 were observed for holes in poly(phenylene ethynylene) (PPE) and electrons in polythiophene (pT).



Electrons were also added chemically to pF (solid line in Figure 1) and pT. Their optical spectra were indistinguishable from those found in pulse radiolysis; knowledge of radiation chemistry tells us that free ions are created in the pulse radiolysis experiments, though ion-pairs are possible in some cases. These observations provide a preliminary answer of "no" to a question proposed at the outset of this work: Would adventitious ions pair with and trap charges in wires, rendering them immobile? At present this conclusion is based on spectroscopy and the comparison has not interrogated the low-energy sides of the NIR bands.

While charges are very delocalized, the experiments also show that they are somewhat confined as "polarons." Measurements at LEAF determined delocalization lengths for electrons to be 3.8 nm in polyfluorene and 3.1 nm in polythiophene in THF. This and other results present insight into what charges are like and how they move in these long molecules.

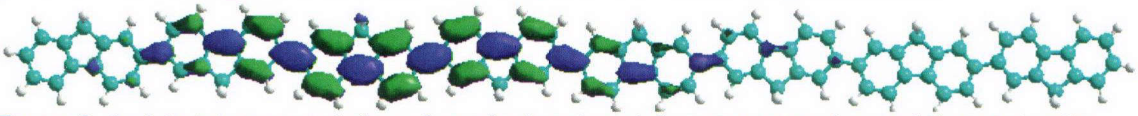
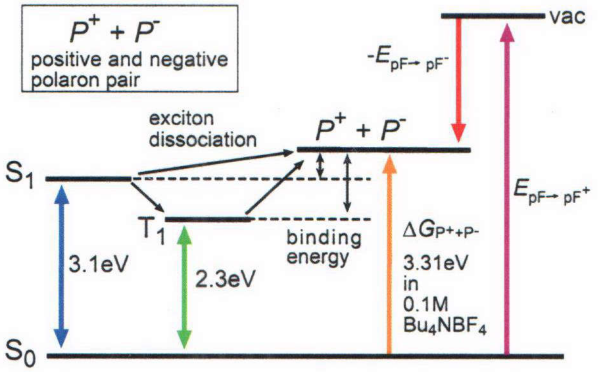


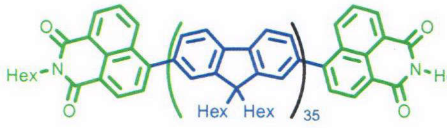
Figure 2. A pictorial representation of an electron in polyfluorene spread over 4.5 repeat units.

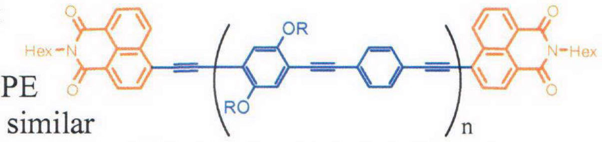
At the same time paired like charges ("bipolarons") are shown not to be formed, except at very high doping when electrons or holes are "squeezed" together.

Electrochemistry is effective for determination of redox potentials of small molecules and oligomers of moderate lengths, but often fails to obtain energetics for injection of charges into long oligomers or polymeric wires. Pulse radiolysis measurements of charge transfer equilibria obtained reversible redox potentials for electron injection into polythiophene and electron and hole injection into polyfluorene (E^0(pF$^{+/0}$) = +0.69 V and E^0(pF$^{0/-}$)= -2.65 V vs Fc$^{+/0}$) The figure at right summarizes energetics of optical excitation in pF, evaluating the exciton binding energy to be 0.2 eV under electrochemical conditions (high electrolyte concentration).



Polyfluorenes (pF) were synthesized with appended anthraquinone (AQ) or naphthylimide (NI, shown at right) electron traps. While most electrons should be captured by the long pF chains, they appeared on the AQ or NI trap groups within 2 ns, signaling fast electron transport in the pF chains. Planned experiments will examine charge transport in these molecules utilizing the newly-developed ultrafast single-shot detection system to measure charge transport with 10 ps time resolution. We also plan to synthesize PPE with NI end-cap groups (shown right) and perform similar experiments. Planned experiments will develop methods to utilize laser pulses to re-inject charges trapped on end-caps and observed their transport to end-caps with ~ 1 ps time resolution.





Additional planned experiments will refine the methods for determination of delocalization lengths and redox potentials, facilitating their application to additional types of conjugated polymer and oligomers, including polymers in which metal atoms are part of the conjugated chain. Investigations of oligomers of defined lengths will deepen our insight into the natures of charges in conjugated molecules.

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EXCITED ELECTRONIC STATES IN CARBON NANOTUBES

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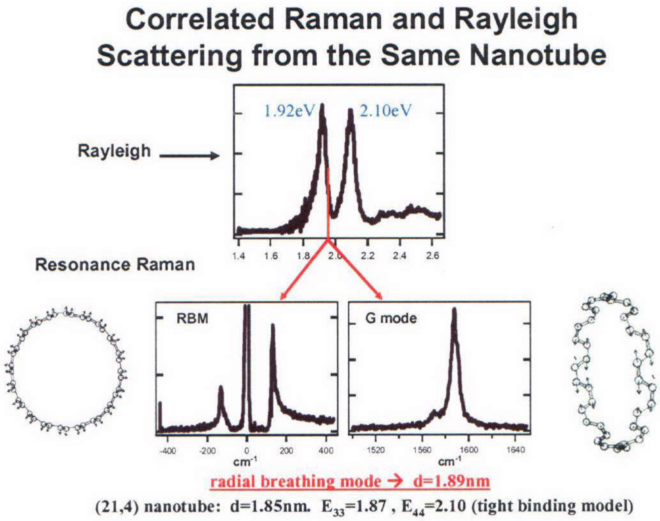
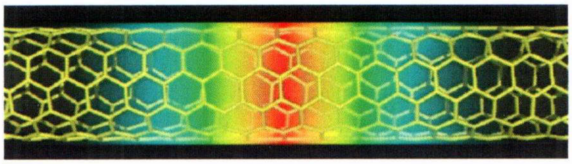
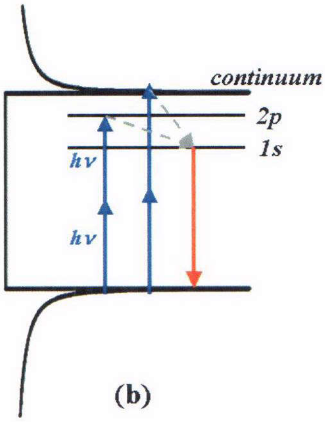
The goal of our DOE research is to understand how visible light interacts with nanoparticles and nanowires that have the potential for photogenerated charge separation. Our recent experiments focus on electromagnetic field enhancement around metallic particles, and single wall carbon nanotubes SWNT -- the subject of this talk.


Correlated Raman and Rayleigh Scattering from the Same Nanotube

(21,4) nanotube: d=1.85nm. E_{33}=1.87 , E_{44}=2.10 (tight binding model)

In SWNT two issues have been addressed: 1) can we find a spectroscopic way to identify *uniquely* an arbitrary metallic or semiconducting tube? Can we establish general spectroscopic assignments? Can we identify a single tube? 2) what is the fundamental nature of excited states, that is, are they bound excitons or free electron-hole pairs? On 1), we have discovered it is possible to characterize single tubes by resonant Rayleigh scattering, using a white light "supercontinuum" of laser brightness. The figure shows resonant Rayleigh and Raman data from one single tube. Resonant Rayleigh scattering gives essentially the same information as the absorption spectrum, and can be measured against a zero background. It should be a general characterization method for nano-objects that does not depend upon the sample's ability to luminescence. To establish assignments we have a continuing collaboration with the Yimei Zhu high resolution TEM group at Brookhaven, to do electron diffraction on the same single tubes.


(a)



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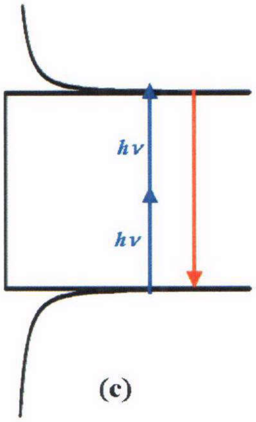

(c)

On 2) we have proven the transitions in the optical spectra are actually excitons (about 20 Angstroms in size) by a comparison of two photon and one photon absorption spectra, in micellar solutions of luminescing semiconductor tubes. Because of the high symmetry and selection rules, different transitions appear in the two spectra. The binding energy is about 0.4 eV. Previously these transitions were thought to be spatially delocalized van Hove band edge singularities. In a study of fast SWNT photophysics we found a very high rate of exciton-exciton interaction and decay by Auger recombination. This fast Auger process is also seen in a study of endoperoxide side wall groups present for tubes handled in air. Such sidewall endoperoxide groups protonate at acid pH in aqueous solution. This protonation dopes holes into the tubes, which in turn first quench band gap luminescence and (at higher doping levels) bleach the band gap optical absorption. DNA is an excellent surfactant for carbon nanotubes in water, as shown by careful work at DuPont. In collaboration we have shown that DNA wrapped SWNT show strong circular dichroism. This CD signal is induced quantum mechanically by the chiral DNA; there is no evidence for SWNT enantiomer separation.

In our Ag metal nanocrystal work, we are now trying to understand if charge transfer photochemistry is possible for plasmon excited states. This research has occurred in several steps. Previously, the excited electron coherent metallic polarization in such particles was shown to cause Surface Enhanced Raman Scattering. Confocal microscopic optical techniques have shown how a single molecule at 23 C, under optimal circumstances, can show a spectrally integrated Stokes Raman signal that is 10^2-10^3 stronger than a fully allowed, free space single molecule luminescence signal. This huge Raman cross section occurs at the junctions of ca. 40nm touching Ag nanocrystals. There is simultaneously an optical squeezing effect on the junction. We did a numerical calculation of the force due to the mutual induced metallic polarizations. The resulting force is dipole-dipole at long separations. At short distance, as the ac electronic polarization inside the metal concentrates at the junction, the force increases much faster than dipole-dipole. We calculate that these forces might be used to organize Au or Ag particles into lines under laser irradiation. On photochemistry, we had showed earlier that Ag local field enhancement can also photocatalyze reduction of adsorbed Ag ion leading to nanocrystal growth. The shape of the growing Ag nanocrystal can be controlled by the choice of laser wavelength with respect to the dipolar plasmon resonant wavelength. Currently we are studying photoelectrochemistry of Au particles on ITO electrodes in an electrochemical cell. Under negative bias the local field causes excited (hot) electron tunneling to nearby Cu++ ions in the water electrolyte. These ions are reduced to Cu atoms which then deposit on the Au field enhancing particles. These studies are being done with photolithographically generated Au particles, so that we might have precise relative geometries between particles, with known local field distributions. In a separate project, a previously unrecognized type of Ostwald ripening was found for reduced metallic Ag particles on conductive ITO substrates in pure water. Electrons travel from smaller to larger particles through the substrate, while simultaneously Ag+ ions travel through the water. The net result is that larger particles grow at the expense of smaller particles.

We have a close collaboration with the Friesner group on geometrically optimized DFT calculations on nanostructures important to the DOE solar energy program. At present 500 atom sections of carbon nanotubes, and realistic models of solvated anatase and rutile TiO_2 particles (as in the Gratzel cell) are under study. We have also looked carefully at the basic nature of electrical doping in Si nanocrystals and nanowires.

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NOVEL SOLAR PHOTON CONVERSION PROCESSES INVESTIGATED BY TERAHERTZ SPECTROSCOPY

Matthew C. Beard, James E. Murphy, Kelly P. Knutsen, Xin Ai, Garry Rumbles, Randy J. Ellingson, and Arthur J. Nozik

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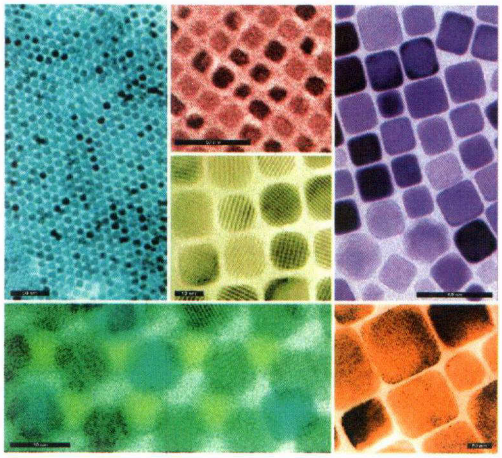
Three dimensional arrays of semiconductor nanocrystals (NCs) are a novel approach to solar energy conversion that offers the potential to control the microscopic charge generation, separation, and transport so as to maximize solar energy conversion efficiencies. Beneficial hot-carrier effects such as slowed hot-carrier cooling and multiple exciton generation may be engineered in these novel nanostructures. Efficient carrier transport requires strong inter-NC coupling while minimizing carrier trapping. We present measurements using time-resolved THz spectroscopy (TRTS) of treated PbSe NC arrays that exhibit inter-NC electronic coupling and discuss the various factors that determine efficient long range transport. TRTS is a powerful and relatively new experimental tool that measures both inter-NC coupling, in a non-contact fashion, and carrier dynamics, with sub-picosecond temporal resolution, simultaneously.

A necessary characteristic of all solar photon conversion approaches that are based on NC arrays is that the arrays exhibit very high mobility (or conductivity) for electrons and holes; this requires strong inter-NC electronic coupling and the subsequent formation of extended states called minibands. The inter-NC spacing is a critical parameter that determines, in large part, the required inter-NC coupling. However, in addition to the inter-NC spacing other factors contribute to efficient carrier transport, for example, site energy dispersion, NC size and shape, cross linking, and Coulomb charging. Inter-NC separations are controlled, in large part, by the surface capping chemistry. Semiconductor NCs are prepared via an organometallic synthesis, where an organic molecule, such as oleic acid, terminates the surface preventing agglomeration, allowing the NCs to be suspended in a variety of solvents, and controlling the surface chemistry, for example, by reducing the rate of oxidation. To achieve efficient inter-NC coupling the capping ligand must be exchanged to allow for smaller inter-NC spacing. In addition, carrier trapping at the surface of the NCs must be minimized. To achieve both strong coupling and minimized trapping requires knowledge of the surface chemistry. All of these factors are highly interdependent. THz spectroscopy is the only technique that can measure both the degree of coupling and the carrier dynamics simultaneously. Furthermore, the usually prevalent contact issues are irrelevant for THz measurements, while charge transfer at the contact and long range transport (measured via dc conductivity) are important factors for solar energy applications, the microscopic intrinsic dynamics must be investigated and understood.



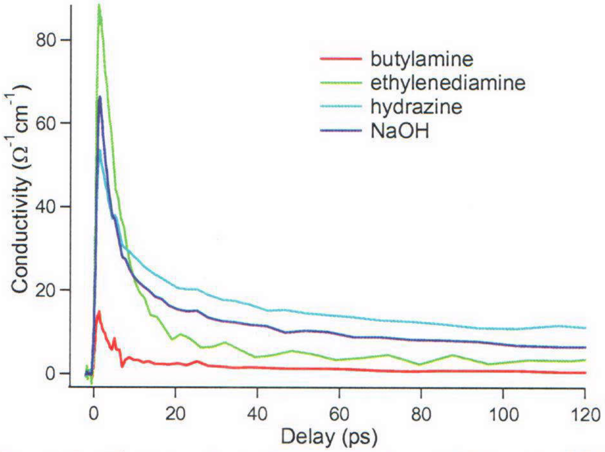


Figure 1. Photoconductivity (excitation at 800 nm) of 5.6 nm PbSe NC arrays with different surface treatments.

THz photoconductivity in ordered arrays of 5.6 nm PbSe NCs with varying inter-NC separation was measured. The following surface capping ligands produced arrays with average inter-NC separation of oleic acid (OA), 1.8 nm, aniline (AN), 0.8 nm, ethylenediamine (EDA), 0.4 nm, butlyamine (BA), 0.4 nm, and hydrazine (HY), 0.25 nm. NCs were treated with NaOH to achieve intimate contact. The TRTS results are shown in Fig. 1. All of the films except for those with OA capped NCs show a photoconductive response, indicative of strong inter-NC coupling. The extracted mobility, a measure of inter-NC electronic coupling, decreases from EDA > NaOH > HY > BA > AN > OA. These results do not follow the expected increase in coupling with a decrease in inter-NC spacing. Comparing the EDA treatment to the BA, the mobility is 6 times greater in EDA; however, the inter-NC spacing is of comparable magnitude

In addition to NC arrays, we have begun studying the fundamental carrier transport dynamics in blends of PCBM/P3HT. Organic semiconductors, such as P3HT, share many advantageous properties with traditional inorganic semiconductors (ISCs) (e.g., silicon); however, their potentially low-cost processing, light weight, and flexibility make them highly attractive for renewable energy applications. In contrast to dc conductivity measurements, THz spectroscopy measures transport phenomena on a localized length scale given by $L=\sqrt{D/\omega}$, where D is the electron (hole) diffusivity and ω is the radial frequency; L is on the order of several nanometers. This relation makes THz spectroscopy the most sensitive technique to measure the microscopic conductivity, which is precisely where the fundamental processes that determine conductivity occur. Furthermore, TRTS is the only technique that can measure the photoconductivity on a sub-picosecond timescale. We find that the photon-to-carrier conversion efficiency is very low ~ 5×10^{-4}, however, the AC mobility is high. Carrier transport in the P3HT, extracted from the frequency-dependent conductivity, can be modeled by a localized transport mechanism, whereby long range transport is hindered. Our measurements as a function of the PCBM weight fraction show that in neat P3HT or a blend of 80% PCBM the excited carriers have a fast decay time. In the neat P3HT case, photogenerated free carriers geminately recombine within 100 ps. In contrast, in films with a PCBM weight percent between 20% and 50% the photogenerated carriers survive to much longer times due to charge transfer between the PCBM (an electron acceptor) and the P3HT (hole acceptor). Our results indicate that the increased performance of the blends results from the survival of the photogenerated carriers to long times.

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Session VI

Interfacial Charge Transfer

GROUND- AND EXCITED-STATE CHARGE TRANSFER IN MOLECULAR- AND NANO-SCALE SYSTEMS

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Scope:

Coordination chemistry is used to address problems in interfacial charge transfer and homogeneous electron and atom transfer processes essential in solar photoconversion to fuels.

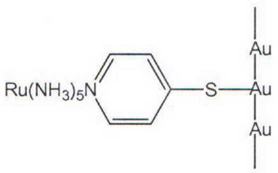
Recent Results:

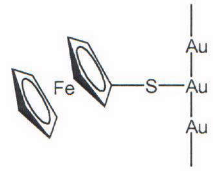
The overall purpose of nanoparticle work during the past two years was to elucidate the nature of electron- and energy-transfer processes between metal complexes or organic molecules and metal nanoparticles as a function of the electronic structure of the nanoparticle. (1) Spectroscopic methods were used to try to detect light-induced electron transfer from molecules and metal complexes either free in solution or attached to gold nanoparticles. New absorption features due to optically induced electron transfer were sought and the emission intensities and lifetimes of emissive complexes as a function of the concentration of gold nanoparticles were probed. (2) An important emergent issue in this work became the nature of metal nanoparticle surfaces and, for that reason, research also focused on the coordination chemistry of these surfaces. (3) Finally, as it became clear that the electronic interaction between the metal complex and the metal nanoparticle was very difficult to detect, we began an effort to model the properties (molar absorptivity and wavelength profile) to be expected for optical interfacial charge transfer between a molecular adsorbate and a band of electronic levels in a nanoparticle.

Interfacial charge-transfer absorption. Optically induced charge transfer between adsorbed molecules and a metal electrode was predicted by Hush to lead to new electronic absorption features, but has not been experimentally observed. Interfacial charge transfer absorption (IFCTA) provides information concerning the barriers to charge transfer between molecules and the metal/semiconductor and the magnitude of the electronic coupling and could thus provide a powerful tool for understanding interfacial charge-transfer kinetics. We are developing a framework for modeling and predicting IFCTA spectra.

The key feature of optical charge-transfer to or from a band of electronic levels, assumed to have a constant density of states and absorption probability, is that the molar absorptivity attains a plateau and reaches half-plateau intensity at $h\nu = \lambda + \Delta G^{\theta}$, where λ and ΔG^{θ} are the reorganization energy and free-energy gap for the optical charge transfer. In contrast, from the Mulliken –Hush expression modified for a multi-state system for metals, the molar absorptivity ($M^{-1}cm^{-1}$) drops at high energy and $\leq$ $2.5\times10^{3}\rho_{M}H_{12}^{2}r^{2}/(\lambda+\Delta G^{\theta})$, giving rise to a peaked absorption profile, where H_{12} is the electronic coupling between states 1 and 2, r is the distance over which electron transfer occurs, and ρ_M is the metal density of states (energies in wavenumbers, r in Å, 298 K).

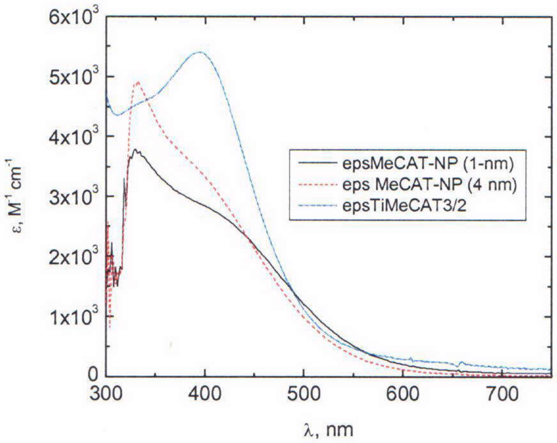
Electrochemical studies of the distance dependence of electron-transfer kinetics in the $(NH_3)_5Ru[4\text{-py}(CH_2NHC(O)(CH_2)_nS\text{-}]^{2+/+}$ and $(C_5H_5)Fe[(C_5H_4)(CH_2)_nS\text{-}]^{+/0}$ systems were used to gauge the intensities to be expected for IFCTA in these systems. From the Mulliken–Hush expression above, the molar absorptivity for IFCTA in these systems is estimated as $> 3 \times 10^3\ M^{-1}cm^{-1}$ for the $n = 0$ systems. Such intensities should be observable for $n = 0$ gold nanoparticle assemblies.





Plans:

Preliminary comparisons of methylcatechol-complexed 1- and 4-nm TiO_2 nanoparticles (corrected for the TiO_2 absorption) are compared with that of the tris(methylcatechol)titanium(IV) complex (left). After correction of the nanoparticle spectra for residual TiO_2 absorption, multiple absorption features (not previously reported) are evident. These spectroscopic measurements suggest a localized excitation process, consistent with the results of a number of electronic structure calculations. Systems such as those shown are being studied computationally and experimentally.



Proton-coupled Electron Transfer vs. H-atom Transfer. An understanding of the factors controlling the energetics of electron, proton, hydrogen atom, and hydride ion transfer reactions in transition metal complexes will be required to rationally develop fast, energy-efficient catalysts for the various fuel generation reactions that will be needed in the future.

We will begin to examine the reactions of photogenerated metal radicals ($Re(CO)_5$, $Re(bpy)X(CO)_2$, $OsCp(CO)_2$, etc.) with electron and hydrogen donors (aniline derivatives, NADH, other metal hydrides) in aqueous and organic media. These H-donors (acceptors) present a range of thermodynamic and intrinsic barriers. As data become available, we will test the relationship between observed rate constants and those predicted from Marcus and other models.

$$M_2 \xrightarrow{h\nu} 2M\bullet$$
$$AH + M\bullet \longrightarrow A\bullet + MH$$
$$MH + A\bullet \longrightarrow M\bullet + AH$$

Publications 2004-2006

“Henry Taube: Inorganic Chemist Extraordinaire”
C. Creutz, P. C. Ford, T. J. Meyer
Inorg. Chem., submitted

"Transition State Characterization for the Reversible Binding of Dihydrogen to Bis(2,2'-bipyridine)rhodium(I) from Temperature- and Pressure-Dependent Experimental and Theoretical Studies," Fujita, E.; Brunschwig, B. S.; Creutz, C.; Muckerman, J. T.; Sutin, N.; Szalda, D.; Eldik, R. v. *Inorg. Chem.* 2006, *45*, 1595 – 1603

“Interfacial Charge Transfer Absorption:Applications; Metal-Molecule Assemblies
Carol Creutz, Bruce S. Brunschwig, and Norman Sutin,
Chem. Phys. (in press, Hush issue)

“Far-Infrared Study of the Au-S Stretch of Alkanethiol-Capped Au Nanoparticles
Janet Petroski, Mei Chou, and Carol Creutz, *J. Phys. Chem. B* (submitted)[§]

“Interfacial Charge Transfer Absorption: Semiclassical Treatment
Carol Creutz, Bruce S. Brunschwig, and Norman Sutin, *J. Phys. Chem. B* **2005**, *109*, 10251-10260

“Implications of an Electron-Hopping Model for Charge Transport through Donor-Bridge-Acceptor Assemblies Connected to Metal Electrodes,”
Sutin, N.; Brunschwig, B. S.; Creutz, C.; Feldberg, S. W.
J. Phys. Chem B **2004**, *108*, 12092 -12102

“Synthesis, Structure and Reactivity of a Hydroxymethyl Complex in Water”
Carol Creutz, Mei H. Chou, Etsuko Fujita and David J. Szalda
*Coord. Chem. Rev.***2005**, 249, (3-4), 375-390

“Rapid Phosphine Exchange on 1.5-nm Gold Nanoparticles”
Janet Petroski, Mei H. Chou, and Carol Creutz
Inorg. Chem. **2004**, *43*, 1597-1599

“Using the Marcus Inverted Region for Rectification in Donor-Bridge-Acceptor "Wire" Assemblies”
Norman Sutin, Bruce S. Brunschwig and Carol Creutz
J. Phys. Chem B. **2003**, *107*, 10687 - 10690

105 Electron transfer from the molecular to the nanoscale
Carol Creutz, Bruce S. Brunschwig and Norman Sutin
Comprehensive Coordination Chemistry II, J. McLeverty and T. J. Meyer Editors, Elsevier, Amsterdam, Vol. 7, pp 731-777 (2004)

ELECTRON TRANSFER AT ZnO/LIQUID CONTACTS : ELUCIDATION OF THE RATE CONSTANT AT OPTIMAL EXOERGICITY, DIRECT OBSERVATION OF THE MARCUS INVERTED REGION, EVALUATION OF REORGANIZATION ENERGIES AT A SEMICONDUCTOR ELECTRODE, AND DIRECT MEASUREMENT OF DRIVING FORCE AND ELECTRONIC COUPLING EFFECTS ON INTERFACIAL CHARGE TRANSFER

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Electron transfer across the semiconductor/liquid interface is one of the most fundamental processes in the operation of a photoelectrochemical energy conversion system. Control of the interfacial electron-transfer rate is required to optimize the solar energy conversion efficiency of such devices. Some of the factors that govern these interfacial electron-transfer rate constants, however, remain relatively poorly understood. While in principle semiconductor electrodes have advantages over metal electrodes in addressing some of the basic predictions of interfacial electron-transfer theories, such measurements are difficult because extraordinarily low defect densities at the semiconductor/liquid interface are required to prevent adsorption and surface-state related reactions from dominating the observed interfacial kinetics processes.

Under DOE support, carefully prepared n-type ZnO/H_2O contacts with a series of $Os^{3+/2+}$ redox couples have recently been reported to exhibit the predicted dependence of interfacial charge-transfer rate constants, k_{et}, on changes in standard interfacial free energies, $\Delta G^{\circ\prime}$, for driving forces up to and beyond that of optimum exoergicity. The rate constants were observed to decrease for high driving force contacts, indicating, by a straightforward application of Marcus theory, that interfacial charge-transfer processes of some electrodes can operate in the inverted region.

Our DOE-supported work has addressed another basic prediction of the Marcus model for interfacial electron-transfer reactions at semiconductor electrodes. The interfacial electron-transfer rate constant should be strongly dependant on the reorganization energy, λ, of the acceptor species in solution. At constant driving force, in the normal region, k_{et} should decrease as λ increases. Previous measurements in our laboratory of the stability of n-Si/CH_3OH contacts as a function of the reorganization energy of the electron donor in the electrolyte provided indirect evidence of this prediction. To directly verify this basic theoretical prediction, we synthesized a series of one-electron redox couples having relatively constant potentials in the band-gap region of ZnO and having reorganization energies that span approximately 1 eV. Charge-transfer rate constants were measured for these systems in contact with n-type ZnO electrodes. This investigation provided a detailed comparison of interfacial electron-transfer reactions at an "ideally" behaving semiconductor/electrode interface with the predictions of Marcus theory for such systems.

The interfacial energetic and kinetics behavior of n-ZnO/H_2O contacts were determined for cobalt trisbipyridine ($Co(bpy)_3^{3+/2+}$), ruthenium pentaamine pyridine ($Ru(NH_3)_5py^{3+/2+}$), cobalt bis-1,4,7-trithiacyclononane ($Co(TTCN)_2^{3+/2+}$), and osmium bis-dimethyl bipyridine bis-imidazole ($Os(Me_2bpy)_2(Im)_2^{3+/2+}$), which have similar formal reduction potentials yet which have reorganization energies that span approximately 1 eV. Differential capacitance vs. potential and current density vs. potential measurements were used to measure the interfacial electron-transfer rate constants for this series of one-electron outer-sphere redox couples. Each interface displayed a first-order dependence on the concentration of redox acceptor species and a first-order dependence on the concentration of electrons in the conduction band at the semiconductor surface, in accord with expectations for the ideal model of a semiconductor/liquid contact. Rate constants varied from 1×10^{-19} to 6×10^{-17} $cm^4\ s^{-1}$. The interfacial electron-transfer rate constant decreased as the reorganization energy, λ, of the acceptor species increased, and a plot of the logarithm of the electron-transfer rate constant vs. $\left(\lambda + \Delta G^{0'}\right)^2 / \left(4 \lambda k_B T\right)$ (where $\Delta G^{o\prime}$ is the driving force for interfacial charge transfer) was linear with a slope of ≈ -1. The rate constant at optimal exoergicity was found to be $\approx 5 \times 10^{-17}$ $cm^4\ s^{-1}$ for this system. These results show, for the first time to our knowledge, that interfacial electron-transfer rate constants at semiconductor electrodes are in good agreement with the predictions of a Marcus-type model of interfacial electron-transfer reactions.

In another study under DOE support, we have addressed another key prediction of electron-transfer theory. The inverted region is the regime in which an increase in driving force produces a decrease in the electron-transfer rate constant. For a semiconductor electrode, changes in the conduction band edge energy will affect the driving force of interfacial electron transfer, and thus change the interfacial charge-transfer rate constant to a pH-independent redox species. Such a variation of the conduction band edge energy is predicted for metal oxide electrodes when the pH is varied due to the protonation / deprotonation equilibrium of –OH sites on the oxide surface but to our knowledge has not yet been rigorously observed for any semiconductor electrode system to date.

The driving force dependence of the interfacial electron-transfer rate constant was investigated in our work by using pH changes to shift the band edges of n-ZnO electrodes in contact with $[Co(bpy)_3]^{3+/2+}$ and $[Ru(bpy)_2(MeIm)_2]^{3+/2+}$. Differential capacitance vs. potential and current density vs. potential measurements were used to determine the energetics and kinetics, respectively, of the interfacial electron-transfer processes. All rate processes were observed to be kinetically first-order in the concentration of surface electrons and first-order in the concentration of dissolved redox acceptors. The band-edge positions of the ZnO were essentially independent of Nernstian potential of the solution and were shown to vary as predicted with pH. Measurements of $[Co(bpy)_3]^{3+/2+}$, which has a low driving force and high reorganization energy, and measurements of $[Ru(bpy)_2(MeIm)_2]^{3+/2+}$, which has a high driving force and low reorganization energy, allowed for the evaluation of both the normal and inverted regions of interfacial electron-transfer processes, respectively. The rate constant at optimum exoergicity was observed to be approximately 5×10^{-17} $cm^4\ s^{-1}$. The rate constant vs. driving force dependence at n-type ZnO electrodes exhibited both normal and inverted regions, and the data were well-fitted by parabolas generated using classical electron-transfer theory. These results are in excellent agreement with theoretical predictions of the free energy dependence of interfacial electron-transfer reactions.

Finally, we have addressed changes in the rate constant that occur as a result of steric hindrance to the redox species lowering the electronic coupling in both the self-exchange process and in the interfacial charge transfer process at ZnO electrodes. Taken together with previous results of the standard driving force and reorganization energy dependence of k_{et}, the entire set of data offers strong proof, and arguably the most complete verification in any system to date, of the Marcus model of interfacial charge-transfer reactions. This work also offers guidelines for future work to achieve molecular level chemical control over charge separation processes in photoelectrochemical systems for efficient solar energy conversion.

DOE-Supported Publications in Last Two Years

Nick Prokopuk and Nathan S. Lewis, "Eneretics and Kinetics of Interfacial Electron-Transfer Processes at Chemically Modified InP/Liquid Junctions," *J. Phys. Chem., B,* 2004, *108 (14): 4449-445.*

Jae-Joon Lee, George M. Coia, and Nathan S. Lewis, "Current Density vs Potential Characteristics of Dye-Sensitized Nanostructured Semiconductor Photoelectrodes. I. Analytical Expressions." *J. Phys.Chem.B,* 2004, *108 (17): 5269-5281.*

Jae-Joon Lee, George M. Coia, and Nathan S. Lewis, "Current Density vs Potential Characteristics of Dye-Sensitized Nanostructured Semiconductor Photoelectrodes. II. Simulations." *J. Phys.Chem.B,* 2004, *108 (17): 5282-5293.*

Thomas W. Hamann, Florian Gstrein, Bruce S. Brunschwig, and Nathan S. Lewis, "Measurement of the Free Energy Dependence of Interfacial Charge-Transfer Rate Constants Using ZnO/H_2O Semiconductor/Liquid Contacts", *J. Am .Chem. Soc.*, 2005, *127 (21): 7815-7824.*

Thomas W. Haman, Florian Gstrein, Bruce S. Brunschwig, and Nathan S. Lewis, "Measurement of the Dependence of Interfacial Charge-Transfer Rate Constants on the Reorganization Energy of Redox Species at n-ZnO/H_2O Interfaces", *J. Am. Chem. Soc.*, 2005, *127 (40): 13949-13954.*

Thomas W. Hamann, Florian Gstrein, Bruce S. Brunschwig, and Nathan S. Lewis, "Measurement of the Driving Force Dependence of Interfacial Charge-Transfer Rate Constants in Response to pH Changes at n-ZnO/H_2O Interfaces", *Chem. Phys.*, special invited issue, *in press.*

William J. Royea, Thomas W. Hamman, Bruce S. Brunschwig, and Nathan S. Lewis "A Comparison Between Interfacial Electron-Transfer Rate Constants at Metallic and Graphite Electrodes", *J. Phys. Chem, B., in press.*

Matthew C. Traub, Julie S. Biteen, David J. Michalak, Lauren J. Webb, Bruce S. Brunschwig, Nathan S. Lewis, "High-Resolution X-Ray Photoelectron Spectroscopy of Chlorine-Terminated GaAs(111) Surfaces" *J. Phys. Chem., B, in press.*

Nathan S. Lewis, "Chemical Control of Charge Transfer and Recombination at Semiconductor Photoelectrode Surfaces", *Inorg. Chem.*, invited article in Forum issue on solar energy, 2005, *44 (20): 6900-6911.*

Session VII

Dye-Sensitized Solar Cells

ELECTRON TRANSFER DYNAMICS IN EFFICIENT MOLECULAR SOLAR CELLS

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A key objective of our research is to provide kinetic models for surface mediated photochemical processes relevant to solar energy conversion.[1-15] Our emphasis is on metal-to-ligand charge-transfer (MLCT) excited states, energy transfer, electron injection, and charge recombination processes with $(d\pi)^6$ coordination compounds of our own design (Re(I), Ru(II), and Os(II) compounds, termed sensitizers), anchored to ~ 20 nm diameter nanocrystalline (anatase) TiO_2 particles in mesoporous 10 μm thick films. A new research direction is to quantify iodine redox chemistry in fluid solution and at these sensitized interfaces.

Excited State Injection. Electron injection into TiO_2 from molecular excited states often occurs on pico- to femto-second time scales. In support of this we have recently found that the injection yields from Ru(II) ammine compounds are excitation wavelength dependent and are sensitive to deuteration of the ammine ligands. The presence of low-lying ligand field (LF) excited states in these compounds shortens the lifetimes to < 10 ns. Efficient, wavelength dependent electron injection is therefore consistent with ultrafast injection from vibrationally 'hot' excited states. This finding indicates that energy conversion and interfacial electron transfer can be controlled by nuclear substitution. The interfacial isotope affects are kinetic in origin and likely emanate from changes in the non-radiative decay rate constants. Experiments designed to probe this are underway.

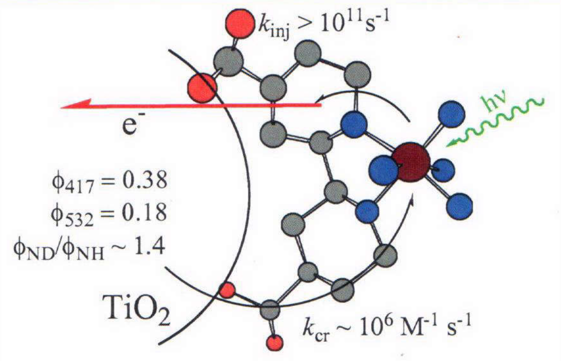

Figure 1. Excitation wavelength and isotope dependent electron injection quantum yields measured after 417 and 532.5 nm excitation of $Ru(dcb)(NH_3)_4/TiO_2$.

The tetra-ammine compound shown in Figure 1 has only a single chromophoric ligand. In the more commonly studied sensitizer *cis*-$Ru(dcb)_2(NCS)_2$, where dcb is 4,4'-$(COOH)_2$-2,2'-bipyridine, the dcb ligands may be inequivalent leading to ambiguity about the direction of the excited state dipole relative to the surface. The compound *cis*-$Ru(dpp)_2(eina)_2(PF_6)_2$, where dpp is 4,7-diphenyl-1,10-phenanthroline, and ina is isonicotinic acid, was prepared and characterized to directly quantify the yields of 'remote injection'. Visible light excitation promotes an electron to the 'remote' dpp ligand. Interfacial proton concentration was employed to tune the relative sensitizer-semiconductor energetics. Injection quantum yields, ϕ_{inj}, varied from ~ 0.2 at pH = 5 to ~ 1 at pH = 1, with a slope of ~ 0.15/pH. At pH = 12, long-lived excited states were observed with $\phi_{inj} < 0.05$. At pH ≤ 2, ϕ_{inj} became temperature dependent. A mechanism was proposed wherein population of LF states at elevated temperatures lowers ϕ_{inj}. The results demonstrate quantitative electron injection from an MLCT excited state localized on a ligand that is not anchored directly to the TiO_2 surface.

Intermolecular Energy Transfer. The yields and dynamics for energy transfer from the MLCT excited states of $Ru(dcb)(bpy)_2(PF_6)_2$, Ru^{2+}, and $Os(dcb)(bpy)_2(PF_6)_2$, Os^{2+}, anchored to TiO_2 thin films were quantified. Lateral energy transfer from Ru^{2+*} to Os^{2+} was observed and the yields were measured as a function of the relative surface coverage and the external solvent environment (CH_3CN, THF, CCl_4, and hexanes). Excited-state decay of Ru^{2+*}/TiO_2 was well described by a parallel first- and second-order kinetic model, whereas Os^{2+*}/TiO_2 decayed with first-order kinetics within experimental error. The first-order component was assigned to the radiative and non-radiative decay pathways ($\tau = 1$ μs for Ru^{2+*}/TiO_2 and $\tau = 50$ ns for Os^{2+*}/TiO_2). The second-order component was attributed to intermolecular energy transfer followed by triplet-triplet annihilation. An analytical model was derived that allowed determination of the fraction of excited-states that follow the two pathways. The fraction of Ru^{2+*}/TiO_2 that decayed through the second-order pathway increased with surface coverage and excitation irradiance. Monte-Carlo simulations were performed to estimate the $Ru^{2+*} \rightarrow Ru^{2+}$ intermolecular energy transfer rate constant of $(30\ \mathrm{ns})^{-1}$.

Iodine Redox Chemistry. Iodide remains the sole electron donor that yields high efficiencies, > 10% under AM 1.5 illumination, in sensitized regenerative solar cells. It is not clear why. To address this question we have begun characterization of sensitized iodide oxidations. The MLCT excited states of $Ru(bpy)_2(deeb)(PF_6)_2$, where deeb is 4,4'-$(CO_2CH_2CH_3)_2$-2,2'-bipyridine, in dichloromethane were found to be efficiently quenched by iodide at room temperature. The ionic strength dependence of the UV-Visible absorption spectra gave evidence for ion pairing. Iodide was found to quench the excited states by static and dynamic mechanisms. Stern-Volmer and Benesi-Hildebrand analysis of the spectral data provided a self-consistent estimate of the iodide-$Ru(bpy)_2(deeb)^{2+}$ adduct in dichloromethane, $K = 59{,}700\ M^{-1}$. Transient absorption studies clearly demonstrated an electron transfer quenching mechanism with transient formation of $I_2^{\cdot-}$ in high yield, $\phi = 0.25$ for 355 or 532 nm excitation. The parent $Ru(bpy)_3^{2+}$ compound also ion pairs with iodide in CH_2Cl_2 and light excitation gave a higher $I_2^{\cdot-}$ yield, $\phi = 0.50$. X-ray crystallographic, IR, and Raman data gave evidence for interactions between iodide and the coordinated deeb ligand in the solid state. Similar ion-pairing and quenching of MLCT excited states was observed with tri-iodide however the mechanism(s) remain speculative.

Driving 'Uphill' Redox Reactions with Hot Electrons. With interfacial energetics like that shown in Figure 2, ultrafast electron injection can drive redox reactions that would be thermodynamically uphill from the emissive excited states. We have recently provided proof-of-principle demonstrations of this important step toward exceeding the well-known Schockley-Queisser limit of single junction photovoltaic cells. For example, the thermally equilibrated MLCT and the reduced form of $[Os(bpy)_2(deebq)](PF_6)_2$, where deebq is 4,4'-diethylester-2,2'-biquinoline, do not inject electrons into TiO_2. Injection into TiO_2 from vibrationally hot excited states is followed by acceptor reduction with quantum yields of $\phi(417\ \mathrm{nm}) = 0.18 \pm 0.02$, $\phi(532.5\ \mathrm{nm}) = 0.08 \pm 0.02$, and $\phi(683\ \mathrm{nm}) = 0.05 \pm 0.01$. Acceptor reduction is several hundred meVs uphill from the emissive excited state and does not occur.

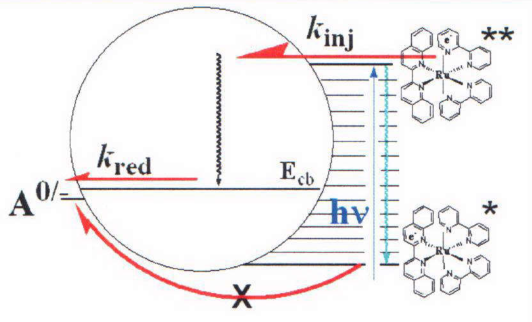

Figure 2. Schematic of interfacial energetics necessary to drive redox reactions that would be uphill from the emissive excited state.

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1. **Sensitization and Stabilization of TiO_2 Photoanodes with Electropolymerized Films of Ruthenium and Zinc Polypyridyl Complexes.** Moss, J.A.; Yang, J.C.; Stipkala, J.M.; Wen, X.; Bignozzi, C.A.; Meyer, T.J.; Meyer, G.J. *Inorg. Chem.* **2004**, *43*, 1784-1792.

2. **Cation Effects in Nanocrystalline Solar Cells.** Watson, D.F.; Meyer, G.J. *Coord. Chem. Rev.* **2004**, *248*, 1391-1406.

3. **Influence of Surface Protonation on the Sensitization Efficiency of Porphyrin-Derivatized TiO_2.** Watson, D.F.; Marton, A.; Stux, A.M.; Meyer, G.J. *J. Phys. Chem. B* **2004**, *108*, 11680-11688.

4. **Excited State Electron Transfer from Ru(II) Polypyridyl Compounds Anchored to Nanocrystalline TiO_2 Through Rigid-Rod Linkers.** Wang, D.; Galoppini, E.; Hoertz, P.G.; Carlisle, R.A.; Meyer, G.J. *J. Phys. Chem. B.* **2004**, *108*, 16642 – 16653.

5. **A Nuclear Isotope Effect for Excited State Electron Transfer Across Semiconductor Interfaces.** Liu, F.; Meyer, G.J. *J. Am. Chem. Soc.* **2005**, *127,* 824-825.

6. **Dye-Sensitized SnO_2 Electrodes with Iodide and Pseudohalide Redox Mediators.** Bergeron, B.V.; Marton, A.; Oskam, G.; Meyer, G.J. *J. Phys. Chem. B* **2005**, *109*, 937-943.

7. **Electron Injection at Dye-Sensitized Semiconductor Electrodes.** Watson, D.F.; Meyer, G.J. *Ann. Rev. Phys. Chem.* **2005**, 56, 119-156.

8. **Evidence for Static Quenching of MLCT Excited States by Iodide.** Clark, C.C.; Marton, A.; Meyer, G.J. *Inorg. Chem.* **2005**, *44*, 3383-3385.

9. **Intermolecular Energy Transfer Across Nanocrystalline Semiconductor Surfaces.** Higgens, G.T.; Bergeron, B.V.; Hasselmann, G.M.; Farzad, F.; Meyer, G.J. *J. Phys. Chem. B* **2006**, *110*, 2598-2605.

10. **Molecular Approaches to Solar Energy Conversion with Coordination Compounds Anchored to Semiconductor Surfaces**. Meyer, G.J. *Inorg. Chem.* **2005**, *44*, 6852-6864.

11. **Remote and Adjacent Excited State Electron Transfer at TiO_2 Interfaces Sensitized to Visible Light with Ru(II) Compounds**. Liu, F.; Meyer, G.J. *Inorg. Chem.* **2005**, *44*, 9305-9313.

12. **Static and Dynamic Quenching of Ru(II) Polypyridyl Excited States by Iodide.** Marton, A.; Clark, C.C.; Srinivasan, R.; Freundlich, R.E.; Narducci Sarjeant, A.A.; Meyer, G.J. ***Inorg. Chem.*** **2006, *45*,** 362-369.

13. **Tri-iodide Quenching of Ruthenium MLCT Excited State in Solution and on TiO_2 Surfaces: An Alternate Pathway for Charge Recombination.** Clark, C.C.; Marton, A.; Srinivasan, R.; Narducci Sarjeant, A.A.; Meyer, G.J. *Inorg. Chem.* **2006**, *45, in press.*

14. **Towards Exceeding the Shockley-Queisser Limit: Photo-Induced Interfacial Charge Transfer Processes that Store Energy in Excess of the Equilibrated Excited State.** Hoertz, P.G.; Staniszewski, A.; Marton' A; Higgins, G.T.; Incarvito, C.D.; Rheingold, A.L.; Meyer, G.J. *J. Am. Chem. Soc.* **2006**, *128, in press.*

15. **Tuning Open Circuit Photovoltages with Tripodal Sensitizers.** Clark, C.C.; Meyer, G.J.; Wei, Q.; Galoppini, E. *submitted.*

LINKERS FOR SEMICONDUCTOR NANOPARTICLE SENSITIZATION: MODELS FOR ELECTRON TRANSFER AND SOLAR CELLS APPLICATIONS

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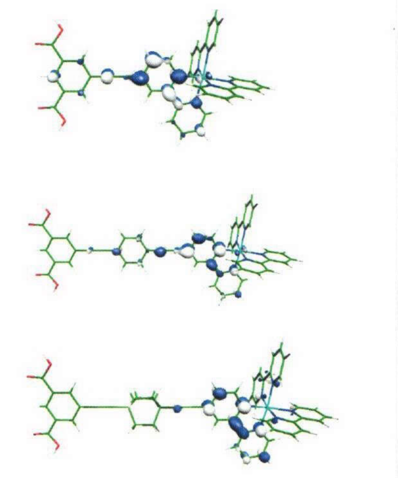

Figure1. Lowest Unoccupied Molecular Orbitals (LUMO) for conjugated and saturated Rigid-rod Ru-bpy chromophores in acetonitrile.

Recent progress in the following research areas will be presented in this talk:

Rigid Linkers Varying in Length as Models for Electron Transfer *(with Gerald J. Meyer, Johns Hopkins, and Petter Persson, Lund University)* We have studied with Piotrowiak a series of rigid-rod (Figure 1) and tripodal linkers varying in length and saturation of the bridging unit to study the distance dependence of electron injection and the effect of the linker structure.[1] Electron injection events were quantified by femtosecond laser spectroscopy studies at improved time resolutions (< 40 fs) on well-characterized films.[1] Also, Ru-bpy rigid rods have been investigated using DFT and TD-DFT calculations to elucidate the influence of the rigid rod on their absorption spectra and oxidation processes in different chemical environments (Figure 1).[2] In addition, the control of the sensitizer-TiO_2 distance is important for efficient power optimization, as the open circuit photovoltage (Voc) increased markedly with the distance between the Ru center and the surface.[3] A description of IR experiments designed to characterize the bond between the anchoring groups of the described models and the nanoparticles surfaces will be included in the discussion.

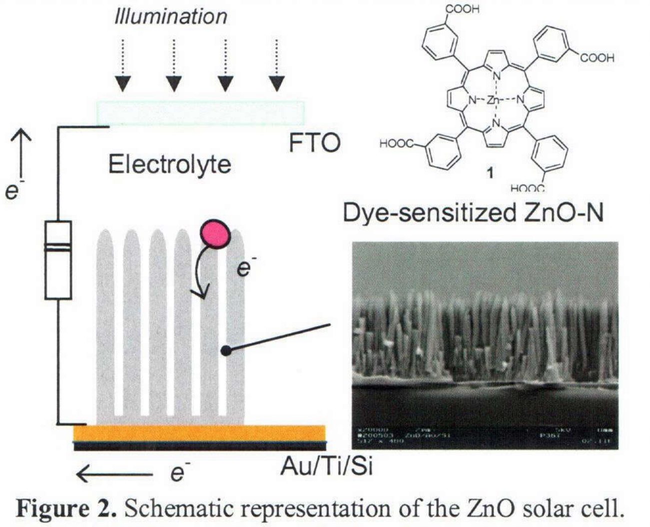

Figure 2. Schematic representation of the ZnO solar cell. The ZnO-N film is~1.8 μm thick and the rods diameter is ~ 0.15 μm. The ZnO uniformly covers the gold surface.

Fast Electron Transport in Dye-Sensitized ZnO Nanorod Solar Cells[4,5] *(with Anders Hagfeldt, KTH Stockholm and Yicheng Lu, Rutgers New Brunswick)* Over the past few years ZnO has emerged as the material of choice for the preparation of nanostructured electrodes, especially those based on columnar structures called nanorods or nanowires. We will describe **(a)** the functionalization of Lu's MOCVD-grown ZnO nanorods (ZnO-N) with linkers and chromophores, and **(b)** the efficiency and electron transport properties of a dye-sensitized solar cell with the working electrode made of ZnO-N on gold/Si (Figure 2), measured at the KTH Center of Molecular Devices. The dye employed was zinc(II) porphyrin, **1**, with four COOH *meta* anchoring groups, which is an efficient sensitizer for TiO_2 electrodes. Dye-sensitized solar cells prepared from vertically aligned, single-crystalline, ZnO-N electrodes displayed much faster (~ 2 orders of magnitude) electron transport than comparable cells with mesoporous ZnO nanoparticle electrodes (ZnO-C). The difference was attributed to the difference in number of grain boundaries that the electron has to pass.

List of Publications:

1. **in preparation:** *Ru(II)-Polypyridyl Complexes Bound to Nanocrystalline TiO_2 Films Through Rigid-Rod Linkers: Effect of the Linkers Length on Electron Injection Rates* Piotrowiak, P.; Galoppini, E.; Wang D.; Myahkostupov, M.

2. *Calculated Optoelectronic Properties of Ruthenium tris-bipyridine Dyes Containing OPE Rigid Rod Linkers in Different Chemical Environments* Lundqvist, M. J.; Galoppini, E.; Meyer, G. J.; Persson P. *J. Phys. Chem. B* **2006**, submission planned by end of April).

3. *Tuning Open Circuit Photovoltages with Tripodal Sensitizers* Clark, C.C.; Meyer, G.J.; Wei , Q.; Galoppini, E. *J. Phys. Chem.* **2006**, submitted 11 Apr 2006.

4. *Fast Electron Transport in Dye-Sensitized ZnO Nanorod Solar Cells* Galoppini, E.; Rochford, J.; Hagfeldt, A.; Boschloo, G.; Chen, H; Saraf, G.; Lu Y. *J. Am. Chem. Soc.* **2006**, submitted 10 April 2006.

5. *Binding Studies of Molecular Linkers to ZnO Nanotips* Taratula, O.; Galoppini E.; Wang, D.; Chu, D.; Zhang, Z.; Chen, H.; Saraf, G. and Lu, Y. *J. Phys. Chem. B* **2006**, *110*, 6506-6515.

6. *Excited State Electron Transfer from Ru(II) Polypyridyl Complexes Anchored To Nanocrystalline TiO2 Through Rigid-Rod Linkers,* Wang, D.; Mendelsohn, R. Galoppini, E. Hoertz, P. G.; Carlisle, R. A. and Gerald J. Meyer *J. Phys. Chem B.* **2004**, *108*, 16642.

7. *Tripodal Ru(II) Complexes with Conjugated and Nonconjugated Rigid-Rod Bridges for Semiconductor Nanoparticles Sensitization* Wei, Q. Galoppini, E. Tetrahedron **2004**, *60*, 8497.

8. *Linkers For Anchoring Sensitizers to Semiconductor Nanoparticles* Elena Galoppini, *Coord. Chem. Rev.* **2004**, *248*, 1283-1297.

ULTRAFAST ELECTRON INJECTION FROM ADSORBATES TO NANOCRYSTALLINE SEMICONDUCTOR THIN FILMS: pH AND SEMICONDUCTOR DEPENDENCE

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The long-term goal of the proposed research is to understand electron transfer dynamics in nanoparticle/liquid interface. This knowledge is essential to many semiconductor nanoparticle based devices, including photocatalytic waste degradation and dye sensitized solar cells. The specific objectives of this budget period are two folds: 1) To understand the dependence of injection rate on the strength of electronic coupling strength in the ultrafast injection regime, and 2) To develop vibrational sum-frequency mixing as a probe for adsorbate geometry and electron injection dynamics at the interface. In the past year we have finished the following two main projects and started to develop the SFG setup.

1) Dependence of injection rate on solution pH. (ref. 6)

Unlike intramolecular ET, the existence of a quasi-continuum of electronic states in the solid leads to a dependence of ET rate on the density of accepting states in the semiconductor, which varies with the position of the adsorbate excited-state oxidation potential relative to the conduction band edge. For metal oxide semiconductors, their conduction band edge position varies with the pH of the solution, leading to pH dependent interfacial ET rates in these materials.

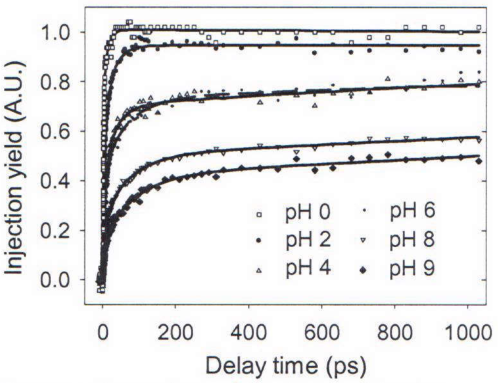

Figure 1. Comparison of the electron injection kinetics for ReC1P/TiO_2 films at pH 0-9 range after 400 nm excitation. The symbols are experimental data and the solid curves are best three-exponential fits.

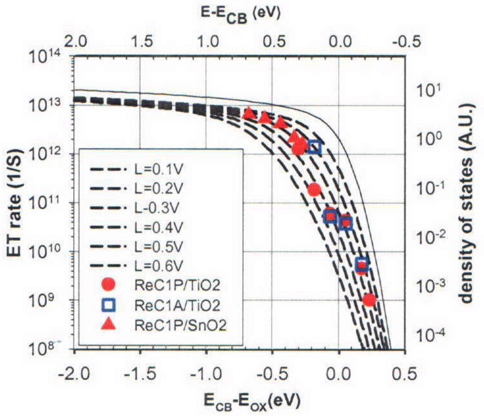

Figure 2. Comparison of calculated electron injection rate (dashed line) as a function of E_{CB}-$E_{OX}(S^*/S^+)$ and measured electron injection rate in ReC1A and ReC1P on TiO_2 and ReC1P on SnO_2 at different pH. The measured injection rates for ReC1P/SnO_2 and ReC1A/TiO_2 have been multiplied by a factor of 15 and 11, respectively, to allow comparison on the same curves. A plot of the density of states in the semiconductor (right axis) as a function of energy relative to the band edge (top axis) is shown by the thin solid curve.

In this work we examine this dependence in $Re(L_P)(CO)_3Cl$ (or ReC1P) [L_P = 2,2'-bipyridine-4,4'-bis-$CH_2PO(OH)_2$] and $Re(L_A)(CO)_3Cl$ (or ReC1A) [L_A = 2,2'-bipyridine-4,4'-bis-CH_2COOH sensitized TiO_2 and ReC1P sensitized SnO_2 nanocrystalline thin films using femtosecond transient IR spectroscopy. ET rates are measured as a function of pH by monitoring the CO stretching modes of the adsorbates and mid-IR absorption of the injected electrons. The injection rate to TiO_2 was found to decrease by 1000 fold from pH 0 to 9, while it reduced by only a factor of a few to SnO_2 over a similar pH range. Comparison with the theoretical predictions based on Marcus' theory of nonadiabatic interfacial ET suggests that the observed pH dependent ET rate can be qualitatively accounted for by considering the change of density of electron accepting states caused by the pH dependent conduction band edge position.

2) Semiconductor dependence:

One of the most interesting aspects of interfacial ET is the strong dependence on the nature of semiconductors. In addition to TiO_2, Nb_2O_5, and ZnO, we have extended similar studies of injection dynamics from RuN3 to SnO_2 and In_2O_3. Similar studies using organic dyes were also conducted.

a) Electron injection from Ru dyes to SnO_2: (ref. 5) Ultrafast infrared spectroscopy was utilized to investigate the electron transfer dynamics from $Ru(dcbpy)_2(X)_2$ complexes (dcbpy = 4,4'-dicarboxy-2,2'-bipyridine; X_2 = SCN^-, $2CN^-$, and dcbpy; referenced as RuN3, Ru505, and Ru470, respectively) to nanocrystalline SnO_2 films. Injection kinetics in all case are biphasic, with a small ultrafast component (less than 10%) and a much larger nonexponential slow component, indicating that most injection occurs from thermalized excited state. Comparing RuN3, Ru505, and Ru470, the rate of both the fast and slow components slow down in correlation with less negative excited-state oxidation potentials in these dyes. Comparing injection from RuN3 to different semiconductors, the amplitude of fast component on SnO_2 is similar to that on ZnO but much smaller than that on TiO_2, suggesting a significantly slower electron injection rate from the unthermalized state to SnO_2 and ZnO than to TiO_2. The ET rate variation among these semiconductors is attributed to considerably lower density of conduction band states in s-type (SnO_2 and ZnO) than that in d-type (TiO_2) semiconductors.

b) Electron injection from Ru dyes to In_2O_3: (ref. 8) Photoinduced electron injection dynamics from RuN3, Ru505, and Ru470 to In_2O_3 nanocrystalline thin films were also studied using ultrafast transient IR spectroscopy. Following 532 nm excitation of the adsorbates, the injection kinetics were non-single-exponential. The half rise times, defined as the time of 50% injection yield, are 5, 85, and >200 ps for RuN3, Ru505 and Ru470 respectively for samples exposed to air. For samples in pH 2 buffer, the corresponding half time for injection from these complexes becomes 6, 105 and 18 ps respectively. The injection kinetics from RuN3 to In_2O_3 was found to be similar to that to SnO_2. These kinetics traces show negligible < 100fs injection component and are very different from those to TiO_2. The dependences of the injection kinetics on adsorbate energetics and the nature of the semiconductors are consistent with previously observed trend in other semiconductors.

Publications acknowledging DOE Grant # DE-FG02-98ER14918 (2004-2006)

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Manuscript in preparation

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INTERFACIAL PHOTOCHEMICAL PROCESSES IN SENSITIZED NANOSTRUCTURED ELECTRODES

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We are conducting basic studies to understand the principal physical and chemical factors (e.g., electrolyte composition, molecular adsorbents, network morphology, defect structure, trap state distribution, band edge movement, and light intensity) that influence or limit the kinetics and energetics of electron transport and recombination in (Grätzel-type) dye-sensitized photoelectrochemical solar cells. Some specific recent achievements are summarized below.

Molecular adsorbent effects on recombination and band-edge movement. The mechanism by which molecular adsorbents affect the photovoltage of dye-sensitized TiO_2 solar cells is not well understood. In principle, an adsorbent could change the photovoltage by either altering the recombination rate between photoelectrons in TiO_2 and oxidized redox species in the electrolyte or inducing band-edge movement. Often the proposed mechanism for improved cell performance is based on measurements that do not distinguish between shielding and band-edge movement. We investigated the mechanisms by which the adsorption of chenodeoxycholate (collaboration with M. Grätzel, Swiss Institute of Technology) and guanidinium to the TiO_2 surface alters the band-edge position, recombination rate, and cell performance. Cografting chenodeoxycholate with a sensitizer onto the TiO_2 surface is found to both shift the conduction-band-edge upward to negative potentials (favoring a higher photovoltage) and enhance the recombination rate by fivefold (favoring a lower photovoltage). The collective effect of both the upward band-edge shift and faster recombination was an improved photovoltage. It was also found that the coadsorbent reduced the dye loading significantly – by as much as 60% – but had only a modest effect on the photocurrent. Calculations and experiments revealed that even at low dye loading enough dye was present to absorb a significant fraction of incident light. In marked contrast to chenodeoxycholate, we found that the adsorbent guanidinium slows recombination by 20-fold. In addition, the guanidinium cation was found to induce a downward shift of the conduction-band edge. The net effect of these opposing phenomena was an improved photovoltage. To our knowledge, this is the first experimental evidence of a molecular adsorbent that passivates surface recombination sites in dye-sensitized solar cells. These studies draw attention to the possibility of enhancing the photovoltage by developing adsorbents that not only shift the band edges upward but also shield the surface against recombination.

Temperature & photoelectron density dependences of electron diffusion coefficient. The nature and origin of the distribution of traps in TiO_2 nanoparticle films have been two of the most important and elusive issues in understanding the electron-transport dynamics in dye-sensitized solar cells. The experimental results from several studies are consistent with trap-limited electron transport. It has generally been inferred from these and other results that the distribution of energy levels for these traps forms an exponential conduction band tail. However, the evidence for an exponential trap-state distribution in TiO_2 nanoparticle films is inconclusive. In particular, critical experimental measurements are missing to test the predictions of this model. Toward this end, we investigated (collaboration with E.A. Schiff, Syracuse U) the temperature and photoelectron-density dependences of the electron transport dynamics in TiO_2 nanoparticle films. While the electron diffusion coefficient was found to depend strongly on the photoelectron density, surprisingly, the activation energy displayed little, if any, dependence on the photoelectron density. These results are inconsistent with the widely used transport model that assumes multiple trapping of electrons in an exponential conduction band tail. Importantly, our results also suggest that structural disorder, rather than energetic disorder, limits electron transport in mesoporous TiO_2.

Spatial location of transport-limiting traps. We addressed a long-standing issue in the understanding of electron transport in dye-sensitized TiO_2 solar cells – namely, the spatial location of transport-limiting traps or, equivalently, the spatial location where electrons predominantly reside during their transit through porous nanoparticle films. The dependences of the electron-diffusion coefficient and photoinduced-electron density on the internal surface area of dye-sensitized TiO_2 nanoparticle films were investigated by photocurrent transient measurements. With the aid of expressions derived from the waiting-time distribution used in the continuous-time random walk model, we showed that traps located at the surface of particles – rather than in the bulk of particles or at grain boundaries between particles – predominantly limit transport. This study also shows, for the first time, that the photogenerated electrons spend most of their time on the surface of particles as they diffuse through films. Identifying their spatial location provides important scientific information and insight into effective surface modification strategies to improve cell performance.

Nonideal statistics of electron diffusion. We investigated the ideality of electron statistics in disordered nanoparticle films and its effects on transport and cell performance. Experimental and theoretical studies showed that the Einstein diffusion equation does not apply to dye-sensitized nanoparticle solar cells and that the electron statistics in disordered nanoparticle films are nonideal. Previous studies on electron diffusion have explicitly or implicitly assumed that the applicability of the Einstein diffusion relation. Our results also suggest that individual electrons move slower than the electron density profile by a constant factor owing to a distribution of localization sites. No evidence was found for Coulomb interaction, although it is likely to be important in high efficiency (>10%) dye cells or at high light intensities (> one sun). This study is relevant to understanding the electron transport mechanism in other disordered systems, such as organics, amorphous materials, quantum dot arrays, and polycrystalline materials. Small perturbation techniques (e.g., photocurrent transient) were shown to measure the chemical diffusion coefficient of electrons, which corresponds to the movement of the electron density profile with time instead of – as is normally assumed – the movement of individual electrons with time, which corresponds to the tracer diffusion coefficient. The latter diffusion coefficient is shown to determine the actual electronic charge in the film.

Core-shell nanoparticle films. The morphological properties of core-shell nanoparticle films involving a ZnO-like shell on SnO_2 and TiO_2 cores were characterized (collaboration with N.-G. Park, Korea Institute of Science and Technology) by XRD, SEM, XANES, and EXAFS. Detailed information was obtained about the uniformity, composition, and crystallinity of the shell surrounding the cores and the effect of shell morphologies on the film morphology, adsorbed dye concentration, light scattering, electron transport, recombination, and overall cell efficiency. XANES and EXAFS studies reveal thin ZnO-like shells around the nanoparticles at low Zn levels. In the case of SnO_2 cores, ZnO nanocrystals are formed at high Zn/Sn ratios (ca. 0.5). SEM studies show that Zn-modification of SnO_2 nanoparticles changes the film morphology from a compact mesoporous structure to a less dense macroporous structure. In contrast, Zn-modification of TiO_2 nanoparticles is found to have no apparent influence on film morphology. For SnO_2 cores, adding ZnO improves the solar cell efficiency by increasing light scattering and dye uptake and decreasing recombination. In contrast, adding a ZnO shell to the TiO_2 core decreases the cell efficiency, largely owing to a loss of photocurrent resulting from slow electron transport associated with the buildup of the ZnO surface layer.

Future plans are directed toward understanding photochemical processes in ordered nanostructured systems.

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"Effect of an Adsorbent on Recombination and Band-Edge Movement in Dye-Sensitized TiO_2 Solar Cells: Evidence for Surface Passivation" Kopidakis, N; Neale, N.R.; Frank, A.J. *J. Phys. Chem. B*, in press.

"Temperature Dependence of the Electron Diffusion Coefficient in Electrolyte-Filled TiO_2 Nanoparticle Films: Evidence Against Multiple Trapping In Exponential Conduction Band Tails" Kopidakis, N; Benkstein, K.D.; van de Lagemaat, J.; Frank, A.J.; Yuan, Q.; Schiff, E.A. *Phys. Rev. B*, **2006**, 73, 045326.

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ULTRAFAST DYNAMICS AND CHROMOPHORE DESIGN IN DYE-SENSITIZED TiO_2-BASED SOLAR CELLS

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The 1991 report by O'Regan and Grätzel of a high-efficiency photoelectrochemical device using colloidal nanoparticle TiO_2 sparked a significant research effort toward the further development of solar cells based on the concept of dye sensitization.[1] Currently, the best performing devices employ a Ru^{II} polypyridyl-based chromophore in which photoexcitation results in the formation of a metal-to-ligand charge-transfer (MLCT) excited state that then undergoes interfacial electron transfer to yield a conduction band electron in the TiO_2 nanoparticle. The reliance of these devices on molecular substrates covalently attached to the surface of the nanoparticles has spurred research on a wide variety of chromophores as potential sensitizers in an effort to increase the overall efficiency of the device.[2] In 1998 Ferrere and Gregg reported the production of photocurrent from a TiO_2-based solar cell employing an Fe^{II} analog of the Ru^{II} complexes more commonly employed.[3] Although the photocurrent measured was a factor of 100 less than that of an analogous Ru^{II} chromophore, the incipient production of photocurrent was nevertheless encouraging: successful utilization of a first-row transition metal complex as a sensitizer presents a number of potential advantages ranging from reduced cost to more facile redox chemistry which could lead to a significant increase its overall efficiency.

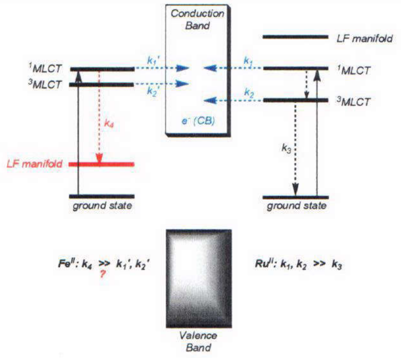

Figure 1. *Simplified energy level diagram for a TiO_2-based dye-sensitized photocathode.*

A schematic energy level diagram for the cathodic half of the Grätzel Cell is shown in Figure 1. Whereas the second- and third-row metal-based chromophores typically employed in the Grätzel cell have relatively high-energy charge-transfer states as their lowest energy excited states, the electronic structures of most first-row complexes are characterized by low-lying ligand-field states. These states are not good candidates for facilitating injection due to their energies and spatial characteristics. From these considerations we can infer that the results obtained by Ferrere and Gregg indicate that (a) hot injection – electron transfer from a non-thermalized excited state of the chromophore – is likely responsible for the production of photocurrent, and (b) intramolecular deactivation of the initially formed MLCT state may be competing with interfacial electron transfer to reduce the injection yield. The goal of our work is therefore two-fold: (1) to determine the origin of the low photocurrent obtained in Fe^{II}-based solar cells by elucidating the nature of the excited-state dynamics of these systems following MLCT excitation, and (2) to use that information toward the design new chromophores based on first-row transition metals that we believe will open up new avenues of study for improving the performance characteristics of this class of photoelectrochemical cells.

Our initial efforts focused on the development of a prototype Fe^{II} chromophore in order to gain some basic insights into the ultrafast excited-state dynamics endemic to this ion.[4a] Time-resolved spectroscopic studies of the $[Fe(tren(6\text{-}R\text{-}py)_3)]^{2+}$ system (where R = H or CH_3) indicated an exceedingly rapid deactivation of the initially formed ^{1}MLCT excited state (τ_{obs} = 80 ± 20 fs), followed by slower but still remarkably fast formation of the lowest-energy excited state of the molecule ($\tau_{obs} \approx 300$ fs); this lowest energy excited state corresponds to the $^5T_2$ high-spin ligand-field state as evidenced by a number of spectroscopic studies, most recently through picosecond time-resolved XAS measurements we have carried out in collaboration with a group at the Advanced Light Source at Lawrence Berkeley National Laboratory.[4b] We have now extended work on Fe^{II} polypyridyl chromophores and have examined the solution-phase dynamics of a number of different compounds including $[Fe(bpy)_3]^{2+}$, $[Fe(tpy)_2]^{2+}$, and $Fe(bpy)_2(CN)_2$, the latter corresponding to a variant of the sensitizer used by Ferrere and Gregg. Femtosecond time-resolved absorption data on this compound (Figure 2) clearly reveal that the charge-transfer state formed following $^1A_1 \rightarrow {}^1$MLCT excitation in the visible decays extremely rapidly (τ_{obs} = 70 ± 30 fs), resulting in the formation of the $^5T_2$ excited ligand-field state. We believe this is at least partly responsible for the low photocurrent observed by Ferrere and Gregg. Current efforts involve studying the excited-state dynamics of the $Fe(bpy)_2(CN)_2$ sensitizer on TiO_2-based electrodes (along with related chromophores) in order to establish this hypothesis, as well as excitation wavelength-dependent studies directed toward understanding the origin of the pronounced wavelength dependence of the photocurrent reported by Ferrere and Gregg.

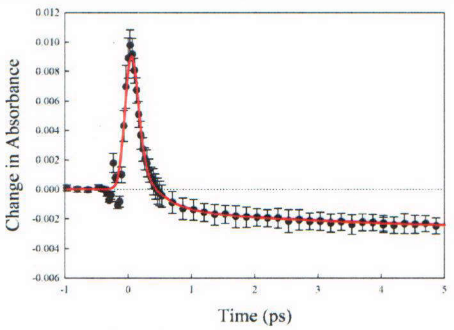

***Figure* 2** *Femtosecond time-resolved absorption data for $Fe(bpy)_2(CN)_2$ in CH_3CN solution at 680 nm following ~100 fs excitation at 405 nm. The rapid decay from positive to negative ΔA (τ = 70 ± 30 fs) is indicative of conversion from the charge-transfer to ligand-field manifold of the chromophore.*

The coupling to the ligand-field manifold that is giving rise to the rapid non-radiative decay of charge-transfer states represents an important issue that must be dealt with in order to facilitate the use of Fe^{II} (and by inference other first-row) chromophores in dye-sensitized photovoltaics. Our approach at present is focusing on the design of new ligands around nuclear coordinates that have been implicated in non-radiative ground-state recovery dynamics of related Fe^{II} chromophores.[5] In addition, recent work on Fe^{II} complexes with extended π systems[6] as well as Cr^{III} complexes[7] suggests that mixing of ligand-localized (e.g., $\pi\pi^*$) and ligand-field states can yield circumstances that may be favorable for electron injection from non-thermalized excited states of the chromophore.

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DOE-Supported Research (2004 – Present)

1. “Time-Resolved Relaxation Studies of Spin-Crossover Systems in Solution”, Clare Brady, John J. McGarvey, James K. McCusker, Hans Toftlund, and David N. Hendrickson, in *Spin Crossover in Transition Metal Compounds*, Topics in Current Chemistry vol. 235, P. Gütlich and H.A. Goodwin, eds., Springer-Verlag, 2004, pp. 1-22.

2. “Picosecond X-Ray Absorption Spectroscopy of a Photo-induced Iron(II) Spin-Crossover Reaction in Solution”, Munira Khalil, Matthew A. Marcus, Amanda L. Smeigh, James K. McCusker, Henry H.W. Chong, and Robert W. Schoenlein, *J. Phys. Chem. A* **2006**, *110*, 38-44.

3. “Ultrafast Dynamics of Ligand-Field Excited States”, Eric A. Juban, Amanda L. Smeigh, Jeremy E. Monat, and James K. McCusker, *Coord. Chem. Rev.*, in press.

4. “Solvent Effects on Ring Rotation Dynamics in the Charge Transfer-State Evolution of Arylated Ruthenium Bipyridyl Complexes”, Niels H. Damrauer, Aimee E. Curtright, and James K. McCusker, *J. Phys. Chem. A*, submitted for publication.

5. “Electrolyte Effects on the Thermodynamics and Kinetics of Electron Transfer in Dye-Sensitized TiO_2-based Solar Cells”, Jordan Katz, Amanda L. Smeigh, James K. McCusker, and Nathan S. Lewis, manuscript in preparation.

6. “Femtosecond Time-Resolved Absorption Study of a Sub-Picosecond $\Delta S = 2$ Non-Radiative Relaxation Process”, Amanda L. Smeigh and James K. McCusker, manuscript in preparation.

7. “Photophysics of d^6 Metal Polypyridyls: A Classic Paper Revisited”, Amanda L. Smeigh and James K. McCusker, in preparation for inclusion in the *J. Phys. Chem.* special issue honoring Norman Sutin.

Session VIII

Quantum Dots and Hybrid Assemblies for Solar Photoconversion

MOLECULARLY WIRED HYBRID ASSEMBLIES FOR PHOTOELECTROCHEMICAL CONVERSION OF LIGHT ENERGY

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Nanocluster-molecular assemblies provide innovative strategies for designing next generation solar cells. Of particular interest are photoresponsive organic-inorganic hybrids which when assembled as two- or three-dimensional architectures provide new ways to modulate optical and photochemical properties. The present work focuses on designing ordered assemblies of semiconductor and metal nanoparticles and carbon nanostructures and elucidating their behavior in light energy conversion devices.

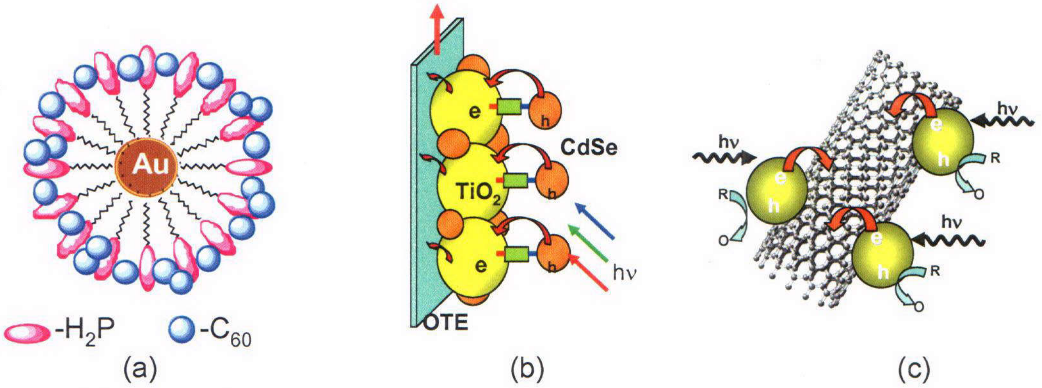

Figure 1. Modulating photoinduced charge separation and charge transport in a nanostructured hybrid assembly. (a) Porphyrin-C_{60} functionalized gold particles, (b) CdS nanoparticles anchored on carbon nanotubes and (c) CdSe nanoparticles linked mesoscopic TiO_2 films via a bifunctional linker.

Photoactive hybrid systems with different architectures assembled on electrode surfaces are shown in Figure 1. When excited with visible light these hybrid assemblies undergo charge separation and direct the electron flow towards the collecting electrode surface. The ability to convert light energy into electricity or chemical energy opens up new ways to develop efficient photovoltaic devices. The highly colored composite clusters of porphyrin gold nanoparticles and fullerenes have been assembled as three-dimensional arrays onto nanostructured SnO_2 films using an electrophoretic deposition method. Porphyrin and fullerene are known to form charge transfer complexes that facilitate rapid photoinduced electron transfer and slow charge recombination, leading to the generation of a long-lived charge-separated state with a high quantum yield. The composite cluster electrode exhibits an incident photon-to-photocurrent efficiency (IPCE) as high as 54% and broad photocurrent action spectra (up to 1000 nm).

The salient features of semiconductor quantum dots (QD) have been explored by assembling TiO_2 and CdSe nanoparticles using bifunctional surface modifiers of the type HS-R-COOH. Photochemical processes that follow the excitation of CdSe quantum dots were elucidated by photoelectrochemical and transient absorption measurements (Figure 2). Femtosecond transient absorption and emission quenching experiments confirm the injection

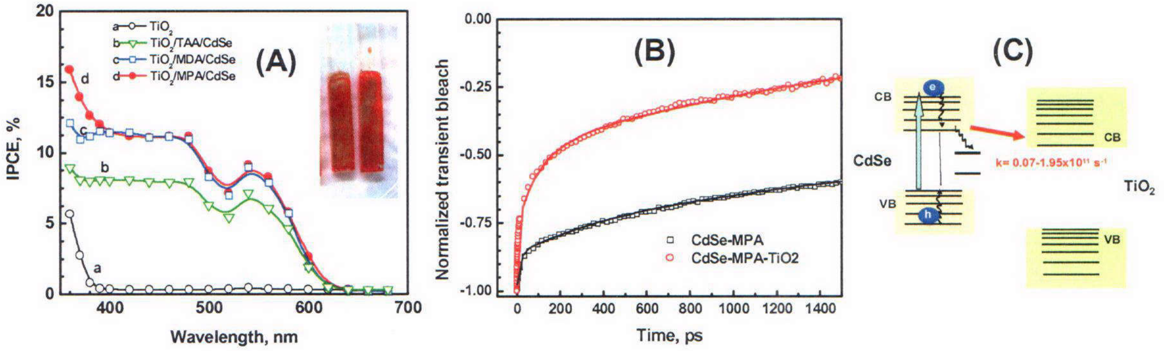

Figure 2. **(A)** Photocurrent action spectra of TiO$_2$ (a), and OTE/TiO$_2$/Linker/CdSe films (b-d) Electrolyte 0.1 M Na$_2$S and Pt counter electrode. (B) Recovery of bleaching at 530 nm recorded following 387 nm laser pulse excitation of CdSe, in the absence and presence of TiO$_2$ (C) Schematic diagram illustrating the charge injection process.

from the excited state of CdSe QDs into TiO$_2$ nanoparticles. Electron transfer from the thermally relaxed s-state occurs over a wide range of rate constant values between 0.073-1.95×10^{11} s^{-1}. The TiO$_2$-CdSe composite, when employed as a photoanode in a photoelectrochemical cell, exhibits a photon-to-charge carrier generation efficiency of 12%. The generation of photocurrents upon visible light excitation of such composites demonstrates our ability to transport photogenerated electrons to the collecting electrode.

Another interesting approach that we are currently exploring is the use of carbon nanotubes as a support for anchoring light harvesting assemblies. For example, the deposition of CdS nanoparticles on single-walled carbon nanotubes produces a photoactive composite that undergoes charge transfer interactions following excitation with visible light. The adsorption of Cd^{2+} ions on the SWCNT surface followed by its reaction with S^{2-} provides a simple and convenient method to prepare SWCNT-CdS composites. Unlike the starting material, viz., SWCNT, the composite is readily suspendable in polar solvents. The luminescence of CdS is quenched by SWCNT. Transient absorption experiments confirm the quick deactivation of excited CdS on the SWCNT surface as the transient bleaching recovers in about 200 ps. Excitation of CdS deposited on SWCNT films produces photocurrent with a maximum incident photon to current generation efficiency of 0.5% and thus provides evidence for the electron transfer pathway in the composite.

Ordering the semiconductor and metal nanostructures on an electrode surface is an important aspect since it can provide the basis for charge rectification and improved charge transport in a mesoscopic film. Efforts will be made to design organized assemblies of donor-acceptor molecules and probe the charge separation processes using transient spectroscopy and spectroelectrochemical experiments. By directly anchoring light harvesting assemblies on single wall carbon nanotube supports it should be possible to promote charge transport across the nanostructured film and improve the charge collection efficiency at the collecting electrode surface. In addition, our quest to harvest infrared photons will be pursued using cyanine dyes and PbS and PbSe semiconductor quantum dots. Extending the photoresponse of light harvesting assemblies into the infrared will be one of the challenges to tackle in the future.

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COUPLING OF TiO_2 NANOCRYSTALLITES TO PROTEINS

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Multidirectional assembly of nanostructures for solar-energy conversion requires functionalization of the semiconductor surface in such a way that enables efficient separation of photogenerated charges. Proteins may be a class of biomolecules capable of fulfilling this requirement. Due to structure and dynamics of the local and global environments, proteins can enhance charge separation, as in natural photosynthesis. Additionally, because of the specific, selective and complementary ("lock and key") recognition of proteins, efficient nanoparticle assembly/scaffolding can be achieved. Our approach in achieving enlarged separation distances is to employ reconstructed surfaces of TiO_2 nanocrystallites (particles, rods, tubes and cubes) for obtaining a strong coupling with electron-donating and electron-accepting biomolecules in order to achieve stabilization of charges analogous to the supramolecular triads.

We have developed a rational design of protein-TiO_2 hybrid architectures that enable coupling of photoinduced charge separation in nanocrystallites with the charge-transfer induced chemistry on proteins using avidin-biotin "lock and key" recognition. Avidin-biotin complex was chosen as a model system for protein-TiO_2 hybrid architecture because of the high association constant (10^{15} M^{-1}) of noncovalent binding between protein (avidin, ~ 60 kDa) and molecule (biotin). In the construction of TiO_2 nanocrystallites functionalized with biotin we used dopamine as a conduit of photogenerated holes. The conjugation was performed by condensation reaction of amino groups on dopamine and N-hydroxy-succinimide on biotin derivatives. Dopamine end-labeled biotin binds to the surface of TiO_2 nanocrystallites through the bidentate complex of dopamine OH groups with undercoordinated Ti atoms. Selective conjugation of biotin to axially anisotropic nanocrystallites was obtained by linking biotin to corner sites of ~ 300 nm elongated rods. The high curvature of the surface at the tips of the nanorods gives rise to undercoordinated Ti atoms, promoting the binding of dopamine end-labeled biotin exclusively to these sites. As a consequence, the resulting binding of avidin with biotin produces almost exclusively tip-to-tip assembly of TiO_2 nanorods resulting in wire-like or tripod supramolecular architecture, Figure 1.

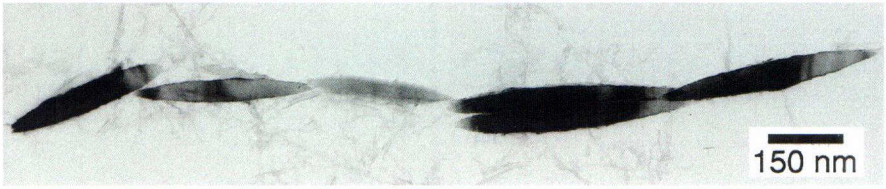

Figure 1. Transmission electron micrograph of the tip-to-tip assembled TiO_2 nanorods using biotin-avidin as the connector.

Upon excitation of this hybrid system, the photogenerated electrons localize on TiO_2 nanocrystallites while holes localize on tyrosine (Tyr) 33 of avidin, as was detected by low temperature Electron Paramagnetic Resonance (EPR), Figure 2. The yield of oxidation of Tyr 33 decreases with the extension of the valeric acid side chain in biotin derivatives from 13.5 Å (biotin) to 22.4 Å (LC-biotin). Thus in this optimally designed hybrid system, dopamine modified TiO_2 acts as light-harvesting material, while avidin acts as an electron-donating species producing site-specific chemistries in protein. The question as to what are the consequences of photoinduced redox chemistry in these hybrid systems was addressed examining photoelectrochemistry of the avidin-biotin complex conjugated onto thin film nanocrystalline TiO_2 electrodes. Specifically, two potential outcomes resulting from accumulation of the holes in avidin were addressed: the capability to manipulate its binding properties, or the possibility of discharging its capacitance. Combining different electrochemical methods (chronopotentiometry, cyclic voltammetry and photocurrent action spectroscopy) with the direct determination via chemiluminescence of bound avidin on biotinylated TiO_2 electrodes, we have shown that site-specific oxidation of avidin in TiO_2-dopamine-biotin-avidin hybrids alters the proteins' binding properties causing dissociation of the avidin-biotin complex.

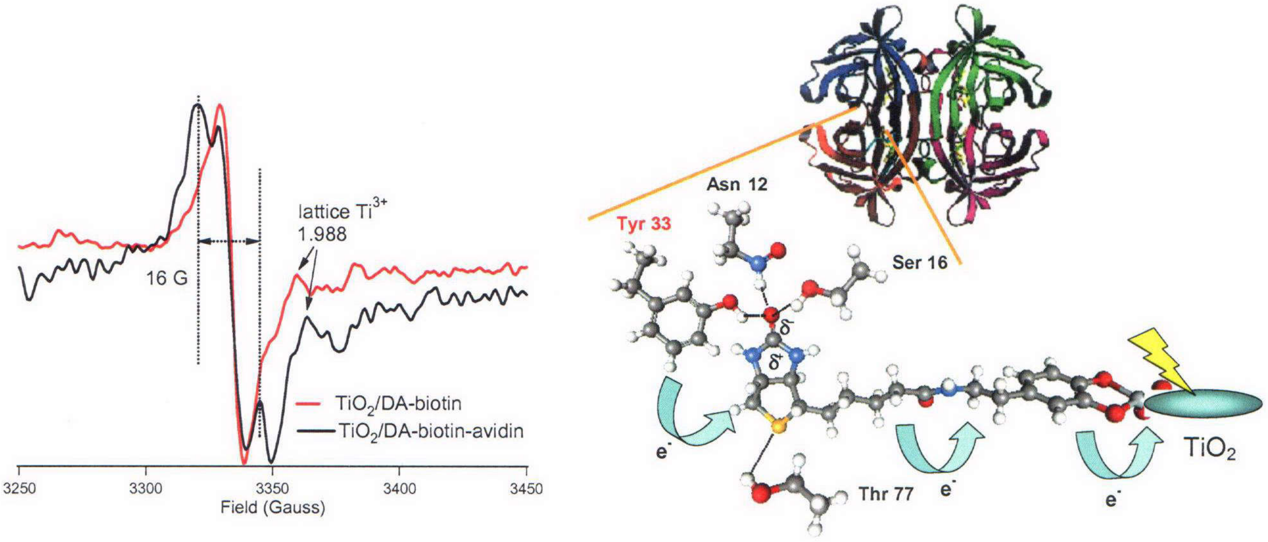

Figure 2. X-band EPR spectra of TiO_2/DA-biotin-avidin hybrids under illumination showing tyrosine radical, and salient presentation of amino acids involved in binding of avidin to biotinylated TiO_2.

Coupling electron-accepting biomolecules onto the surface of TiO_2 in order to use them as conductive leads for electrons is a further step towards assembly of nanoscopic triads. An alcohol dehydrogenase protein cofactor, pyrroloquinoline quinone (PQQ), provides several binding sites for metal cations such as surface Ti(IV). Additionally, the redox potential for PQQ reduction (0.09 V vs. NHE) is such as to allow transfer of TiO_2 conduction band electrons. The binding of PQQ on the surface of 4.5 nm nanocrystalline TiO_2 particles was found to constitute a tridentate site: the $Ti(IV)_{surf}$ is coordinated to the 7-carboxilate oxygen, 6-pyridine nitrogen, and 5-quinonic oxygen atoms, with $K = 500\ M^{-1}$ per $Ti(IV)_{surf}$. The photoexcitation of PQQ-TiO_2 results in the formation of a PQQ^- semiquinone radical, as determined by X- and W-band EPR measurements at helium temperature. At temperatures less than 40 K, only PQQ attached to the surface undercoordinated Ti sites can participate in one-electron charge transfer reaction. Attaching dopamine as the electron donor and PQQ as the electron acceptor ligand onto TiO_2 particles promotes efficiency of charge separation by enlarging charge separation distance, the result being a twofold increase of the PQQ^- semiquinone radical concentration. The effect of temperature on the kinetics of semiquinone formation was studied in order to determine the energetics of lattice trapped electrons in nanocrystalline TiO_2.

Future directions include employing photoinduced redox chemistry obtained by the PQQ-TiO_2 hybrid system for the reduction of CO_2 with consecutive transformation of formate to methanol in the presence of protein methanol dehydrogenase.

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ELECTROSYNTHESIZED OXIDE SEMICONDUCTORS FOR PHOTOELECTROCHEMICAL APPLICATIONS

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Semiconductors are generally prepared by high temperature methods or by the use of vapor phase and ultra-high vacuum environments. Milder temperatures coupled with the use of condensed media, using water or other solvents (organic compounds or ionic liquids), represent interesting and economic alternatives for the growth of semiconductors in either bulk or thin film form. Electrodeposition is one such preparative methodology in this category, which already has seen widespread acceptance in the metallurgical and microelectronics sectors. On the other hand, electrodeposition of semiconductors has a relatively recent history dating back only to the 1970s. This method is attractive from both fundamental and practical perspectives in terms of applicability to large and irregular device areas and the ability to prepare composite (e.g., metal/semiconductor) structures and unique semiconductor morphologies (e.g., nanotubes, nanodots). In this regard, it is worth noting that respectable photovoltaic conversion efficiencies have been already demonstrated for solar cells based on electrodeposited semiconductor absorber layers, both in our laboratory[1] and by other research groups.[2] This talk will focus on the electrosynthesis and use of oxide semiconductor thin films for photoelectrochemical applications using recent data drawn from our laboratory as illustrative examples.

Compound semiconductors for photoelectrochemical solar energy conversion applications generally involve Group III-V compounds or Group II-VI chalcogenides. On the other hand, oxide semiconductors offer the potential of avoiding precious elements (such as Ga or In) and environmental issues related to disposal or recycling (after the lifetime of the solar device) that beset semiconductors based on As, Se or Te. Nonetheless, the electrodeposition of oxide semiconductor films has an even shorter history and is only now gaining momentum as a serious process candidate. Anodic and cathodic electrosynthesis of metal oxide films will be briefly reviewed in terms of the underlying chemistry/electrochemistry and the mechanistic aspects.

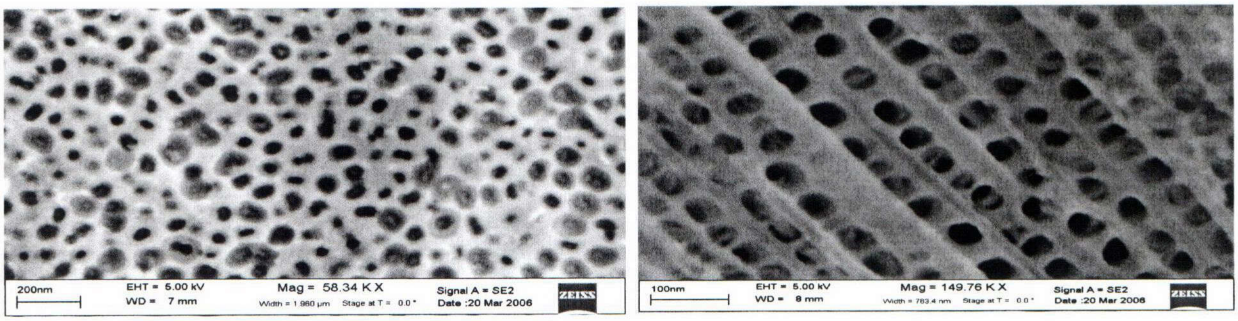
Oxide semiconductors based on Group II metal cations (Zn^{2+} and Cd^{2+}) and their alloys have a wide range of applications in photovoltaic solar energy conversion. For example, CdO is an n-type semiconductor with nearly metallic conductivity. The combination of high transparency in the visible range of the electromagnetic spectrum, high electrical conductivity, and high carrier concentration (even in undoped samples because of inherent non-stoichiometry) has prompted its use in CdO/CdTe and CdO/Cu_2O heterostructure solar cells and in photoelectrochemical devices.[3] The cathodic electrosynthesis of CdO thin films from aqueous media will be described. The mechanistic aspects of CdO film formation were characterized by a variety of techniques. The photoelectrochemical behavior of these films will be presented.

Since the first report in 1996,[4] a raft of studies have begun to appear on Zn-Cd-O films, nanowires and nanorods. These materials have been prepared by a variety of techniques (e.g., sol-gel process, spray pyrolysis, pulsed laser deposition, molecular beam epitaxy); however, conspicuously absent from this array of thin film deposition techniques is electrodeposition. Oxygenated KCl electrolytes containing $ZnCl_2$ and $CdCl_2$ in varying molar ratios were used to cathodically prepare thin films of ZnO, either admixed with CdO or doped with Cd. Remarkably, whether mixed or doped films were obtained, depended crucially on the electrosynthesis potential. Evidence for doping of ZnO with Cd was obtained from X-ray diffraction (XRD), optical transmission, chronopotentiometry, and X-ray photoelectron spectroscopy data. The Cd-doped ZnO samples showed superior photoelectrochemical response relative to undoped ZnO in the ~300-450 nm wavelength range.

Copper (I) oxide has a bandgap energy of 2.0-2.2 eV and a high absorption coefficient over the wavelength span of the solar spectrum. Its component elements are non-toxic and highly abundant. Thin films of Cu_2O were cathodically electrodeposited on Sn-doped indium oxide substrates. The influence of electrodeposition bath pH on grain orientation and crystalline shape was carefully examined using XRD and scanning electron microscopy. In addition to the (100) and (111) preferred orientations identified in two previous sets of studies, as the bath pH was varied in the present study from ~7.5 to ~12, a third preferred orientation, (110), was identified in a narrow pH range, ~9.4-~9.9. An unusual shift in the flat-bad potential (spanning ~500 mV) was measured in a non-aqueous electrolyte medium for the various Cu_2O samples obtained from baths of varying pH. A photoelectrochemical cell for H_2 evolution was constructed and studied using the electrosynthesized p-Cu_2O film samples. Data from a variety of electrolytes containing hole acceptors in the anode compartment will be presented along with the photocurrent densities measured for H_2 evolution with visible light.

Composite WO_3-TiO_2 films have been the subject of many recent studies especially because WO_3 and TiO_2 have complementary electronic, optical, photoelectrochemical, and electrochromic properties. Pulsed electrodeposition will be shown to be a useful technique for preparing composite WO_3-TiO_2 films over a wide compositional range. Specifically, a variant of this cathodic electrodeposition strategy that relies on the sequential deposition of WO_3 and TiO_2 from two separate baths will be shown to afford composite films with superior photoresponse relative to counterparts obtained from a single bath.

Finally, our earlier template semiconductor growth studies[5,6] have been very recently extended to the anodic growth of nanoarchitectures of WO_3 and TiO_2 (as shown by examples in the figure below) starting from tungsten and titanium. The next step in these studies will be to use highly-ordered WO_3 and composite WO_3-TiO_2 nanotube arrays to photocleave water under solar irradiation.



SEM images of nanotube arrays of WO_3 and TiO_2 obtained by anodization of a W foil at 34.5 V for 1 h in 0.3 M oxalic acid/water and a Ti foil at 20 V for 10.5 h in 0.15 M NH_4F/glycerol.

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ULTRA-EFFICIENT AND ULTRA-FAST MULTIPLE EXCITON GENERATION FROM SINGLE PHOTONS ABSORBED IN SEMICONDUCTOR QUANTUM DOTS AND ITS IMPACT ON HIGH EFFICIENCY SOLAR PHOTON CONVERSION

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We have demonstrated ultra-efficient Multiple Exciton Generation (MEG) in three different IV-VI semiconductor QDs: PbSe, PbS, and PbTe. The dependence of the MEG quantum yield (QY) on photon energy is very similar for all three types of QDs with the same size; the QY reaches 300% at photon energies about 4 times the HOMO-LUMO energy (i.e., band gap) of the QDs with band gaps (after quantization) of about 0.9 eV (see Fig. 1). Thus, three excitons are produced for each photon absorbed by a QD within these samples. The creation of multiple excitons from single photons in bulk semiconductors via impact ionization is very much less efficient at equivalent photon energies relative to the band gap.

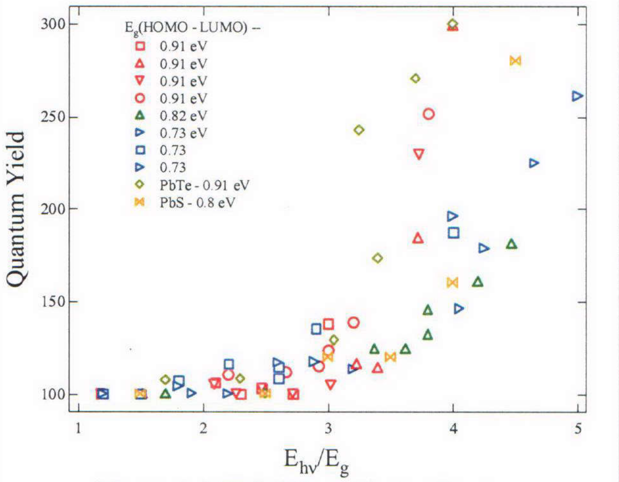

Figure 1. MEG QY vs Photon Energy

Highly efficient MEG with single photons having wavelengths spanning the solar spectrum has dramatic implications for the theoretical conversion efficiency of solar photon conversion to both fuel and electricity. We present thermodynamic calculations of the enhanced ultimate conversion efficiency for various QD-based solar cells. The small band gap of bulk IV-VI semiconductors and the UV wavelengths required to obtain carrier multiplication via impact ionization in optimum band gap semiconductors like Si, render the effect of carrier multiplication in bulk semiconductors useless for enhancing the efficiency of solar photon conversion.

Our experiments show that MEG is extremely fast (< 200 fs) in our samples and is the dominant channel for the relaxation of the highly energetic excitons created initially by the absorption of high energy photons. The reverse process, non-radiative Auger recombination of multiexcitons, is considerably slower (25-50 ps) than MEG. This dramatic difference in rates between the forward and reverse processes with the same matrix elements plus the exceptionally high MEG QY indicates that the usual model of carrier multiplication via impact ionization is incapable of describing MEG.

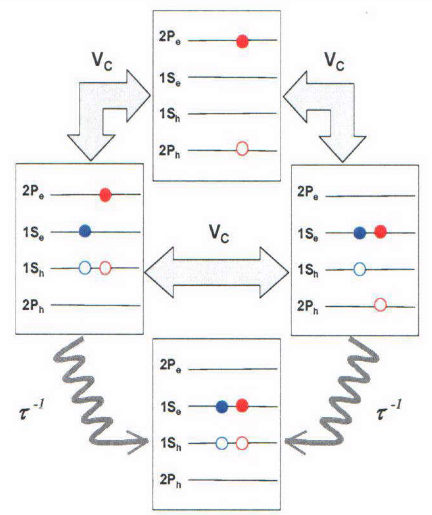

Figure 2. Schematic of coherent superposition model of MEG.

We have developed an alternative new description of MEG (collaboration with Al. L. Efros and A. Shabaev) in which the initially highly-excited single exciton state couples directly with multiple-exciton states via Coulomb interactions (see Fig. 2). This produces a coherent superposition of single- and multi-exciton states immediately upon photoexcitation. The wavefunction at early times will evolve between primarily single- and multi-exciton character, with the superposition being destroyed by irreversible dephasing processes. If multi-exciton states dephase much more rapidly than single-exciton states, the QY can be as high as allowed by simple conservation of energy, since rapid dephasing would "collapse" the wavefunction while it resides in the multi-exciton state. This explanation of MEG depends upon the details of the symmetry of the quantum states of the QDs and the selection rules for the initial photoexcitation. The model includes preferential dephasing rates through strong electron-phonon interactions for asymmetric charge distributions of the correlated electron-hole pairs of multiexcitons compared to weak electron-phonon interactions for symmetric charge distribution of single excitons created by symmetric initial transitions (e.g., nS_h-nS_e, nP_h-nP_e, nD_e-nD_h, …..)

Another consequence of the coherent superposition model is that the wavefunction will oscillate (quantum beating) between single- and multi-exciton character. It is expected that this oscillation should appear in the early time transient absorption data. However, initial experiments were not able to definitively show clear quantum beating. If the Coulomb coupling is strong (about 33 meV), the oscillation period is 125 fs and it was shown that our instrument response of 200 fs would damp out well-defined quantum beats and produce a simple half-oscillation in the transient absorption rise time, as was observed experimentally.

Studies have been initiated to dissociate the multiexcitons, and then separate and extract the multiple electrons and holes generated in QDs as photocurrent in an external circuit. This is a critical next step for developing higher efficiency solar photon conversion cells. Three different cell configurations are being investigated for this purpose. One configuration involves synthesis of QDs dispersed in a blend of hole and electron-conducting phases, such as polymers. A second configuration uses QDs as chromophores sensitizing wide band gap nanocrystalline oxides such as TiO_2 and SnO_2. A third configuration is to form arrays of QDs as the intrinsic region of a p-i-n structure. Recent results and future directions for these experiments will be discussed.

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Poster Abstracts

Poster #1

PHOTOINDUCED CHARGE CARRIER GENERATION IN BULK HETEROJUNCTIONS OF P3HT AND PCBM STUDIED BY TIME-RESOLVED TERAHERTZ SPECTROSCOPY

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Time-resolved THz spectroscopy (TRTS), a non-contact probe of the photoconductivity with sub-ps to ns temporal resolution has been effectively used to measure photoconductivity in non-conventional photoconversion materials such as colloidal nanoparticles, organic semiconductors, colloidal TiO_2. Recently, the use of TRTS has been extended to investigate charge separation dynamics in conjugated polymer systems due to its unique sensitivity to the free-carrier production and capability distinguishing free-carrier from excitons. In this work, TRTS was employed to investigate photoinduced charge carrier generation in bulk heterojunctions of regioregular poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C61-butyric acid methyl ester) (PCBM), which are the active components of a relatively efficient (4.4%) excitonic, photovoltaic solar cell. The precise composition of the blended films plays an important role in determining the cell performance, for example, a P3HT:PCBM ratio of 1:1 by weight tends to perform better than other ratios. However, the reason for this ratio is not clear, as it differs from other polymer systems, such as the soluble phenylene vinylene polymer MDMO-PPV with PCBM. A systematic study of the interfacial interaction between P3HT and PCBM including microscopic charge generation, separation, migration and collection as a function of composition is important and will help to further understand the fundamental photoconversion process, which ultimately lead to an improvement in device performance. Here, we present the photoinduced charge carrier generation dynamics of P3HT:PCBM blended films with PCBM weight fractions of 0, 0.2, 0.5 and 0.8 studied by TRTS. The samples were excited by 500 nm light and the differential transmitted far-infrared electric field is measured as a function of temporal delay between pump and THz probe. By comparing the differential transmitted field to the transmitted field strength without a pump, the time-resolved frequency-dependent photoconductivity was extracted and used to reveal the origination of signal in blended films on sub-picosecond timescale.

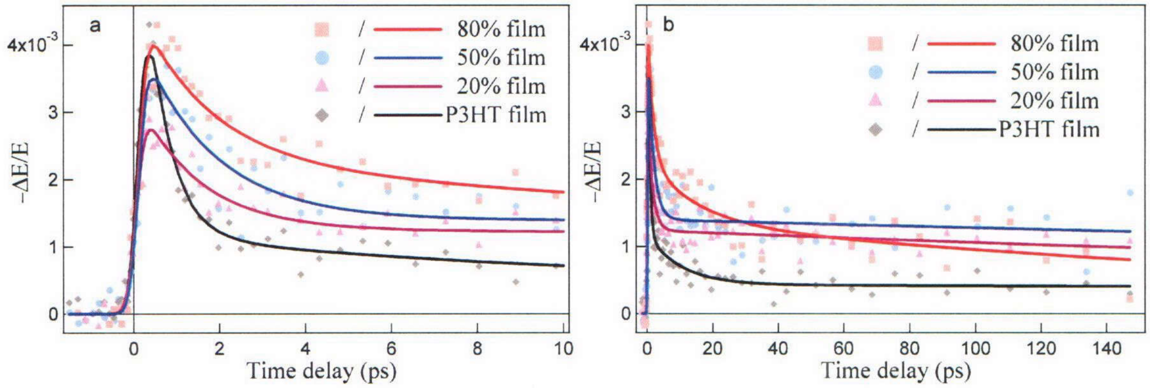

Figure 1. Time-resolved THz spectroscopy pump scans for P3HT, 20%, 50% and 80% PCBM films at (a) short and (b) long delay times.

DYNAMICS OF CARBON MONOXIDE IN MESOPOROUS SILICA MONITORED BY TIME-RESOLVED FOURIER TRANSFORM-INFRARED SPECTROSCOPY

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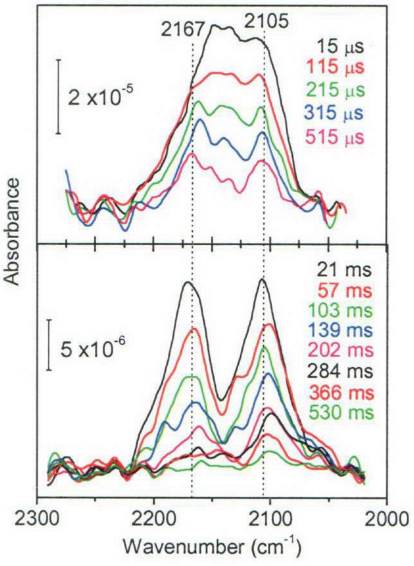
We have recently employed mesoporous silica as high surface area supports for single or binuclear metal sites for the photoreduction of CO_2 to CO. For the material $ZrCu^I$-MCM-41 featuring Zr^{IV}-O-Cu^I sites covalently anchored on the pore surface, excitation of the MMCT transition resulted in the splitting of CO_2 to CO when the gas was loaded into the pores (*J. Am. Chem. Soc.* **2005**, *127*, 1610). Understanding of the behavior of the CO molecules in the mesopores, and of the temporal aspects of the escape into the surrounding gas phase is crucial for maximizing the yield of the product. For example, knowledge of the sites encountered by CO as it diffuses through the pore system and analysis of the kinetics of escape will facilitate the selection of nanoporous structures that minimize the possibility of back reaction. Yet, no such measurements for small molecules like CO on mesoporous supports have been reported to date due to the insufficient time-resolution of available techniques such as PFG-NMR. We have employed step-scan FT-IR spectroscopy (25 nanoseconds to 10 milli-seconds) as well as the slower rapid-scan technique (10 milliseconds to seconds) to explore the dynamics of CO in silica mesopores.

Carbon monoxide was generated inside the 30A channels of the silica material MCM-41 by excitation of a loaded precursor (diphenylcyclopropenone) with a nanosecond laser flash. CO exhibits a surprisingly broad, inhomogeneous absorption band from 2200 to 2080 cm^{-1} on the nanosecond and early microsecond time scale, which decays within 500 microseconds as CO escapes from the pores into the gas phase. The large bandwidth originates from CO molecules transiently interacting with siloxane oxygen (physisorption) and, weakly, with silanol groups of the pore surface. In agreement with the expectation that the physisorbed molecules escape from the pores most readily, the center part of the profile around 2125 cm^{-1} erodes most rapidly. Two residual peaks at 2167 and 2105 cm^{-1} subsequently decay on a much longer time scale of 130 millisecond and are attributed to CO molecules more strongly held by silanol groups, either C or O end on. Comparison with a parallel study of MCM-41 with methyl-derivatized silica pores gave further insight into the nature of the infrared band profile.



This is the first study to provide spectroscopic data on the sites occupied by CO, and on the diffusion kinetics in a mesoporous material at room temperature. The detailed insight into the behavior of CO in the mesopores obtained here is crucial for the understanding of time-resolved FT-IR results of CO_2 photoreduction in transition metal silicates.

Poster #3

"ELECTROCHEMICALLY WIRED" SEMICONDUCTOR NANOPARTICLES: TOWARD VECTORIAL ELECTRON TRANSPORT IN HYBRID MATERIALS AND SOLAR-ASSISTED HYDROGEN PRODUCTION

Neal R. Armstrong, Zhiping Zheng, Dominic McGrath, Jeffrey Pyun

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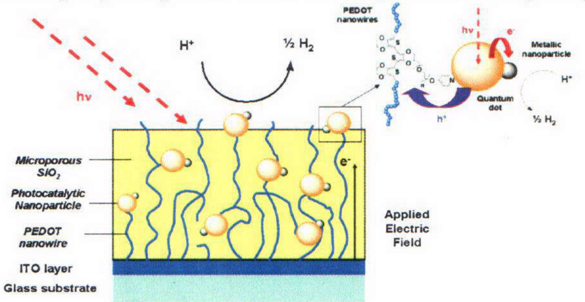

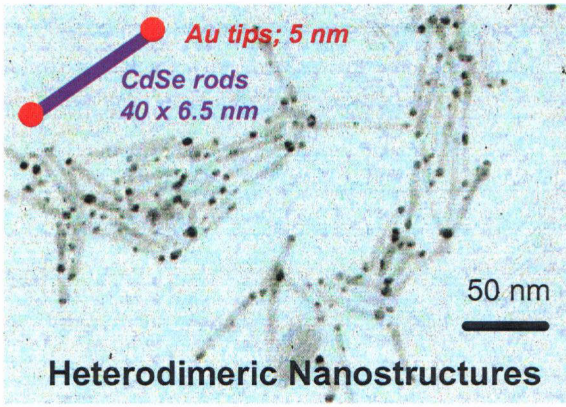

This new DOE-BES program is focused on the creation of new "electrochemically wired" semiconductor nanoparticles (SC-NPs) which are designed to function as photocatalysts for solar-assisted hydrogen production. Our global strategy is to prepare dendrimers, semiconductor nanoparticles and heterodimeric nanostructures that can be copolymerized with polythiophene nanowires grown through a porous sol-gel thin film. The initial work on this project has focused on the synthesis of CdSe colloids (particle size = 2-5 nm) and functionalization of semiconductor particle surfaces with electroactive thiophene monomers (e.g., EDOT and Pro-DOT). Upon either dispersion in a sol-gel film, or direct deposition on an ITO substrate, these SC-NPs can be electrochemically linked to growing polythiophene wires, or to the ITO surface creating pathways for electron injection into the photoexcited SC-NP, coincident with its photoelectrochemical reduction of solution acceptors (e.g. MV^{+2}, H^+). Our approach is inspired by our recent success in "wiring" dendrimers which have been rendered electrochemically active with both pendant ferrocene (Fc) and 3,4 ethylenedioxy-thiophene (EDOT) groups, in porous sol-gel matrices.[1] We have also synthesized heterodimeric nanoparticles that directly conjugates a single metal colloid (e.g., Au, FePt, Pt) to a SC-NP.[2] By the direct alloying of disparate metal and semiconductor nanoparticles, vectoral charge dissociation of photo-generated excitons within quantum dots, or rods is envisioned to be a potential driving force for solar assisted hydrogen generation.

This presentation will focus on the synthesis of these novel photocatalytic nanomaterials and the fabrication of brush-like thin films of PEDOT and related conducting polymers on activated indium-tin oxide surfaces.

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Poster #4

SINGLE MOLECULE SPECTROELECTROCHEMISTRY (SMS-EC)

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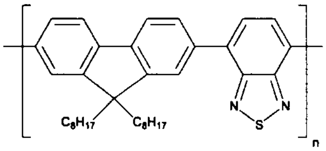
We describe an approach to the determination of the thermodynamics and kinetics of electron transfer (eT) to single immobilized molecules based on single molecule spectroelectrochemistry (**SMS-EC**). Such eT reactions are of interest in solar cells, flat-panel displays and chemical sensors.[1-4] The extreme heterogeneity of inorganic/organic interfaces has been a key obstacle to developing a quantitative, molecular-level understanding of such devices.[5-7] Here we introduce a powerful new technique for studying eT processes at highly heterogeneous interfaces, **SMS-EC** measures electrochemical behavior one molecule at a time, offering for the first time the distribution of key electrochemical variables, e.g. the half-wave potential, $E_{1/2}$, not just the ensemble average. **SMS-EC** is used herein to study the oxidation at an indium tin oxide (ITO) electrode of single molecules of the organic conjugated polymer poly(9,9-dioctylfluorene-*co*-benzothiadiazole) (F8BT), used in solar cells and OLEDs.

F8BT



ENHANCING SOLAR ENERGY CONVERSION EFFICIENCIES BY LIGHT MANIPULATION

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Dye-sensitized solar cells (DSSCs) are an inexpensive alternative to traditional solid-state photovoltaics with conversion efficiencies approaching 11%. This number becomes more competitive with silicon when considering that silicon-based solar cells rated at 17% under laboratory conditions actually operate in the field at 11-13% due to heating. Furthermore, flat plate systems are advantageous under high diffuse radiation conditions while concentrator systems allow for lower material consumption and lower overall costs. We propose a hybrid approach that combines DSSCs, Si, flat plate and concentrator solar cell systems: use DSSCs for the diffuse and visible radiation while directing near-IR photons to Si concentrator cells by mirrors built into the DSSC cells. By lowering the Si concentrator cell temperature as well as using diffuse radiation, the solar spectrum is utilized more efficiently. One embodiment of this tandem cell prototype will consist of a 3-D parabolic array of ~1 cm^2 DSSCs interconnected in series-parallel with a Si module placed at the parabola's focal point.

The major challenge in the construction of the tandem device has been the optimization and reproducibility of individual DSSC performance. We have found that depositing a dense ~100 nm TiO_2 layer (i.e. underlayer, UL) on top of the FTO by spray pyrolysis at ~370 °C results in a ~15% increase in cell performance. Treating nanoTiO_2/UL/FTO cells with $TiCl_4$ (aq) leads to a considerable 40% gain in cell current density thus transforming 5% cells to 7-8% cells. In addition, the cell efficiency is highly influenced by the procedure used to make the nanocrystalline TiO_2 particles and paste. Our best results have been obtained using the TiO_2 literature preparation first reported by Gregg et al. and commonly used by Frank et al. Consistent with the results of Frank et al, the interconnectivity of TiO_2 nanoparticles and the porosity of the mesopores are crucial factors in DSSC performance.

Realizing 10% DSSCs reliably from our current level will require the incorporation of a light scattering layer as previously reported by Grätzel et al. and Arakawa et al. These particle based scattering approaches enhance absorption at ~ 550-700 nm. We use an inverse opal photonic crystal (PC), structure, which is a more efficient scatterer. We have shown that TiO_2 inverse opals enhance 550-700 nm photon absorption in a transparent counter electrode DSSC configuration. The wavelength region at which enhanced backscattering occurs can be tuned by controlling the PC interlayer spacing or the filling fraction during TiO_2 infiltration. We have verified theoretical predictions by Miguez, et al., that the ideal structure for optimizing DSSC cell performance is PC/nanoTiO_2/UL/FTO. Our method of building ordered and disordered photonic crystals on top of disordered nanoTiO_2 layers will be presented along with photoelectrochemical results.

Poster #6

GROUND-STATE HOLE TRANSFER IN PORPHYRIN ARRAYS

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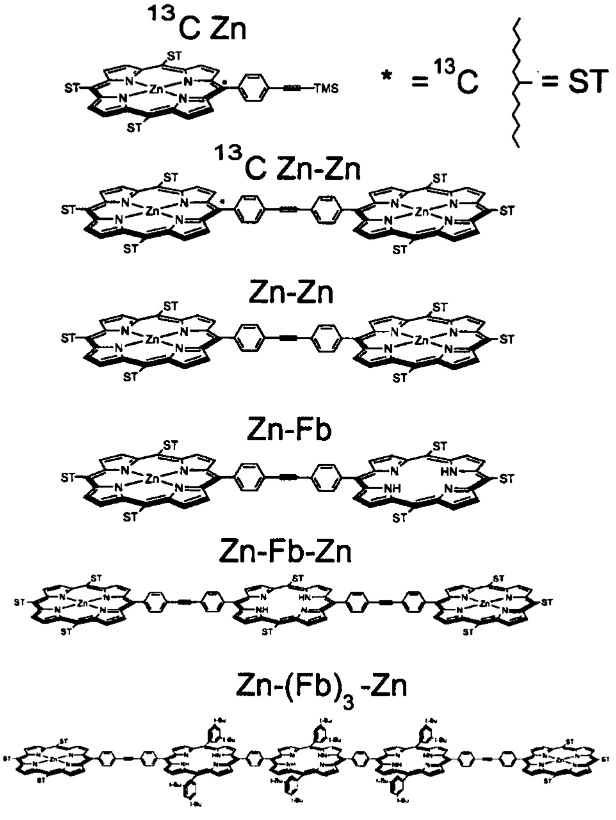
Efficient solar-energy conversion requires that holes generated after excited-state electron-injection can move efficiently away from the anode, thereby preventing charge-recombination. Thus, understanding hole mobility in prototypical light-harvesting and charge-separation systems is of fundamental interest. Towards this goal, the ground-state hole-transfer characteristics of the monocations of symmetrical porphyrinic arrays of different length have been investigated using EPR spectroscopy. In these arrays, the terminal porphyrins are identical Zn chelates and the intervening porphyrins are units whose structure is varied to tune the redox potentials to a desired value. The immediate objective of studies is to determine how the energies of the intervening porphyrins affect hole transfer. One class of porphyrin arrays that has been investigated includes a triad, tetrad, and pentad in which the intervening (one, two, or three) porphyrins is/are a free base. The structures of a triad and a pentad along with the structures of several benchmark dyads and monomers, including ^{13}C-labeled molecules, are shown in the chart. The redox potential of the central free base porphyrin(s) in the arrays is several hundred mV higher than that of the terminal Zn chelates; thus, hole transfer can only occur via a process wherein the free-base porphyrins serve as superexchange mediators. The EPR signatures for the monocations of the triad and two larger arrays indicate that hole transfer is slow on the EPR timescale ($<10^6$ s^{-1}).



PHOTOINITIATED ELECTRON COLLECTION IN MIXED-METAL SUPRAMOLECULAR COMPLEXES: DEVELOPMENT OF PHOTOCATALYSTS FOR HYDROGEN PRODUCTION

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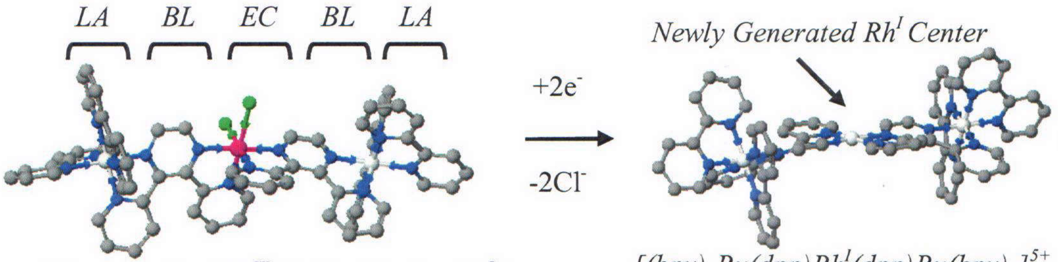
Supramolecular complexes used in this forum are large molecular assemblies built of smaller sub-units. Each sub-unit contributes properties to the supramolecular assembly, allowing the assembly to display complex functions. Supramolecular complexes are of interest in many forums including the harvesting of solar energy. The coupling of multiple charge transfer light absorbing units has been proposed as a means to use light to collect multiple reducing equivalents. This light activated collection of reducing equivalents is known as photoinitiated electron collection (PEC) and represents a means to use sun light to produce fuels from chemical feedstocks. Supramolecular assemblies coupling two ruthenium light absorbers (LA) through bridging ligands (BL) to a central Rh core have been constructed and shown to undergo photoinitiated electron collection at the Rh center, Figure 1.



$[(bpy)_2Ru(dpp)Rh^{III}Cl_2(dpp)Ru(bpy)_2]^{5+}$ *$[(bpy)_2Ru(dpp)Rh^{I}(dpp)Ru(bpy)_2]^{5+}$*

Figure 1. Rearrangement of $[\{(bpy)_2Ru(dpp)\}_2RhCl_2]^{5+}$ following reduction.

The ability of these assemblies to collect electrons at a metal center with the assembly remaining intact is unusual. The newly generated Rh^I site produced through PEC is available for binding to substrates for the catalysis of multi-electron reductions. The photoreduced forms of these supramolecular assemblies act to produce molecular hydrogen through a multi-electron process. The ability to most effectively use this new structural motif for solar hydrogen production will depend on the development of an understanding of the factors governing this multi-electron photochemistry. A study of the factors impacting electron collection and hydrogen production using this structural motif will be described.

Poster #8

ELECTROCHEMICAL SYNTHESIS OF PHOTOELECTRODES WITH CONTROLLED MICRO- AND NANO-STRUCTURES FOR USE IN SOLAR HYDROGEN PRODUCTION

Kyoung-Shin Choi

Department of Chemistry, Purdue University, West Lafayette, IN 47907

Among the various approaches for utilizing semiconducting materials for solar hydrogen production, direct water photoelectrolysis by photoelectrochemical cells (PECs) has the potential to achieve the lowest production cost. Because of the high manufacturing cost of single crystalline devices, commercially viable PECs will be built based on polycrystalline photoelectrodes, the efficiency of which is significantly affected by the interfacial structures (e.g. surface areas, individual crystal shapes and sizes, grain boundaries). Therefore, gaining synthetic abilities to accurately control polycrystalline interfacial structures and understanding their effects on photoelectrochemical properties are critical for the development of highly efficient, low-cost polycrystalline photoelectrode materials. In this presentation, we will introduce new electrochemical synthetic strategies to produce photoelectrodes with controlled nano- and micro-scale architectures (Figure 1), and discuss the morphological dependence of photoelectrochemical properties in detail. The results obtained by our study will form a solid foundation to construct multi-stack and multi-component photoelectrodes with optimum junction structures that can maximize the efficiency of solar energy conversion.

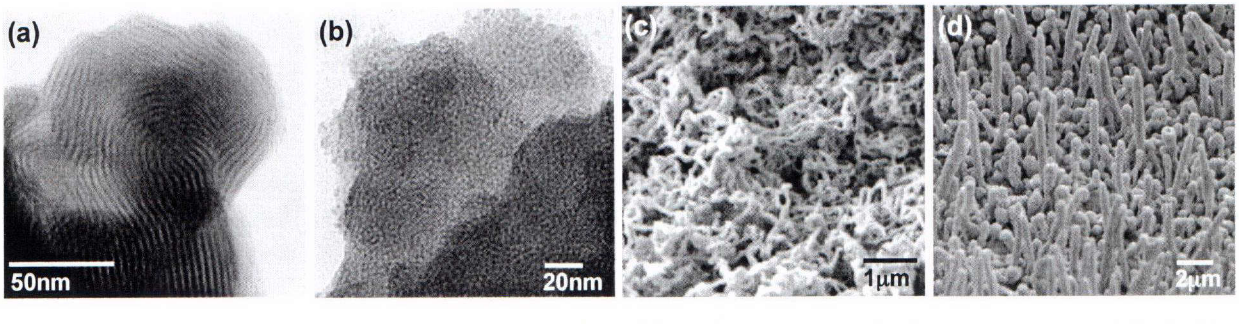


Figure 1. TEM and SEM images of photoelectrodes with various nano- and micro-structures; (a) ZnO, (b) SnO_2, (c) ZnO, and (d) SnO_2.

Poster #9

HIGH-RESOLUTION TIME-RESOLVED CRYSTALLOGRAPHY: THE GEOMETRY OF MOLECULAR EXCITED STATES IN CRYSTALS AND ITS INTERPRETATION BY THEORETICAL CALCULATIONS

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Knowledge of the geometry of molecular excited states at atomic resolution is crucial for a full understanding of photochemically induced processes. Time-resolved pump-probe X-ray diffraction methods are now capable of providing the geometry of excited states of molecular complexes in crystals,[1] and can lead to a unique assignment of the states responsible for observed spectroscopic features.

We will present several results on metal-metal bond shortening on excitation to microsecond lifetime triplet states in organometallic solids. Advanced chemical theory provides a qualitative interpretation, but often does not reproduce the quantitative aspects of the observed excited-state geometry.[2,3] The energy difference between the experimental results and the predicted theoretical geometry may be small even when the two geometries differ significantly (Figure 1), in such cases the molecular environment in the crystal may have a pronounced influence.[4] Supramolecular solids, in which reactive molecules are embedded in an inert host matrix are ideally suited for studying the effect of the molecular environment on the photophysical properties of complex molecules. The first examples of time-resolved diffraction in complex solids will be presented.

The monochromatic technique used in our experiments provides the necessary accuracy, but has disadvantages in terms of the length of the experiment and the accumulated laser-photon flux on the sample. The application of Laue techniques is to be explored in upcoming experiments. The development of a fast shutter and the possibility for single pulse selection in regular synchrotron operating modes will be discussed.[5]

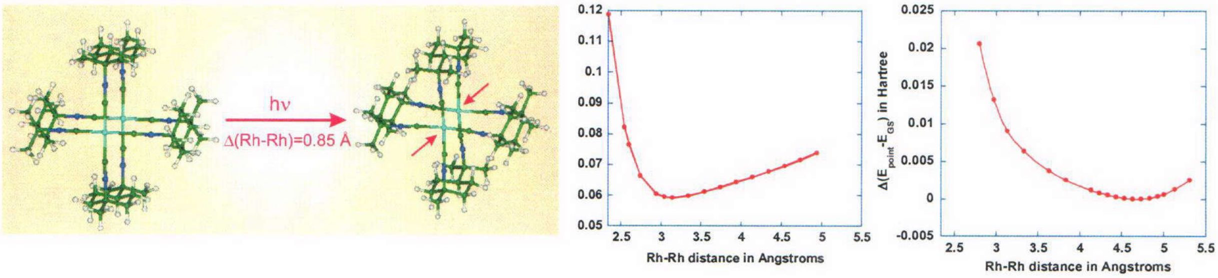

Figure 1. Left: Shortening of the Rh-Rh distance on excitation of $[Rh_2(1,8\text{-diisocyano-}p\text{-menthane})_4]^{2+}$. Middle and right: Rh-Rh potential in the first excited and ground states.

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Poster #10

SPECTROSCOPIC AND MICROSCOPIC CHARACTERATION OF QUANTUM DOT BIOASSEMBLY

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Energy Sciences Directorate, National Renewable Energy Laboratory, Golden, Colorado

Our goal is to understand exciton/charge transfer processes occurring in defined quantum dot (QD) arrays assembled using biomolecules. We have demonstrated that amino acids and bio-engineered proteins can be used to build QD conjugates of high order, as well as linear arrays of individual QDs on cellulose nanocrystals using carbohydrate-binding modules (CBMs) (Fig. 1). This strategy resulted in the production of arrays where the average inter-(CdSe)ZnS QD distance on the cellulose crystal was ~2 nm. These QD bioconjugates have been characterized using steady state and time-resolved photoluminescence (PL) spectroscopy. The average PL decay lifetime of protein-conjugated-QDs is slightly longer than that of amino-acid-capped QDs solution. We also observed that the PL lifetime increases at the red end of the emission peak. Also, the emission peak red shifts in QD arrays strongly suggest energy transfer from the smaller to the larger QDs (Fig. 2). Based on literature reports, we noted that the magnitude of the lifetime and PL peak change is often much larger for close packed QDs. This observation is attributed to very close inter-QD distances (~1.1 nm). To obtain more effective energy transfer from protein conjugated QDs, the inter-QD distances require further optimization. To this end, we propose to integrate advanced microscopic techniques (e.g. scanning probe and total internal reflection fluorescence microscopy) to isolate and promote precision control of donor/acceptor QD distance. Besides time-resolved PL spectroscopy, advanced spectroscopic approaches, including transient absorption (TA) and time-resolved THz photoconductivity (TRTP) will also be employed to study electron and energy transfer processes and surface modification effects.

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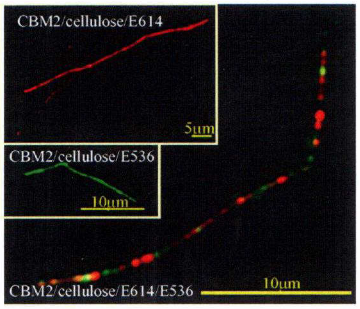

Fig. 1. Fluorescence micrographs showing two sizes (E614 red and E536 green) arrayed on cellulose nanocrystal.

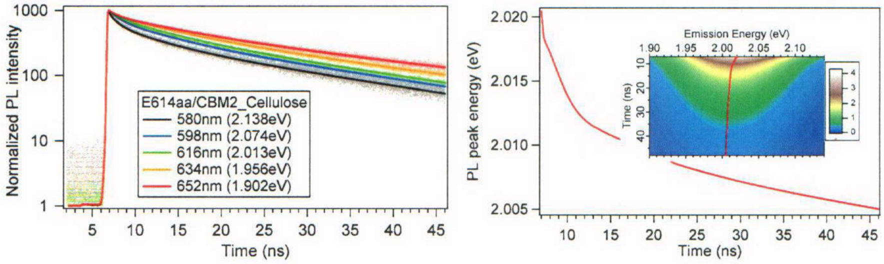

Fig. 2. E614 (CdSe)ZnS QDs (max emission at 614 nm) were arrayed on a cellulose crystal using CBM2. The average PL lifetime at the blue end of the E614 emission peak was about 17 ns. At the red end of the emission peak, the PL lifetime increased to 25 ns. The emission peak red shifts about 15 meV over 40 ns. Most of this shift takes place within the first 10 ns.

Poster #11

PHOTOACTIVE INORGANIC MEMBRANES FOR CHARGE TRANSPORT

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Molecular assemblies, which upon visible light absorption result in long-lived charge separated states, are critical in the first step for solar to chemical energy conversion. However, in order to exploit the charge separation, the molecular assemblies need to be integrated into a specific membrane architecture, and methodology for doing so just does not exist. We propose that microporous zeolitic inorganic membranes with the following properties: 1) internal porosities consistent with the size of photochemical assemblies, 2) stability with respect to appropriate temperatures, pH and solvents, 3) ease of chemical manipulation and 4) capable of maintaining charge balance, meets the requirements for making practical advances towards the goal of solar energy conversion. In this project that is just beginning, our goals are to connect molecular assemblies to zeolites, transport charge into the zeolite with the help of suitable acceptors and then propagate the charge through the membrane.

The immediate plans are fourfold:

(a) Choice of a suitable photosensitizer: We have decided to focus on a Ru polypyridyl complex [$(bpy)_2$Ru(II)L , bpy = bipyridine, L = 1, 2-bis [4-(4′ – 2,2′ – bipyridyl) ethene], with the goal that the L part of the ligand can be incorporated into the zeolite. Current focus is on understanding the photophysics and photochemistry of this molecule with time resolutions extending from femtosecond to millisecond time scales

(b) Synthesis of CdSe in zeolite Y: Using zeolite Y as a host, we are examining ways to synthesize CdSe quantum dots within the zeolite.

(c) Dynamics of Electron transfer: We will be examining the electron transfer from $(bpy)_2$ Ru(II)L tethered to the zeolite surface to CdSe in the zeolite. Transient spectroscopic studies will define the efficiency of the charge injection process and the ability to move charge from the molecule into the zeolite.

(d) Synthesis of zeolite Y membrane: Studies will focus on synthesis and characterization of meso-defect free membranes and will be verified by state-of-the-art porosimetry. The zeolite membrane provides the opportunity to build cascades of molecules with graded reduction potential to investigate if vectorial electron transfer within the membrane promotes the charge transport process.

Based on fundamental studies of the charge transport process, this research program will establish guidelines for coupling photochemical molecular assemblies to inorganic membranes for spatial charge separation.

Poster #12

MULTIPLE EXCITON GENERATION IN SEMICONDUCTOR QUANTUM DOTS

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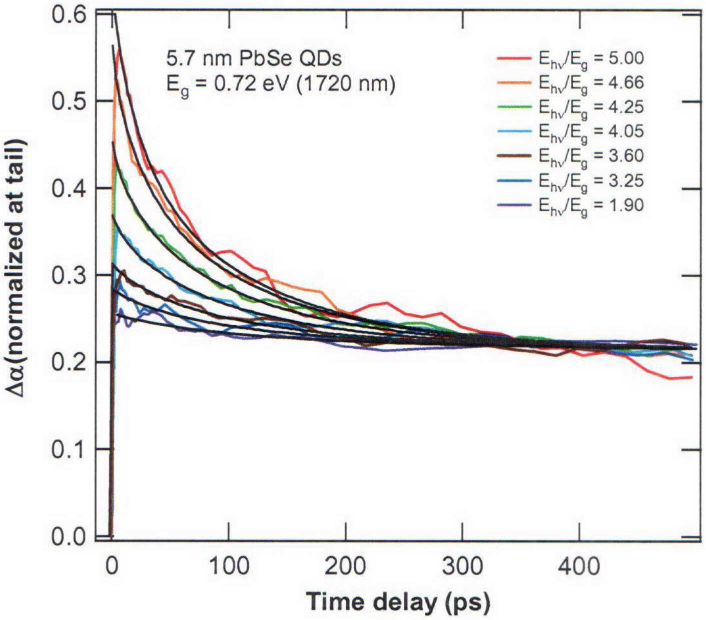
National Renewable Energy Laboratory, Golden, Colorado

The process of multiple exciton generation (MEG), recently discovered in colloidal semiconductor quantum dots (QD), has the potential to improve solar cell power conversion performance by nearly 50% beyond what is thermodynamically possible for conventional devices based on one exciton per absorbed photon. Exceptionally high yields (300% or 3 excitons per photon) in several QD colloidal samples of different lead salts, which have an excellent match with the solar spectrum, have been observed utilizing ultrafast spectroscopic techniques. After photoexcitation, the initial dynamics of coupling between single- and multi-exciton states and with lattice phonons are important for elucidating the mechanism of MEG; although several theories have been developed to explain the effect, MEG remains poorly understood. Along with ultrafast pump-probe studies, nonlinear coherent spectroscopy is being employed to test predictions of MEG theories and aid in determining the fundamental QD exciton dynamics that are relevant to the MEG process. Initial attempts to observe MEG in an actual solar cell device have also been made, and we are guided by conclusions drawn from these studies as well as by detailed balance calculations of theoretical efficiencies toward realizing the full potential of this unique phenomenon.



Exciton population decay dynamics obtained by probing intraband transitions in the mid-IR at 5.0 μm for a sample of 5.7 nm diameter PbSe QDs. The photoexcited density of excitons is held constant with varying wavelength to achieve an initial *average* excitation level of 0.25 photogenerated excitons per QD in the sample. The increasingly prominent fast decay results from Auger recombination of multiple excitons within each photoexcited QD.

Poster #13

PHOTOINDUCED CHARGE-SEPARATION IN DYE-SENSITIZED SOLAR CELLS AND MOLECULAR ASSEMBLIES

C. Michael Elliott[a], Matthew Rawls[a], John M. Weber[a], Ulrich E. Steiner[b] ,Silvia Cazzanti[c], Stefano Caramori[c], Roberto Argazzi[c], and Carlo Alberto Bignozzi[c]

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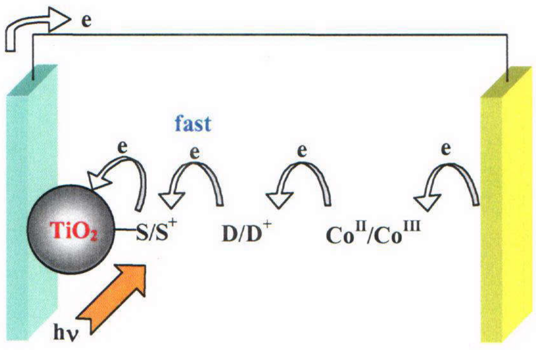
In dye sensitized solar cells (DSSC) the photoexcited dye adsorbed on the surface of a wide-bandgap semiconductor (TiO_2, SnO_2, NiO) injects into the semiconductor's conduction band. The resulting oxidized dye is reduced by a redox couple mediating the transport of holes from the photoanode to the "dark" cathode. Historically, the best efficiencies have been obtained with I^-/I_3^- as mediator. The I^-/I_3^- couple has ideal kinetic properties; specifically, the regeneration of the dye by I^- is very fast and the recombination of I_3^- with photoinjected electrons in the TiO_2 is extremely slow[7] yet I^-/I_3^- has a number of other drawbacks. Recently, certain polypyridine Co(II) complexes have been shown to be moderately efficient mediators in solar cells; however, compared to I^-/I_3^-, they exhibit slower dye re-reduction and faster recombination with photoinjected electrons. In the first part of this poster we report the photoelectrochemical characterization of mediator mixtures in which a co-mediator, characterized by a fast electron transfer reaction, is used in conjunction with the previously studied $Co(DTB)_3^{2+}$ complex (DTB = 4,4'-di-*t*-butyl-2,2'-bipyridine).



Similarly, photoinduced charge separation can be effected at the molecular level by systems incorporating a chromophore (C), an electron donor (D) and an electron acceptor (A). Commonly, these systems have low to modest quantum efficiencies for forming charge-separated states because the rate of geminate recombination of the initial photoproducts is faster than or, at least comparable with, the rate of charge separation. Donor-chromophore-acceptor molecular assemblies where the chromophore is a ruthenium bipyridine complex and the donor is an azine (i.e., phenoxazine, phenothiazine or phenoselenazine); however, behave differently. These assemblies have uncharacteristically large quantum efficiencies for charge separated state formation, often approaching 1. To understand the origin of this large efficiency, studies were conducted on photoinduced electron transfers in systems consisting of a chromophore-acceptor diad (C-A) and freely diffusing azine donor. These results clearly show that the donor is not oxidized in a bimolecular event, rather it is in an equilibrium ground-state association with the chromophore prior to photoexcitation. This observation leads to the conclusion that a similar intramolecular C/D association happens in the D-C-A triad assembly and it is this association that is responsible for the near-unity quantum efficiency for charge separation.

Poster #14

INTEGRATION OF PHOTOACTIVE ORGANIC MOLECULES INTO DISPERSIONS OF CARBON SINGLE-WALLED NANOTUBES: PROBING THE MOLECULE-NANOTUBE INTERFACE

Chaiwat Engtrakul, Timothy J. McDonald, Jeff L. Blackburn, Yong-Hyun Kim, Mark F. Davis, Shengbai Zhang, and Michael J. Heben

National Renewable Energy Lab, Golden, Colorado

We are conducting basic studies on neat carbon single-walled nanotubes (SWNTs) and SWNTs assembled with photoactive molecules. These studies seek to provide the scientific principles for designing systems, which can efficiently convert sunlight into electricity and fuels. It is critical to understand how the structural properties of the interface between these two components control the degree of electronic coupling in the hybrid system. To this end, we prepared luminescent SWNT solutions in which polyaromatic hydrocarbons (PAHs) were adsorbed onto the nanotube's surface. Raman, photoluminescence excitation (PLE),[1] and nuclear magnetic resonance[2] spectroscopies were used to investigate the noncovalent functionalization of the SWNTs with the PAHs. The spectroscopies provided structural, chemical, and electronic information regarding the accessibility of the molecules to the SWNT's hydrophobic surface. Specifically, we observed a change in the electronic structure of the nanotubes due to the close proximity of certain polyaromatic molecules. For example, the addition of perylene showed a preferential photoluminescence (PL) quenching of the small band-gap tubes and a red shift in the PL for the larger diameter tubes (Figure 1). The perturbation of a nanotube's electronic structure is strongly dependent on the degree of electronic coupling with the PAH and the strength of the binding of the various surfactant molecules. Details on the mechanism of the interaction between SWNTs and noncovalent solubilizing agents will be provided by molecular dynamics simulations based on the first-principles density functional theory and local density approximation.

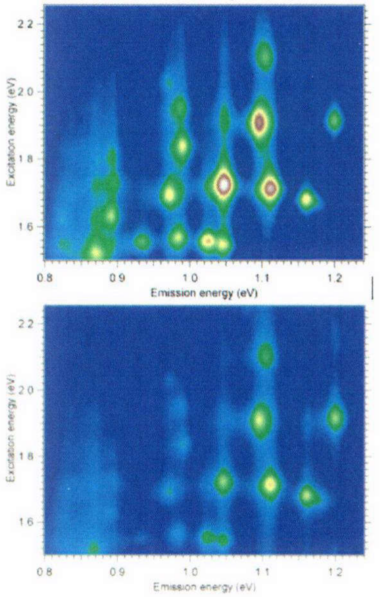


Figure 1. PLE spectroscopy of SWNTs (top) and SWNTs and perylene (bottom) in sodium cholate. The intensities have been adjusted so that the large band-gap tubes have the same color in both plots.

Studies on SWNTs in communication with photoactive molecules would be greatly simplified if homogenous collections of a single nanotube type could be prepared. To this end, we have developed a chirality-selective purification method that leads to chiral-pure SWNT samples. This purification method exploits selective interactions of nanotubes with common surfactants (e.g., sodium dodecylsulfate, sodium cholate). The chirality-dependent nature of the measured surfactant binding energies allows us to devise strategies for producing chiral-pure suspensions.

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VISIBLE LIGHT-ABSORBING Ti-O-Co CHARGE TRANSFER SITES IN MESOPOROUS SILICA

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University of California, Berkeley, CA 94720

Nanoporous inorganic oxides such as those made of silica offer opportunities for organizing and coupling photocatalytic components for solar to fuel conversion in a robust, inert scaffold. The pore chemistry is well suited for the covalent anchoring of the components, and the compartmentalized nature of the framework offers opportunities for instant separation of evolving oxygen from reduced products. For driving water oxidation and CO_2 or proton reduction with visible light, multi-electron catalytic sites need to be coupled directly to visible light electron pumps. Binuclear metal-to-metal charge-transfer (MMCT) units embedded in the silica pores are ideally suited for driving charge transfer; the variety of available metals and oxidation states offers great flexibility in terms of visible light absorption properties and matching of redox potentials with those of the catalytic sites. We have recently introduced visible charge-transfer units featuring group IV metals Ti or Zr oxo-bridged to d^{10} metals Cu^I or Sn^{II}, and were able to drive CO_2 reduction at one of these sites ($ZrOCu^I$). Here, we introduce visible MMCT units in mesoporous silica featuring Ti linked to a group VIII transition metal, Co^{II}.

The binuclear Ti^{IV}-O-Co^{II} units were assembled in the mesopores of MCM-41 silica sieve (30 A diameter) by exposing a solution of $Co^{II}(NCCH_3)_2Cl_2$ precursor in acetonitrile to Ti-MCM-41 powder. The latter contained TiOH groups tripodally anchored on the silica pore surface (Ti/Co = 0.01). The optical Co^{II}(d-d) spectrum revealed that Co^{II} was anchored on the pore surface in tetrahedral coordination. The infrared spectrum confirmed that both CH_3CN ligands were replaced by oxo bridges to Ti or Si, with stretching modes of Co-O-Si and Co-O-Ti linkages observed at 846 and 756 cm^{-1}. No Co oxide clusters were formed by this synthetic procedure. The diffuse reflectance spectrum of the $TiCo^{II}$-MCM-41 material showed a continuous absorption band extending from the UV region to 520 nm, which originates from the Ti^{IV}-O-Co^{II} $\rightarrow$ Ti^{III}-O-Co^{III} MMCT transition. The absorption is absent in a MCM-41 sample containing both isolated Ti and Co center; this material was obtained by grafting Co^{II} centers on a Ti-MCM-41 material that had the Ti protected by a cyclopentadiene ligand, thus preventing reaction of $Co^{II}(NCCH_3)_2Cl_2$ precursor at Ti sites. The finding strongly supports the conclusion that observation of MMCT absorptions requires an oxo bridge between the two metal centers, which is further supported by the results from XANES spectroscopy.

In summary, robust visible light-absorbing binuclear Ti-O-Co^{II} metal-to-metal charge-transfer units were synthesized on the pore surface of mesoporous silica by a simple step-wise solution loading technique. Identification of labile metal precursors that react preferentially at metal sites and do not lead to cluster formation is a crucial aspect of the approach. Considering the redox potential of tetrahedral Co^{III}, the excited charge-transfer state of the Ti-O-Co moiety is suitable for driving a multi-electron water oxidation catalyst.

A QUALITATIVELY IMPROVED DENSITY FUNCTIONAL METHODOLOGY EMPLOYING LOCALIZED EMPIRICAL CORRECTIONS

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We have developed an empirical localized orbital correction model which improves the accuracy of DFT methods for the prediction of thermochemical properties for molecules of first and second row elements. The B3LYP localized orbital correction version of the model (B3LYP-LOC) improves B3LYP DFT atomization energy calculations on the G3 data set of 222 molecules from a mean average deviation (MAD) from experiment of 4.8 to 0.8 kcal/mol. The almost complete elimination of large outliers and the substantial reduction in MAD yields overall results comparable to the G3 wavefunction based method; furthermore, the new model has zero additional computational cost beyond standard DFT calculations. The following four classes of correction parameters are applied to a molecule based on standard valence bond assignments: corrections to atoms, corrections to individual bonds, corrections for neighboring bonds of a given bond, and radical environmental corrections. A particularly important result is the identification of systematic underbinding in ionic bonds; a single correction parameter, which can be derived from the observed B3LYP error in the atomization energy of NaCl (4.5 kcal/mole), yields a very large improvement in the ~35 molecules in the G2 data set which exhibit formal charge separation.

We have recently extended this work to improve the calculation of electron affinities and ionization potentials. Additional correction parameters are identified which involve systematic DFT errors in electron-electron interactions in different environments. The MAD for a set of 134 electron affinities and ionization potentials, taken from the G2 data set, is reduced from 0.137 eV to 0.039 eV, an improvement similar to that obtained for atomization energies. The ration of adjustable parameters to experimental data points is smaller in this case (22 new parameters in all), so verification of the robustness of the results using an independent test set will be necessary in order to establish a degree of confidence in the parametrization that is analogous to that achieved for neutral molecules, described above. A suitable test set can for example be generated using high level ab initio computational methods.

We plan to apply this new method to improve the accuracy of the treatment of the electronic structure of materials of importance to the DOE program. For example, in silicon nanoparticles, or in TiO_2 particles, localized trapping states of an excited electron are critical to functioning of solar energy devices. In systems such as TiO_2, there is additionally a strong ionic character in the localized electronic structure of the bulk material. The methodology we are developing will be essential in providing an accurate description of these states.

PHOTOINDUCED REACTION OF FUNCTIONALIZED POLYPYRIDYLRUTHENIUM COMPLEXES WITH AN NAD$^+$/NADH MODEL LIGAND

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Take-aki Koizumi[2] and Koji Tanaka[2]

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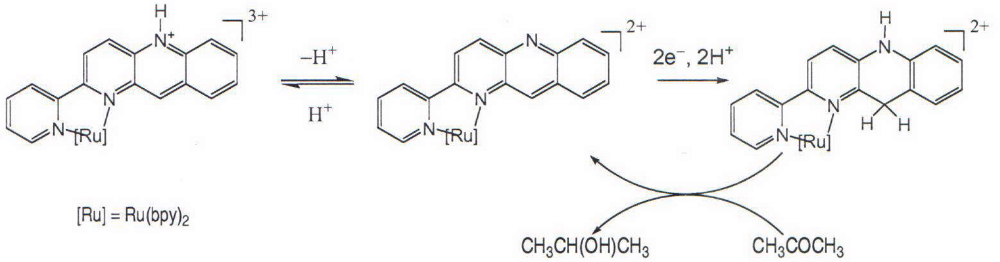
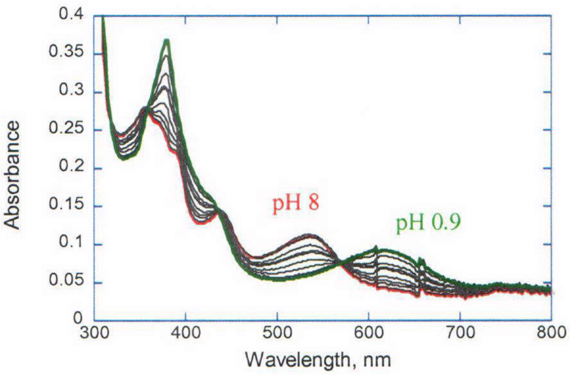
NAD$^+$/NADH is one of the most important redox mediators in biological systems and acts as a reservoir/source of two electrons and a proton. A polypyridylruthenium complex with an NAD$^+$/NADH model ligand, $[Ru(bpy)_2(pbn)](PF_6)_2$ (bpy = 2,2′-bipyridine, pbn = 2-(2-pyridyl)-benzo[*b*]-1,5-naphthyridine) catalyzes the electrochemical reduction of acetone to isopropanol at -1.14 V vs Fc/Fc$^+$.[a]



We found that the complex with the hydrogenated pbn ligand, $[Ru(bpy)_2(pbnH_2)](PF_6)_2$, is cleanly produced by two electrons and two protons upon visible light irradiation with triethylamine or ^{60}Co irradiation with formate. The results open a new door to photo-induced hydride transfer reactions in artificial photosynthetic systems. In order to understand factors controlling the energetics of coupled proton and electron transfer reactions involved in this system, we initiated a study of the mechanism and kinetics of the formation of $[Ru(bpy)_2(pbnH_2)](PF_6)_2$ and its reaction with acetone. The acid-base properties of the ground- and excited-state complexes and the reduced species were investigated to identify the intermediates for the formation of $[Ru(bpy)_2(pbnH_2)](PF_6)_2$.



pH dependent spectra of $[Ru(bpy)_2(pbn)](PF_6)_2$

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[a] Koizumi and Tanaka, *Angew. Chem. Int. Ed.*, **2005**, *44*, 5891

ELECTRON TRANSPORT IN ORGANIC SEMICONDUCTORS AND COMPARISONS TO EXISTING MODELS

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Electron motion through actual, rather than ideal, organic semiconductors is still quite poorly understood. One problem is that many measurements are made on impure and poorly characterized systems. We studied clean, polycrystalline perylene diimide films, doped and undoped, to understand transport in a relatively ideal experimental system. With simplifying assumptions, we derived an equation for the transport. Our model is an analytical approximation to a nonlinear set of coupled processes, yet it fits the data remarkably well (Fig. 1). The current density is given by

$$J = q\, F\, \mu^0\, n_{\mathrm{d}}\, exp((-E_{\mathrm{aJ,0,nd}} + \eta\, F^{1/2})/k_{\mathrm{B}}T) \qquad (1)$$

where F is the applied electric field, μ^0 represents the "pristine" single crystal mobility of free carriers unperturbed by dopants, traps, electrostatic fluctuations, etc, n_{d} is the dopant density, $E_{\mathrm{aJ,0,nd}}$ is the activation energy for the current at zero field for a given n_{d}, and η is a modified Poole-Frenkel factor.

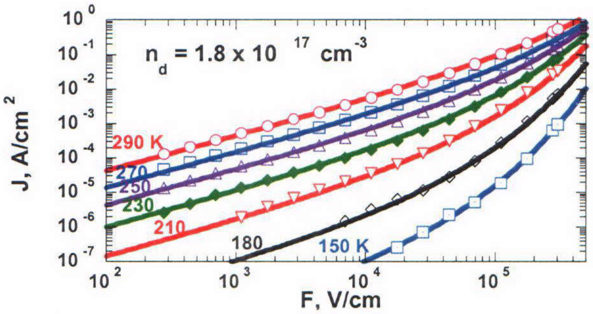

Figure 1. Typical current density-average field data at various temperatures for a film doped at 1.8×10^{17} cm^{-3} with an electrode spacing of 3.6 μm. The curves are fits to eq. 1.

Being based on simple electrostatics, our model should also apply to less ideal systems, even to π-conjugated polymers which suffer from both covalent and non-covalent disorder as well as chemical impurities. Thus we studied a poly(p-phenylenevinylene) derivative and compared our results to those in the literature. Experimentally our results were identical but our intepretation was quite different. Such data are routinely fit to the space-charge-limited current (SCLC) model. Yet the Poole-Frenkel-like model (eq. 1) seems to fit the available data better and with fewer assumptions than the SCLC model (Fig. 2).

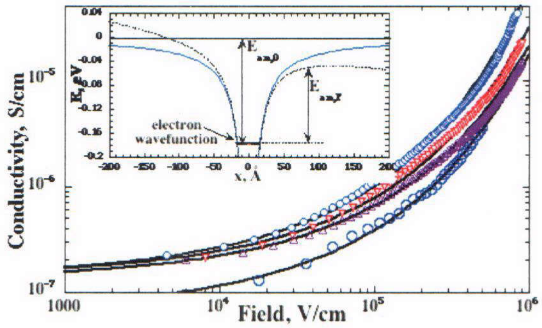

Figure 2. Conductivity vs. applied field for two PPV derivatives. The top three curves are from 660 nm, 375 nm, and 500 nm films of $OC_1C_{10}PPV$ derivatives, respectively. The lowest curve is from literature data. Data are fit to eq. 1. The inset shows the basis of the Poole-Frenkel model.

PHOTOCHEMICAL CO_2 REDUCTION IN NONCOORDINATING SOLVENTS AND SUPERCRITICAL CO_2

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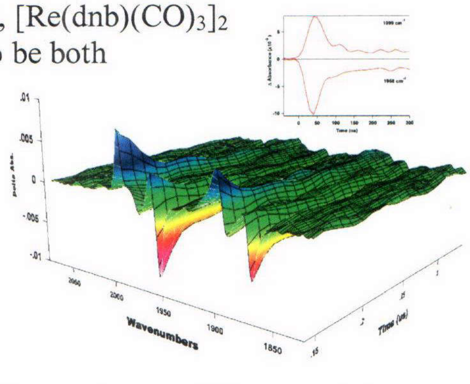
Previous studies on the homogeneous catalytic photoreduction of CO_2 into useful chemicals using transition metal complex catalysts have shown promising results. However, the turnover frequencies (TOFs) for these reactions are often disappointing. We have previously shown that polar solvents, which are required to dissolve the current generation of catalysts, can coordinate to a vacant site at the metal center upon photolysis, resulting in drastically reduced rate constants for reaction with CO_2 and thus low catalytic activity.

We propose to synthetically modify a series of CO_2 photoreduction catalysts from the family with general formula, $[Re(CO)_x(\alpha\text{-diimine})L_{4-x}]^{0,+}$ ($x = 2$ or 3; L = halide, phosphine, phosphite or amine) in such a way as to render them soluble in *noncoordinating solvents*, such as hexane and in high-pressure *supercritical CO_2* ($scCO_2$) itself. This will involve the addition of long alkyl and/or CO_2-philic polyfluoro chains to the ligand framework, and the replacement of anions with CO_2-philic anions, such as $[BAr^F_4]^-$ ($[BAr^F_4]^- = B[3,5\text{-}(CF_3)_2C_6H_3]_4^-$). The elimination of coordinating solvents should significantly increase the reactivity of the active photogenerated catalytic species toward CO_2 and thus improve TOFs. Furthermore, by eliminating organic solvents completely and using $scCO_2$ as the solvent, a number of advantages will be enjoyed. Most notably, the available concentration of CO_2 reactant molecules will increase substantially, by 2 orders of magnitude (to ~20 M). In addition, the physical properties of $scCO_2$ are easily tuned as a function of pressure and temperature, offering the possibility to enhance reaction rates and select desired products.

Preliminary results will be presented on the dimeric complex, $[Re(dnb)(CO)_3]_2$ (dnb = 4,4'-dinonyl-2,2'-bipyridine). This dimer was found to be both solvatochromic and thermochromic. Variable temperature FTIR has been used in conjunction with DFT calculations to investigate this behavior in terms of its conformation. 532 nm excitation of the dimer in hexane resulted in the formation of a short-lived (< 100 ns) MLCT excited state, followed by Re-Re bond homolysis to give the Re-based $17e^-$ radical, $Re(dnb)(CO)_3$ (see Figure). This radical was found to be 10^6 times more reactive toward re-dimerization in hexane compared to in the coordinating solvent, THF. Results of preliminary investigations into the reactivity of the radical toward CO_2, both in hexane and in $scCO_2$, will be presented.



Nanosecond step-scan FTIR spectroscopy in hexane shows that upon 532 nm excitation, the MLCT excited state of $[Re(dnb)(CO)_3]_2$ lives less than 100 ns and produces the metal-based radical, $Re(dnb)(CO)_3$.

Poster #20

AN ELECTROCHEMICAL STRATEGY TO INCORPORATE NITROGEN INTO TiO_2 NANOTUBE-ARRAY THIN FILMS: MODIFICATION OF BANDGAP AND PHOTOELECTROCHEMICAL PROPERTIES

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and Craig A. Grimes

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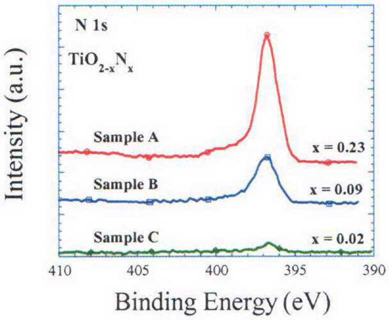
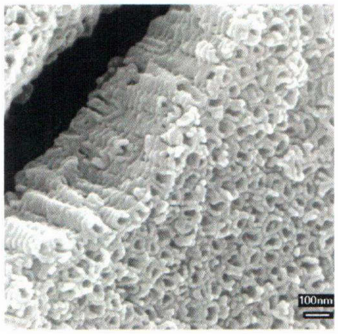
The Pennsylvania State University

We describe a simple electrochemical method to introduce anionic dopants into TiO_2 nanotube-array films made by anodization of a Ti film. N-doped thin films with chemical composition $TiO_{2-x}N_x$, up to $x = 0.23$, were fabricated by anodic oxidation of a pure titanium sheet in electrolyte solutions containing ammonium ions, nitrate ions and fluoride ions enabling simultaneous nanostructuring and doping of the growing anodic oxide. Analysis by X-ray photoelectron spectroscopy (XPS) indicates that nitrogen atoms substitute for oxygen sites within the TiO_2. F atoms were present in the amorphous, as-anodized samples but were resubstituted by O atoms upon annealing in oxygen at temperatures higher than 600°C. For nitrogen doped films UV-vis spectroscopy indicate a shift in the primary absorption threshold as well as significant optical absorption in the visible wavelength range from 400 to 530 nm. The concentration of the incorporated anionic dopants, and the morphology of the doped thin film are strong functions of electrolyte chemistry and anodization time. Longer anodization periods resulted in a well-developed nanotube-array structure but smaller amounts of incorporated nitrogen. XPS depth profiling reveals the nitrogen doping to be inhomogeneous, with maximum nitrogen incorporation occurring near the oxide-electrolyte interface at the surface of the anodized film.





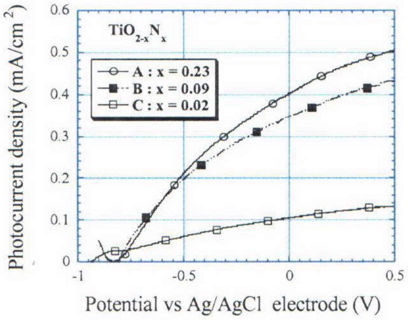


Fig. 1 (L). N 1s XPS spectra for samples made by variable anodization chemistries with respective nitrogen doping levels denoted by 'x'.

Fig. 2 (C). FESEM image of sample anodized for 6 hours in an electrolyte containing 2.5 M NH_4NO_3 at 15 V.

Fig. 3 (R). Photocurrent generation of samples A, B and C under AM 1.5 illumination.

Poster #21

CONCATENATION OF ANTENNA FUNCTION AND PHOTOINDUCED ELECTRON TRANSFER IN PORPHYRIN-CONTAINING MOLECULAR SYSTEMS

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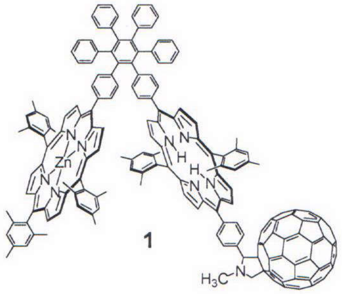
Various structural motifs are found in natural photosynthetic antenna systems. In several organisms, antennas include rings of chlorophyll and carotenoid molecules. Light absorbed by these pigments generates excited states that can migrate among the ring chromophores by energy transfer processes, and ultimately move out of the ring to another antenna or to the reaction center. With such systems as inspiration, we are constructing model antenna systems based on hexaphenylbenzene as an organizing framework.



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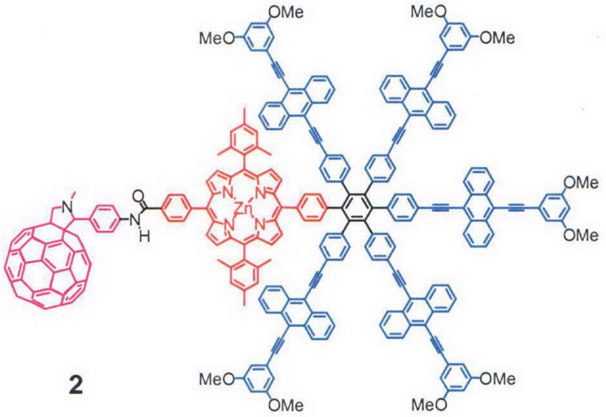
To begin to investigate this approach, we synthesized model triad **1**, which features two porphyrins, a free base (P_{2H}) and a zinc (P_{Zn}) porphyrin, linked to the hexaphenylbenzene core. The free base porphyrin, with its lower-lying excited singlet state, acts as an excitation energy trap. In addition, it bears a fullerene (C_{60}) as an electron acceptor. Spectroscopic studies in 2-methyltetrahydrofuran show that excitation of the zinc porphyrin antenna moiety to form $^1P_{Zn}\text{-}P_{2H}\text{-}C_{60}$ is followed by singlet-singlet energy transfer to the free base porphyrin (τ = 59 ps), yielding $P_{Zn}\text{-}^1P_{2H}\text{-}C_{60}$. The free base porphyrin first excited singlet state decays by photoinduced electron transfer to the fullerene (τ = 25 ps), producing a $P_{Zn}\text{-}P_{2H}^{\bullet+}\text{-}C_{60}^{\bullet-}$ charge-separated state. Charge shift (τ = 167 ps) yields $P_{Zn}^{\bullet+}\text{-}P_{2H}\text{-}C_{60}^{\bullet-}$. This final charge-separated state is formed with quantum yields >90% following excitation of any of the three chromophores. Charge recombination in 2-methyltetrahydrofuran (τ = 50 ns) occurs by an apparently endergonic process to give triplet states of the chromophores, rather than the ground state. In benzonitrile, charge recombination yields the ground state (τ = 220 ns).

Heptad **2** is a more complex example of an antenna-reaction center system based on a hexaphenylbenzene core. The bis(phenylethynyl)anthracene (BPA) units are antennas that absorb at longer wavelengths than the porphyrin Soret band. Results from a variety of spectroscopic studies show that excitation from these antenna chromophores is ultimately transferred to the porphyrin with time constants of a few ps and a quantum yield of ~1.0. Electron transfer from the porphyrin to the fullerene occurs with a time constant of 80 ps, yielding a charge-separated state that decays with a lifetime of 15.3 ns. A variety of other antenna-reaction center structures based on this molecular framework have been synthesized.



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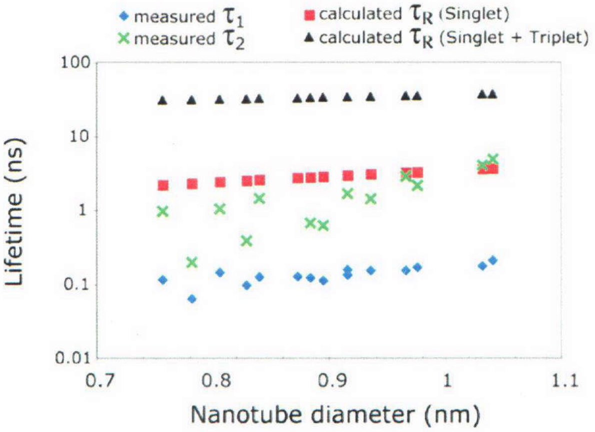
Poster #22

TIME AND SPECIES RESOLVED PHOTOLUMINESCENCE MEASUREMENTS ON SOLUBILIZED SINGLE-WALL CARBON NANOTUBES

Wyatt Metzger, Timothy J. McDonald, Chaiwat Engtrakul, Randy J. Ellingson, Garry Rumbles,
and Michael J. Heben
National Renewable Energy Laboratory, Golden, Colorado

Despite a substantial amount of work, the photoexcitation relaxation mechanisms in carbon single-wall nanotubes (SWNTs) are not well understood. There is a wide range of reported photoluminescence (PL) lifetime (τ_{PL}) values likely due to the fact that time windows, excitations levels and energies, and the samples themselves vary from lab to lab. In fact, Hagen et al. reported τ_{PL} values for different tubes of the same (6,4) type that range from ~20 to ~180 ps at 87 K.[1] We recently completed an extensive study in which we measured the PL dynamics from 15 individual SWNT species in aqueous surfactant solution using time-correlated single photon counting.[2,3] Each tube was resonantly excited at E_{22} in an effort to prepare similar excited states. Room-temperature PL decay curves were measured by time-correlated single-photon counting. Photoexcitation at the desired wavelength was provided by an optical parametric amplifier pumped by the output of a titanium:sapphire laser system with a regenerative amplifier. The sensitivity of the method permitted experiments at very low excitation levels such that fast exciton-exciton recombination could be avoided. The majority of the PL (> 90%) decayed with a time constant that scaled from 60 to 200 ps with increasing diameter (τ_1). The trend is qualitatively consistent with that expressed in a recent theory for the dependence of the radiative lifetime as a function of diameter.[4] Interestingly, for some tubes, we observed a substantial component of the PL (1 – 8%) to have long lifetimes (τ_2 - see figure), in the range of 0.5 to 5 ns, that are comparable in magnitude to values that have been calculated for the *radiative* lifetime from singlet states across the same tube diameter range. The results suggest that excitonic emission occurs from mixed singlet-triplet states, and that the long lifetime component may be attributed to tubes that are "more perfect". These findings will be presented and discussed with regard to possible tube-tube and tube-surfactant interactions in the solutions.



Measured τ_1 and τ_2 and calculated τ_R values (from Perebeinos et al.) versus nanotube diameter.

References: (1) Hagen, A. et al. "Exponential decay lifetimes of excitons in individual single-walled carbon nanotubes". Physical Review Letters 95 (2005); (2) Jones, M. et al. "Analysis of photoluminescence from solubilized single-walled carbon nanotubes". Physical Review B 71 (2005); (3) Jones, M. et al. "Diameter Dependence of Photoluminescence from Single-Walled Carbon Nanotubes: Long-Lived Emissive States". in preparation (2006); (4) Perebeinos, V. et al. "Radiative lifetime of excitons in carbon nanotubes". Nano Letters 5, 2495-2499 (2005).

Poster #23

ORDERING QUANTUM DOTS USING BIOMOLECULES

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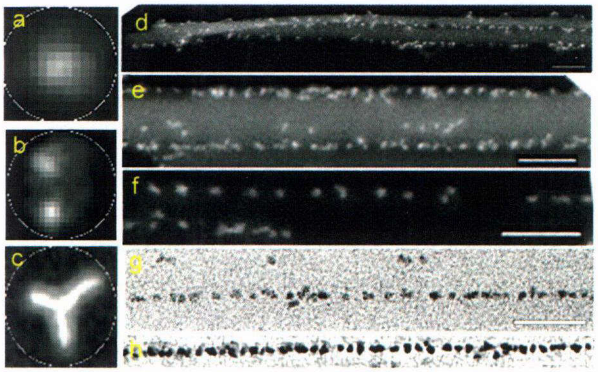
Energy Sciences Directorate, National Renewable Energy Laboratory, Golden, Colorado

Our goal is to understand exciton/charge transfer processes occurring in defined quantum dot (QD) arrays assembled using biomolecules. We term the strategy to use bioengineered molecules to gain such controlled QD-QD organization, bioassembly.

We have reviewed the potential for cellulosomal proteins from *Clostridium thermocellum* to be used individually or collectively to position QDs using cellulose templates. We first reported the use of amino acid conjugated, genetically engineered cellulosomal proteins to solubilize (CdSe)ZnS QDs in 2003. We also showed that selected amino acids and amino acid derivatives could be used to cap surfaces of (CdSe)ZnS QDs so that no loss of native fluorescence was observed in aqueous solvents. In 2004, we reported the assembly of large water soluble clusters of (CdSe)ZnS QDs demonstrating energy transfer photoluminescence. We then exploited the CBMs from the cellulosome scaffoldin assembly that have very high binding specificity for the 1,1,0 cellulose face to create linear arrays of CBMs on cellulose crystals. Later in 2004, we successfully arrayed photoluminescent biotinylated (CdSe)ZnS QDs on cellulose crystals in linear arrays using complex assemblies of Strept-II tagged, type3 carbohydrate binding domains (CBMs) and cohesin/dockerin proteins mediated by streptavidin biotin interaction. In 2005, we extended this approach by reducing the size of the protein bioconjugate to simply the bi-polyhistidine tagged, type 2 CBM, which appeared to further reduce the inter-QD distances in arrays visualized by STEM and TEM (see Figure). PL measurements and transient absorption spectroscopy showed that the protein arrayed QDs were indeed fully luminescent and demonstrated similar carrier decay kinetics to the toluene soluble, TOPO QDs.



Electron micrographs of QD bio-assemblies. a-c: single (a), pair (b), and trefoil (c) QDs capped by genetically engineered proteins. d-f: CBM-QD arrays on cellulose crystal. Bar=100 nm.

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PATHWAYS AND DYNAMICS OF EXCITED-STATE ENERGY TRANSFER IN LIGHT HARVESTING ARRAYS CONSISTING OF A HEXAMERIC WHEEL OF PORPHYRINS AND CENTRAL GUEST CHROMOPHORE

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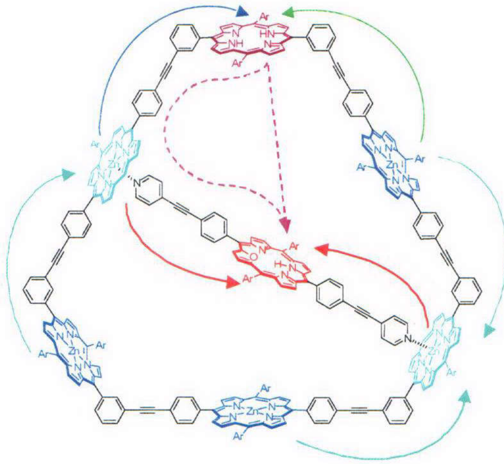
David F. Bocian[3], Jonathan S. Lindsey[2], and Dewey Holten[1]

Chemistry Departments [1]Washington University,
[2]North Carolina State University, [3]University of California Riverside

A hexameric wheel of porphyrins with a ~35 Å cavity provides an effective host for a dipyridyl-substituted free base porphyrin, forming a self-assembled light harvesting system containing a central energy trap. Each cyclic hexameric array contains zinc porphyrins plus zero, one, two, or three free base porphyrins (denoted **Zn_6**, **Zn_5Fb**, **Zn_4Fb_2**, **Zn_3Fb_3**, respectively). The dipyridyl-substituted guest chromophore is either a free base porphyrin (***N_4Fb***) or a hybrid in which one of the central nitrogens has been replaced by an oxygen atom (***N_3OFb***) to lower the excited-state energy. These host-guest architectures have energy gradients derived from the nature of the constituent porphyrins and from the binding of the dipyridyl-substituted guest chromophore to opposing zinc porphyrins in the hexameric wheel. The pathways, rate constants, and yields of energy flow were determined using ultrafast transient absorption kinetic spectroscopy, in conjunction with static and time-resolved fluorescence measurements. In addition to the various host-guest complexes, a number of relevant control compounds were analyzed. In the **Zn_6•*N_4Fb***, **Zn_6•*N_3OFb*** arrays, for example, light energy absorbed by the uncoordinated Zn porphyrins is transferred quantitatively through-bond to the pyridyl-coordinated Zn porphyrins in the hexamer with the rate constant of ~(40 ps)$^{-1}$. Subsequently, energy flows to the ***N_4Fb*** guest with a rate constant of ~(1.5 ns)$^{-1}$ for the ***N_3OFb*** guest with a rate constant of ~(0.75 ns)$^{-1}$. Transfers from host to guest have a significant Förster through-space contribution. Additional pathways for energy flow are available in **Zn_5Fb•*N_3OFb*** and **Zn_4Fb_2•*N_3OFb***. These processes include though-bond superexchange mediated energy transfer between nonadjacent constituents of the cyclic hexamers, and a combination of through-bond superexchange-mediated or through-space energy transfer from the Fb porphyrin of the hexameric host to the ***N_3OFb*** guest chromophore (as shown for **Zn_5Fb•*N_3OFb*** in the figure).



Poster #25

COORDINATIVELY ASSEMBLED SUPRAMOLECULES FOR LIGHT COLLECTION AND CHARGE SEPARATION

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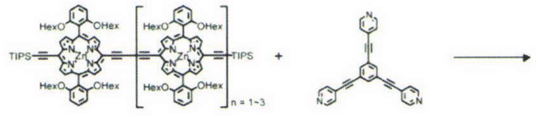
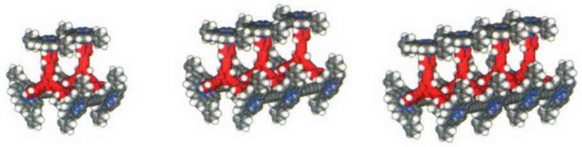
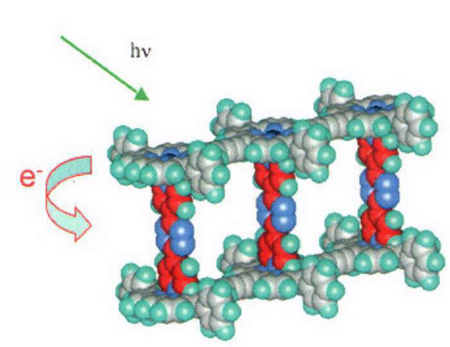
Sheridan Road, Evanston, IL 60208

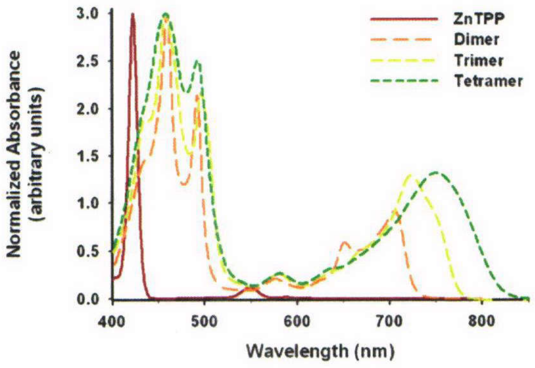
As amply demonstrated by Therien, Anderson, and others, highly conjugated porphyrin oligomers are often much broader blue absorbers and much stronger red absorbers than are simple monomers such as tetra-phenyl porphyrin (TPP). The striking spectral changes, which are due in part to symmetry reduction, make the conjugated oligomers particularly attractive as light harvesters, especially if conjugation is introduced in a way that does not adversely affect excited-state lifetimes; see figure. Well-defined supramolecular prism, ladder, and box-like assemblies of conjugated dimeric, trimeric, and tetrameric porphyrin chromophores have been constructed via reversible, cooperative coordination chemistry. Assembly formation allows other functionalities and other chromophoric components to be incorporated in well-defined ways. In addition, it further broadens the oligomers' blue absorption and further intensifies their red absorption.

This poster will describe: 1) formation and photophysical characterization of simple assemblies, 2) transient DC photoconductivity studies of charge-separation within more complex assemblies, and 3) solution-phase X-ray structural characterization of assemblies (synchrotron-based studies in collaboration with D. Tiede and co-workers). Preliminary investigations of surface immobilization and solar cell incorporation may also be described.









PHOTOPHYSICS OF COVALENTLY LINKED DIMERS BASED ON AN *O*-QUINODIMETHANE BIRADICAL: EVIDENCE FOR SINGLET FISSION

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[2]Department of Chemistry, University of Colorado, Boulder, Colorado

We report the first systematic theoretical and experimental investigation of tailored molecular chromophores intended to exhibit singlet fission (SF), the splitting of one singlet excitation into two triplets. Covalently-linked 1,3-diphenylisobenzofuran (DPIBF) dimers were synthesized, and the photophysics were measured with respect to the monomer. Triplet-triplet absorption spectra were collected in solution via sensitization, and triplet quantum yields (TQY) of the directly-excited molecules were measured. While no triplet formation was detected for the monomer, the TQY was found to depend upon the coupling strength between the chromophoric units in the dimer. TQY's for the dimer range from 1.0 - 6.0 %, with the highest yield being obtained for molecules with the closest coupling that still inhibited conjugation of the two monomeric units. The TQY was found to depend highly on solvent polarity, indicating that triplet formation proceeds via an intermediate with considerable charge-transfer character. Ultrafast transient absorption studies have revealed details about the nature of this intermediate and its possible role in triplet formation. A model is developed which details the possible mechanisms of triplet formation, including singlet fission, a potentially important process to be utilized in ultraefficient light-harvesting devices. A variety of device configurations utilizing SF are considered, and the efficiency of such devices is compared with similar schemes that employ multiple exciton generation, an analogous process to SF that occurs in semiconductor nanocrystals.

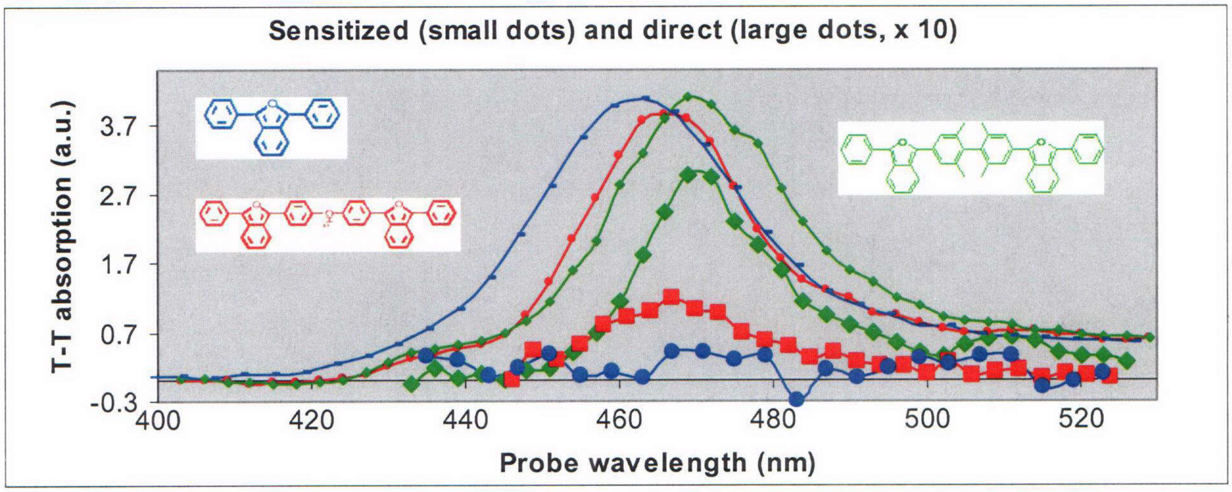

Figure 1: Triplet-triplet absorption spectra in solution for the molecules coded by color. The intensities of the absorptions of directly excited molecules are compared with those sensitized with anthracene to obtain triplet yields. For SF, triplet formation is only possible in dimers.

SPECTROSCOPY AND DYNAMICS IN GaSe-InSe NANOPARTICLE HETEROJUNCTIONS

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Femtosecond polarized transient absorption results are obtained for several sizes of GaSe and InSe nanoparticles in solution. Assignments of the observed absorptions are made in terms of the known band structures and an effective mass model in which the electron and hole states are described by particle-in-a-cylinder wavefunctions. The results indicate that the transient absorption spectrum of large GaSe particles is dominated by a size-independent, z-polarized hole intraband transition.[1] The small GaSe particles exhibit the same z-polarized hole transition and a much more intense x,y-polarized transition that is assigned to an electron charge transfer transition from the conduction band to particle surface (edge) states. This absorption is absent in larger particles. The intensity of this transition depends on the electron momentum state (Γ or M), and Γ to M electron momentum relaxation results in a 15 ps transient in the absorption intensity and anisotropy. InSe nanoparticles exhibit a similar z-polarized hole intraband transition and a somewhat weaker, size-independent z-polarized electron intraband transition.[2] The differences between GaSe and InSe transient absorption spectra may be understood in terms of their respective band structures. The intensity of the electron intraband transition also depends on the electron momentum state, and a loss of the z-polarized electron intraband transition is observed upon Γ to M relaxation.

Both GaSe and InSe nanoparticles form strongly interacting solution-phase aggregates.[3] Mixed InSe-GaSe aggregates are also readily formed, i.e., the nanoparticles form heterojunctions. The transient absorption results on both types of nanoparticles are used to interpret analogous results obtained for mixed aggregates. The static absorption spectrum of the mixed aggregates exhibits a very strong absorption feature not seen in either type of nanoparticle alone. This feature is assigned to a charge transfer absorption band at an energy slightly higher than the InSe bandgap.[4] Photoexcitation of this band results in a polarized transient absorption spectrum and kinetics characteristic of InSe valence band holes and GaSe conduction band electrons. These features are present immediately after excitation, indicating that direct InSe to GaSe electron transfer occurs upon photoexcitation. The kinetics indicate that this charge-separated states persists for at least several hundred picoseconds.

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Poster #28

MAGNETIC RESONANCE AND ELECTRON TRANSFER STUDIES OF HOST-GUEST COMPLEXES OF CAROTENOIDS

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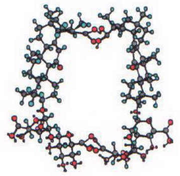
[2]Institute of Chemical Kinetics & Combustion, Novosibirsk, Russia
[3]Department of Biochemistry and Medical Chemistry, University of Pécs, Hungary

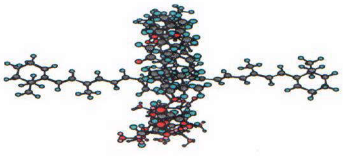
Carotenoids, intrinsic components of reaction centers and pigment-protein complexes in photosynthetic membranes, play a photoprotective role and as an alternative electron donor where the primary electron donor pathway is inhibited in plants and bacteria. Their robust nature in living materials requires extensive characterization of their electron transfer and radical trapping ability, stability, structure in and on various hosts, and photochemical behavior. Such information is needed before optimum use of them can be made in artificial photosynthetic systems.

Host-guest complexes of carotenoids with the triterpene glycoside, β-glycyrrhizic acid (GA) at <1 mM forms 1:2 complexes [$Car(GA)_2$] in aqueous solutions as well as polar organic solvents, methanol, acetonitrile and dimethylsulfoxide. A tube-like dimer of GA encapsulates a carotenoid molecule with stability constants in all solvents near 10^4 M^{-1}. In addition inclusion complexes are formed with carotenoid radical cations, which results in their stabilization. Complex formation (a) decreases the rate of electron transfer from carotenoids to electron acceptors (Fe^{3+} or quinone). (b) considerably increases the lifetime of their carotenoid-quinone charge-transfer complex, (c) increases the yield of the carotenoid-quinone adduct and (d) increases the oxidation potential of the carotenoids in the complex which leads to a multiple (10 times) increase in the scavenging rate of the OOH peroxyl radical by carotenoids with a high oxidation potential (~.7 V) and has no influence on the activity of carotenoids with lower potential (~0.5 - 0.6 V). Above 1 mM GA concentrations, the structure of the complex changes, the stability of the complex decreases and its influence on the reactivity of the carotenoids lessens. A thermodynamic study shows that hydrophobic interactions are the main driving force for the formation of the $Car(GA)_2$ complex.

Use of Density Functional Theory (DFT) calculations to interpret ENDOR measurements have shown that carotenoids embedded on activated silica-alumina solid supports form the carotenoid radical cation but upon exposure to UV photolysis, loss of H^+ from the 5, 9 or 13 methyl group occurs to form a neutral carotenoid π-radical, previously deduced from electrochemical measurements. These calculations solve a reported mystery in comparing DFT calculations to previously used RHF-INDO/SP methods where large 13-16 instead of 8-9 MH_z couplings were predicted for the carotenoid radical cation.



GA Dimer



$Car(GA)_2$ Complex

Poster #29

ULTRAFAST SPECTROSCOPY OF SINGLE WALL CARBON NANOTUBES: NEAT, BORON-DOPED AND COUPLED HETEROSYSTEMS

Kelly P. Knutsen, Jeff L. Blackburn, Chaiwat Engtrakul, Matthew C. Beard, Timothy J. McDonald, Wyatt Metzger, Garry Rumbles, Randy J. Ellingson, and Michael J. Heben

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Single-wall carbon nanotubes (SWNTs) are of great interest for their optoelectronic properties. Understanding the mechanisms of charge and energy relaxation in these unique high aspect-ratio molecules may permit new approaches to converting solar energy into electricity and fuels. We recently measured the dynamics of charge carriers within polydisperse aqueous solutions of semiconducting and metallic HiPCO SWNTs[1] using femtosecond transient absorption (TA) spectroscopy. The photoresponse of metallic tubes was mostly invariant to the excitation pump frequencies, whereas the semiconducting tubes showed a clear difference in the TA spectrum when excited above and below the first excitonic transition. The latter finding indicates the presence of a true bandgap in semiconducting SWNTs. These efforts are being extended to explore heteroatom-doped SWNTs produced by laser vaporization[2] as well as nanoscale heterosystems in which molecules or quantum dots are in contact with tube surfaces.

We compare the ultrafast photoresponse for B-SWNTs and neat C-SWNTs with regard to the dynamics of charge carrier relaxation and recombination, as well as the spectral response in the regions of excitonic transitions. Ultrafast TA measurements were performed from 450 to 2000 nm, to delay times as long 1.6 ns. Double-exponential fits yield different τ_1 and τ_2 values for the B-doped and all-carbon SWNTs for some tube chiralities (Fig. 1), while other tubes show similar decay constants. The differences are evaluated by considering the effect of B-doping on the π electron distribution, the SWNT Fermi level, and the oscillator strength of the suspended SWNTs. Results are also compared to recent time-resolved PL data collected in our lab which showed that the radiative lifetime of the tubes were governed by both an intrinsic diameter dependence as well as extrinsic effects such as tube length, defect sites and bundling.

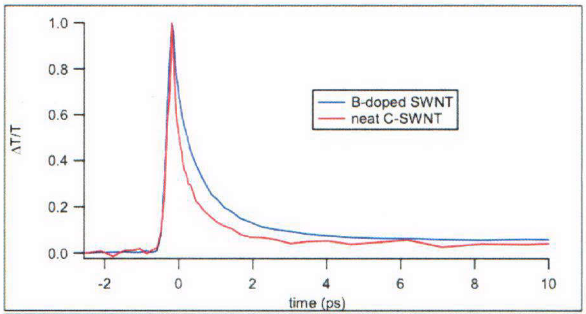

Figure 1. Normalized transient absorption dynamics of semiconducting SWNTs, comparing the response of B-doped and neat C-SWNTs when pumped above the second exciton transition and probed at the first exciton transition.

We have also begun studying SWNTs in contact with adsorbed quantum dots and aromatic hydrocarbons. In the former case we observe quantum dot photoluminescence quenching due to the presence of the nanotubes, while the latter case shows changes in the photoluminescence excitation spectrum for the contacted nanotubes. Preliminary TA data for both of these systems will be presented, as well as discussions of the challenges faced in exploring these coupled systems.

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(1) R. J. Ellingson, et al., *Phys. Rev. B* **71**, 115444 (2005); (2) J.L. Blackburn, et al., *Chem. Mater.*, accepted (2006).

Poster #30

CONJUGATED DENDRIMERS: A MODEL SYSTEM FOR STUDYING STRUCTURE-PROPERTY RELATIONS OF ORGANIC SEMICONDUCTORS

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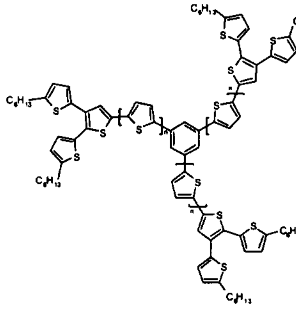
We discuss a family of pi-conjugated dendrimers as a model system for studying structure-property relations in organic semiconductors. Using dendrimers circumvents problems due to polydispersity, ill-defined molecular weight and the presence of impurities, which make it difficult to study structure-property relations in conjugated polymers.

We have synthesized a family of conjugated organic dendrimers based on a phenyl core and thiophene dendrons (**1** and **2**). The molecules have a well-defined structure and were synthesized at moderate to high yields with very high purity and monodispersity. We show that fundamental properties of the dendrimers, like conformation, conjugation length, energies of the HOMO and LUMO levels and optical absorption onset, can be controlled by changing the number and the length of dendrons around the core. For example, dendrimers with three dendrons around the core (**1**) are more planar than those with four dendrons (**2**); in the latter, steric interactions between the closely-packed dendrons cause them to twist and form more three-dimensional structures, with further implications on the optical and electronic properties.

In addition, the degree of local order in self-assembled thin films of the dendrimers varies according to molecular conformation; while some dendrimers self-assemble into highly ordered structures, others form amorphous films. We used the electrodeless Time-Resolved Microwave Conductivity technique to characterize charge transport in solution-cast thin films of the dendrimers, and showed that the mobility of charge carriers increases with increasing conjugation length of the dendron, reaching values close to those of standard organic polymers like poly(3-hexylthiophene).



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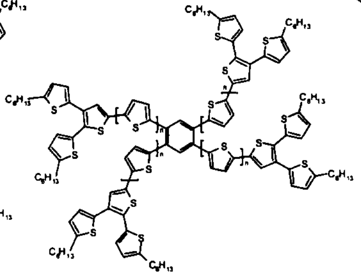

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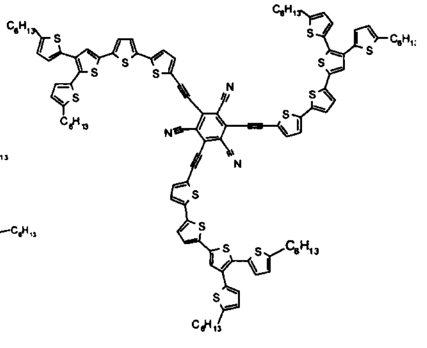


3

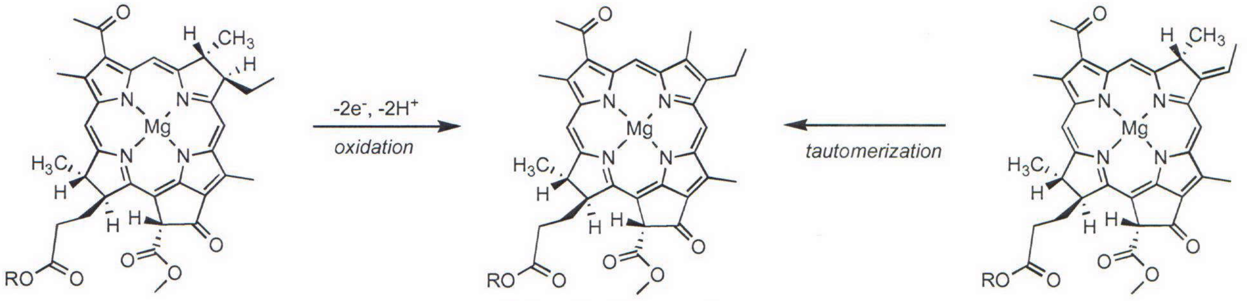
The control of the conformation and the correlation to the properties of self-assembled thin films of the phenyl-cored thiophene dendrimers has led us to investigate further modifications of the dendrimers. An example is shown in molecule **3**, where electron-withdrawing cyano groups have been attached to the core and acetylene groups have been added to the dendrons to reduce steric hindrance. Thin films of **3** exhibit clear evidence for crystalline structure, as shown by X-ray diffraction, and a reduced optical band gap relative to the analogous dendrimer in **1**.

Poster #31

CRYSTALS OF STABLE SYNTHETIC BACTERIOCHLORINS FOR POSSIBLE USE AS LIGHT-HARVESTING ANTENNAS

Masahiko Taniguchi,[1] Han-Je Kim,[1] David F. Bocian,[2] Dewey Holten[3] and Jonathan S. Lindsey[1]
Departments of Chemistry, [1]NC State University, [2]UC Riverside, and [3]Washington University

Photosynthetic systems employ collections of hydroporphyrins (chlorins, bacteriochlorins) to absorb sunlight and convey the energy to reaction centers. The construction of synthetic analogues of such antennas has generally relied on the more synthetically accessible porphyrins rather than hydroporphyrins. To achieve antennas with strong near-IR absorption requires use of bacteriochlorins rather than porphyrins. Although one can imagine using naturally occurring bacteriochlorins in artificial antennas, the natural compounds are somewhat fragile toward laboratory handling and are not very malleable from a synthetic standpoint. Indeed, only about 10 single-crystal X-ray structures of bacteriochlorins have been reported. One source of instability stems from conversion to the corresponding chlorin.

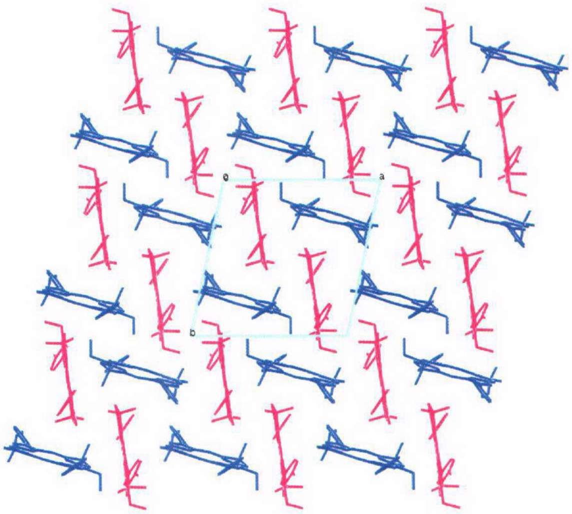


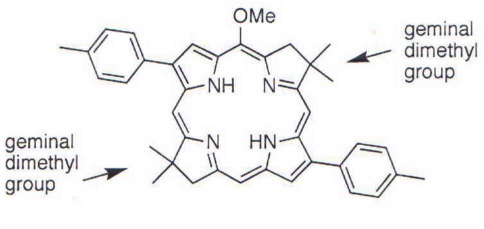
bacteriochlorophyll *a*

3-desvinyl-3-acetyl chlorophyll *a*

bacteriochlorophyll *b*

A new route to synthetic bacteriochlorins has yielded stable macrocycles and opened the door to systematic structural tailoring. A geminal dimethyl group in each reduced ring blocks decomposition pathways that lead to chlorins or porphyrins. The bacteriochlorins are robust toward diverse conditions (heat, acid/base, metalation/demetalation, chromatography, recrystallization) and exhibit characteristic strong near-IR absorption features. The bacteriochlorin compound shown below was crystallized and gave the packing pattern and unit cell shown at right. Our current objectives are to investigate the use of crystalline bacteriochlorins as light-harvesting assemblies, and understand whether different substituents and central metals can be employed to alter crystal-packing patterns and light-harvesting properties.





Poster #32

SOLVATION, REACTION, AND DYNAMIC HETEROGENEITY IN IONIC LIQUIDS

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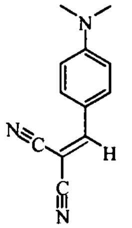
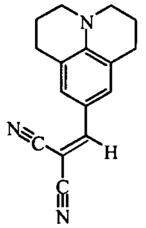
104 Chemistry Building, University Park, PA 16802

We have been using time-resolved emission spectroscopy to measure solvation dynamics, rotational diffusion, and the kinetics of ultrafast reactions in room temperature ionic liquids. Solute rotation times of a variety of probe solutes in ionic liquids generally exhibit the same relationship to hydrodynamic predictions as in conventional solvents. However, in contrast to the typically exponential correlation functions observed conventional liquids, rotational correlation functions are often stretched exponential functions of time with exponents in the range 0.5-1. Dynamic Stokes shift measurements show that solvation is also a highly non-exponential process. In some cases it is clear that the response is biphasic, consisting of an ultrafast component in the few hundred femtosecond range and a slower, highly non-exponential component extending into the nanosecond range. In some cases (where both the cation and anion are large) the division into two components is not obvious and one simply finds relaxation occurring over over 4-5 decades in time. Broad distributions of relaxation times such as these are characteristic of conventional glass-forming systems. In the latter case, much recent research has shown that such temporal distributions are the result of "dynamic heterogeneity" – the fact that the observed response is made up responses from different spatial locations whose dynamics differ greatly. We have been attempting to confirm this assignment in the case of ionic liquids by measuring the excitation dependence of solute rotation times and, most recently, of the internal conversion of the two benzylidene malononitriles DMABMN and JDMN.

DMABMN



JDMN



The ultrashort lifetimes of these two solutes is due to an isomerization about one or more bonds which may or may not involve significant charge transfer (as in TICT processes). This requirement for large-amplitude torsional motion renders the emission of DMABNB and JDMN a sensitive probe of the "free-volume" available in solvents. We will report our most recent experimental and computational studies of these solutes and the evidence they provide on the question of dynamic heterogeneity in room-temperature ionic liquids.

PHOTOELECTROCHEMISTRY OF SEMICONDUCTOR NANOWIRE ARRAYS

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Departments of Chemistry, Materials Science and Engineering,[1] Engineering Science and Mechanics,[2] and Electrical Engineering[3], The Pennsylvania State University, University Park, PA 16802

Semiconductor nanowire arrays offer an interesting alternative to single crystal and polycrystalline semiconductor electrodes. Because the frequency of crystal nucleation is proportional to surface area, it is possible to make arrays of single crystals of Si and compound semiconductor nanowires by scalable vapor phase methods. These arrays are interesting for photoelectrochemistry because in principle they allow one to eliminate grain boundary recombination, and to make multijunction devices within individual wires. Metal oxide nanowire arrays offer the advantage of quasi-1D transport of carriers for efficient excitonic solar cells, such as dye sensitized cells. We are synthesizing and studying nanowire photoelectrochemical cells based on vertical nanowire arrays of Si, CdSe, and dye-sensitized TiO_2.

Nominally undoped Si nanowires grown by vapor-liquid-solid (VLS) methods in anodic aluminum oxide (AAO) templates were found to be p-type with resistivities on the order of 1-3 Ω-cm. Si nanowires grown under similar conditions on oxidized Si substrates were also p-type but with much higher resistivities ($\sim 10^4$ Ω-cm), indicating that the AAO membranes are a major source of acceptor-type impurities. In order to circumvent the impurity problems, the growth of epitaxially-oriented Si nanowires on (111) Si substrates was investigated. High density Si nanowire arrays were obtained at 900°C using $SiCl_4$ as the source gas. The Si nanowires had a predominant <111> growth direction with diameters on the order of 100-150 nm and lengths up to ~100 μm. Mott-Schottky plots of the nanowire arrays in contact with acetonitrile solutions were linear and consistent with a p-type carrier density on the order of $10^{15}/cm^3$.

The *in-situ* doping capabilities were used to fabricate Si nanowire p-n and n-p axial homojunctions. The i-V characteristics of junctions fabricated with nearly equal p- and n-type resistivities (5×10^{-2} Ω-cm) showed rectifying behavior in both cases, but the reverse leakage currents of n-p junctions were considerably higher. The variation in reserve currents suggest that the dopant profiles of the p-n and n-p junctions are graded differently during VLS growth possibly due to solubility differences of B and P in the Au-Si alloy melt. Preliminary studies of individually aligned p-n Si nanowires showed measurable photocurrent under illumination.

TiO_2 nanowire arrays were grown by oblique angle deposition onto conducting SnO_2 electrodes and studied as anodes for dye-sensitized solar cells. The individual nanowires have diameters of 3-5 nm and cluster into columnar or helical bundles that are 50-100 nm in diameter. We are now synthesizing dye-donor diads that will form a contiguous self-assembled monolayer on the columns to prevent contact between the hole-conducting species and the photoanode.

Poster #34

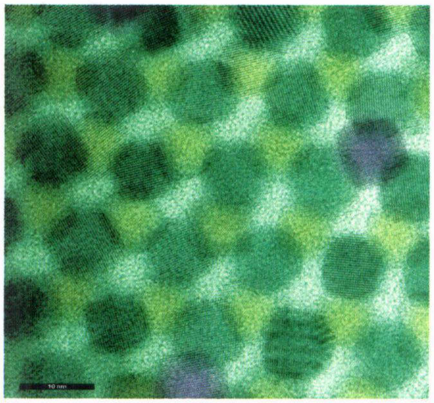
SEMICONDUCTOR NANOCRYSTALS AND NANOCRYSTAL ARRAYS: SYNTHESIS, CHARACTERIZATION, AND TIME-RESOLVED TERAHERTZ SPECTROSCOPY PHOTOCONDUCTIVITY MEASUREMENTS

James E. Murphy, Qing Song, Matthew C. Beard, Randy J. Ellingson, Olga I. Mićić, Arthur J. Nozik

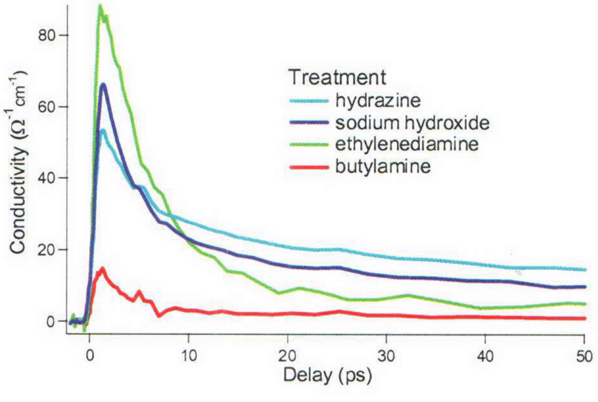
National Renewable Energy Laboratory, Golden, Colorado

Semiconductor nanocrystals (NCs) offer promising new approaches for efficient solar energy conversion structures, and understanding and maximizing charge transport in NC arrays is critical in improving the efficiencies of these structures. We report new synthetic methods to semiconductor NCs, the fabrication of ordered, conductive arrays, and the first characterization of conductive NC arrays using time-resolved terahertz spectroscopy (TRTS).

Spherical PbSe, PbS and PbTe NCs were synthesized, having a size distribution as low as 6%, with first excitonic transitions tuned from about 1 μm to 2.4 μm. The synthesis of colloidal cubic-like PbSe and PbTe NCs using this PbO "one pot" approach are also reported. This TEM image shows the beginning of a third layer of near-cubic PbTe NCs in an ordered hexagonal close-packing configuration. We report the first detection of photoluminescence in PbTe NCs, with the photoluminescence quantum yield measured to be 52%. We compare the electronic band structure and optical properties of these lead salt NCs.



Finally, we report TRTS photoconductivity measurements on NC arrays of InP and lead salts. THz spectroscopy is the only experimental technique that can measure both the degree of coupling and the carrier dynamics simultaneously, and it does so in a noncontact fashion with subpicosecond resolution. Several methods were explored to increase the conductivity in NC solids by decreasing the average interdot distance. Treating NC arrays with solutions containing various short-chained amines resulted in the greatest enhancement in photoconductivity, and pump power dependent TRTS studies indicate that Auger recombination is an efficient loss mechanism in these arrays.



Poster #35

VISIBLE LIGHT-DRIVEN WATER OXIDATION BY Ir OXIDE CLUSTERS COUPLED TO SINGLE Cr CENTERS IN MESOPOROUS SILICA

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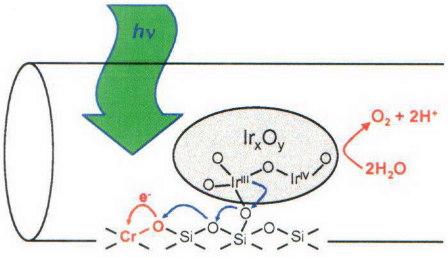
Physical Biosciences Division, Lawrence Berkeley National Laboratory
University of California, Berkeley, CA 94720

Inert nanoporous oxides such as silica offer opportunities for assembling and coupling photocatalytic components for the direct conversion of water and carbon dioxide to fuel molecules under visible light. Framework substitution or covalent anchoring of metal centers and polynuclear components, and spatial separation of oxidizing from reducing sites can be explored in these materials by virtue of their surface chemistry and compartmentalized structure. A particular challenge of this or any other approach to artificial photosynthesis is the photo-driven water oxidation. Specifically, the oxygen-evolving catalyst needs to be coupled directly to a visible light electron pump that can be coupled to a reducing site in the nanoporous scaffold. We have assembled a photocatalytic unit inside silica mesopores that consists of a single Cr^{VI} center as visible light electron pump coupled to an Ir oxide nanocluster. The unit evolves oxygen under visible light. Single or dinuclear metal sites as charge-transfer chromophores may offer ways of coupling the water oxidation half reaction with CO_2 or proton reducing sites for direct solar to fuel conversion in these nanoporous photoreactors.



Exposure of $Cr^{IV}(=O)_2$ sites at the surface of mesoporous framework-substituted CrMCM-41 silica to $Ir^{III}(acac)_3$ precursor resulted in the formation of Cr-O-$Ir^{IV}(acac)_2$ units. The reaction was monitored by FT-Raman (growth of Cr-O-Ir mode at 808 cm^{-1}, loss of Cr=O at 986 cm^{-1}), FT-IR (Cr=O mode at 889 cm^{-1}), and optical spectroscopy (loss of $Cr^{IV}O$ LMCT absorption). Calcination at 300 C gave Ir oxide nanoclusters which could directly be observed inside the mesopores by Z-contrast HRTEM combined with EDX spectroscopy. Oxygen evolution was observed by mass spectroscopy upon visible light excitation of the $Cr^{IV}O$ LMCT absorption of an aqueous suspension of Ir_xO_y-CrMCM-41 particles. Materials that contain only isolated Cr centers were the most active ($Cr/Si < 0.02$); spectroscopic evidence showed that dichromate and polychromate species present in $Cr/Si = 0.05$ samples are not active as charge-transfer chromophores. While oxygen evolution leveled off rapidly due to stoichiometric reduction of Cr^{VI}, addition of persulfate acceptor led to linear oxygen yield with time due to re-oxidation of Cr by $S_2O_8^{2-}$. Progress on the coupling of a biomimetic Mn dimer complex to Cr centers on the silica pore surface will also be discussed.

In conclusion, water oxidation has been demonstrated at a polynuclear catalyst coupled directly to a molecular visible charge-transfer moiety. Covalently anchored metal centers as charge-transfer chromophores open up opportunities of coupling the oxygen-evolving site to a reducing metal-to-metal charge-transfer unit in the nanoporous solid for accomplishing CO_2 reduction under H_2O oxidation in a sequential two-step process.

Poster #36

MECHANISTIC ANALYSIS OF HOMOGENEOUS AND INTERFACIAL ELECTRON TRANSFER

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Upton, New York 11973-5000

Mechanistic analysis of electron transfer (ET) processes, both in homogeneous solution and at interfaces, remain a major fundamental research goal driven by the need for basic insights into energetics and dynamics pertinent to solar conversion and the behavior of electronic junctions. Aside from the well-known Franck-Condon (FC) control of nonadiabatic ET kinetics for weakly-coupled donor (D) and acceptor(A) sites, the full range of possible ET mechanisms involves tradeoffs among a number of competing electronic and nuclear degrees of freedom (governed by their respective timescales). The latter, including molecular and collective medium modes, may modulate electronic coupling and lead to several types of rate-determining step (rds) in dynamical regimes beyond the simple two-state transition state theory model. Commonly used approximations such as factorization of electonic prefactors and nuclear activation factors, and separability of different types of nuclear modes, become inadequate in many ET situations, especially for cases of wide-amplitude variation of molecular coordinates and rearrangement of bonding in the course of activated ET.

Solvent control of precursor complex formation for bimolecular ET is another example of the role of nuclear modes in controlling the ET mechanism. The paramagnetic [1:1] encounter complex $(\mathrm{TCNE})^{2-\bullet}$ has been established experimentally as the important precursor in the kinetics and mechanism of electron-transfer for the self-exchange between tetracyanoethylene (TCNE) acceptor (A) and its radical-anion as the donor (D). The spectroscopically observed intervalence absorption band of the dimeric $(\mathrm{TCNE})^{2-\bullet}$ has been analyzed with the aid of Mulliken-Hush theory, revealing sizable coupling ($H_{DA} = 1000\ \mathrm{cm}^{-1}$) between the TCNE moieties. Ab initio quantum-mechanical methods as applied to independent theoretical computations of both the reorganization energy and H_{DA} confirm the essential correctness of the Mulliken-Hush formalism for fast electron transfer via strongly coupled donor/acceptor encounter complexes, but imply a significant role of solvent in controlling the encounter geometries, yielding structures appreciably displaced from the face-to-face contact observed in related dianion dimeric crystal structures.

The transfer of electronic charge at interfaces involves a number of specific issues related to the geometrical and electronic structure at the interface, eg, metal-organic interfaces comprised of close-packed monolayer films. Taking the interface associated with a phenylthiolate (PT) film-modified metal electrode interface (111 Au or Cu), we have exploited band structure techniques to examine the interfacial charge redistribution in terms of the charge distributions of the isolated individual components of the interfacial assembly. The results imply aignificant interference effects between direct through-space (TS) and indirect substrate-mediated interactions of adsorbate molecules. A unique feature of the organic thiolate/substrate interface is attributed to the presence of two quasi-degenerate S radical states, leading to large dispersion effects (transverse k components) in partially occupied bands. These special electronic effects are not expected for closed shell 'contact' linker groups such as $-NH_2$ or -NC.

Poster #37

HANGMAN CATALYSTS FOR PHOTO- AND PHOTOELECTROCHEMICAL OXIDATION OF WATER

Daniel G. Nocera

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Massachusetts Institute of Technology, 6-335
Cambridge, MA 02139-4307

The water splitting problem is defined by fundamental steps of:

(1) Assembly of water molecules at a redox cofactor by controlling the secondary coordination sphere
(2) Activation of water by proton-coupled electron transfer (PCET)
(3) Oxygen-oxygen bond formation involving the transfer of four electrons encompassed by atom transfer of oxygen from a metal center

To address these challenges, we have constructed Hangman active sites in which a hydrogen-bond functionality hangs over a redox-active macrocyclic platform. The Hangman constructs allow proton transfer to be coordinated with redox reactions at the metal center for (1) kinetics studies of PCET involving oxygen activation and (2) small molecule catalysis involving oxygen activation. At the metal center of the Hangman, our intent is to generate an oxo of sufficient electrophilicity that it can be attacked by hydroxide. We have established the production of such oxos with the metal salophen, salen and porphyrin constructs. The results of kinetics and catalysis studies at these platforms will be presented.

INTER- AND INTRAMOLECULAR EXCITED STATE ELECTRON TRANSFER DYNAMICS IN POLYPYRIDYL COMPLEXES

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Department of Chemistry, University of North Carolina, Chapel Hill, NC 27599

We have used a combination of time-resolved near infrared (TRNIR) and ultrafast laser spectroscopies to map out the potential energy surfaces for the solvated metal-to-ligand charge transfer (MLCT) excited states of $Os(phen)_3^{2+}$. We have also applied TRNIR to the observation of intervalence transfer in the MLCT excited state of the pyrazine(pz)-bridged complex, $[(bpy)_2ClRu^{III}(pz^{\cdot-})Ru^{II}Cl(bpy)_2]^{2+*}$.

Application of TRNIR to $Os(phen)_3^{2+}$ in CD_3CN, following visible (450 nm) laser flash excitation, reveals an absorption feature at $\nu_{max} = 5460\ cm^{-1}$ ($\varepsilon_{max} \gtrsim 5000\ M^{-1}\ cm^{-1}$, $\Delta\nu_{½} = 1840\ cm^{-1}$) for the MLCT excited state $Os(phen)_3^{2+}$*. Based on an electronic structure model, including spin-orbit coupling, the absorption is tentatively assigned to three overlapping ligand-to-ligand charge transfer (LLCT) bands two of which have $d\pi \rightarrow d\pi$ interconfigurational character *(Figure 1)*. Analysis of the spectra provide a direct measure of the solvent reorganization energy, λ_o. Femtosecond polarization anisotropy spectroscopy has been used to follow interligand electron transfer (ILET) dynamics following MLCT excitation of $Os(bpy)_3^{2+}$ and a mixed ligand analog. ILET takes place on the sub-10 ps timescale in both systems, is solvent and temperature dependent, and is adiabatic occurring between strongly coupled ligands.

The pz-bridged complex is stabilized toward photochemical ligand loss in rigid PMMA films. Following Ru→pz MLCT photoexcitation to give $[(bpy)_2ClRu^{III}(pz^{\cdot-})Ru^{II}Cl(bpy)_2]^{2+*}$, an intervalence transfer (IT) band appears in the near IR with $\nu_{max} = 6880\ cm^{-1}$, $\Delta\nu_{½} = 3740\ cm^{-1}$, and $\varepsilon_{max} \geq 970\ M^{-1}cm^{-1}$. Comparison with near IR measurements for the analogous ground state mixed valence complex, $[(bpy)_2ClRu^{III}(pz)Ru^{II}Cl(bpy)_2]^{3+}$, in CH_3CN allows pz and $pz^{\cdot-}$ to be assessed as bridging ligands. A model has been developed to explain the decrease in IT band energy and width in the rigid medium PMMA compared to CH_3CN.

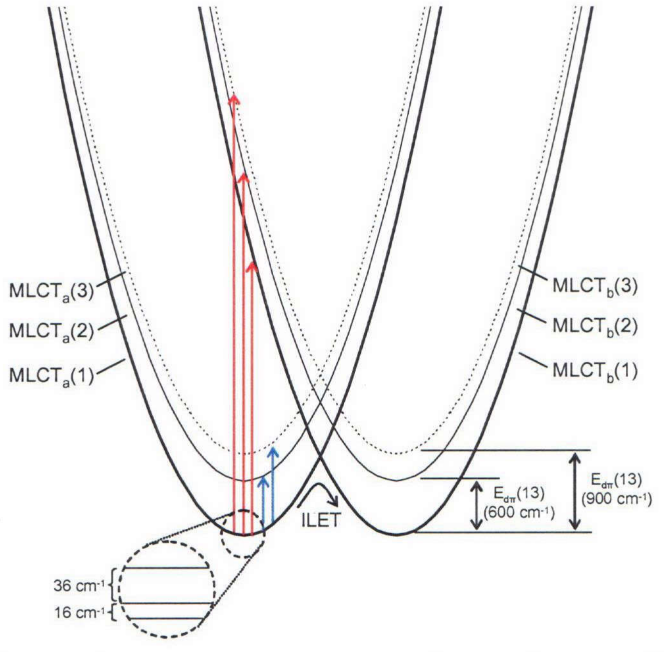

Figure 1: Schematic energy-coordinate diagram for Os(phen)32+* illustrating low lying MLCT excited states, the three LLCT transitions in red, the two inter-configurational $d\pi \rightarrow d\pi$ transitions in blue, and thermally activated interligand electron transfer (ILET).

Poster #39

A COMBINATORIAL METHOD TO IDENTIFY NEW OXIDE MATERIALS FOR THE PHOTOELECTROLYSIS OF WATER

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Hydrogen obtained from renewable energy will be the fuel of choice when fossil fuels become depleted, or when the environmental consequences of burning fossil fuels are no longer acceptable. Direct photoelectrolysis of water using solar energy is the ideal method for producing hydrogen from a renewable, inexpensive and abundant raw material. We strongly believe that semiconducting oxides are the best candidate materials for efficient photoelectrolysis of water. No such oxide material has been identified thus far.

We have employed a combinatorial search strategy using ink jet printing of overlapping gradient patterns of metal oxide precursors onto a conductive glass substrate. We have investigated several oxide precursors for printing including metal nitrates that are soluble in water, can be easily loaded into ink jet cartridges and are easily pyrolyzed into metal oxides at relatively low temperatures. Recently we have been also printing oxometallates, sol gels and oxide nanoparticles. The printed and pyrolyzed thin films are immersed in an aqueous electrolyte and scanned with a visible wavelength laser to detect any photocurrent due to either the photooxidation or photoreduction of water.

Our initial high throughput approach involves screening four metals, three at a time, in triangular patterns that represent the faces of an unfolded tetrahedron (Figure 1A) akin to the pattern used by Mallouk et al for printing mixtures of precious metals for screening as fuel cell catalysts[1]. Figure 2B shows a photograph taken after printing the pattern in 2A twice with Fe, Cu, Nd and Cs and firing the film. Areas showing considerably higher photocurrent, relative to the internal standards, then represent promising new compositions.

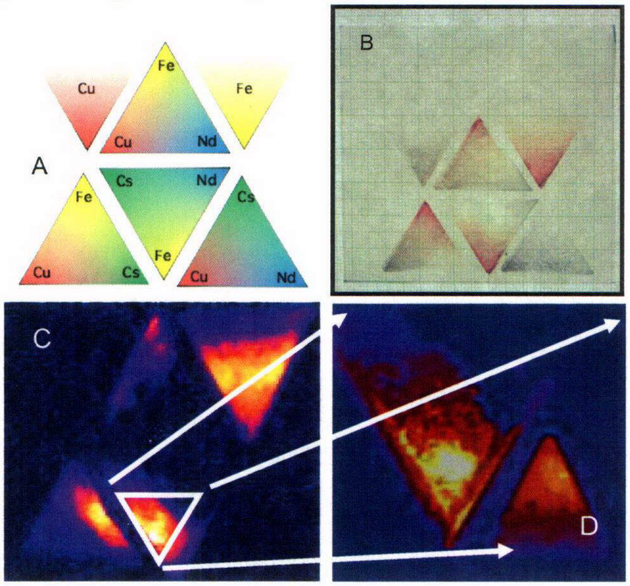

Figure 1. Printing and screening a four-metals-three-at-a-time pattern and a compositional zoom for the Fe-Cs-Nd-Cu system. A. False color template showing the positions and gradients used for printing the four metal precursor solutions. B. Photograph of the printed and fired film. Note the triangular internal standards of α-Fe_2O_3 and CuO (upper right and left respectively) with thickness gradients (bottom to top) that are used as internal standards. C. False color photocurrent image of the film shown in B using 514.5 nm illumination under a 0.5 V bias in 0.5M NaOH solution. D. Photocurrent scan at 514.5 nm of a triangular composition "zoom in" on the brightest area of the Fe-Cs-Nd triangle shown in C that has a maximum IPCE value approximately twice that of the α-Fe_2O_3 internal standard (smaller triangle to the lower right).

We will present our recent results of screening hundreds of new compositions and the physical characterization of the promising oxide phases we have identified.

1. Reddington, E.; Sapienza, A.; Gurau, B.; Viswanathan, R.; Sarangapeni, S.; Smotkin, E. S.; Mallouk, T. E. *Science* **1998**, *280*, 1735.

Poster #40

PHOTOEXCITATION DYNAMICS IN DYE-SENSITIZED SEMICONDUCTORS, CARBON NANOTUBES AND QUANTUM DOTS

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Time-dependent density functional theory for electron-nuclear dynamics is applied to study ultrafast photoinduced dynamics in dye-sensitized TiO_2, quantum dots and carbon nanotubes in real-time and at the atomistic level of detail.

The dye/semiconductor systems derive from the Gratzel solar cell and address the general problems of the organic/inorganic interface that commonly arise in photovoltaics, photochemistry and molecular electronics. The simulation resolves the controversy regarding the origin of the ultrafast ET by showing that ultrafast transfer is possible with both adiabatic and non-adiabatic (NA) mechanisms, depending on the system. The alizarin-TiO2 system constitutes a particularly interesting and novel case. The molecular architecture of the alizarin-TiO2 system permits efficient electron injection into the edge of the TiO_2 conduction band (CB) by the adiabatic mechanism without the energy loss associated with injection high into the CB by the NA process seen in typical Gratzel cell systems. The simulation indicates that the electron is injected from alizarin into a localized surface state within 8 fs and spreads into the bulk on a 100fs or longer timescale. Vibrational motions of the chromophore are particularly important in both generating a nonuniform distribution of photoexcited states and driving the ET process.

Following a photoexcitation between the second van Hove singularities, the electrons and holes in the (7,0) zig-zag carbon nanotube decay to the Fermi level on characteristic subpicosecond timescales. Surprisingly, despite a lower density of states, the electrons relax faster than the holes. The relaxation is primarily mediated by the C-C stretching G-phonons. Hole dynamics are more complex than the electron dynamics. In addition to G-phonons, holes couple to the lower frequency breathing modes and decay over multiple time-scales.

The electron and hole charge carriers in a PbSe quantum dot show slow nearly symmetric relaxation through multiple intermediate states. The relaxation is non-exponential, in agreement with the observed strongly non-Lorentzian spectral line-shapes. Both electrons and holes interact with low frequency phonons. Holes decay only slightly faster than electrons rationalizing the highly efficient carrier multiplication in PbSe nanocrystals reported recently in relation to improved solar power conversion.

Poster #41

BIOINORGANIC HYBRID SYSTEMS FOR LIGHT ENERGY CONVERSION

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Recent progress in understanding the surface structure of TiO_2 nanoparticles enables synthesis and control of the surface sites in differently shaped nanocrystals. The surface structures of the anisotropic nanocrystallites were found to have different reconstructions depending on the curvature of exposed surfaces, and therefore display diverse chemical reactivity of the flat and high curvature regions. Site-selective reactivity of these differently shaped nanoparticles was demonstrated by EPR spectroscopy and microscopy techniques. Paramagnetic Mn^{2+} ions incorporated in anatase lattice at substitution sites were used as probes of the reactivity of bulk and surface atoms. EPR spectroscopy indicates different coupling of Mn ions with electronic states of TiO_2 nanoparticles in the surface and bulk regions. The presence of Mn ions in the bulk region of nanoparticles results in superparamagnetic behavior, while Mn ions doped in the surface layers participate in light excitation, however those trapped deeply in the bulk of nanoparticles do not show any photoactivity. These results suggest that while doping of the bulk region contributes to magnetic properties, doping of the surface region plays an important role in the primary events of charge separation and can be used for tuning the charge separation processes in nanoparticles.

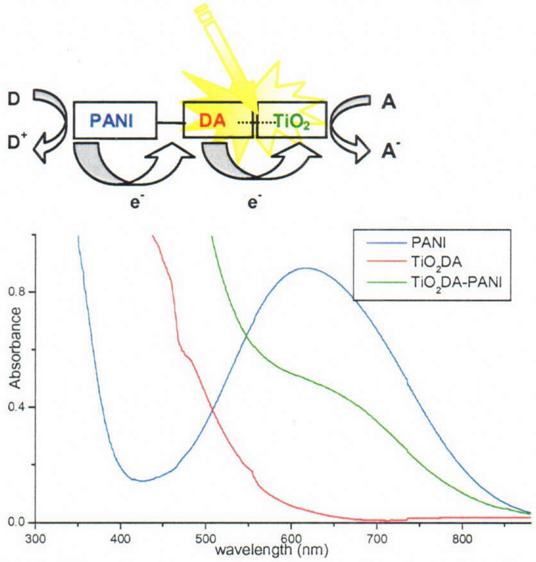

Fig. 1. Charge separation in dopamine functionalized TiO2 nanoparticles linked to polyaniline.

Molecular structure and reactivity of local surface sites associated with corner, edge and high curvature interfaces in nanoparticles were also used for electronic coupling of nanoparticles with electroactive molecules. Manipulation of the surface charge of TiO_2 nanoparticles using surface-active ligands was found to alter the kinetics of chemical reactions. A shift in the Fermi level to more positive potentials was detected for nanoparticles modified with the negatively charged ligand (3,4-dihydrophenylacetic acid) compared to those modified with the positively charged ligand (dopamine). These biolinkers are used as "leads" that bridge the electronic properties of semiconductors to electroactive moieties such as conductive polymers. Therefore, these unique conjugate hybrid systems provide the means for assembling nanoscopic triads capable of performing redox functions at the nanoscale level, depending on the electronic properties of the triad constituents. Covalent coupling of polyaniline through dopamine conductive linkers results in a change of electronic structures of both the TiO_2 nanoparticle and conductive polymer. Upon coupling the absorption band of polyaniline disappears with concomitant appearance of a charge transfer band that improves the optical properties of the TiO_2/dopamine nanoparticle (Fig. 1). The efficiency of extended charge separation in semiconductor triads is correlated to the electronic properties of electroactive materials and the length of bridging bioligands.

TRANSIENT PHOTOCUNDUCTIVITY STUDIES OF EXCITON DISSOCIATION AT CONJUGATED MOLECULE:FULLERENE INTERFACES

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We will report on some studies of the soluble derivative of C_{60}, PCBM, dispersed in thin films of the conjugated polymer, poly (3-hexylthiophene), (P3HT) at varying weight fractions from 0 to 80%. Using both transient microwave conductivity (TRMC) and transient terahertz spectroscopy (TRTP), we will show how the two techniques can be used to probe the kinetics of charge carriers over a range of time scales from picoseconds to milliseconds. We will also report some preliminary studies of a related donor-acceptor heterojunction, where the P3HT is replaced with one of a number of conjugated dendrimers that have been synthesized with the same thiophene repeat unit. Unlike their polymeric counterpart, however, these dendrimers are monodispersed, free of defects and impurities. More importantly, they offer greater control of the molecular electronic structure, enabling a more detailed understanding of the role of the interface in the photoconversion step.

Using the two techniques, the production and loss of both electrons and holes produced by excitons photogenerated in a P3HT film and dissociated at a P3HT:PCBM heterojunction have been followed from <1 ps up to >100 μs as a function of the amount of PCBM dispersed in the polymer matrix. The data will be used to demonstrate the efficiency with which PCBM acts as an electron acceptor, and how the network can be used to extend the lifetime of the charges. The data also show how the presence of the PCBM in the P3HT serves to control the morphology of the polymer, influence the hole transporting properties and ultimately influence the overall control of the photoconversion process. The two photoconductivity techniques of transient microwave conductivity and transient terahertz spectroscopy are complementary. While the former provides good sensitivity and covers a wide temporal range (ns to s); the latter offers higher time-resolution (ps to ns), detects over a wider frequency range (0.1 – 2.5 THz) and can resolve complex conductivity and mobility mechanisms. The P3HT:PCBM data will be used to examine how truly complementary these two techniques are and how the results, specifically carrier mobilities, compare with other techniques.

We will also report results from a study of P3HT deposited onto thin films of magnesium doped Zinc Oxide ($Zn_{1-x}Mg_xO$), which has been used to replace the fullerene as the acceptor. By increasing the fraction, x, of magnesium from 0 to 0.4, the conduction band level can be raised by almost 1 eV, and provides a mechanism of studying the impact of band offset on both the exciton dissociation and the carrier recombination processes. Unlike the fullerene studies, the P3HT and oxide form a simple, planar interface and therefore the importance of polymer morphology is significantly reduced, with the polymer forming a well-ordered film on the oxide surface. We will report TRMC studies of this system and demonstrate the effectiveness of the interface to act as a photoconversion site, and also reveal the impact on electron mobility of inserting magnesium into the zinc oxide lattice.

PHOTOINDUCED ELECTRON TRANSFER REACTIONS OF Pt(II) TERPYRIDYL COMPLEXES

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In a recent publication, Tung and Wu demonstrated that a group of Pt(II) terpyridyl acetylide complexes yield hydrogen upon photolysis in the presence of dihydropyridines.[1] In addition, others have demonstrated that this class of Pt(II) complexes have excited state behavior that is strongly dependent on terpyridyl substitution and the nature of the fourth ligand. The mechanism of hydrogen production was postulated to involve H atom abstraction from the dihydropyridine by the Pt(II) complex excited state. Our efforts in this area have been to use time resolved absorption and emission spectroscopy to investigate the nature of the excited state of a group of these complexes and to explore formation and decay of photoproducts formed in the presence of reductive quenchers.

Excited state behavior of four complexes was examined in detail : $[(DMAtpy)Pt(II)Cl]^+$, $[(mpt)PtCCPhCl]^+$, $[(mpt)PtCCPhOMe]^+$ and $[(mpt)PtCCPhMe]^+$ (DMAtpy = 4'-dimethy lamino-2,2'6',2"-terpyridine; mpt = 4'-(p- methylphenyl) 2,2',6',2"-terpyridine). Excited state lifetimes, emission maxima and emission quantum yields were strongly dependent on both the terpyridyl substituent and the phenylacetylide substituent.

The photoredox reactions of $[(DMAtpy)PtCl]^+$ and $[(mpt)PtCCPhCl]^+$ with a variety of reductive electron transfer quenchers was also examined. With quenchers such as N-methylphenothiazine and triethylamine, excited state quenching rate constants were in excess of 10^9 $M^{-1}s^{-1}$ and laser flash photolysis indicated that single electron transfer products were formed.[2] When dihydropyridines, potential H atom donors, were used as quenchers, transient absorption spectra provided evidence that the species formed were the result of electron transfer quenching of the excited state of the Pt complex. The results suggest that formation of the Pt hydrido intermediate in H_2 production with dihydropyridine quenchers involves protonation of the one electron reduced species formed in the excited state reaction.

References

(1) Tung, C.-H et. al. *J. Am. Chem. Soc.* **2004**, 126, 3440-3441.
(2) Prabhu, R. N.; Hester, H.; Schmehl, R. H. *Inorg. Chem.*, in press.

Poster #44

A NEW FAMILY OF RUTHENIUM COMPLEXES FOR WATER OXIDATION

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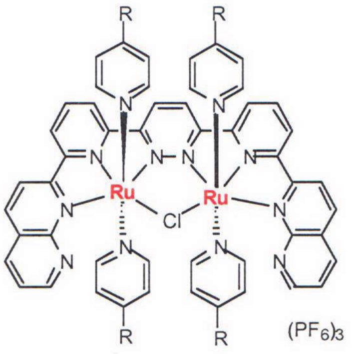
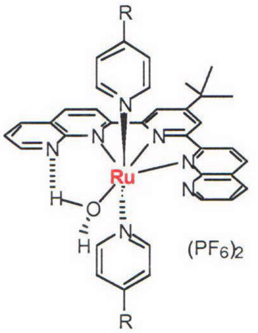
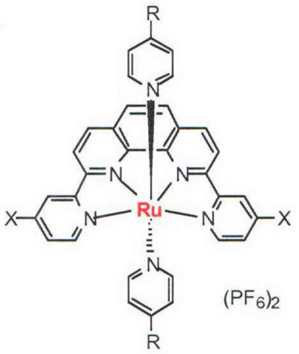
A bis-tridentate bridging ligand has been designed to hold two metal centers in close proximity. When this ligand is combined with $Ru(DMSO)_4Cl_2$ and excess 4-substituted pyridine in the presence of triethylamine, the complexes **1a-e** assemble in yields of 44-56%. The addition of these catalysts to an aqueous solution of $Ce(IV)\text{-}CF_3SO_3H$ (pH = 1.0), results in copious oxygen evolution. The highest catalyst turnover (TN ≈ 3200) is observed for **1b**. When the axial ligand is N-methylimidazole, no oxygen is evolved. The series of mononuclear complexes **2a-c** was prepared to evaluate the importance of dinuclear coordination. Surprisingly, these systems also generate oxygen with modest efficiency (TN ≈ 580 for **2b**). Utilizing a series of 2,9-di(pyrid-2'-yl)-1,10-phenanthrolines as tetradentate ligands, the coordinatively saturated complexes **3a** were prepared and were likewise effective in catalyzing water decomposition. Variations in the equatorial ligand together with a careful analysis of the photophysical and electrochemical properties of these systems are aimed at understanding and optimizing their performance. Several of the catalysts have been anchored to TiO_2 in an effort to drive the oxidation process with light.



1a R = NMe_2 (56%)
b R = CH_3 (44%)
c R = CF_3 (44%)
d R = OCH_3 (43%)
e R = C_6H_5 (27%)
f R = *t*-butyl (20%)



2a R = NMe_2 (59%)
b R = CH_3 (50%)
c R = CF_3 (19%)
d R = OH (30%)
e R = CN (11%)



3a R = NMe_2, X = H
b R = CH_3, X = H
c R = CF_3, X = H
d R = CH_3, X = NMe_2
e R = CH_3, X = CH_3
f R = CH_3, X = CO_2Et

Poster #45

EVALUATION OF NONCONJUGATED DENDRITIC ARCHITECTURES FOR ENERGY AND CHARGE TRANSFER

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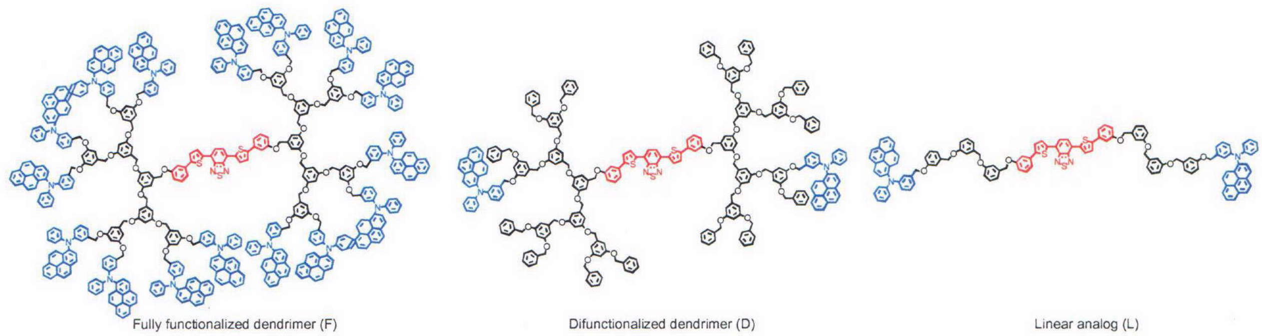
Multichromophore dendrimers provide the ability to surround a single energy acceptor with a dense periphery of energy donors. These types of structures are of interest as artificial light-harvesting systems for use in solar energy conversion devices. Both conjugated and non-conjugated dendrimers have been extensively studied for this purpose. Light harvesting represents only the first step in the photosynthetic process, which also involves the creation of a long-lived charge-separated state, in order to convert photon energy into an electrochemical potential. There has been a relatively number of limited reports on charge transfer within dendritic architectures. Recently, we have reported a system that combines both electronic energy transfer (EET) and charge transfer (CT) events sequentially within the same dendrimer. Using these dendrimers, it is interesting to be able to gain fundamental insights in to the possible advantages that dendritic architectures provide for intramolecular EET and CT processes by comparing dendrimers with the corresponding linear analogs. This comparison in light harvesting dendrimers is more complicated. Classical dendrimers with periphery fully decorated by donor moieties and a single acceptor unit at the core are represented by **F** in the Figure. Comparison of **F** with the linear analog **L** accounts for the donor-acceptor distance that dendrimers and the linear oligomers provides, but fails to provide the equivalent chromophore densities (number of EET/CT donors *vs.* acceptor). However, comparison of the dendrimer **D** with a difunctionalized periphery with the linear analog **L** accounts for both these factors. In other words, comparison of **D** and **L** eliminates the chromophore density variable and directly addresses the advantages of dendritic scaffold in light harvesting. On the other hand, comparison of **F** and **D** provide information on the advantages of chromophore density in dendrimers. We have used time-resolved fluorescence experiments on these three families of molecules to carry out this systematic structure-property relationship study. This poster will outline the results of these studies, which outline the advantages that dendrimers provide in EET and CT properties.



Fully functionalized dendrimer (F)

Difunctionalized dendrimer (D)

Linear analog (L)

Figure. Examples of fully functionalized, difunctionalized dendrimers and the corresponding linear analogs. Triarylamines at the periphery are energy and electron donors. The benzthiadiazole core is the energy and electron acceptor.

X-RAY DIFFRACTION “FINGERPRINTING” FOR QUANTITATIVE EVALUATION OF COORDINATE MODELS FOR SOLUTION STATE SUPRAMOLECULAR STRUCTURE AND DYNAMICS

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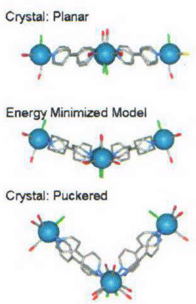
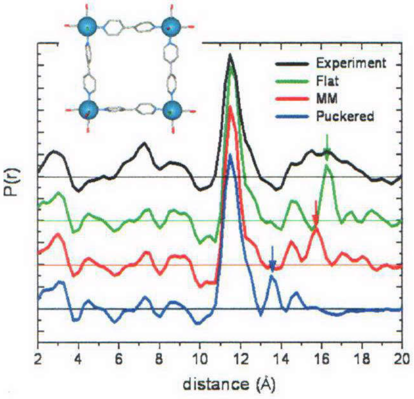
Advances in synchrotron x-ray scattering techniques offer new opportunities for characterization of photosynthetic supramolecular structures and dynamics in non-crystalline media that build upon crystallographic, NMR, and molecular dynamics (MD) databases, but are applied to conditions relevant to *in-situ* solar function. Advances include extension to the high-angle domain where measurements can be routinely made to a spatial resolution of 1 Å, and the development of coordinate-based analyses that allows scattering data to be quantitatively analyzed in terms of atomic models for structure and dynamics. Fourier transforms of coordinate data are used to produce reciprocal space ‘‘fingerprints’’ of atomic pair distance correlations that are characteristic of the ensemble and are the direct numerical analogues of solution x-ray diffraction (SXD) experiments. We present applications on two supramolecular systems: DNA that serves as a model for a π-stacked framework for long-range electron transfer, and Re-cornered molecular squares that serve as prototype hosts designed for catalysis and solar energy conversion

For several DNA sequences a series of crystallographic, NMR, and MD structures are available. SXD experiments are found to discriminate between these different models and identify the best-fit structure. MD simulations analyzed in terms of SXD fingerprints are shown to deviate from experiment, most significantly for poly(A)-poly(T) duplex DNA. MD simulation shortcomings were found to include both mismatches in simulated conformer structures and number population within the ensembles. This work demonstrates an experimental approach for quantitatively evaluating MD simulations for a range of *in situ* applications.

Re molecular squares have been crystallized in planar and puckered conformations and have been analyzed by molecular energy minimization. The different molecular square conformations are distinguished by differing diagonal Re-Re pair distances. SXD experiments and atomic pair distribution function (PDF) analyses have resolved both the pair-distances along the sides and diagonals of the molecule. The experiments show that unlike the sides, the Re-Re diagonal distances are configurationally broadened, consistent with a “butterfly” motion of ~ 20° in the Re dihedral angle. These results demonstrate the opportunity to use SXD measurements for quantitative analysis of dynamic solution state ensembles, and set the stage for extension to the ps time domain.





HIGH-FREQUENCY EPR OF PROTEIN-COFACTOR SITES INVOLVED IN PHOTOSYNTHETIC ELECTRON TRANSFER

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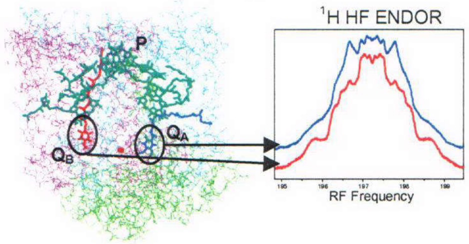
The experimental determination of the local protein-cofactor interactions that fine-tune electron transfer reactions and couple these reactions with secondary reactions, such as proton transfer, remains a challenge. To address this challenge, we have developed new methodologies that utilize both specialized "spin-edited" samples (i.e., samples that involve both isotopic labeling and intrinsic paramagnetic metal ion extraction or replacement) and high-frequency (HF) pulsed electron paramagnetic resonance (EPR) techniques. These approaches allow us to directly probe the details of electron donor-acceptor geometry variations by measuring electron spin-spin interactions, and allow us to investigate the details of the unpaired electron environments by measuring electron spin-nuclear hyperfine couplings. We have applied these methods to investigate local protein environments involved in photosynthetic electron transfer. In photosynthetic bacteria, light-initiated reactions occur in integral membrane proteins called reaction centers (RCs). Following photoexcitation of a bacteriochlorophyll dimer, P, the electron is transferred through one set of cofactors terminating in the electron transfer between two quinone molecules, Q_A and Q_B.

The heterogeneous kinetics, temperature trends, and pH dependencies of the $Q_A^-Q_B \rightarrow Q_AQ_B^-$ reaction show that this interquinone electron transfer in isolated RCs is intimately linked to a complex conformational landscape. Observed alterations of reaction kinetics by illumination while cooling have been linked to trapping the RC in altered conformations induced by charge separation. We have initiated a detailed spectroscopic study of the heterogeneous polypeptide environments surrounding the redox cofactor site Q_B to explore the physical basis for the dramatic variation in low temperature $Q_A^-Q_B \rightarrow Q_AQ_B^-$ electron transfer. HF pulsed D-band (130 GHz) matrix electron nuclear double resonance (ENDOR) was applied to directly look for differences in the protein environments surrounding the quinones in "active" vs. "inactive" conformations with respect to electron transfer. No structural differences in the protein structure near Q_B^- or reorientation (within 5°) of Q_B^- was observed for HF ENDOR spectra of "active" and "inactive" $P^+Q_B^-$ states. These results reveal a remarkably enforced local protein environment for Q_B in its reduced semiquinone state and suggest that the conformational change that controls reactivity resides beyond the Q_B local environment. Future studies will include application of these HF matrix ENDOR techniques to investigate local protein structures and electron-transfer induced changes in protein structure near other active radical centers in the bacterial RC, Photosystem I and Photosystem II.



Poster #48

SYNTHESIS OF DISCOTIC LIQUID CRYSTALLINE SILSESQUIOXANES

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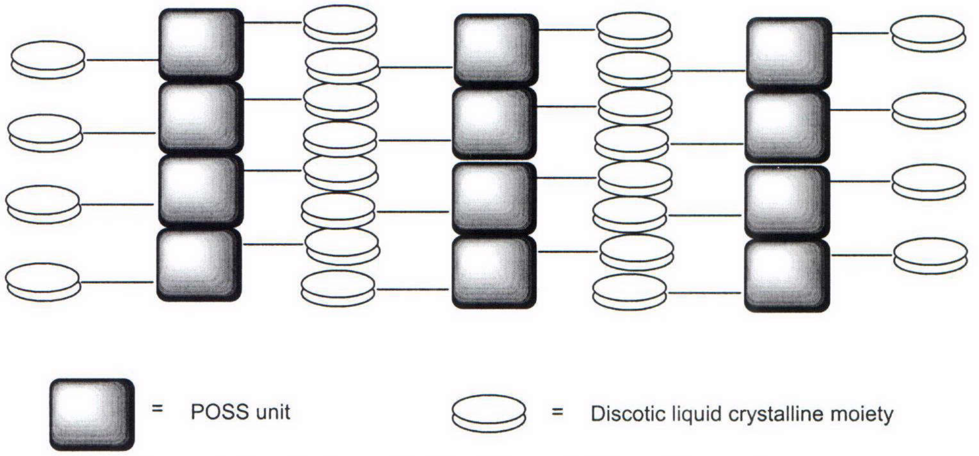
Polyhedral oligomeric silsesquioxanes (POSS) are a class of cage macromolecules with diameters ranging between 1 and 3 nm, depending on the number of silicon atoms in the central cubic cage and on the peripheral substitution groups surrounding the core. A cubic T_8 silsesquioxane unit has a rigid inorganic (silica) core comprised of Si_8O_{12} surrounded by surface hydroxyl groups or chemically bound organic groups. POSS have been recognized as well-defined building blocks for nano-structured materials and organic/inorganic hybrids. Many linear polymers containing POSS groups bound to the main or side chains or at the core of star branched dendrimers have been prepared. Recently, specially designed POSS were found to have the ability to form ordered structures via supramolecular self-assembly: POSS units grafted to polymer chains aggregate into a closely packed crystalline lattice, in which the attached polymer chains forced crystallization into a two-dimensional raftlike structure. Octakis(3-aminopropyl)-silsesquioxane could be assembled layer-by-layer onto a planar support, forming organic-inorganic composite multilayers of well-defined morphology.

In our search for photoresponsive organic-inorganic hybrids, we have focused on liquid crystalline molecules that can self-assemble into highly ordered structures. Two-dimensional polymeric molecules have been prepared via formation of a smectic phase derived from specially designed chiral monomers that pack into rod-like liquid crystals. Discotic monomers can self-assemble into a columnar mesophase through face to face π stacking of the aromatic core. When a discotic liquid is grafted on to a cubic silsesquioxane unit, an ordered organic-inorganic structure is formed through supramolecular interactions. In this work, we describe the synthesis of discotic liquid crystalline silsesquioxanes, their supramolecular structures, and their light responsiveness.



Expected ordering of a liquid crystalline silsesquioxane

Poster #49

COORDINATE-BASED SOLUTION X-RAY SCATTERING ANALYSES FOR SUPRAMOLECULAR SYSTEMS

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Self-assembling supramolecular materials are increasingly being designed for applications in solar energy conversion and storage. The dynamic features of these molecular materials make in-situ structural characterization a critical challenge. Our early studies have demonstrated that wide-angle solution X-ray scattering (WAXS) is a powerful, discriminating, high-throughput technique for in-situ supramolecular structural characterization that can be applied with 100 ps time resolution for mapping structural dynamics along excited state reaction coordinates.. In order to accelerate WAXS data analysis, we have generated a computer program package, *molX* (Solution ***mol****ecular* ***X****-ray Scattering*), which can predict normal and anomalous WAXS and pair distance distribution function (PDDF) for supramolecular system from its coordinates.

With the aid of this program, we can distinguish real structural information from artifacts in data processing, determine molecular structures from WAXS measurements, and study the solvation of supramolecules. For example, as shown in Fig. 1, comparing with the calculated PDDF of γ-cyclodextrin (γ-CD), we found that 6-Å spatial resolution X-ray scattering measurements cannot provide accurate structural information for γ-CD by completely losing the CD height peak and significantly shifting other distance correlation peaks. However, 1-Å resolution scattering reproduces the theoretical prediction very well while the difference between them partially represents the solvation for γ-CD. In addition, *molX* also helps interpret the different behaviors of CDs observed in various solvents.

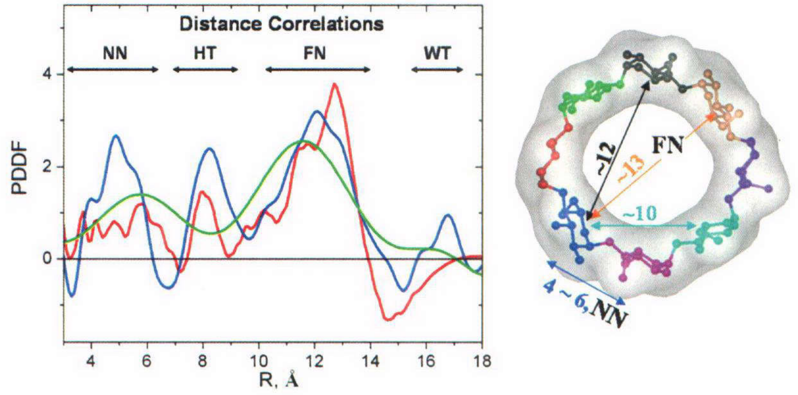

Fig. 1. Experimental PDDF at spatial resolutions of 6.0 Å (green) and 1.0 Å (blue) for γ-CD in water and calculated PDDF (red) from the right model structure, and contributions from structural unit correlations, e.g., nearest neighbors (NN), far neighbors (FN), height (HT) and water shell (WT) in solution phase γ-CD.

Anomalous X-ray scattering provides additional structural data for metallic supramolecules. *molX* can predict anomalous WAXS and PDDF patterns at various energies around the X-ray absorption edges, which were used to guide anomalous scattering data analyses. This approach was applied in structural determinations of metallic complexes designed for solar energy conversion and catalysts, for example, Re bipyridyl molecular squares and metallic porphyrin assemblies.

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