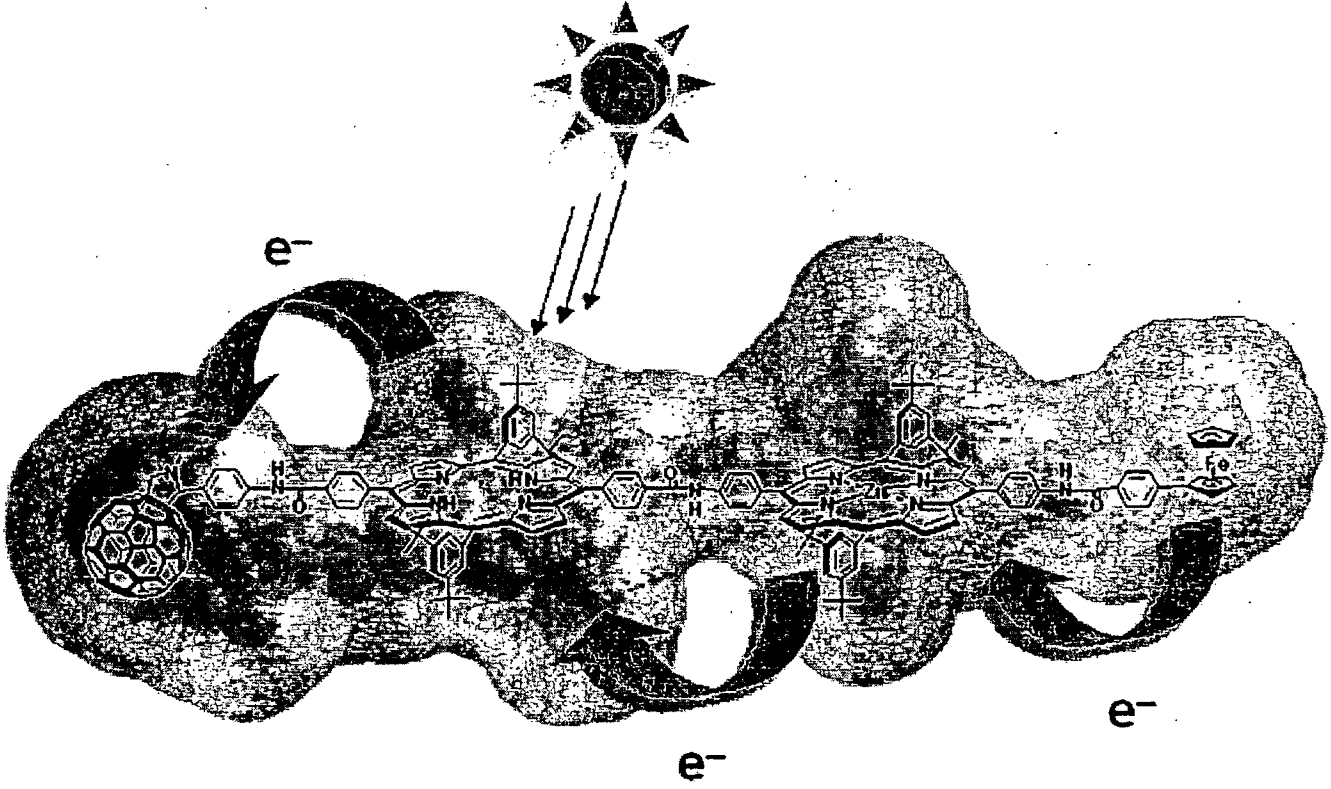
Proceedings of the
Twenty-Fifth DOE Solar Photochemistry Research Conference



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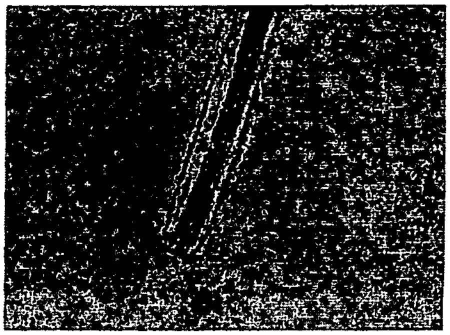
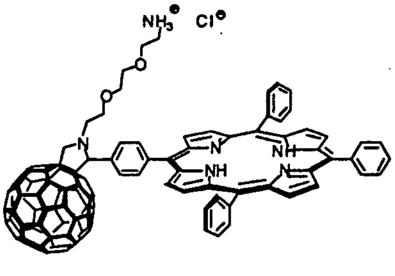


Held at
Airlie Conference Center
Warrenton, Virginia
June 9-12, 2002



Cover Graphics

The figure in the center of the cover portrays light absorption by a fullerene-freebaseporphyrin-zincporphyrin-ferrocene (C_{60}-H_2P-ZnP-Fc) tetrad. The cascade of multielectron electron transfer events evolves from the singlet excited state of $^{1*}H_2P$ to a final charge separated state, $C_{60}^{\bullet -}$-H_2P-ZnP-Fc^+, which has a remarkably long lifetime of 0.38 seconds and is formed with a quantum yield of 0.24. 54 % (~1.1 eV) of the initial excited state energy is stored. The transmission electron microscopy image (250 x 190 nm) at the lower right shows a nanotubule formed by the fullerene-freebaseporphyrin (C_{60}-H_2P) dyad depicted at the lower center.

(Dirk Guldi, Notre Dame Radiation Laboratory)

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FOREWORD

The 25th Department of Energy (DOE) Solar Photochemistry Research Conference, sponsored by the Chemical Sciences, Geosciences and Biosciences Division of the Office of Basic Energy Sciences, is being held June 9-12, 2002, at the Airlie Conference Center, in Warrenton, Virginia. The purpose of the meeting is to foster collaboration, cooperation, and exchange of ideas among DOE grantees and contractors who are engaged in fundamental research on solar photochemical energy conversion. These proceedings include the program, a list of participants, and abstracts of the formal presentations and posters presented at the conference.

The DOE solar photochemistry research program emphasizes fundamental processes aimed at the capture and conversion of solar energy. Photoelectrochemical and molecular based biomimetic systems are explored with the goal of providing the knowledge needed for development of future energy technologies. Biomimetic models seek to mimic the key aspects of photosynthesis - antenna, reaction center, catalytic cycles, and product separation. The program encompasses organic and inorganic photochemistry, photoinduced electron and energy transfer, photoelectrochemistry, biophysical aspects of photosynthesis, and molecular assemblies for artificial photosynthesis. In the past year, a number of projects have been added to the program as a result of new awards by the Office of Basic Energy Sciences in nanoscale science, engineering, and technology. Thus, there should be apparent at this conference an increased level of activity in research that employs the distinctive properties of matter at the nanoscale.

Our special guest plenary lecturer is Professor Frans De Schryver of the Catholic University of Leuven, Belgium, who will discuss energy dissipation in dendritic structures. The topical sessions that follow will address charge separation in molecular model systems; charge separation in homogeneous solution; photoelectrochemistry; photosynthetic membranes, reaction centers, and light harvesting; and characterization and reactions of excited states. The program also features a keynote lecture by Professor Nathan Lewis of the California Institute of Technology on challenges in development of renewable energy technologies. In this volume may be found the program, abstracts of the 25 formal presentations, 46 poster abstracts, and an address list for the 85 participants.

Special thanks are due to the staff of the Airlie Conference Center for their hospitality, and to Rachel Smith and Andreene Witt of the Oak Ridge Institute of Science and Education for logistics support and for preparation of this volume. The real success will be due to interactions among all of the participants that will make the conference a stimulating and rewarding experience.

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

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Poster Sessions

Program

25th DOE SOLAR PHOTOCHEMISTRY RESEARCH CONFERENCE

June 9-12, 2002

Airlie Conference Center
Warrenton, Virginia

PROGRAM

Sunday, June 9

4:00 - 9:00 p.m.	Registration, Garden Room
5:00 - 7:00 p.m.	Reception, Roof Terrace
7:00 - 8:00 p.m.	Buffet Dinner
8:00 - 11:30 p.m.	Reception, Roof Terrace

Monday Morning, June 10

7:30 - 8:30 a.m. Registration

SESSION I
Plenary Session
Mary E. Gress, Chairman

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

8:45 a.m. **Plenary Lecture:** Energy Dissipation in Dendrimers
Frans C. De Schryver, Katholieke Universiteit Leuven, Belgium

9:45 a.m. Coffee Break

SESSION II
Charge Separation in Molecular Model Systems
Frederick D. Lewis, Chairman

10:15 a.m. Chromophore-Laden Dendrimers as Highly Absorptive, Multielectron Redox Centers
Marye Anne Fox, North Carolina State University

10:45 a.m. Dynamic Structural Studies of Light-Induced Charge Transfer in Molecular Systems
Joseph T. Hupp, Northwestern University

11:15 a.m. Towards Long-Lived Charge Separation in C_{60}-Based Donor-Acceptor Ensembles
Dirk M. Guldi, Radiation Laboratory, University of Notre Dame

<u>Monday Afternoon, June 10</u>

1:30 p.m. Magnetic Resonance and Electron Transfer Studies of Carotenoids
Lowell D. Kispert, The University of Alabama

2:00 p.m. Molecular Orbital Symmetry Effects in Donor-Acceptor Systems Linked by Cage Molecules and Heteroatoms
Piotr Piotrowiak, Rutgers University

2:30 p.m. Coffee Break

SESSION III

Charge Separation in Homogeneous Solution

Kenneth B. Eisenthal, Chairman

3:00 p.m. Photoinduced Dipoles and Charge Separation in Condensed Media
Charles L. Braun, Dartmouth College

3:30 p.m. Hydrogen Bond Dynamics in Hydrogen Bonding Liquids Probed with Ultrafast Infrared Experiments
Michael D. Fayer, Stanford University

<u>Monday Evening, June 10</u>

SESSION IV

7:30 p.m. **Keynote Lecture:** Challenges for the Chemical Sciences in Development of Renewable Energy Technology
Nathan S. Lewis, California Institute of Technology

8:30 p.m. Posters (Odd numbers), Meadow Room

<u>Tuesday Morning, June 11</u>

SESSION V

Photoelectrochemistry

Gerald J. Meyer, Chairman

8:30 a.m. Doping Processes and Photoconversion Mechanisms in Organic Semiconductor Films
Brian A. Gregg, National Renewable Energy Laboratory

9:00 a.m. Studies of High Quantum Yield Sensitization Processes at Semiconductor Electrodes
Bruce A. Parkinson, Colorado State University

9:30 a.m. Theoretical Studies of Electron Transfer and Optical Spectroscopy in Complex Molecules
Richard A. Friesner, Columbia University

10:00 a.m. Coffee Break

10:30 a.m. Carrier Dynamics in Quantum Dots and Quantum Dot Arrays and Their Role in Solar Photon Conversion
Arthur J. Nozik, National Renewable Energy Laboratory

11:00 a.m. Electron and Hole Dynamics in Layered Semiconductor Nanoparticles
David F. Kelley, Kansas State University

11:30 a.m. Semiconductor-Based Nanocomposites: Preparation, Properties, and Performance
Krishnan Rajeshwar, The Univeristy of Texas at Arlington

12:00 a.m. Photocatalysis and Photoelectrochemistry Using Inorganic Colloids and Nanocrystals
Thomas E. Mallouk, The Pennsylvania State University

Tuesday Afternoon, June 11

SESSION VI

1:30 p.m. Posters (Even numbers), Meadow Room

Tuesday Evening, June 11

6:00 p.m. Barbecue at the Smokehouse

Wednesday Morning, June 12

SESSION VII

Photosynthetic Membranes, Reaction Centers, and Light Harvesting

Graham R. Fleming, Chairman

8:30 a.m. Light-Powered Ca^{++} Transport by an Artificial Photosynthetic Membrane
Devens Gust, Arizona State University

9:00 a.m. Design and Fabrication of Optimal Near-Field Optical Probes for Imaging Photosynthetic Membranes
X. Sunney Xie, Harvard University

9:30 a.m. Bridging the Gap between Molecular Models and Photosynthetic Function
David M. Tiede, Argonne National Laboratory

10:00 a.m. Coffee Break

10:30 a.m. Metal Ion Modulated Electron Transfer in Photosynthetic Bacterial Reaction Centers
Lisa M. Utschig, Argonne National Laboratory

11:00 a.m. Polarized NMR Spectra from Photosynthetic Reaction Centers: Mechanism and Interpretation
Ann E. McDermott, Columbia University

11:30 a.m. Electron Transfer Pathways and Structure of Charge Separated States in the Photosynthetic Reaction Centers as Studied by High-Frequency EPR Spectroscopy
Oleg G. Poluektov, Argonne National Laboratory

Wednesday Afternoon, June 12

SESSION VIII

Characterization and Reactions of Excited States

Guillermo J. Ferraudi, Chairman

1:30 p.m. Photodriven Chemical Reactions of Metal Complexes Involving CO_2, H_2, H^+, CO, and N_2
Etsuko Fujita, Brookhaven National Laboratory

2:00 p.m. Electron-Transfer and Spectroscopic Behavior of Multi-Transition Metal Donor-Acceptor Complexes
John F. Endicott, Wayne State University

2:30 p.m. Electroabsorption Studies of the MLCT Transition in Transition Metal Complexes
Bruce S. Brunschwig, Brookhaven National Laboratory

3:00 p.m. Closing Remarks
Mary E. Gress, U.S. Department of Energy

Session I

Plenary Session

ENERGY DISSIPATION IN DENDRIMERS

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To an increasing extent coupling of photophysical and photochemical techniques to microscopy has allowed to obtain information heterogeneous organic and bioorganic and macromolecular systems by mapping their spectral and (photo) chemical properties.
In this contribution photophysical properties of in particular dendritic structures eventually containing either a single central chromophore or decorated with chromophores at the rim and presented in Figure 1 will be addressed. The single molecule results will be complemented with ensemble measurements (1). The importance of the substitution pattern and the size of the dendrimer generation will be illustrated using these rigid dendrimer core scaffolds.

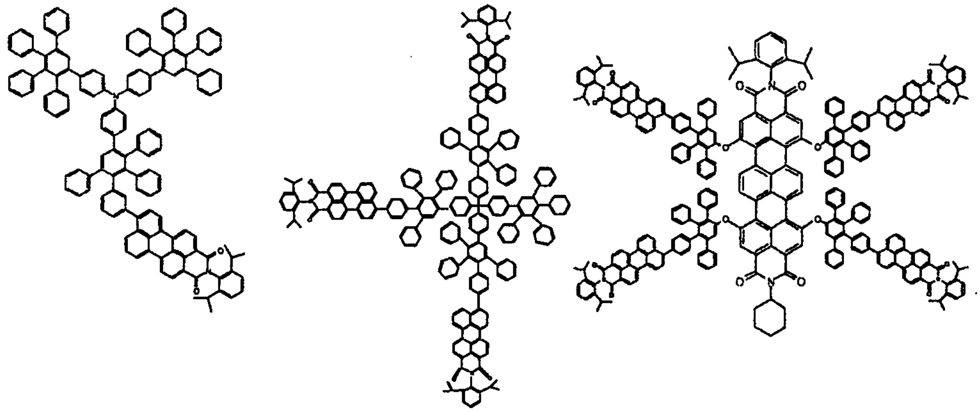

Figure 1. Dendritic structures

The energy dissipation processes including annihilation, energy hopping , energy transfer and electron transfer at the ensemble and single molecule level will be discussed.
One of the most intriguing findings at the single molecule level was the presence of collective on/off jumps in the fluorescence intensity traces of the dendrimers (2). This phenomenon can be explained by assuming both a radiative trap (energetic lowest chromophoric site) and a non-radiative trap (triplet state of one chromophore) within the individual dendrimers. It was shown that a similar scheme can explain the collective on/off jumps in the fluorescence intensity traces of biologically important systems. A first example of single electron transfer of a single molecule will be presented.

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Session II

Charge Separation in Molecular Model Systems

CHROMOPHORE-LADEN DENDRIMERS AS HIGHLY ABSORPTIVE, MULTIELECTRON REDOX CENTERS

Marye Anne Fox, James K. Whitesell , Tarek H. Ghaddar, James F. Wishart, and David W. Thompson

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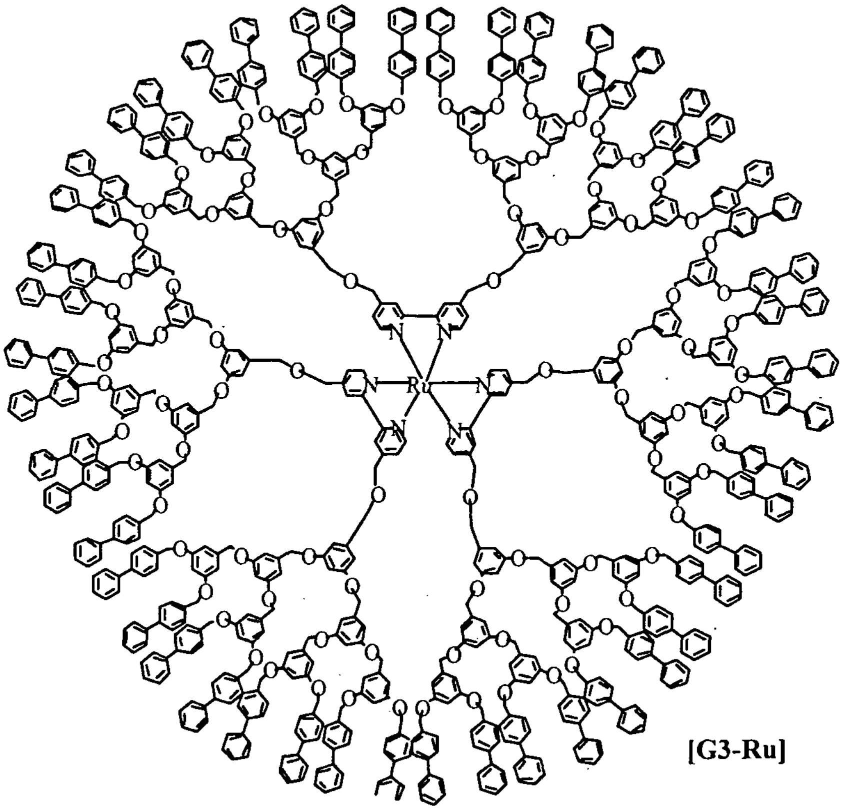
Electron transfer (ET) is a key reaction in most natural photosynthetic systems. These reactions are usually driven by an absorbed photon in which sunlight is converted into chemical energy by successive ETs to a precisely positioned chemical redox site. The primary reaction is charge separation, ultimately driving proton pumping and creating an electrochemical potential across a photosynthetic membrane. The first critical electron transfer reaction is initiated by light harvested in a complex array of antenna pigments. The excitation energy then migrates by energy transfer to a primary electron donor with near unit efficiency. In complex reaction centers, the excited donor transfers an electron to the acceptor. The accumulation of the separated charges required for multielectron redox reactions (as in the reduction of carbon dioxide or the oxidation of water) then ensue in subsequent chemical steps. Since multi-photon processes are important in several emerging applications, such as fluorescence microscopic imaging and optical data storage and microfabrication, their demonstration within a well-characterized model establishes a link between fundamental studies of biological electron transfer and these exciting new applications.

Many synthetic model systems have been proposed as vehicles to understand the fundamental structural parameters governing electron transfer. Models employing a donor D separated from an acceptor A by a spacer S of variable length and chemical composition (**D – S – A**) have provided invaluable information about the effects of distance, energetics, orientation, and local solvation on the rates of intramolecular electron transfer. Systems with multiple donors (D1, D2, etc.) and/or multiple acceptors (A1, A2, etc.) have similarly provided arrays in which multiple hops separate charges over even longer distances, e.g., $\mathbf{D1^+ - S - D2 - S - A1 - S - A2^-}$. The nanoscale equivalents of these multiple hop arrays are block polymers for donor-acceptor gradients arrayed in one-dimension, thin films in two-dimensions, and concentric spheres (sometime called 'quantum onions') in three-dimensions. In the last two years, we have synthesized and studied several new dendrimers with redox active cores and highly functionalized peripheries bearing multiple absorptive chromophores. As models for nanoscaled, roughly spherical arrays, we have shown these molecules to exhibit interesting properties distinct from the individual component of the array. Among their most interesting features is their ability to sustain multiple electron transfers over relatively long times.

Functionalized dendrimers provide an architectural framework on which relatively large numbers of chromophores can be chemically bound within a single molecule. Thus, they represent interesting systems in which multi-electron events might reasonably be expected to derive from near-concurrent multiple excitations that can take place in the array of linked chromophores, even at low incident light intensities. Recently, dendrimers with redox cores and/or absorptive periphery-bound chromophores have been studied as models, but to our knowledge no demonstration of multiple ET from multi-photon absorption has been achieved. For some time, we have been interested in studying such electron transfer centers and exploring their utility in chemical catalysis. Here we report the first observation of electron transfer derived from multiple photon absorptions within a chromophore-laden synthetic dendrimer containing a viologen core marker that serves as an electron trap.

Electron transfer reactions in Frechet-type dendrimers with biphenyl peripheral groups and a ruthenium core were investigated by pulse radiolysis techniques. Second and third generation ruthenium dendrimers (for example, **G3-Ru**) were prepared by the complexation of ruthenium trichloride and the respective bipyridine ligand. Pulse radiolysis by 30 ps pulses of 8 MeV electrons of the resulting dendrimers in THF produced electron adducts. The edge-to-edge distances between the biphenyl groups and the bipyridine were estimated from molecular mechanics calculations to be about 14 and 18 A in the two dendrimers with a 14 and a 19 bond separation, respectively, as the shortest distance between the biphenyl peripheral groups and the ruthenium core.



[G3-Ru]

The reaction kinetics were measured by monitoring the transient absorption of the reactants between 350 nm and 1050 nm. Small differences in rates between dendrimers of succeeding generations may be the result of the restricted geometry of the biphenyl groups within the dendrimer, or may reflect small contributions from exciplex formation between the adjacent biphenyl groups. The observed rates are consistent with a very fast electron transfer from an initially produced biphenyl anion to the ruthenium tris-bipyridine core. Fast electron transfer rates found in the two ruthenium dendrimers suggest a very efficient electronic coupling between the peripheral donor groups and the core acceptor.

In a second set of functionalized dendrimers, paired electron transfers (ET) induced by the absorption of two photons by a synthetic dendrimers are observed in first, second, and third generation dendrimers comprised of a viologen-like core and an array of naphthalene peripheral groups. Flash photolysis and transient absorption techniques show that the yield of photoinduced double ET depends on laser intensity in the two largest dendrimers. Their photochemical behavior thus requires an unusual multi-photon kinetic scheme. These dendrimers constitute the first synthetic models capable of multiple electron redox events deriving from a defined molecular architecture, thus mimicking natural light-collecting antenna systems.

LIST OF DOE–SPONSORED PUBLICATIONS 2000-2001

"Competitive Photochemical Reactivity in a Self-Assembled Monolayer on a Colloidal Gold Cluster," Jun Hu, Fang Liu, Jian Zhang, Kevin Kittredge, James K. Whitesell, and Marye Anne Fox, *J. Am. Chem. Soc.* **2001**, *123*, 1464.

"Photoreactivity of Self-assembled Monolayers of Azobenzene or Stilbene Derivatives Capped on Colloidal Gold Clusters," Jian Zhang, James K. Whitesell, and Marye Anne Fox, *Chem. Mater.* **2001**, *13* , 2323.

"Photophysical Quenching and Photocurrent Effects Mediated by Guanine in Pyrene End-labeled Oligonucleotides," Eran Zahavy, Scott Reese, and Marye Anne Fox, *J. Biol. Chem. Lumines. Spectr.* **2000**, *15*, 75.

DYNAMIC STRUCTURAL STUDIES OF LIGHT-INDUCED CHARGE TRANSFER IN MOLECULAR SYSTEMS

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This projects focuses on three mechanistic questions central to molecule-based solar energy conversion: 1) How far do electrons transfer? 2) How do electrons get "from here to there"? 3) How can molecular energy flow within the larger assemblies be usefully manipulated, extended, accelerated, or modulated? Much of the work relies upon the development of supramolecular chromophoric assemblies, in many cases via directed coordination chemistry. Described below are recent results.

Stark emission spectroscopy has been used in a unique way to assess the nature of light-induced charge-injection occurring at representative molecular-dye/colloidal-semiconductor interfaces. The systems examined were eosin Y and coumarin-343, both on TiO_2. Recent literature reports have described sensitization for these systems as direct charge-transfer (CT) processes, as opposed to processes involving localized excitation (LE) of the dye, followed by injection into the semiconductor's conduction band. Our Stark studies show that eosin-Y injects via a conventional LE mechanism. Coumarin-343 conceivably may react via an interfacial CT state, although a simpler explanation centering on an environmentally perturbed LE state is also consistent with the experimental evidence.

Stark emission spectroscopy, transient DC photoconductivity (TDCP), and ground state dipole moment measurements have been used to evaluate light-induced charge transfer within several (X_2-bipyridine)$Re(CO)_3Cl$ complexes following ^{3}MLCT excited state formation. The Stark technique reports on vector dipole moment differences, which can be transformed directly into CT distances. The TDCP technique, on the other hand, reports on scalar dipole moment differences. For high symmetry systems, the scalar and vector quantities are equivalent. For low symmetry systems, however, they can differ enormously. By combining the two kinds of data, we find that we can move beyond simple CT distance measurements and begin to understand light-induced charge *redistribution*, including ground-state/excited-state dipole rotation. The dependence of both distance and redistribution parameters upon molecular structure (chromophoric ligand structure) has been elucidated.

Tetrametallic "molecular rectangles" designed and synthesized in our lab provide the basis for a new class of mixed valence compounds featuring ligand-to-ligand rather than metal-to-metal charge transfer. The rectangular framework enforces a cofacial geometry for the ligands comprising the longer edges of the rectangle. Stepwise electrochemical reduction of the electronically interacting ligands yields mixed-valence (ligand^{1-}/ligand^{0}) species that display intense intervalence charge transfer (IVCT) absorptions. The IVCT lineshapes, energies, and oscillator strengths provide quantitative information about reorganization energies and electronic coupling energies for the ligand-based optical electron transfer process.

Stark absorption spectroscopy and TDCP techniques have been applied to a family of ethynyl-linked porphyrin assemblies developed in Michael Therien's lab. The experiments unexpectedly showed that charge-transfer accompanies the optical excitation of nominally symmetrical assemblies. The observation may reflect slight reductions in symmetry. Another explanation, however, is one derived from our computational studies: application of the Stark field itself evidently is sufficient to break the symmetry and engender charge-transfer behavior to a degree great enough to be observed experimentally.

A family of rhenium-linked porphyrin dyads has been synthesized via coordinative directed assembly. Despite the presence of heavy atoms, the dyads readily fluoresce at room temperature in fluid solution. The rhenium centers enforce a rigid, coplanar geometry for the porphyrins, thereby offering a particularly well defined structural configuration for the investigation of ultrafast light-initiated energy transfer reactions. By using mixed dyads, selective excitation of one of two available porphyrins is possible. We observe, upon excitation of the porphyrin featuring the higher emissive-state energy, rapid transfer of the energy and efficient re-emission by the remote second porphyrin. Energy transfer rates exceeding 10^{10} s^{-1} have been obtained, implying that excitons can be propagated over a large number of porphyrin units in extended arrays. We have initiated studies of this kind using well defined surface-templated porphyrin multilayer structures that permit us to control array size to within one porphyrin repeat unit and array length to within 2 nm. This work comprises much of our current effort and is a primary focus of future work. Returning to the dyads, we are currently seeking to control energy transfer pathways synthetically, and to extend pathway control to light-induced electron transfer reactions. While information gained here will be of significant fundamental scientific value, it will also usefully instruct us in our ongoing optimization work on energy-converting arrays.

DOE Supported Publications 2000-2002

1. "Hyper-Rayleigh Scattering: A Spectroscopic Tool for Nonlinear Optical Property Characterization, Charge Transfer Symmetry Investigation, and Nanoscale Interface Interrogation", R. C. Johnson and J. T. Hupp, **2000**, *13*(2), 1-8.

2. "Using Resonance Raman Spectroscopy to Examine Vibrational Barriers to Electron Transfer and Electronic Delocalization", J. T. Hupp and R. D. Williams, *Acc. Chem. Research*, **2001**, *34*(10), 808-817.

3. "Comparative Absorption, Electroabsorption and Electrochemical Studies of Intervalence Electron Transfer and Electronic Coupling in Cyanide-Bridged Bimetallic Systems: Ancillary Ligand Effects", F. W. Vance, R. V. Slone, C. S. Stern, and J. T. Hupp, *Chem. Phys.*, **2000**, *253 (2-3)*, 313-322.

4. "An Inorganic Application of Transient DC Photoconductivity: Corroboration of a Charge-Transfer Assignment for the Luminescing States of Pt(dpphen)(ecda)", F. W. M. Vanhelmont, R. C. Johnson, and J. T. Hupp, *Inorg. Chem.*, **2000**, *39*, 1814-1816.

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7. "Singlet and Triplet Excited States of Emissive, Conjugated Bis(porphyrin) Compounds Probed by Optical and EPR Spectroscopic Methods", R. Shediac, M. H. B. Gray, H. T. Uyeda, R. C. Johnson, J. T. Hupp, P. J. Angiolillo, and M. J. Therien, *J. Am. Chem. Soc.*, **2000**, *122*, 7017-7033.

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11. “Vibrational Coherence Due to Promoting Mode Activity in the Relaxation Dynamics of the Class III Mixed-Valence Molecule $[Ru_2TIEDCl_4]^{+}$”, T. W. Marin, B. J. Homoelle, K. G. Spears, J. T. Hupp, L. O. Spreer, *J. Am. Chem. Soc.*, **2002**, *106*, 1131-1143.

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13. “Luminescence Based Assessment of Thermodynamic Constants for Electrostatic Binding of Non-Luminescent Dyes and Atomic Ions to Colloidal Semiconductor Surfaces”, X. Dang and J.T. Hupp, *J. Photochem. Photobio. A: Chemistry,* **2001**, *143*, 251-256.

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15. “Synthesis, Characterization, and Preliminary Intramolecular Energy Transfer Studies of Rigid, Emissive, Rhenium-linked Porphyrin Dimers," K. E. Splan, M. H. Keefe, A. M. Massari, K. A. Walters, and J. T. Hupp *Inorg. Chem.*, **2002**, *41*, 619-621.

16. "Experimental Studies of Light-Induced Charge Transfer and Charge Redistribution in $(X_2\text{-bipyridine})Re(CO)_3Cl$ Complexes," K. A. Walters, Y. Kim, and J. T. Hupp *Inorg. Chem.*, **2002**, in press.

17. "The Creutz-Taube Ion: Electronic Structure of an Archetypal Mixed-Valence Complex,", J. T. Hupp, *Comp. Coord. Chem. II*, **2002**, submitted.

18. "Collapsed Molecular Rectangles based on Rhenium (I) Coordination of Ethynylpyridyl Porphyrins, Synthesis, Structure, and Bending-Induced Charge-Transfer Beharior," K.D. Benkstein, C. L. Stern, K. E. Splan, R. C. Johnson, K. A. Walters, F. W. M. Vanhelmont, J. T. Hupp, **2002**, submitted.

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TOWARDS LONG-LIVED CHARGE SEPARATION IN C_{60}-BASED DONOR-ACCEPTOR ENSEMBLES

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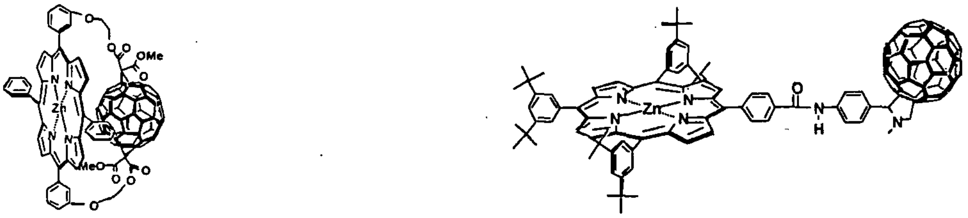
Combining the rapidly evolving fields of nanostructured materials and supramolecular chemistry is an attractive strategy for constructing large and complex, yet highly ordered, molecular and supramolecular entities, with specific functions. We develop novel super- and supramolecular donor-acceptor architectures through careful design, and probe them in condensed media and organized thin films at semiconductor surfaces as viable tools for efficient conversion of solar energy. The application of the proposed donor-acceptor conjugates is relevant to the mission of the DOE's solar photochemistry program and is of interest to scientists working in the fields of photo- / radiation-chemistry, electron donor-acceptor interactions, supramolecular chemistry and photovoltaics.

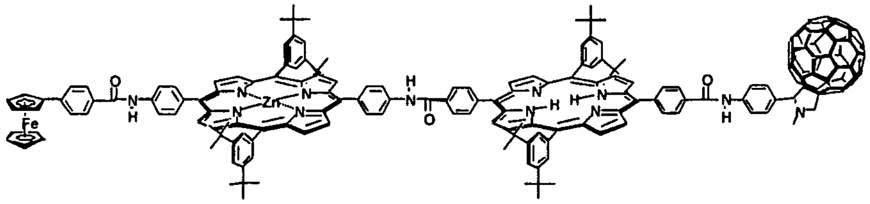
Fullerenes and porphyrins / phthalocyanines are molecular architectures ideally suited for devising integrated, multicomponent model systems to transmit and process solar energy. Implementation of $\mathbf{C_{60}}$ as a 3-dimensional electron acceptor holds great promise on account of its small reorganization energy in electron transfer reactions and has exerted noteworthy impact on the improvement of light-induced charge-separation. The current contribution describes how the specific composition of porphyrin chromophores (i.e., **ZnP**, zinc tetraphenylporphyrin and $\mathbf{H_2P}$, free base tetraphenylporphyrin) linked to $\mathbf{C_{60}}$ – yielding artificial light harvesting antenna and reaction center mimics – has been utilized to tune the electronic coupling, orientation and separation between donor and acceptor sites and the total reorganization energy. Specifically, the effects that these parameters have on the rate, yield and lifetime of the energetic charge-separated states will be discussed.



Scheme 1: $\mathbf{ZnP\text{-}C_{60}}$ molecular dyads with edge-to-edge separations of 3 Å and 12 Å.

The most far-reaching observation of our work is that charge-recombination in $\mathbf{ZnP^{\bullet+}}$ / $\mathbf{C_{60}^{\bullet-}}$ couples (*i.e.*, molecular dyads – $\mathbf{ZnP\text{-}C_{60}}$, $\mathbf{H_2P\text{-}C_{60}}$ – and triads – $\mathbf{ZnP\text{-}H_2P\text{-}C_{60}}$) is located deep in the "inverted region" of the Marcus parabola, regardless of linkage, distance and orientation. By contrast, lowering the driving force *via* replacing the **ZnP** with the better electron acceptors ferrocene (**Fc**) or tetrathiafulvalene (**TTF**), while keeping all other parameters (*i.e.*, distance, acceptor, solvent, temperature, etc.) constant, shifts the dynamics into the normal region. This variation is of great advantage in determining parameters such as electronic coupling (V), reorganization energy (λ) and damping factor (β) with high accuracy. These parameters have key character for material design considerations with the objective being to prolong the lifetime of the energetic charge-separated state, while, simultaneously, optimizing the efficiency of charge separation.

The success in mimicking the primary events in photosynthesis using **ZnP-H$_2$P-C$_{60}$** and **Fc-ZnP-C$_{60}$** encouraged us to combine these two systems into an integrated single system, **Fc-ZnP-H$_2$P-C$_{60}$**. Indeed, the lifetime of the spatially-separated (R_{ee} = 48.9 Å) radical pair, the product of a sequence of energy and multi-step electron transfer reactions, reaches well beyond milliseconds (0.38 s), into a time domain which has never been accomplished so far in an artificial photosynthetic reaction center. The lifetime is also comparable, for example, to the lifetimes (~1 s^{-1}) of the bacteriochlorophyll dimer radical cation ($(Bchl)_2^{\bullet+}$)-secondary quinone radical anion ($Q_B^{\bullet-}$) ion pair in the bacterial PRC. The relatively low quantum yields (0.17 - 0.24) can be explained by the competition of the various charge-shift reactions, transferring the charge from **Fc-ZnP-H$_2$P$^{\bullet+}$-C$_{60}$$^{\bullet-}$** to **Fc$^{\bullet+}$-ZnP-H$_2$P-C$_{60}$$^{\bullet-}$** *versus* the intrinsic decays of each reactive intermediate. In **Fc-ZnP-H$_2$P-C$_{60}$**, another limiting parameter is the charge injection from **^{1*}H$_2$P** into the fullerene acceptor to yield **Fc-ZnP-H$_2$P$^{\bullet+}$-C$_{60}$$^{\bullet-}$**. To facilitate this crucial step the first charge-separation was probed in a **Fc-ZnP-ZnP-C$_{60}$** tetrad. In general, **ZnP** has a lower oxidation potential than **H$_2$P**, thus providing more thermodynamic driving force, and therefore larger rate constants and quantum yields for the crucial conversion of the **Fc-ZnP-^{1*}ZnP-C$_{60}$** intermediate to the **Fc-ZnP-ZnP$^{\bullet+}$-C$_{60}$$^{\bullet-}$** species.



Scheme 2: **Fc-ZnP-H$_2$P-C$_{60}$** molecular tetrad with an edge-to-edge separation of 49 Å.

One of the major challenges that still lie ahead is to regulate the forces, which will ultimately dictate size and shape in relation to function of the resulting composite. Can molecular tailoring of fullerenes contribute to the induction of new assemblies? We intend to probe novel donor-acceptor ensembles, in which **C$_{60}$** will constitute the acceptor moiety and biomimetic organization principles (*i.e.*, hydrogen-bonding, π-π stacking, metal-mediated complexation and electrostatic motifs) and will ensure the hierarchical integration of multiple components into well-ordered arrays. These organization principles will permit engineering of donor-acceptor composites and, simultaneously, achieve predetermined architectures of controlled sizes and outer-shell structures, with high directionality and selectivity. The most important aspect in this area will be the regulation of the inherently weak forces seen in biomimetic organization principles on a molecular basis. We expect that these systems can be utilized to convert photolytically generated charge-separated states into electrical or chemical energy by constructing integrated artificial photosynthetic assemblies – on modified indium-tin-oxide electrodes (**ITO**) with the use of *layer-by-layer* self-assembly.

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MAGNETIC RESONANCE AND ELECTRON TRANSFER STUDIES OF CAROTENOIDS

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Carotenoids are intrinsic components of reaction centers and pigment-protein complexes in photosynthetic membranes. They play a photoprotective role in plants and bacteria. Their robust nature requires extensive characterization of their electron transfer and radical trapping ability, 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.

Single Two-electron Transfers vs. Successive One-electron Transfers in Symmetrical Carotenoids. In a collaborative electrochemical cyclic voltammetric project with Professor Savéant's group (Paris, France) it has been shown that an inversion of the standard potentials for the first and second electron transfers occurs in the oxidation of β-carotene and 15,15'-didehydro-β-carotene in CH_2Cl_2 solvents but not in their reduction. The same inversion occurs in the reduction of canthaxanthin in CH_2Cl_2 solvents but not in its oxidation. A series of density functional B3LYP/6-31G* calculations to estimate the magnitude of the disproportionation equilibrium constant were carried out. The B3LYP results indicate that all radical ions have a symmetrical structure suggesting that the unpaired electron and the charge are delocalized over the whole molecular framework and not confined to one terminal group. UHF-MP2 calculations confirmed this result. As the number of conjugated double bonds increases, the disproportionation constant decreases, meaning the second electron-transfer step becomes easier and easier as compared to the first. This is apparently due to the increased possibility of the two charges in the di-ion to move apart from one another, thus decreasing the coulombic repulsion energy. The C–C bond length was also found to lie midway between the single and double-bond length in the di-ion, and that the end groups which are not planar in the neutral compounds tend toward planarity upon removal or the addition of two electrons. The charges in the di-ion are localized near the ends of the molecule at large distances from each other. This minimizes the coulombic repulsion and favors the solvation of the di-ion providing additional stabilization. In contrast the charge in the ion radical is delocalized over the whole molecular framework and stabilization by interaction with the solvent is not as favorable. Potential inversion cannot occur when the two electrophores are linked by a saturated bridge. Localization of the charges in the di-ion is favored by electron-accepting terminal groups (two carbonyl groups in canthaxathin) and hole-accepting terminal groups for oxidation (β-carotene).

Variable High Field EPR Measurements of Electron Transfer Between Metal Ions and Carotenoids. With the assistance of Dr. Brunel's group at the National High-Field Magnet Laboratory at Florida State University, we have measured the HF-EPR spectra of several metal-substituted mesoporous molecular sieves with incorporated carotenoids. The 9-287 GHz measurements of Fe(III)-MCM-41 indicated the presence of high-spin Fe(III) and aggregated

Fe(III). Incorporation of carotenoids yields the carotenoid cation radical (Car$^{\bullet+}$) due to electron transfer to the extra framework Fe(III) cations on the outer surface of the pore. For Ni(II)- and Al(III)-containing MCM-41 the photoyield and stability of generated Car$^{\bullet+}$ increased in the order of MCM–41<Ni–MCM–41<Al–MCM–41. EPR signals of Ni(I) provide direct evidence for the reduction of Ni(II) ions detected at 220 GHz by the carotenoids. ENDOR measurements revealed the orientations of Car$^{\bullet+}$ inside the MCM-41. ENDOR evidence suggests that the carotenoids are bound to the MCM–41 pore walls via the ends of the polyene chain in close proximity to the C9,9'–CH_3 groups. Reversible electron transfer between carotenoids and Cu^{2+} ions was observed in Cu–MCM–41 molecular sieves.

In a collaborative project with Dr. M. Bowman at the Pacific Northwest National Laboratory, it was shown that the anisotropic alpha proton couplings could be detected by HYSCORE measurements for Car$^{\bullet+}$ stabilized on activated silica-alumina which were not resolved by ENDOR spectroscopy. It appeared that cis/trans isomerization of carotenoids on silica-alumina results in stabilization of di-cis isomers with large isotropic couplings for some α protons comparable to those of β protons. Detection of ^{27}Al nuclear resonance by 1D three-pulse ESEEM and 2D HYSCORE spectra indicated electron-transfer between carotenoids and Al^{III} ions. Apparently, the HYSCORE is a promising technique to increase spectral resolution for proper assignment of protons with large hyperfine anisotropy which cannot be resolved by ENDOR spectroscopy in powders.

Radical Trapping Ability of Carotenoids as a Function of Oxidation Potential. The role of several natural and synthetic carotenoids as scavengers of free radicals using spin trapping techniques showed that the scavenging ability for the $^{\bullet}$OOH and $^{\bullet}$OH radical increased with the oxidation potential of the neutral carotenoid although the relative rate of scavenging carbon centered radicals decreased by three orders of magnitude. In the presence of Fe^{3+}, an increase in radical concentration occurred due to reduction of Fe^{3+} to Fe^{2+} by the carotenoid suggesting an increase in total radical yield when carotenoids are involved in a reaction cycle with the participation of iron.

Surface Behavior of Thio Substituted Carotenoid on Gold Surfaces. In a collaborative project with Dr. Moore and Dr. Gust (Arizona), the stability, packing density, optical absorption and hydrophobicity of a thio-substituted carotenoid 7'-apo-7'-(4-mercaptomethylphenyl)-β-carotene, (AMC) on gold surfaces was investigated at Alabama using XPS, Fourier transform infrared reflection absorption spectroscopy, UV-Vis spectroscopy, spectroscopic ellipsometry and contact angle measurements. The polyene chains are well packed creating a hydrophobic interface. The saturation coverage was ~4 x 10^{14} AMC molecules/cm^2 and the film thickness ~20 Å.

Photochemistry of Carotenoids in Liposomes. Photodegradation studies in our lab have shown that faster photodegradation of carotenoids occurs in liposomes than in organic solvents. Experimental observations have confirmed this to be due to the suppression of vibrational deactivation due to twisting motions about the polyene; CH stretching and bending in carotenoids. EPR spectra of carotenoids photolyzed in liposomes exhibit intense signals and a discussion of the radical identity will be given. Further studies in liposomes are underway.

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MOLECULAR ORBITAL SYMMETRY EFFECTS IN DONOR-ACCEPTOR SYSTEMS LINKED BY CAGE MOLECULES AND HETEROATOMS

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The important question of the role of structural and molecular orbital symmetry in determining the rate of intramolecular electron and excitation transfer has been studied using two families of donor-acceptor models in which the two active fragments are bridged either by a single tetrahedral Group IV atom, or by a rigid cage molecule. Both sets employ fluorene, or substituted fluorene, as the donor and the acceptor.

Excitation and electron transfer mediated by >C<, >Si<, >Ge< and >Sn< atoms: In comparison with the wealth of data on the propagation of donor-acceptor coupling through organic and bioorganic bridges, little is known about the similar role of heteroatoms and metals. Understanding these interactions will be of increasing importance for the design of new hybrid molecular-semiconductor assemblies that find application in energy conversion, catalysis and other areas. In the present work we focus on the contribution of the valence orbitals of the central heteroatom to the inter-chromophore coupling as one progresses from carbon to the heavier members of Group IV. The strongest S_1 and T_1 inter-chromophore interaction was found for the Si compound, followed by the Ge, with the Sn bridge giving the most "carbon-like" behavior. DFT calculations support the experimental findings and show that the contribution from the orbitals of the central heteroatom X to the LUMOs of the system are largest when X = Si, and diminish for the heavier analogues. This shows that silicon bridges should be particularly efficient in mediating electron transfer between aromatic fragments. Interestingly, the coupling between the HOMO orbitals (responsible for hole transfer) is dominated by the direct "through space" interaction and decreases as the size of the central atom increases.

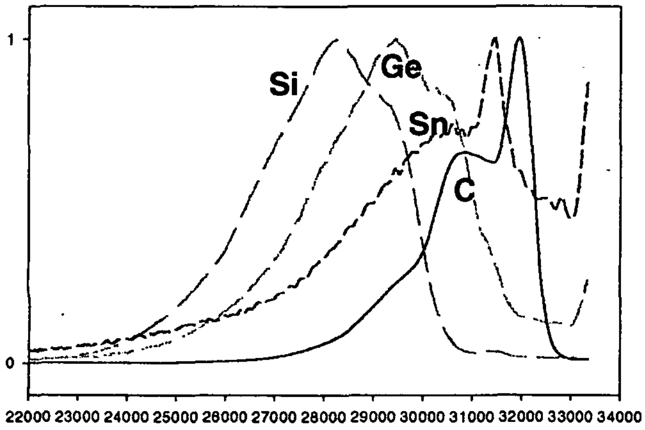

Fig. 1. Fluorescence spectra of spirobifluorenes with heteroatom bridges.

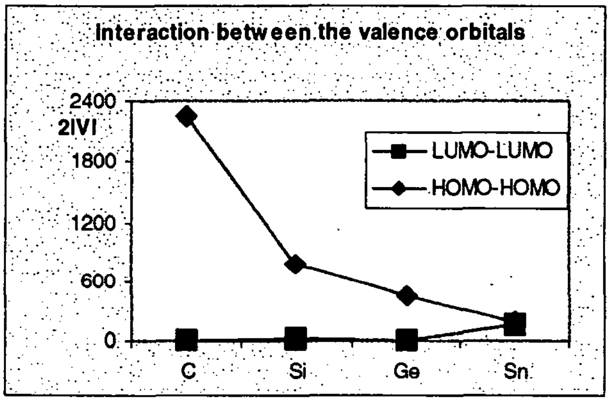

Fig. 2. Electronic coupling between the valence orbitals of heteroatom bridged spiranes.

Energy and electron transfer mediated by adamantane *bis*-homocubane and stellane bridges: Models based on adamantane, stellane and *bis*-homocubane have been developed to probe the role of the donor/acceptor MO symmetry in determining the magnitude of the electronic coupling. In the adamantane system the donor and the acceptor are perpendicular to one another, and the electronic interaction between the respective local MOs is symmetry forbidden. The stellane bridge breaks the orthogonality, thus "turning on" the exchange and dipole-dipole D-A interactions. The *bis*-homocubane unit forces the donor and the acceptor to be coplanar, thus, in principle, maximizing the inter-chromophore electronic interaction.

Bridge	$|V_{HOMO\text{-}HOMO}|$	$|V_{LUMO\text{-}LUMO}|$	$|V_{S1\text{-}S1}|$
Adamantane	10.4 cm^{-1}	0.0 cm^{-1}	0.0 cm^{-1}
Stellane	49.6 cm^{-1}	120.8 cm^{-1}	77.4 cm^{-1}
Bis-homocubane	21.5 cm^{-1}	197.5 cm^{-1}	65.2 cm^{-1}

A quasi-classical molecular dynamics study of symmetry effects on the dynamics of charge-shift reactions in the adamantane and *bis*-homocubane bridged bichromophores was performed. The charge-shift process takes place *via* the most symmetric transition structure and in these systems may be either formally symmetry-allowed or symmetry-forbidden depending on the topology of the connecting bridge, the local MO symmetry of the chromophore pair and on the sign of the migrating charge. The degree to which symmetry breaking vibrations influence the dynamics of charge-shift in these systems was probed using the Landau-Zener trajectory surface hopping (LZ-TSH) model. It was found that frequencies of passage for the formally symmetry-forbidden charge-shift processes were slightly smaller than those for the analogous formally symmetry-allowed processes, demonstrating that symmetry breaking vibrations play a crucial role in the charge transfer dynamics in these molecules. The specific symmetry breaking modes were identified by calculating secondary kinetic isotope effects and by performing FT analyses of the reaction trajectories.

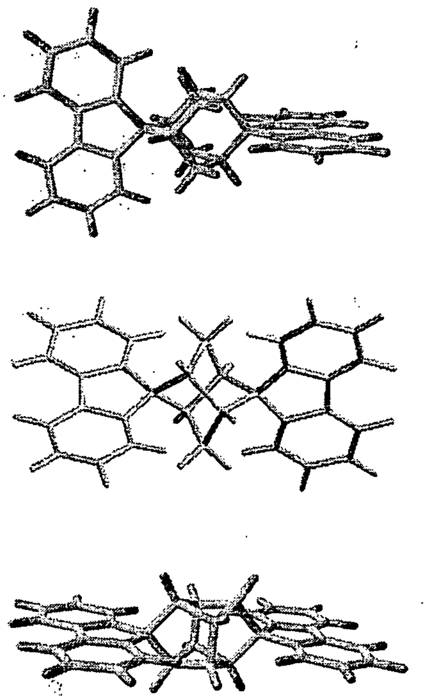

Fig. 3. Bichromophores based on (from top down) adamantane, stellane and *bis*-homocubane bridges.

Future directions: Current experimental efforts concentrate on low temperature fluorescence anisotropy measurements on the adamantane and heteroatom bridged molecules, as well as on the multi-step synthesis of the stellane bridged bichromophore. The recently completed kHz multipass Ti:sapphire amplifier will be used to perform ultrafast transient absorption and time-resolved emission depolarization experiments on the described systems. New series of trajectory surface hopping calculations will be performed on singlet and triplet energy transfer in bichromophores with adamantane, stellane and *bis*-homocubane bridges.

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Session III

Charge Separation in Homogeneous Solution

PHOTOINDUCED DIPOLES AND CHARGE SEPARATION IN CONDENSED MEDIA

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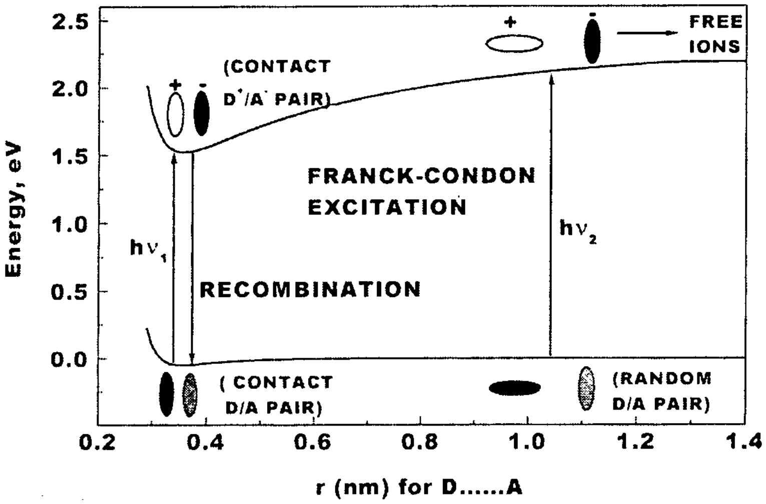
Great progress has been made in understanding the production of free charge carriers (ions) by photoinduced electron transfer from molecular donors to electron acceptors. We have solved the long-standing problem of how photoexcitation of an electron-donor acceptor (**EDA**) complex can result in free ions despite the strong Coulomb force between those ions. Our conclusion is that photoexcitation of these ground state complexes is not important to the production of free ions except in highly polar solvents in which Coulomb binding is weak. Instead, photoinduced electron transfer between unassociated, "random" or statistical donor/acceptor pairs is the critical step in the production of charges that can separate and thus avoid counterproductive back electron transfer.



Our experiments which supported a suggestion by Norman Sutin of Brookhaven National Laboratories led to a fruitful collaboration [2,3] which proved that the free charges come, not from photoexcitation of **EDA** complexes, but from photoabsorption by unassociated, random, or "statistical" pairs (see Figure above). Thus the photoinduced by electron transfer directly produces separated ions or carriers which start life already part way up the Coulomb barrier. Absorption by such random pairs is most probable on the high energy side of a charge-transfer (**CT**) absorption band.

We have recently measured the absorption spectra of random donor/acceptor pairs. Formation of **EDA** complexes was prevented by using donors with large steric bulk. For example, while hexamethylbenzene is flat and forms a stable **EDA** complex with **TCNE**, hexaethylbenzene (**HEB**) does not form such a complex. In another example, we compare durene (1,2,4,5-tetramethylbenzene) with substituted benzene in which each methyl group is replaced by an isopropyl (**TIPB**). The later donor does not form a stable ground state complex with **TCNE**. However, bulky donors like **HEB** and **TIPB** do give weak **CT** absorption spectra in solution with **TCNE**. These spectra are understandable as a result of the interaction between random donors and acceptors.[7]

In a related study, we examined the electron transfer quenching of 9,10-dicyanoanthracene (**DCA**) by sterically hindered as compared to unhindered donors. An example is **TIPB** versus the corresponding durene. Of course, the oxidation potential of those substituted benzenes is almost identical. However, in dichloromethane, **TIPB** quenching of **DCA** gives 40 times the quantum yield of free radical ions as does quenching by durene. We show that this striking result originates in long distance quenching by **TIPB** which is sterically prevented from close approach of its benzene center to **DCA**. We also find that, in a medium-polarity solvent like dichloromethane, the photocurrent risetime is not equal to the exciplex decay time. This means that contact radical ion pairs (**CRIPs**) or exciplexes are not the precursors of free ions. The photocurrent risetime is usually controlled by ion recombination. Thus, the lifetime observations also imply that **CRIPs** are not usually in equilibrium with solvent separated radical ion pairs (**SSRIPs**) in sharp contrast to the assumption of previous workers.

In further work, the recombination rates at a variety of separation distances are measured for geminate radical ion pairs (**RIPs**) formed by electron transfer quenching of excited (**DCA**) using benzene donors substituted with different bulky groups in several moderately polar solvents. For the first time, increased recombination rate constants with increasing **RIP** separation are observed in solution. It is concluded that the dominant mechanism for the recombination of **SSRIPs** involves a direct return electron transfer from **SSRIPs** by tunneling, thus by-passing the **CRIPs**.

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HYDROGEN BOND DYNAMICS IN HYDROGEN BONDING LIQUIDS PROBED WITH ULTRAFAST INFRARED EXPERIMENTS

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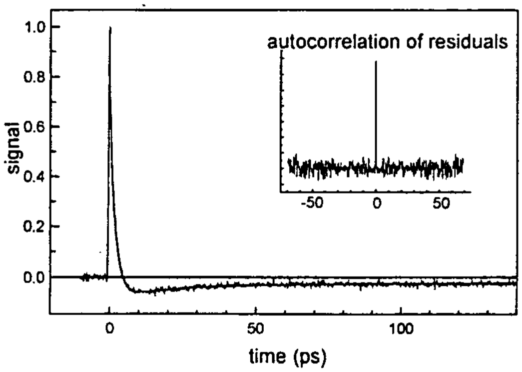
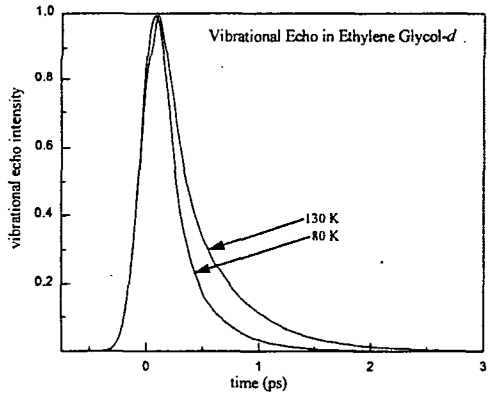
It has been recognized for the last several decades that solvent properties are of fundamental importance in electron transfer. In the Marcus theory, the solvent enters through the outer sphere contribution to the reorganization energy. The solvent is treated as a dielectric continuum with its properties characterized by the optical and static dielectric constants. Solvent dynamics come into play when issues of adiabatic vs. non-adiabatic electron transfer arise. In recent very detailed experimental and statistical mechanics theoretical studies of photoinduced electron transfer in a large number of solvents, we found excellent agreement with theory in many of the solvents.[1] However, anomalies were found as the extent of hydrogen bond network formation increased, with the anomalous behavior being particularly pronounced in ethylene glycol.[2] The H-bonded network solvents resulted in distinct electron transfer behavior in spite of the similarities with other liquids in dielectric constants and donor/acceptor diffusion constants. With these electron transfer observations as a motivation, we have begun a detailed examination of the dynamics of H-bonded oligomers and liquids. The long-range goal is to correlate detailed studies of solvent dynamics and the dynamics of electron transfer with an eye to controlling electron transfer in systems such as reverse micelles.



To investigate hydrogen bond dynamics, we are employing ultrafast infrared experiments. These include IR pump-probe experiments, spectrally resolved pump-probe experiments, and vibrational echo experiments. Using the pump-probe experiments, we are addressing the dynamics and mechanism of H-bond breaking and reformation. Detailed experiments were conducted that examine the relationship between OD vibrational excitation and hydrogen bond breaking in methanol-*d* (MeOD),[3] ethanol-*d*, and propanol-*d* in carbon tetrachloride. At very low concentrations, the alcohols exist as monomers. As the concentration is increased, increasingly large H-bonded oligomers are formed. For example, exciting MeOD at 2690 cm^{-1}, only the free O-D (where the D is not H-bonded) stretching mode was initially populated. For MeOD mole fractions ≤ 0.025, a 2.15 ps single exponential decay was observed. At mole fractions ≥ 0.0375, the signal decays (2.15 ps decay time) below zero (increased absorption) and then recovers on time scales of 22 ps and >>300 ps (see figure). Similar data are observed for ethanol and propanol. The increased absorption indicates the formation of additional free ODs caused by the breaking of H-bonds that are not directly coupled to the initially excited vibration. The two-time scale recovery of this signal arises from geminate recombination (fast) and the generation of heat (slow). The data were fit with a set of kinetic equations that accurately reproduce the data (see figure). The results demonstrate that vibrational relaxation of the initially excited free OD stretch into intramolecular modes of the methanol leads to H-bond breaking. These results call into question the results of studies in other types of hydrogen bonded systems (e.g., water) that suggest direct relaxation of a vibrationally excited OH stretch into an H-bond stretch is responsible for H-bond breaking.

Excitation of the OD stretch in the middle of the broad oligomer OD stretching band (as opposed to the "free" OD peak) results in a fast initial decay of the pump-probe signal (~400 fs). The signal does not decay to zero, but, rather begins to increase again with a time constant of ~750 fs, reaching a second maximum in ~3 ps. Following the second maximum, the signal again decays with a fast component (~13 ps) and a very slow component. A model is presented that describes the initial decay as vibrational relaxation. Following vibrational relaxation, hydrogen bonds are broken. Only MeODs that have two hydrogen bonds absorb at the experimental wavelength. Therefore, breaking an H-bond in the middle of an oligomer removes two MeODs from absorbing the probe pulse. The loss of 2 MeOD absorbers produces additional bleaching, which gives rise to the second maximum. The rise time to the second maximum gives the rate constant for hydrogen bond breaking.

We have recently conducted the first ultrafast vibrational echo experiments on a hydrogen bond network solvent, ethylene glycol, as a function of temperature. The figure shows vibrational echo data taken at two temperatures on the OD stretching mode. The vibrational echo is a direct probe of hydrogen bond dynamics. As an isolated molecule (e.g. methanol-d (MeOD) in very dilute solution in CCl_4), the OD stretch is a relatively narrow peak (~20 cm^{-1} full width at half height) at 2690 cm^{-1}. However, in a pure liquid or highly concentrated solution, the hydrogen bonding has a substantial affect on the spectrum. The maximum of the OD stretch in a hydrogen bonding system is 2490 cm^{-1}, and the FWHH is ~200 cm^{-1}. The hydrogen bonding causes both the red shift and the broadening. The hydrogen bond adds an additional attractive term to the OD stretching potential, opening up the potential and lowering the vibrational energy. Because there is a distribution of hydrogen bond strengths, there is a distribution of OD transition frequency shifts, which produce the broad absorption band. The hydrogen bond structure is not static. Time evolution of the hydrogen bond network will cause the frequency of the OD stretch to evolve in time. Thus, the time evolution of the OD stretching frequency, as measured by vibrational echo experiments, provides direct information on the hydrogen bond/liquid structure dynamics.



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Session IV

Keynote Lecture

CHALLENGES FOR THE CHEMICAL SCIENCES IN DEVELOPMENT OF RENEWABLE ENERGY TECHNOLOGY

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This presentation will describe and evaluate the challenges, both technical, political, and economic, involved with widespread adoption of renewable energy technologies. First, we estimate the available fossil fuel resources and reserves based on data from the World Energy Assessment and World Energy Council. In conjunction with the current and projected global primary power production rates, we then estimate the remaining years of supply of oil, gas, and coal for use in primary power production. We then compare the price per unit of energy of these sources to those of renewable energy technologies (wind, solar thermal, solar electric, biomass, hydroelectric, and geothermal) to evaluate the degree to which supply/demand forces stimulate a transition to renewable energy technologies in the next 20-50 years. Secondly, we evaluate the greenhouse gas buildup limitations on carbon-based power consumption as an unpriced externality to fossil-fuel consumption, considering global population growth, increased global gross domestic product, and increased energy efficiency per unit of globally averaged GDP, as produced by the Intergovernmental Panel on Climate Change (IPCC). A greenhouse gas constraint on total carbon emissions, in conjunction with global population growth, is projected to drive the demand for carbon-free power well beyond that produced by conventional supply/demand pricing tradeoffs, at potentially daunting levels relative to current renewable energy demand levels. Thirdly, we evaluate the level and timescale of R&D investment that is needed to produce the required quantity of carbon-free power by the 2050 timeframe, to support the expected global energy demand for carbon-free power. Fourth, we evaluate the energy potential of various renewable energy resources to ascertain which resources are adequately available globally to support the projected global carbon-free energy demand requirements. Fifth, we evaluate the challenges to the chemical sciences to enable the cost-effective production of carbon-free power on the needed scale by the 2050 timeframe. Finally, we discuss the effects of a change in primary power technology on the energy supply infrastructure and discuss the impact of such a change on the modes of energy consumption by the energy consumer and additional demands on the chemical sciences to support such a transition in energy supply.

Session V

Photoelectrochemistry

DOPING PROCESSES AND PHOTOCONVERSION MECHANISMS IN ORGANIC SEMICONDUCTOR FILMS

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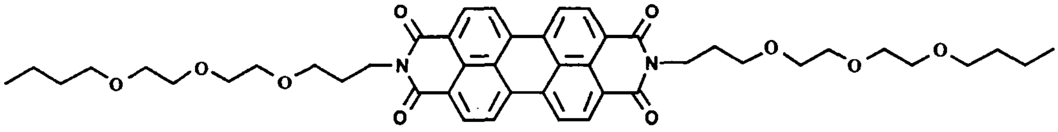
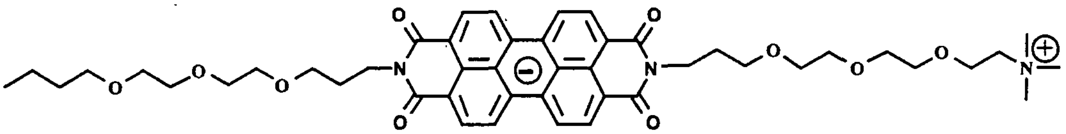
We seek to understand the fundamental photoconversion processes in organic-based systems by studying the energy transfer processes and the generation, separation and recombination of charge carriers in molecular semiconductors. A major focus is on the synthesis and characterization of self-organizing films of liquid crystalline semiconductors, because a high degree of structural order tends to accentuate the intrinsic character of these compounds while minimizing spurious features due to impurities and defects. We are also involved in more theoretical efforts to clarify the similarities and differences in photoconversion mechanisms between organic and inorganic semiconductors.

We have doped organic semiconductors for the first time in a manner that allows the formation of stable electrical junctions. Although organic semiconductors are routinely described as being "p-type" (most commonly) or "n-type", only in rare cases have the dopants been added purposely. Usually the dopants are adventitious and unidentified, which is unsatisfactory and cannot lead to fundamental understanding. But even when added purposely, a crucial aspect of doping has been previously overlooked: if the dopants are mobile, the junctions (Schottky or p-n) cannot be stable. In non-covalent solids like molecular semiconductors, the diffusion coefficients of small molecules (the usual "dopants" like O_2 and Br_2) are so large that electrical junctions may disappear within hours.

Therefore, to "correctly" dope molecular semiconductors, and to enable precise measurements of their properties, we must ensure that: 1) The dopant is fixed in the semiconductor lattice. 2) There are no mobile ions in the film. 3) The dopant is not chemically so distinct from the host that it will tend to phase separate from it. 4) The dopant does not form a deep electrical trap. Our solution to these molecular engineering requirements is: the dopant should be a reduced (for n-type) or oxidized (for p-type) derivative of the host molecule that has a covalently attached counter charge attached to the periphery of the molecule (not in conjugation with the chromophore). We recently synthesized the first example of this idea, shown below with its host molecule.

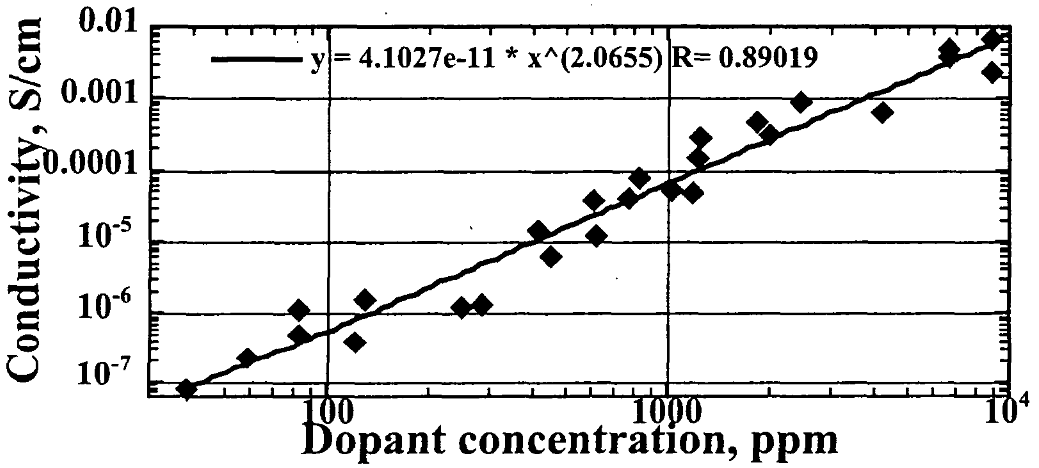


PPEEB



n-type dopant

The measured conductivity in doped PPEEB films is controlled by electron transport through the bulk perylene diimide film, not by the contacts. Up to the highest doping densities yet attempted, ~1 mol%, we observe no evidence for phase separation of the dopant: the conductivity, σ, increases smoothly with increasing doping density and there is no change in σ with time. The conductivity shows an unusual dependence on the dopant concentration, increasing almost exactly with the square of the dopant concentration over five orders of magnitude in conductivity. Coulombic effects almost certainly play a major role in the doping process because of the low dielectric constant of organic materials and the relatively weak delocalization (small Bohr radius) of charge carriers. Most of the added electrons will therefore remain electrostatically confined in the potential well surrounding the counter charge. Nevertheless, doping of just 1% leads to an increase in σ of ~10 orders of magnitude compared to the undoped compound ($\sigma \approx 10^{-12}$ S/cm).



We propose a random dopant-pairing model which explains the dependence of σ on the square of the dopant concentration. Conductivity is given by $\sigma = n\ q\ \mu_n$ where n is the number of free electrons, q is the electronic charge and μ_n is the electron mobility. Variable range hopping models for the mobility are often invoked to describe the conductivity in organic films, but they cannot account for our results. We therefore assume that the quadratic increase of σ implies that the number of *free* electrons, n, is proportional to the *square* of the dopant concentration.

A classical electrostatic calculation of the binding energy of an electron to the nearest positive counterion(s) was performed. It revealed that one of the two electrons near a randomly associated pair of dopants is the most weakly bound of the three expected types of "classical" electrons (i.e., those near isolated dopants, and the two electrons near random pairs of dopants). The decrease in the calculated binding energy of ~100 meV relative to an electron near an isolated dopant arises because the electron-electron repulsion energy of the "second" electron of a dopant pair dominates the additional electron-ion attraction energy. More precise calculations involving the quantum aspects (e.g., electron delocalization, zero point energy, etc.) are in progress; but the simple electrostatic model qualitatively explains these unusual results. This model may also help explain other published results of doping in conducting polymers and small molecule films.

Understanding the doping process in well-characterized organic semiconductor films will be pursued further, both experimentally and theoretically. The synthesis of new dopant molecules, as well as EPR studies, Hall effect and temperature-dependent measurements are planned. In other studies, a model describing the unique characteristics of photoconversion processes based on interfacial exciton dissociation, that is relevant to all organic photovoltaic cells, is being developed.

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STUDIES OF HIGH QUANTUM YIELD SENSITIZATION PROCESSES AT SEMICONDUCTOR ELECTRODES

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During the past three years we have worked in the area of dye sensitization on a number of fronts that are now converging to give us a better overall view of the dye sensitization process. We have worked on the sensitization of two different semiconductor substrates, tin sulfide and titanium dioxide.

The work on tin sulfide was concerned with the sensitization of this substrate with squaraine dyes. The high absorption coefficients, interesting aggregate forms and excellent charge transfer properties of the squaraines made them attractive for the study of the influence of the structure of the dye layer on the sensitization of SnS_2. The sensitization properties of two different squaraine dyes adsorbed onto the van der Waals surface of n-doped tin disulfide single crystals was studied using atomic force microscopy (AFM), vis-NIR absorption spectroscopy and photoelectrochemical techniques. Quantum yields per absorbed photon (QYAP) of near unity were observed for 2,4-bis(4-(*N*-methyl-*N*-hexylamino)phenyl)squaraine (1-6SQ) in aqueous electrolyte when a sufficiently positive bias was applied. Island-like and microcrystalline morphologies associated with aggregate formation, revealed by AFM, could be directly correlated with spectral shifts in both absorbance and photoaction spectra. Another dye 2,4-bis(4-(N,N-dimethyl)-2-hydroxyphenyl)squaraine (1-1OHSQ) at similar coverages showed slightly lower QYAP, ascribed to a recombination path due to the proximity of the oxidation potential of 1-1OHSQ and the SnS_2 conduction band edge. The coverage

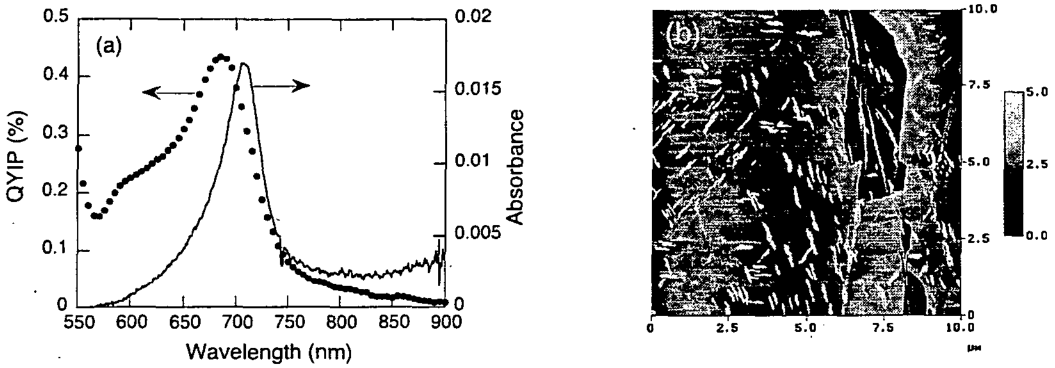

Figure 1 a) Photoaction spectrum and absorption spectrum of about a monolayer of 1-1 OHSQ on a SnS_2 electrode. b) AFM image of the SnS_2 electrode surface showing near monolayer coverage with second layer dye islands oriented along crystallographic directions.

dependence of the quantum yield per absorbed photon could be determined as a function of dye coverage and was seen to drop off when the dye coverage was more than one monolayer.

The accurate determination of the energy band line-up between the SnS_2 conduction band and the excited states of the squaraine dyes required a redox potential for the dye in a similar surface-confined environment. In the process of measuring the redox potential for squaraines confined to the van der Waals surface of HOPG with cyclic voltammetry, we discovered that ordered layers of squaraine dyes have a unique electrochemical behavior. This electrochemical behavior, not previously observed for a two dimensionally ordered system, showed an inert region with no current flow between the separated oxidation and reduction peaks. In this potential region both oxidized and reduced dyes are stable but can only exist in independent domains since the highly ordered two-dimensional domains of reduced dye molecules are immiscible with the two dimensionally ordered oxidized dye molecules, most likely due to the anions incorporated into the oxidized 2D lattice. Small stochastic reduction peaks were observed at more negative potentials that are associated with the reduction of small domains or microcrystallites of the oxidized 1-1OHSQ layers. The structures of both the oxidized and reduced dye layers were imaged at the molecular level using STM.

Natural anatase crystals were also investigated as substrates for dye sensitization by the ruthenium bipyridine based dye, N3, to circumvent the complexity of the nanoporous structure of the nanocrystalline TiO_2 films that are used in the Grätzel solar cell. A crystal face dependence of the sensitization yield was observed and explained with the variation in the distances between the Ti binding sites on the different crystal faces. The dye sensitized photocurrents with the natural anatase crystals had millisecond rise times. The rise time decreased with greater light intensity and greater dye coverage, suggesting that trapping and detrapping of injected electrons at traps in the crystals is involved in the electron transport in the natural anatase crystals. The absorbed photon to current efficiency of the nanocrystalline anatase films was calculated to be approximately three to seven times greater than that of the single crystals, indicating that there is more recombination in the single crystals or that we have a lower than monolayer dye coverage. Despite the many years of work on the dye sensitization of oxide crystals there has been no work where the atomic level order of the surface and the adsorbed dye was verified. Therefore, we are now in the process of stepping back to investigate the sensitization of covalently bound dicarboxylated cyanine dyes on the surface of the various crystal forms of TiO_2 including rutile, anatase and brookite. We are using a combination of UHV, scanning probe microscopy and photoelectrochemical techniques to investigate the binding and sensitization behavior of these dyes on various well-ordered and well-characterized low index TiO_2 crystal surfaces. The cyanine dyes yield some information on their surface structure via the shifts in the photoaction spectra due to aggregate formation on the surface. We will verify the aggregate structures via scanning probe microscopy in both dry and electrolyte environments. Predictions of binding affinity for a given dye on the various low index surfaces can be made based on the geometry of the two carboxyl groups and the positions of the five-coordinate Ti binding sites on the crystal surface.

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THEORETICAL STUDIES OF ELECTRON TRANSFER AND OPTICAL SPECTROSCOPY IN COMPLEX MOLECULES

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During the past several years, we have focused our efforts on the development and applications of quantum chemical methods to the study of solid state and solution phase systems. Rapid advances in electronic structure techniques, coupled with dramatic reductions in the cost/performance of computational hardware, have allowed us for the first time to successfully carry out ab initio calculations on complex molecular systems of interest to the DOE Solar Photochemistry program. Following is a brief description of progress in these areas:

Density Functional Methods for Solids, Nanoparticles, and Large Molecules in Solution: We have continued to develop our ab initio DFT methods to the point where they can be applied to complex structures in the solid state and in solution. It is now straightforward to carry out calculations for clusters containing 100-200 atoms for semiconductors and transition metal oxides. For ionic solids, we have developed an embedding method that allows a cluster treatment to be supplemented with the electric field from the remainder of the solid. This method is able to treat charged species (including electrons)interacting with ionic clusters, something that is very difficult to do with either simple cluster methods that truncate the remainder of the solid or with supercell methods which require reproducing the charge in each supercell, leading to large errors due to a fictitious Coulomb field being produced.

In collaboration with Prof. Louis Brus at Columbia, we are applying these methods to a number of solid state systems of direct interest to the DOE Solar Photochemistry program. These include silicon nanoparticles (where we are investigating the effects of termination of the surface with hydrogen, fluorine, and hydroxyl groups on properties such as the ionization potential and the band gap) and TiO_2 particles, on which we are testing the embedding method described above. Publications in these areas are in preparation.

We have also initiated efforts to use DFT methods to study organic and organometallic systems in solution. As a first step, we have developed a protocol for computing from first principles redox potentials of several different types of molecules; errors are typically in the range of 0.1 ev or less for relative redox potentials, and in many cases at this level for absolute redox potentials (although there are some systems where the errors in absolute redox calculations are larger). In conjunction with our methods for calculating electronic couplings of diabatic states, and modeling electron transfer dynamics (developed in previous granting periods), our goal is to assemble a complete set of tools for predicting electron transfer processes for new molecules in solution and ultimately at the solid/solution interface as well.

Calculation of Electron Transfer Coupling Matrix Elements: We are continuing to use our methods for computing diabatic coupling matrix elements to investigate interesting donor/acceptor pairs. As was discussed above, this technology will be combined with prediction of redox potentials and dynamics methods to produce a complete approach to understanding and predicting electron transfer rates.

Calculation of STM Images: We have used our technology for calculating electron transfer matrix elements to generate first principles predictions of STM images. Our initial application has been to a series of halogenated alkanes on a graphite surface studied by Flynn and coworkers. An analytical theory connecting our ab initio cluster calculations with the expected results for solid state systems has been developed and represents an important step forward with regard to justifying our computational approach. A paper describing this work is in press. The Flynn group is now planning to do experiments on a TiO_2 surface, a material of direct relevance to the DOE Solar Photochemistry program, and we will carry out similar calculations for that system (preliminary studies of TiO_2 electronic structure is in progress, as is discussed above). A major goal is to be able to reliably infer the orientations of molecules on the surface from the STM calculations; some progress was made along these lines for the halogens on graphite system described above.

Future Directions: We are aiming at assembling methods capable of describing solar photochemistry as carried out by complex systems such as the Graetzel cell. This requires treatment of a TiO_2 solid surface, dye molecules adsorbed to the surface, redox partners in solution, and the transfer and trapping of electrons throughout these components. All of the technology described above will be useful in this endeavor. Additionally we will need to use mixed QM/MM methods which are currently under development for this purpose.

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CARRIER DYNAMICS IN QUANTUM DOTS AND QUANTUM DOT ARRAYS AND THEIR ROLE IN SOLAR PHOTON CONVERSION

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One approach we have been investigating to increase the conversion efficiency of solar photon conversion cells above the Shockley-Queisser thermodynamic limit of 32% is to reduce the energy loss caused by the thermal relaxation of photogenerated hot electrons and holes by converting the hot carriers into chemical or electrical free energy before they relax to the band edge. There are two fundamental ways to accomplish this.

One way produces an enhanced photovoltage, and the other way produces an enhanced photocurrent. The former requires that the carriers be extracted from the photoconverter before they cool, while the latter requires the hot carriers to produce a second (or more) electron-hole pair through impact ionization, a process that is the inverse of an Auger process whereby two electron-hole pairs recombine to produce a single highly energetic electron-hole pair. In order to achieve the former, the rates of photogenerated carrier separation, transport, and interfacial transfer across the semiconductor interface must all be fast compared to the rate of carrier cooling. The latter requires that the rate of impact ionization (i.e., inverse Auger effect) is greater than the rate of carrier cooling and other relaxation processes for hot carriers.

We have found that the relaxation dynamics of photogenerated carriers may be markedly affected by quantization effects in the semiconductor. We initially found greatly slowed hot electron cooling in 2-dimensional semiconductor nanostructures (i.e., in semiconductor quantum wells and superlattices). However, to achieve this effect it was necessary to generate a high density of photogenerated hot electrons ($> 10^{18}$ cm^{-3}), producing a *hot* phonon bottleneck and cooling times as long as several hundred ps at carrier densities of 10^{19} cm^{-3}. However, for 0-dimensional semiconductors, i.e., quantum dots where the carriers are confined in three dimensions, slow hot carrier cooling and a phonon bottleneck are predicted at low carrier densities that correspond to unconcentrated solar irradiance.

We have recently demonstrated that slow hot electron cooling in InP QDs can be achieved under certain conditions based on fs transient absorption spectroscopy using 2-beam and 3-beam configurations with pump and probe wavelengths spanning the range from the UV to the mid-IR. For QDs, one mechanism for bypassing the phonon bottleneck, and hence allowing fast cooling, is the Auger process. Here, a hot electron can transfer its excess kinetic energy to a thermalized hole via an Auger process, and then the hole can cool quickly because of its higher effective mass and more closely spaced quantized states. However, if photogenerated electrons are created without holes present or the hole is removed from the QD core (for example by a fast hole trap at the surface), then the Auger process is blocked and the phonon bottleneck effect can occur and lead to slow electron cooling. Slow hot electron cooling by fast hole trapping was first shown for CdSe QDs by P. Guyot-Sionnest and V. Klimov. We have now shown slowed hot electron cooling (3-7 ps) in InP QDs when only electrons are present in the QD core; this condition was achieved either by injecting electrons into the QD from an external reducing agent or by fast hole trapping to an efficient hole trap at the QD surface. When both electrons and holes are confined to the QD core, the cooling time is 350-750 fs. Since surface states and surface chemistry play a critical role in the spectroscopy and carrier dynamics of QDs, ODMR (collaboration with E. Lifshitz, Technion, Israel) and EPR (collaboration with T. Rajh and M. Thurnauer, Argonne) studies of our InP QDs have characterized the surface defect chemistry and we have been able to correlate these results with the unique optical properties and carrier dynamics of the QDs.

An important advance in the area of impact ionization by hot photogenerated electrons was made by the first demonstration of an optical technique (transient vis pump- IR probe spectroscopy) to determine impact ionization. In this method, the wavelength of a visible pump beam is varied and the photogenerated electron density is monitored by a mid-IR probe beam. In the initial experiments, a single crystal wafer of Ge was pumped at wavelengths between 650 and 387 nm, and the quantum yield for electron-hole pair production was determined by varying the pump power at various fixed wavelengths and plotting the absorbance change versus pump power. The relative quantum yield jumped from 1.0 to 1.9 at a phonon energy of about 2.3 eV. The band gap of Ge is 0.7 eV, so the threshold for impact ionization is about 3 times the band gap. This threshold is the same as that measured previously by other researchers by determining photocurrent quantum yields in Ge p-n junctions. A critical advantage of the optical method is that it can be used to measure impact ionization in QDs, where electrical contacts to individual QDs cannot be made to measure photocurrent.

Future research will study the cooling dynamics in QDs in greater detail and determine the maximum cooling time that can be achieved as a function of various QD and QD array parameters, such as QD size, potential barrier height, inter-QD electronic coupling, QD surface chemistry, electric field in p-QD array-n structures, etc. Additional future research will focus on determining the threshold photon energy for impact ionization in InAs QDs, and other low bandgap (< 0.4 eV) semiconductor QDs, compared to bulk material to see if the predicted reduction in threshold energy for QDs is verified. Finally, a detailed kinetic model for the various competing relaxation and electron transfer processes vis-à-vis impact ionization will be developed and confirmed.

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ELECTRON AND HOLE DYNAMICS IN LAYERED SEMICONDUCTOR NANOPARTICLES

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The development of highly photostable semiconductor nanoparticles and the elucidation of their spectroscopy, photophysics and interfacial electron transfer dynamics are the central goals of this research. To this end, nanoparticles of several types of layered semiconductors have been synthesized and studied. The most detailed studies are on GaSe and MoS_2 nanoparticles, and are discussed below.

GaSe nanoparticles

GaSe nanoparticles are synthesized by the reaction of $GaMe_3$ with trioctylphosphine selenium in a solution of TOP/TOPO at high temperature. TEM images show that this synthesis produces GaSe nanoparticles in the size range of 2 – 6 nm. The size distribution of these particles may be narrowed by size selective precipitation. Alternatively, the particles are sufficiently inert that they may be size segregated by column chromatography, with relatively monodisperse nanoparticles samples obtained by taking narrow fractions off the column. Electron diffraction results along with crystallographic simulations indicate that these particles have a two-dimensional, single tetra-layer type structure, i.e., they consist of Se-Ga-Ga-Se sheets.

The photophysics and relaxation dynamics of GaSe nanoparticles have been studied in room temperature solutions, using static and time-resolved emission methods. Bulk GaSe is an indirect bandgap semiconductor with the lowest direct transition at 588 nm. This transition undergoes considerable quantum confinement in the nanoparticles, resulting in an absorption onset in the 360 to 450 nm region. Following excitation with polarized 400 nm light, room temperature particles exhibit intense, polarized emission, with a static emission maximum at 480 nm (Φ_{em}=15%). The anisotropy spectrum peaks on the blue edge of the emission spectrum. Static emission spectra along with wavelength-dependent kinetic results permits the reconstruction of time dependent spectra. The time-dependent spectra may be interpreted in terms of an energetic model which is based on the band edge and trap state energetics in bulk GaSe. The results show an initial 80 ps decay component in the total emission, but not in the anisotropy decay kinetics. There is a ca. 270 cm^{-1} shift in the emission maximum during this decay. This transient is assigned to electron relaxation and corresponds to a direct to indirect band edge relaxation. This is followed by 400 ps and 2.4 ns decay components in both the total emission and the anisotropy kinetics. These transients are assigned to trapping of holes in shallow, followed by deep acceptor levels. As the slow decay occurs, the 480 nm emission is replaced by a much weaker, broad and unpolarized 520 nm emission.

Despite the fact that relaxation to trap states occurs with high quantum efficiency, the particles are extremely photostable, even in the presence of oxygen. This may be understood in terms of a qualitative molecular orbital picture of the bonding in the ground and excited states. Photoexcitation produces a nodal plane between the adjacent gallium atoms, which does not weaken the surface bonds. The relaxation and carrier trapping dynamics are only slightly affected by the nature of the surrounding solvent. This indicates that the carrier traps are intrinsic to the TOP/TOPO capped nanoparticles, rather than associated with solvated dangling bonds on the nanoparticle edges.

MoS_2 nanoparticles

Several different sizes of MoS_2 nanoparticles have been synthesized and their dynamics have been studied using time-resolved optical spectroscopy. Each size is also characterized by TEM images and electron diffraction. We find that different sizes of nanoparticles can be synthesized directly, by controlling the surface binding ligands in the reaction mixture. Alternatively, the same size distribution may be synthesized from samples of polydisperse nanoparticles. The observation that larger or smaller discrete sizes may be obtained from polydisperse samples indicates that these nanocluster sizes are thermodynamically favored, that is, these sizes correspond to free energy minima.

Static and time resolved absorption and emission polarization spectroscopy were used to determine the polarizations of several observed transitions in each case. It is known that the lowest allowed transition in bulk MoS_2 is x-y polarized. We find that the 8 nm particles have a lowest energy absorption maximum at 473 nm which has mixed x-y and z polarizations, 4.5 nm particles have an absorption maxima at 400 and 440 nm which are x-y and z polarized, respectively, and 3.5 nm particles have an absorption maximum at 362 nm which is z polarized. These results indicate that the ordering of the lowest excited states changes as the particle size decreases. The results may be understood in terms of the effects of z-axis and x-y plane quantum confinement on differently polarized transitions, and are summarized in figure 1, below.

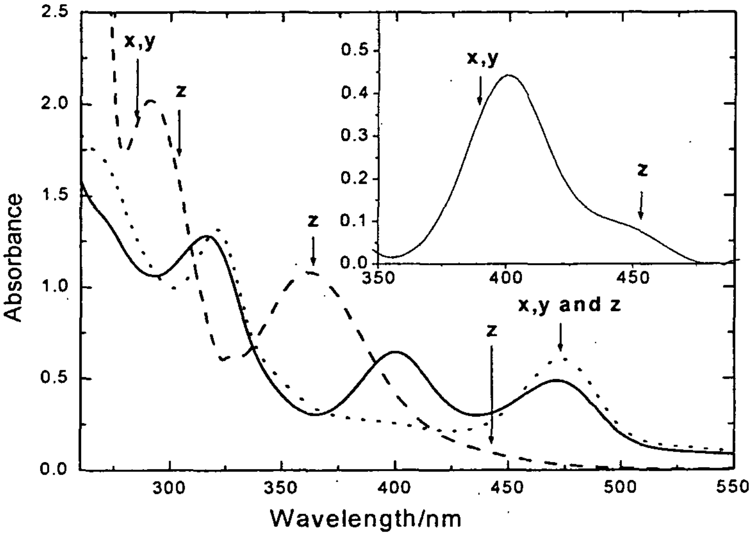

Figure 1. Absorption spectra of 3.5 nm (dashed curve), 8 nm (dotted curve) and of a mixture of 4.5 and 8 nm (solid curve) MoS_2 nanoclusters. A difference curve corresponding to just the 4.5 nm nanoclusters is shown in the insert. The assigned polarizations of the absorption transitions are also shown.

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SEMICONDUCTOR-BASED NANOCOMPOSITES: PREPARATION, PROPERTIES, AND PERFORMANCE

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Nature has produced remarkable composites for millions of years. As in other fields of scientific and technological endeavor, mankind has attempted to develop artificial analogs of these natural materials. The bricks that the ancient Egyptian civilization developed by adding straw to mud are among the earliest examples of man-made composite materials. Within the narrower context of photoelectrochemistry, composite films and particles have been increasingly studied and utilized in many laboratories around the world. Thus a diverse array of semiconductor-based composite materials have been prepared, characterized, and utilized in many applications ranging from photocatalysis, photovoltaic cells, photoelectrochromic windows and displays, light-emitting devices, and sensors.[1] The composite architectures (nanoarchitectures in many cases) are equally diverse. In this discussion we will highlight the many advances that have been made in the chemistry underlying the preparation, properties, and performance of these composite materials. We will use recent data acquired in our laboratory as illustrative examples.

The preparation methods of various types of semiconductor-based composites are first surveyed. We will then present selected examples where these composite materials have shown enhanced performance relative to their counterparts in the "neat" state. Some of the systems discussed fall under the category of nanocomposites in that one of the phase dimensions (length, width, or thickness) is in the nanometer size range. The special properties of these materials arise from the interactions of their component phases at the interfaces. For example, recent work in our laboratory has shown enhanced photocurrents from Ni/TiO_2 composites, relative to "neat" TiO_2 films.[2] This enhancement has been attributed to a site-proximity mechanism based on preferential binding of solution species on Ni sites adjacent to locales in the TiO_2 phase where the photocarriers are generated.[3,4]

The scope of the study of semiconductor-based composites is much enhanced by the recent development of template-based film growth strategies.[1] Thus the photoelectrochemical behavior of a given semiconductor nanodot (p-CuSCN or n-TiO_2) in an alumina template matrix, is remarkably different from that of its macro-sized counterpart. Three separate examples of this distinct difference in behavior are presented. It is shown how the photoresponse (e.g., photocurrent) may be amplified (from a low level typical of the signal emanating from a ~ 10^{-11} cm^2 region corresponding to a semiconductor nanodot) by using a large number of electrically inter-connected Au nanowires to support the overlying semiconductor nanodots. The anomalous photoresponse of p-CuSCN nanodots in the template matrix was also numerically simulated by a simple parallel equivalent circuit consisting of a semiconductor and a photocapacitor. Possible practical application scenarios are finally presented for these nanostructures.

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PHOTOCATALYSIS AND PHOTOELECTROCHEMISTRY USING INORGANIC COLLOIDS AND NANOCRYSTALS

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Our recent DOE-supported work has focused on the use of nanoscale inorganic compounds (metal oxide colloids, layered metal oxide semiconductors, and template-grown semiconductor nanowires) in photocatalysis and photoelectrochemistry. This work is being directed towards the synthesis and characterization of particle-based systems for catalyzing thermodynamically uphill photochemical reactions, such as the photolysis of water.

There are several known oxide semiconductors that evolve hydrogen photochemically in the presence of sacrificial and non-sacrificial electron donors. Visible light absorbing niobates, for example $RbPb_2Nb_3O_{10}$, when catalyzed by noble metals photochemically decompose methanol to hydrogen. Recently, Arakawa, et al. reported overall visible light water splitting using Ni-doped $InTaO_4$ as a photocatalyst. In our previous studies of layered metal oxide semiconductors $K_4Nb_6O_{17}$ and $KTiNbO_5$, we found that sensitization with $Ru(bpy)_3^{2+}$ derivatives gave photochemical hydrogen evolution with I^- as an electron donor. In order to realize efficient water splitting in any of these systems, the problem of oxygen evolution catalysis must be addressed. Currently, the best colloidal catalysts for O_2 evolution (IrO_2 and RuO_2) have turnover rates that are too slow for coupling to sensitized systems in which the charge separation lifetimes are on the order of milliseconds.

We have now studied the IrO_2 system by several techniques in order to understand why oxygen evolution is slow, and to make more active colloidal catalysts that are compatible with layer-by-layer assembly of an overall water splitting system. We found phosphate buffers decompose the oxidized sensitizer molecules, but that silicate-bicarbonate solutions are ideal buffers, giving sensitizer turnover numbers in excess of 200 in persulfate/$Ru(bpy)_3^{2+}$ solutions. Adsorption of Nafion additionally stabilizes the colloidal IrO_2 particles and increases both the turnover rate and the quantum yield for oxygen evolution. Bleaching recovery experiments established that electron transfer between the IrO_2 colloid and the oxidized sensitizer is an order of magnitude faster than the oxygen evolution rates inferred from catalyst turnover numbers. We also found that sensitized IrO_2 colloids could be successfully coupled to solid supports by using a polymeric version of the $Ru(bpy)_3^{2+}$ sensitizer. The most efficient heterogeneous photocatalyst was obtained by the adsorption of a mixture of the polymer and colloidal IrO_2 onto SiO_2 in Na_2SiF_6-$NaHCO_3$ solution. TEM showed that the 10-20 nm diameter colloidal IrO_2 particles were covered with the polymer, and these core-shell catalyst/sensitizer particles adsorbed on the silica surface. This result indicates that the polymer-IrO_2 aggregates retain their activity when immobilized on a support that might be used to organize overall water splitting systems.

In order to more rapidly optimize the composition of these oxygen evolution catalysts and the conditions under which they are used, we developed a parallel screening method. This method relies on the fact that photosensitizer turnover numbers are lower with poorer catalysts, and hence there is more rapid bleaching of these sensitizer/colloid solutions during continuous photolysis. We varied catalyst compositions (IrO_2 doped with Pt, Os, and Ru), pH, sensitizer and colloid concentrations in solutions and screened them in 96-well plates, using an overhead projector as a light source for the photocatalyst array. The array was periodically interrogated with a plate reader to measure the absorbance and emission in each well. This method gave essentially the same ranking of catalysts as serial sampling for O_2, but allowed 96 compositions and/or reaction conditions to be screened at once. We determined that both Pt- and Os-doping enhanced the turnover rate. While the gains in activity were modest (about a factor of 1.5 for compared to IrO_2), this parallel method may be useful for a variety of other optimization problems that involve photosensitizers.

Recently, we have begun work on a new class of visible light-absorbing semiconductors in which some of the lattice oxygen is replaced by nitrogen. This work follows on the recent discovery by Asahi and coworkers that <1% nitrogen doping of TiO_2 films extend their photocatalytic activity into the visible part of the spectrum. We have made layered and three-dimensional oxynitride perovskites by thermal reaction of oxide and carbonate precursors with NH_3. The degree of nitrogen substitution can be controlled by choosing the appropriate charge-balancing cations. For example, $RbCa_2Nb_3O_{10}$, a three-layer perovskite with an indirect band gap of 3.25 eV, reacts with Rb_2CO_3 and NH_3 to yield $Rb_2Sr_2Nb_3O_9N$, in which 10% of the lattice oxygen has been replaced by nitrogen. We have also synthesized $CaTaO_2N$, $SrTaO_2N$ and Sr_2TaTiO_5N, which have higher levels of nitrogen substitution and are structurally analogous to the three-dimensional perovskites $KTaO_3$ and $SrTiO_3$. From UV-visible diffuse reflectance spectra, we estimate indirect bandgaps of 2.90, 2.55, and 3.50 eV for $CaTaO_2N$, $SrTaO_2N$, and $KTaO_3$, respectively. The bandgaps decrease with increasing nitrogen substitution. For a given O/N ratio, the bandgap increases with smaller charge balancing cations, because of cooperative tilting of octahedra. LMTO-ASA band structure calculations on $SrTaO_2N$ and $KTaO_3$ show, as expected, that the conduction band is composed primarily of Ta 5d states. The nitrogen 2p states lie at the top of the valence band, and are primarily responsible for narrowing the bandgap, relative to the analogous oxide. We are currently determining the conduction and valence band edge potentials of these compounds and are investigating their behavior as photocatalysts. We are also studying the intercalation and exfoliation chemistry of the layered oxynitrides, as this represents a means of introducing oxygen- and hydrogen-evolving catalyst particles.

We are also synthesizing semiconductor nanocrystals using anodic aluminum oxide (AAO) membranes as templates. We have electrodeposited CdSe in AAO, and are using it for vapor phase growth of CdSe nanowires. In collaboration with Prof. Joan Redwing (Penn State Materials Science and Engineering) we have made 300 nm diameter bicrystalline Si nanowires in AAO by a vapor-liquid-solid growth technique. The goal of this work is to make arrays of single crystal semiconductor wires for photoelectrochemistry, and series p-n junction nanowires for overall water splitting using visible light.

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Session VII

Photosynthetic Membranes, Reaction Centers and Light Harvesting

LIGHT-POWERED Ca^{++} TRANSPORT BY AN ARTIFICIAL PHOTOSYNTHETIC MEMBRANE

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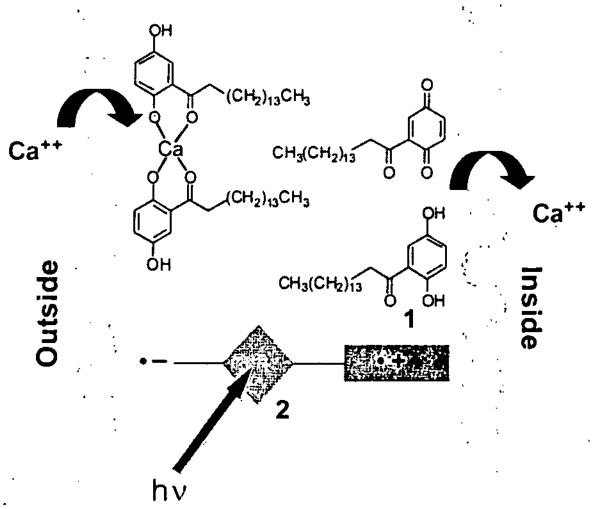
Transport of ions across biological membranes and against a thermodynamic gradient is essential to myriad biological processes, including generation of transmembrane electrochemical potential and various signaling and regulatory functions. Although the pumping of hydrogen ions across membranes lies at the heart of solar energy conversion by living things, the transmembrane transport of metal ions is also of major importance. In spite of the many examples in biology, artificial constructs demonstrating active transport of metal ions across membranes to generate chemical potential are uncommon.



We have prepared a synthetic, light-driven transmembrane Ca^{++} pump based on a redox-sensitive, lipophilic Ca^{++} binding shuttle molecule and powered by an intramembrane artificial photosynthetic reaction center. A schematic representation of the system is shown in the Figure. The artificial reaction center **2** is a carotenoid-porphyrin-quinone (C-P-Q) molecular triad inserted vectorially into the membrane of a liposome, with the carotenoid moiety toward the inside surface. Excitation of the porphyrin is followed by photoinduced electron transfer to the quinone to yield $C\text{-}P^{\bullet+}\text{-}Q^{\bullet-}$. Electron donation from the carotenoid gives a long-lived $C^{\bullet+}\text{-}P\text{-}Q^{\bullet-}$ charge-separated state. At least two molecules of shuttle hydroquinone **1** at the external surface of the membrane lose protons to the aqueous phase (pH 7.5) and bind Ca^{++}. The resulting lipid-soluble complex diffuses across the membrane to the opposite interface. Oxidation of hydroquinone at this location by carotenoid radical cations generates quinone, releasing Ca^{++} to the aqueous phase inside the liposome. Diffusion of quinone and neutral hydroquinone (carrying two protons) to the outside of the membrane followed by reduction of the quinone by the artificial reaction center completes the redox loop and regenerates the reaction center. No net transport of protons is required or observed.

The construct transports calcium ions across the phospholipid membrane of the liposome to develop both a calcium ion concentration gradient and a membrane potential. Although the quantum yield is relatively low (~1%), the electrochemical potential developed is significant (120 mV). Future experiments are designed to elucidate the mechanistic details of Ca^{++} transport and develop other applications of the solar-powered transmembrane charge separation system.

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11. "Active Transport of Ca^{++} by an Artificial Photosynthetic Membrane", I. M. Bennett, H. M. Vanegas Farfano, A. Primak, P. A. Liddell, L. Otero, L. Sereno, J. J. Silber, A. L. Moore, T. A. Moore and D. Gust, submitted for publication.
12. "High Efficiency Energy Transfer from Carotenoids to a Phthalocyanine in an Artificial Photosynthetic Antenna," E. Mariño Ochoa, R. Palacios, G. Kodis, A. N. Macpherson, T. Gillbro, D. Gust, T. A. Moore and A. L. Moore, submitted for publication.
13. "The Design and Synthesis of Artificial Photosynthetic Antennas, Reaction Centers and Membranes," T. A. Moore, A. L. Moore and D. Gust, submitted for publication.

DESIGN AND FABRICATION OF OPTIMAL NEAR-FIELD OPTICAL PROBES FOR IMAGING PHOTOSYNTHETIC MEMBRANES

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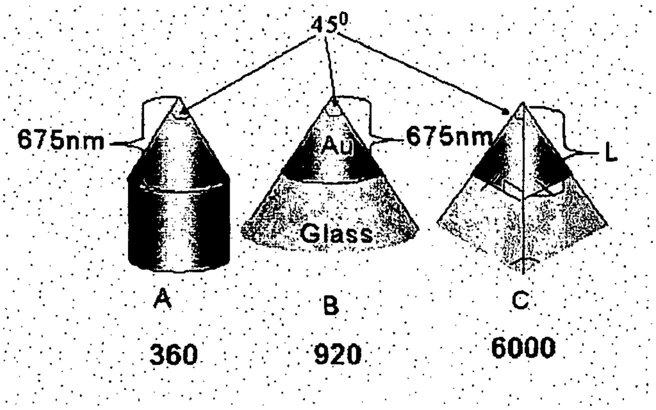
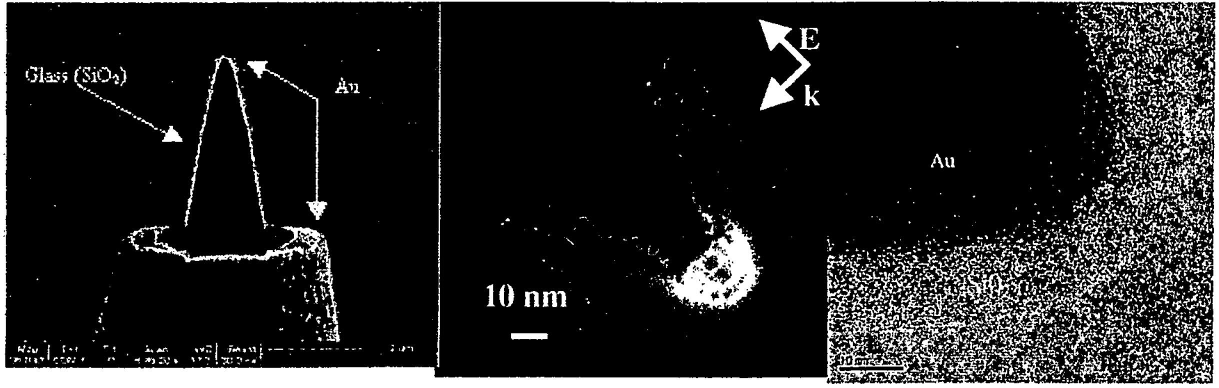
In order to spectroscopically map photosynthetic membranes, we have been developing near-field microscopy with high spatial resolution. In 1991, Betzig et al. pioneered the use of aluminum coated, tapered optical fibers for nearfield microscopy. Their approach popularized the practice of generating near-field optical images with an aperture, which extends many optical contrast mechanisms beyond the diffraction limit. The finite skin depth of metals at optical frequencies, however, places a fundamental limit on the spatial resolution obtainable with coated fiber probes. Typical aperture probes offer resolutions on the order of 50-100 nm. The study of closely packed proteins in photosynthetic membranes requires resolution on the order of 10 nm. Furthermore, the low light throughput of the aperture necessitates a high input power that causes heating of the probe and sample. To overcome these difficulties, a number of groups began work on means of generating near-field images with apertureless probes. Early studies used a solid metal tip as a scattering center, and the signal was collected in the far field at the same wavelength as the illuminating source. In these scattering experiments, the optical signal is sensitively dependent on the topographic features of the samples, so quantitative understanding of the optical contrast is difficult.

Our new method is based on the highly enhanced evanescent wave in the vicinity of a solid metal tip under illumination. The apertureless probe is used as a localized excitation source for spectroscopic measurements, rather than as a scattering center. The spectroscopic response of the sample, such as fluorescence, Raman or nonlinear response, provides a far field detected optical signal at a frequency different from that of the excitation. Images generated in this fashion are simpler to interpret, in that the signal originates in the sample rather than in the probe. This concept was first clearly experimentally demonstrated by two-photon excited fluorescence with 15 nm resolution in 1999. This tip enhanced nonlinear optical microscopy (TENOM) experiment takes advantage of the high field enhancement and nonlinearity to generate contrast above the far-field background. In order to properly treat the interaction of nanoparticles with optical fields, a full electromagnetic solution is needed. The finite difference time domain method (FDTD) is a flexible numerical means of solving electromagnetic problems by integrating Maxwell's equations for an arbitrary geometry. The space is divided into cubic cells, and each cell is assigned the susceptibility for a given material. We have used 3D FDTD simulations to search for optimal probe

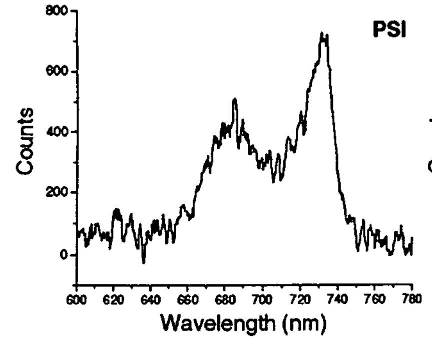


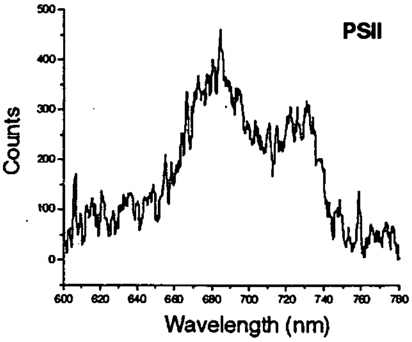
geometries with high field enhancement and high spatial resolution. The above figure shows a conical shape (A), a finite cone (B) and a trigonal pyramid (C) with 10 nm end diameters and the corresponding intensity enhancement factors written below. The results indicate that probes need to be not only sharp, but also finite in length in order to generate the highest field enhancements. The trigonal pyramid probe gives the highest intensity enhancement (6000 higher than the incident intensity).

The trigonal pyramid tip was fabricated using a focused ion beam system, which is capable of milling on the nanometer scale. The electron micrograph of the probe (left figure) is shown together with the corresponding FDTD simulation (middle figure). In order to prevent fluorescence quenching by gold, the tip is coated with a 10 nm of SiO_2 film by electron beam assisted deposition (right figure).



Below is our preliminary result on spatially resolved emission spectra of photosynthetic membrane fragments from green plants, which were taken with our near-field probe under two-photon excitation. Interestingly, we observed position dependent emission spectra, characteristic of PS I and PS II, respectively. This result shows the promise of spectroscopic mapping of photosynthetic membranes. Rationally optimized near-field probes open the door to optical studies of chemical and biological systems on the nanometer scale.





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BRIDGING THE GAP BETWEEN MOLECULAR MODELS AND PHOTOSYNTHETIC FUNCTION

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A central challenge in photosynthesis research lies in resolving the physical and chemical parameters underlying highly efficient photochemical energy conversion. The determination of high-resolution atomic models of photosynthetic proteins and artificial assemblies from crystallographic data represent the first step. However, while single crystals are well-suited for detailed structural resolution, they are typically difficult samples for analysis of photosynthetic function, and a gap exists between the measurement of static structure in crystalline states and the measurement of photosynthesis and energy conversion processes in non-crystalline media.

In this project we are investigating direct correlations between structure, structural dynamics, and function of photosynthetic assemblies using synchrotron wide-angle X-ray scattering techniques. Synchrotron X-ray scattering is useful for structural characterization of molecular assemblies because it is rooted in the same atomic scattering phenomena as crystallographic diffraction, and quantitative comparisons can be made between solution scattering data and crystallographic models. We have been developing approaches for analyzing scattering data parameterized in terms of the well-defined crystallographic observables of time-averaged atomic position, atomic thermal factors (Debye-Waller factors), and incoherent rigid-body motions. The value of this approach is that it provides: i) a quantitative determination of the sometimes differing details of macromolecular structure in crystalline and solution states, ii) a method for extending crystallographic models to fit scattering data recorded under a range of solution conditions not addressable by crystallography, and iii) it can be carried out in time-resolved mode (e.g., see Chen et.al. 2001 Science 292:262). We are utilizing this technique for analysis of structure and light-induced structural change in both natural and artificial photosynthetic systems. The comparison of structure and function in natural and artificial photosynthetic systems provides a means to identify unique features of natural photosynthesis.

Comparison of Wide-Angle X-ray Scattering Data and Protein Crystallographic Models. Small (~ 10 K MW), water-soluble, cofactor-containing proteins ubiquitously serve as redox shuttles between membrane-bound electron protein complexes in biological energy conserving electron transfer chains. We have examined the wide-angle scattering patterns for a number of redox proteins and have found that the wide-angle patterns generally consist of soft, undulatory features that are characteristic for specific structures (figure 1). We have demonstrated the sensitivity of wide angle scattering patterns to protein conformation state by detecting oxidation state and temperature dependent changes

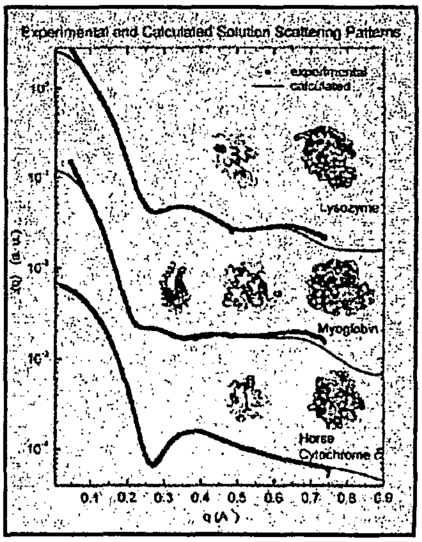

Figure 1. Comparison of experimental and calculated scattering patterns.

in cytochrome *c*. Oxidation dependent changes can be understood to arise from small changes in the time-averaged atomic position (~ 1 Å rms deviation), while the temperature dependent changes can be understood to arise in changes in the amplitudes incoherent rigid-body motions from protein segments. The cytochrome c structures provide useful models for calibrating the sensitivity of wide angle X-ray scattering to subtle reaction-linked structural change.

Reaction Center Conformational States. We have used X-rays scattering to identity conformational states of the reaction center. An unusual temperature-dependent switch from a monomeric to dimeric state was found for detergent solubilized reaction cetners near 4°C. The switch behaves like a protein phase transition that is modulated by divalent metal ions. The dimeric stoichiometry reflects association through a single contact site on the reaction center that may function in the organization of reaction centers in photosynthetic membranes. Low temperature crystal diffraction and solution XAFS (L. Chen, poster this meeting) measurements of trapped, light-induced redox states have detected atomic reorganization associated with quinone reduction. Reorganization of this magnitude is not detected in room temperature scattering measurements, pointing toward a possible consequence of thermally activated mixing of conformational states. These experiments establish an avenue for correlating protein motions to gated electron transfer.

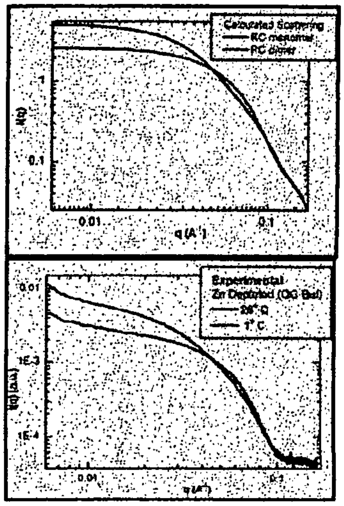

Figure 2. Temperature-dependent changes in RC scattering.

Artificial Photosynthetic Assemblies. We have also begun analyses of wide-angle scattering data for a range of porphyrin-based model compounds. These compounds provide a test for resolving structure and reaction-linked structural change in solution. Characteristic scattering patterns are detected for monodispersed porphyrin compounds, covalently linked porphyrin assemblies, and large, self-assembled organized arrays. Scattering data for the porphyrins are demonstrated to be sensitive to ring substituents, conformation, metal ligation. Significant effects of atomic thermal factors are detected for simple porphyrin compounds and additional rigid body motions are detected for covalently linked porphyrin assemblies. These experiments demonstrate an opportunity to correlate structure and photochemical activity in artificial photosynthetic assemblies.

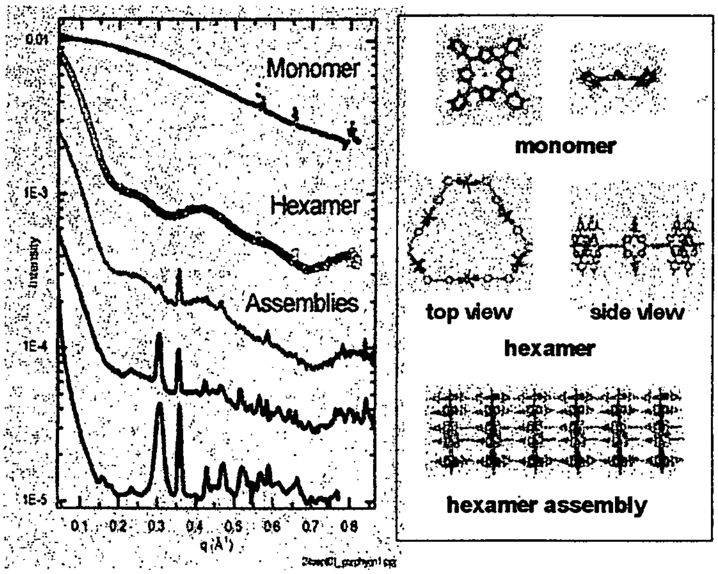

Figure 3. Scattering patterns for porphyrins and porphyrin assemblies.

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METAL ION MODULATED ELECTRON TRANSFER IN PHOTOSYNTHETIC BACTERIAL REACTION CENTERS

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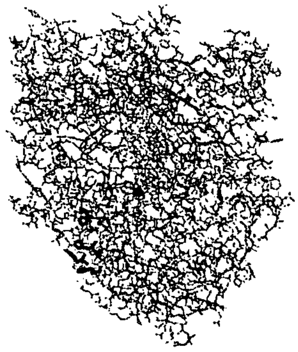
Electron-transfer reactions that occur within proteins are often intimately coupled with other reactions such as conformational changes or proton transfer. Fundamental to understanding biological electron transfer is discerning the involvement of heterogeneous polypeptide environments surrounding the redox cofactor sites in these reaction mechanisms. The structurally characterized photosynthetic bacterial reaction center (RC) provides an important native system to explore intrinsic questions concerning biological electron transfer. In RCs, electron transfer occurs sequentially after photoexcitation of a bacteriochlorophyll dimer (P), through one set of cofactors, terminating in the electron transfer between two quinone cofactors Q_A and Q_B. After a two-electron, two-proton reduction, Q_BH_2 is released from the RC, transporting electrons and protons to other redox components in the bacteria. The electron transfer between Q_A and Q_B is temperature activated, coupled to proton movement, and believed to be rate limited by protein motion. While it is widely accepted that protein conformational changes play an important part in biological electron transfer, there is little experimental information on the role of anisotropic local protein environments in modulating electron transfer. We have discovered a local protein environment, a metal-binding site, which apparently controls protein dynamics important for electron transfer in the RC.

A New Metal Site that Influences $Q_A^-Q_B \rightarrow Q_AQ_B^-$ Electron Transfer. We have found that RCs from *Rb. sphaeroides* R26 stoichiometrically bind Zn(II) and this Zn(II)-binding slows $Q_A^-Q_B \rightarrow Q_AQ_B^-$ electron transfer. Zn(II) influences electron transfer from a remote position on the RC as the Zn(II) site is spatially distinct from the non-heme high-spin Fe(II) site which is buried in the protein interior between the quinones Q_A and Q_B. Thus far, no definitive role for this Fe(II) has been established. Apparently the Fe(II) does not facilitate electron transfer between Q_A and Q_B, and substitution of different divalent metal ions into the Fe site does not significantly alter the electron-transfer characteristics. We have found, however, that divalent metal ions can modulate electron transfer between the quinones when bound to a previously unidentified metal site. Zn^{+2} binding to this site dramatically slows electron transfer from Q_A to Q_B with the room temperature kinetics becoming distributed across the microsecond to millisecond time domain. This effect of metal binding on the kinetics is similar to the more global effect of cooling RCs to 2 °C in the absence of Zn^{2+}. We propose that Zn^{2+} binding alters the conformation of a local protein domain, thereby limiting protein motions that are necessary for efficient electron transfer. Since our initial report of this second metal site, others have extended this work to show that Zn^{2+} and Cd^{2+} binding influences the proton uptake of Q_B.

Structure and Location of the Metal Site. The determination of the location and structure of the metal site and local protein environment is important for understanding the mechanism of metal ion-induced modulation of electron and proton transfer. A second metal ion is not observed in the *Rb. sphaeroides* RC X-ray crystal structure. Thus, we have used paramagnetic Cu^{2+} ($3d^9$) to spectroscopically probe two metal sites on the RC: the well characterized Fe-quinone site and a second surface site, which we believe to be at or near the Zn site that regulates $Q_A^-Q_B \rightarrow Q_AQ_B^-$ electron transfer and Q_B proton uptake. Transient optical measurements show that Cu^{2+} slows $Q_A^-Q_B$

$\rightarrow Q_AQ_B^-$ electron transfer in native Fe-containing RCs from *Rb. sphaeroides*, similar to the observed effect of Zn^{2+} on this electron transfer step.

The continuous wave (cw) and pulsed EPR results clearly indicate two spectroscopically different Cu^{2+} environments on the *Rb. sphaeroides* RC. A cw EPR spectrum typical of a type 2 copper center indicative of a tetragonal Cu^{2+} environment was observed for RCs with Cu^{2+} bound to the surface site. Furthermore, Cu^{2+} bound at the surface site does not magnetically interact with the light-induced radicals and, therefore, based on the observed line broadening, the surface site must be at least 23 Å removed from the primary donor (P^+) and reduced quinone acceptor (Q_A^-). Electron spin-echo envelope modulation (ESEEM) spectroscopy has been used to characterize the magnetic interactions between Cu^{2+} and weakly coupled magnetic nuclei in Cu-RCs. From these pulsed EPR experiments, modulations were observed that are consistent with multiple weakly hyperfine coupled ^{14}N nuclei in close proximity to Cu^{2+}, indicating that two or more histidines ligate the Cu^{2+} at the surface site. The ESEEM results agree with our proposal that a cluster of histidines may be metal binding ligands at the surface site. These histidines are positioned beneath the Q_B binding pocket and surround a water channel that is proposed to be a proton pathway to Q_B. Methods to spectroscopically investigate the interaction of metal ions with the terminal electron acceptor Q_B are being developed.



Crystal Structure of the *Rb. sphaeroides* RC depicting potential Cu-histidine ligands in bold.

General Nature of Metal Ion Modulation of Electron Transfer. We have extended our studies to investigate the metal binding properties of RCs from *Rhodobacter capsulatus* and *Blastochloris* (formerly *Rhodopseudomonas*) *viridis*, specifically searching for a surface metal site involved in electron transfer. We have developed reliable procedures for binding Cu^{+2} to isolated RCs from three species of photosynthetic bacteria. The EPR spectroscopic results have been correlated with transient optical measurements of the solution kinetics. These results provide the first direct spectroscopic evidence that RCs from *Rb. capsulatus* and *Blc. viridis* have a surface metal site involved in electron transfer. Comparison of the cw EPR and ESEEM spectra obtained show that the Cu^{2+} surface site has similar geometry and ligands in each species. The influence of metal ions on the $Q_A^-Q_B \rightarrow Q_AQ_B^-$ electron transfer rates in the less well-characterized RCs of *Blc. viridis* and *Rb. capsulatus* provides evidence of the general nature of metal-ion induced regulation of electron transfer. In each species, the electrochromic response of the bacteriopheophytin cofactors associated with $Q_A^-Q_B \rightarrow Q_AQ_B^-$ electron transfer is slowed in the presence of Cu^{2+}. This slowing is similar to the Zn^{2+} effect observed for RCs from *Rb. sphaeroides*. Interestingly, the cw EPR spectrum of *Blc. viridis* exhibits signals from two spectroscopically distinct Cu^{2+} environments. Temperature-dependent conformational flexibility of the Cu^{2+} environments is currently being investigated. Further elucidation of these Cu^{2+} sites will provide a means to investigate localized proton entry into the RCs of *Rb. capsulatus* and *Blc. viridis* as well as locate a site of protein motions coupled with electron transfer.

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L. M. Utschig, O. Poluektov, D. M. Tiede, and M.C. Thurnauer
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Structure of the $P^{+}_{700}A^{-}_{1}$ Radical Pair Intermediate in Photosystem I by High Time Resolution Multifrequency Electron Paramagnetic Resonance: Analysis of Quantum Beat Oscillations
G. Link, T. Berthold, M. Bechtold, J.-U. Weidner, E. Ohmes, J. Tang, O. Poluektov, L. Utschig, S. Schlesselman, M.C. Thurnauer and G. Kothe
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High-frequency EPR Approach to the Electron Spin-Polarization Effects Observed in the Photosynthetic Reaction Centers
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Chem. Phys. Lett., submitted

POLARIZED NMR SPECTRA FROM PHOTOSYNTHETIC REACTION CENTERS: MECHANISM AND INTERPRETATION

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^{15}N Solid State NMR spectra of illuminated, and electron transfer-blocked reaction centers (*Rb. sphaeroides*, R-26) exhibit strongly emissive signals assignable as the tetrapyrrole nitrogens of the ground state of the special pair P, the bacteriopheophytin acceptor H, and a nearby histidine residue. Computational and experimental studies support a 3-spin coherent mixing mechanism for polarization development, similar to that previously discussed by Norris, Kothe, and others. Nanosecond time scale coherent mixing of nuclear states and electron zero-quantum states are combined with chemical decay kinetics (back electron transfer) leading to nuclear polarization even in absence of a long-lived triplet species. Indeed, the presence of the carotenoid quencher has been shown to be compatible with strong enhancements. Extensions of these initial results for other photosystems have been carried out by our group and others. Chemical shift databases were collected by our group to address the interpretation of the unusual shifts for the histidines in the reaction center. In a separate effort, we have measured the multidimensional NMR spectra of the light-harvesting complex, LH1 from Rhodobacter sphaeroides, in native lipids as well as in detergent-solubilized, hydrated, microcrystalline form. New SSNMR methods allow for site-specific assignments, and possibly for structure and dynamics studies of moderate sized systems such as this α,β dimer.

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ELECTRON TRANSFER PATHWAYS AND STRUCTURE OF CHARGE SEPARATED STATES IN THE PHOTOSYNTHETIC REACTION CENTERS AS STUDIED BY HIGH-FREQUENCY EPR SPECTROSCOPY

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The main objective of our research is to understand the relationship between structure, dynamics, and function of the natural photosynthetic reaction center proteins of bacteria and green plants. We examine their structural and mechanistic aspects of electron and energy transfer in order to determine the crucial parameters required for efficient functioning. Here we report on results which provide new information on two outstanding questions – what is the electronic structure of the primary donor in photosystem I, and what is the photoprotection mechanism in photosystem II? Both of these studies became feasible owing to recent developments of modern EPR techniques, such as high-frequency EPR, and rely on the complete resolution of the g-tensor anisotropy of the ion radical cofactors.

Photosystem I. Photosynthetic energy conversion performed by bacteria, plants, and algae occurs in membrane protein complexes known as reaction center proteins (RCs). The primary light reactions involve electron transfer from the photoexcited primary electron donor (P) to a series of electron acceptors resulting in charge separation across the membrane. Based on magnetic resonance data, it was proposed that the primary donors for different RCs consist of a closely positioned pair of specific chlorophyll (Chl) molecules, i.e. a pair of bacteriochlorophyll *a* (Bchl*a*) molecules (P_{850}) in *Rhodobacter sphaeroides*, and a pair of chlorophyll *a* (Chl*a*) molecules (P_{700}) in photosystem I (PS I) of green plants. In the case of the bacterial RCs from *Rhodobacter sphaeroides*, it has been established that the primary donors are "real" dimers, i.e. excitation in P^* and densities of unpaired electrons in $P^{+\bullet}$ and P^T states are delocalized over both chlorophyll molecules. As for the primary donor in PS I, data confirming either monomeric or dimeric electronic structures are very controversial. The initial interpretation of EPR data on $P_{700}^{+\bullet}$ suggested that this species is a dimer. However, later results and interpretations claimed both monomeric or dimeric structures. Thus, the question is still not resolved. High-frequency EPR spectroscopy provides precise g-tensor measurements of the radical species involved in the photosynthetic reactions. The anisotropy of g-tensors reflects the symmetry properties, electron density distribution, intermolecular interactions, and helps to identify intermediate states in the redox reactions. Our new data on the $P_{700}^{+\bullet}$ and P_{700}^T states in PS I in comparison with that of the Chl$a^{+\bullet}$ and Chla^T states give unambiguous proof that the electronic structures of the primary donor cation radical and triplet state are different from those of monomeric chlorophyll *a*. The g-value anisotropy of $P_{700}^{+\bullet}$ is smaller, and the g_z component considerably deviates from that of Chl$a^{+\bullet}$. In contrast to previous reports, the triplet state of P_{700}^T also differs from Chla^T. In the present study, this difference is resolved due to the high g-value resolution of the high-frequency EPR and characterized by the switching of directions of the *x* and *y* g-tensor axes with respect to the zero-field axes. These results can be explained by a dimeric structure of the primary donor and delocalization of the spin density in $P_{700}^{+\bullet}$ and P_{700}^T. We believe that the observed spectral effects are not the result of a strong interaction between

P_{700} and the protein environment. Such an interaction can not account for the larger shift of the g_z component compared to the g_x and g_y in $P_{700}^{+\bullet}$ relative to Chl$a^{+\bullet}$. For the same reason, we reject the proposed protein interaction-induced mixing of the ground state with a closely lying excited state. As an alternative explanation, we suggest that trapping of the active species on the primary donor of PS I may occur on a molecule different from chlorophyll *a*. Evidence that a reversible rearrangement of the geometric and electronic structure of Chl*a* can account for the observed differences in the magnetic resonance and redox properties between P_{700} and Chl*a in vitro* has been previously reported (M. R. Wasielewski, J. R. Norris, L. L. Shipman, C.-P. Lin, W. A. Svec, Proc. Nat. Acad. Sci. USA 78 (1981) 2957). It was proposed that an enolization of the ring V β-keto ester of Chl*a* is responsible for the change of the electronic properties of P_{700}. Additional confirmation of this hypothesis came recently from the X-ray crystal structure of PS I, where a strong hydrogen bond with a keto group of ring V had been reported for only one of the chlorophylls - Chl*a'*. Thus Chl*a'* might have at least a small admixture of the enol state. In order to resolve this question, we are conducting further studies on the Chl*a* enol cation radical and its triplet state by using high-frequency EPR.

Photosystem II. When the primary electron-donation pathway from the water-oxidation complex in photosystem II (PS II) is inhibited, chlorophyll z (Chl_Z) and cytochrome b_{559} are alternate electron donors that are believed to function in a photoprotection mechanism. Recently, it has been proposed that this photoprotection electron transfer pathway also includes a carotenoid (Car) cofactor. We were able to observe EPR spectra of Car and Chl_Z cation radicals in PS II (work was done in cooperation with K. V. Lakshmi and G. W. Brudvig, Yale University). Deuteration of PS II results in significant narrowing of the EPR lines in comparison to the protonated sample when recorded at high-frequency, 130 GHz. This allows us to resolve EPR lines from Car and Chl_Z cation radicals and to confirm the hypotheses that both chlorophyll and carotenoid are involved in the protection electron transfer pathway in Photosystem II.

Although a high resolution X-ray diffraction structure of PS II is available, the location of the Car is not known. In order to determine the location of the Car molecule in the PS II protein, the spin-lattice relaxation rates of the Car^+ and Chl_Z^+ radicals in Mn-depleted and Mn-depleted plus cyanide-treated PS II have been measured by high-field saturation-recovery EPR spectroscopy. In these two samples, the nonheme Fe(II) is high-spin (S=2) and low-spin (S=0), respectively. The Car^+ and Chl_Z^+ radicals exhibit dipolar-enhanced relaxation rates in the presence of high-spin Fe(II) that are eliminated when the Fe(II) is low-spin. The relaxation enhancements of Car^+ and Chl_Z^+ by the nonheme Fe(II) are smaller than that of $Tyr_D^\bullet$, indicating that the Car^+-Fe(II) and Chl_Z^+-Fe(II) distances are greater than the known $Tyr_D^\bullet$-Fe(II) distance of 37-38 Å. Car^+ exhibits a slightly greater relaxation enhancement by Fe(II) than Chl_Z^+, consistent with Car being an earlier electron donor than Chl_Z. Future measurements on the formation and decay kinetics of Car^+ and Chl_Z^+ are planned. These data will provide insight into the sequence of electron transfers in the alternate electron-donation pathway of PS II.

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Session VIII

Characterization and Reactions of Excited States

PHOTODRIVEN CHEMICAL REACTIONS OF METAL COMPLEXES INVOLVING CO_2, H_2, H^+, CO, AND N_2

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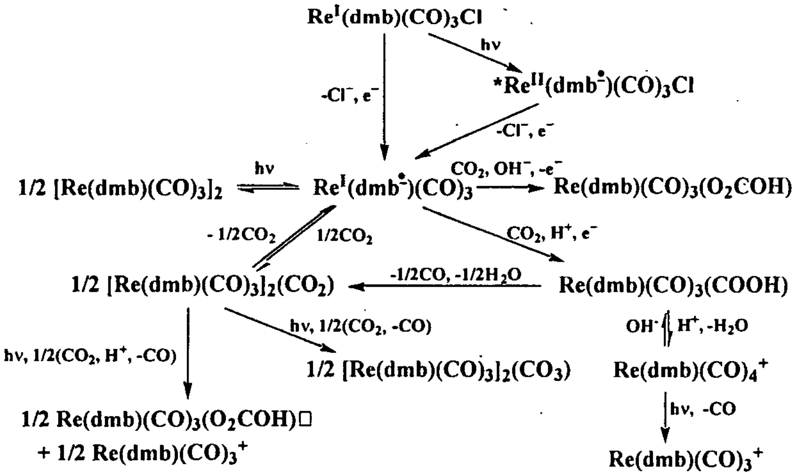
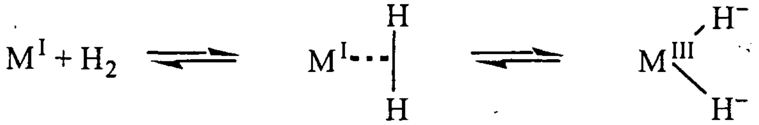
We continue to investigate fundamental processes for the efficient capture and chemical conversion of solar energy using transition metal complexes. The long-term storage of solar energy as fuels and valuable chemicals requires an efficient coupling between photo-induced multi-electron transfer reactions and bond forming (and/or breaking) reactions. Mechanistic and kinetic knowledge about bond forming (and/or breaking) reactions is crucial to understand photocatalytic reactions of CO_2, water, and other species and is necessary to design more efficient photoconversion systems.

CO_2 Reduction with fac-Re(α-diimine)$(CO)_3X$: Rhenium(I) diimine complexes have been shown to act as photocatalysts and/or electrocatalysts for CO_2 reduction to CO. Metallocarboxylates (M-CO_2) and metallocarboxylic acids (M-COOH) have been proposed as intermediates for CO production, but have not been observed directly in the rhenium(I) diimine catalyzed systems. Furthermore, the published characterizations of the possible intermediates are inconsistent. We have investigated the excited state properties of $Re(dmb)(CO)_3Cl$; $Re(dmb)(CO)_3(CH_3CN)^+$ and $[Re(dmb)(CO)_3]_2$ (where dmb = 4,4′-dimethyl-2,2′-bipyridine) and the reactivities of the photochemically produced species by transient UV-vis, transient FTIR, and NMR spectroscopy. $Re(dmb^{\bullet -})(CO)_3$ produced from these complexes is a π anion radical, reacts slowly with CO_2 ($k_{CO2} < 0.1\ M^{-1}\ s^{-1}$), and liberates CO. However when CO_2 is not present, $Re(dmb^{\bullet -})(CO)_3$ dimerizes ($k_d = 35 \pm 3\ M^{-1}\ s^{-1}$ in THF). We have found clear evidence for the involvement of $(CO)_3(dmb)Re$-CO(O)-$Re(dmb)(CO)_3$ and $Re(dmb)(CO)_3$-COOH as intermediates in CO formation. $[Re(dmb)(CO)_3]_2(CO_3)$, $Re(dmb)(CO)_3(O_2COH)$ and $Re(dmb)(CO)_3^+$ were detected as oxidation products. Mechanistic and kinetic information of various reactions involving these intermediates will be presented. The mechanism for the formation of $(CO)_3(dmb)Re$-CO(O)-$Re(dmb)(CO)_3$ with CO and H_2O from $Re(dmb)(CO)_3$-COOH found in our study is quite different from that previously reported. (with B. S. Brunschwig and Y. Hayashi)



Dihydrogen Reactions with Rh(bpy)$_2^+$ and Other Complexes: Metal hydrides are important catalysts and/or intermediates in many catalytic hydrogenation, hydroformylation and dihydrogen-generating reactions. Thus dihydrogen and hydride complexes have been implicated in solar energy conversion schemes directed toward the photoreduction of water and of CO_2 (to formate), respectively. We had previously measured the kinetics of the oxidative addition of dihydrogen to $Rh(bpy)_2^+$ (bpy = 2,2′-bipyridine) and of photo-induced reductive elimination of dihydrogen from $Rh^{III}(bpy)_2(H^-)_2^+$. We have extended our study to gain more detailed mechanistic insight into the nature of the transition state associated with the formation of the dihydride complex: i.e. the extent to which dihydrogen acts as a two-electron σ-bonding ligand to form the $Rh^I(bpy)_2(H_2)^+$ intermediate as shown below.



$$M^I + H_2 \rightleftharpoons M^I\cdots\overset{H}{\underset{H}{|}} \rightleftharpoons M^{III}\begin{smallmatrix} H^- \\ H^- \end{smallmatrix}$$

The thermodynamic parameters were determined from the UV-vis spectrum of an equilibrium mixture of $Rh^I(bpy)_2^+$ and $Rh^{III}(bpy)_2(H^-)_2^+$ as a function of H_2 concentration, temperature and pressure in acetone and methanol. Photolysis of a solution containing $Rh^{III}(bpy)_2(H^-)_2^+$ results in the dissociation of dihydrogen, followed by the regeneration of $Rh^{III}(bpy)_2(H^-)_2^+$. Kinetic parameters were obtained from plots of observed rate constants ($k_{obs} = k_f[H_2] + k_r$) for the return to equilibrium as a function of H_2 concentration, temperature and pressure. The most surprising result is that the activation volumes for the forward reaction are relatively small (between −14 and −15 cm^3 mol^{-1}) and are similar to the overall volume changes, indicating a remarkably late transition state in the oxidative addition of dihydrogen. We are currently investigating photo-induced reactions of $IrCl(CO)(PPh_3)_2L$ (PPh_3 = triphenylphosphine, L = H_2 and D_2) and $W(CO)_3(PCy_3)_2L$ (PCy_3 = tricyclohexylphosphine, L = H_2, D_2, N_2, and CO), and radiation-induced reactions of CoL^{2+} (L = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene) with H^+ and CO. These results and their implication will be discussed. (with R. van Eldik, B. S. Brunschwig, C. Creutz, N. Sutin, and J. Wishart)

CO_2 Reduction with Cobalt and Iron Corroles: Chemical, electrochemical, and photochemical reductions of $Co^{III}(tpfc)(PPh_3)$ (tpfc = 5,10,15-tris(pentafluorophenyl)corrole, $Fe^{IV}(tpfc)Cl$ and $Fe^{IV}(tdcc)Cl$ (tdcc = 5,10,15-tris(2,6-dichlorophenyl)corrole) have been carried out. Photochemical reduction in CO_2-saturated solution containing corrole, *p*-terphenyl and triethylamine led to production of CO and H_2. Cyclic voltammetry in CO_2-saturated solutions indicated that the Co^I and Fe^I complexes reacts with CO_2 and that the reduced Fe(tdcc) complex is the most efficient electrocatalyst among these corroles. The finding that the M^I oxidation states of the cobalt and iron corroles can react with CO_2 is in contrast with the case of the respective porphyrins and phthalocyanines, which do not react with CO_2 until they are reduced beyond the M^1 state. (with P. Neta and Z. Gross)

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

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Summary. Our studies of the electron-transfer behavior of several series of covalently linked transition metal donor-acceptor complexes have led us to re-examine the basic metal-to-ligand charge-transfer (MLCT) spectroscopy of some relatively simple complexes containing polypyridine ligands, to search for the vibronic fine structure in the electron transfer emissions of several series of complexes, and to synthesize and characterize some "σ-bridged" systems.

Certain MLCT excited states have been implicated in superexchange mechanisms for electron-transfer in polypyridine ligand-bridged transition metal complexes. In some linked D/A systems the bridging ligand CT states do not facilitate D/A coupling, contrary to superexchange mechanism-based expectations (Macatangay, *et al.*, *J. Phys. Chem.*, **1998**; *Inorg. Chem.*, **2000**). Other systems exhibit substantial deviations from the expected CT/electrochemical correlations (Seneviratne, *et al.*, *Inorg. Chem.*, **2002**). Features such as these can be related to the nature of the low energy MLCT excited states. We have examined the properties of several series of monometallic complexes in order to obtain experimental information about the nature of these excited states.

We have initiated studies of a series of complexes in which the D/A transition metal complexes are bridged by a halide ion (Udugala-Ganehenege, *Inorg. Chem.*, **2001**). The behavior of these complexes is strongly dependent on the electronic configurations of the transition metal centers. Among the interesting properties observed are large (up to 600 mV) shifts in the M^{III}/M^{II} potentials of the bridged metals. This is large enough to bring some unusual electronic configurations into the range of possible sensitization by the $Ru(bpy)_3^{2+}$ ^{3}MLCT excited state. A strategy for linking these complexes to a polypyridine ligand is progressing.

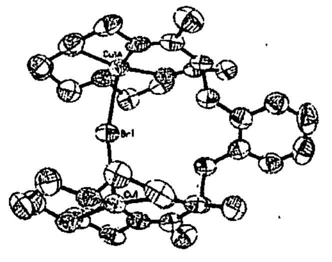
Some details. 1.Studies of polypyridyl complexes. *Ab initio* calculations (by Prof. H. B. Schlegel) of polypyridine π*-orbital energies are the basis for assignment of the lowest energy, highest intensity metal-to-ligand charge transfer (MLCT) transitions in simple ammine-polypyridine-ruthenium(II) complexes. The LUMO doe 2,3-dipyridylpyrazine (dpp) does not correlate with the pyrazine LUMO. Gaussian analysis of the absorption and emission spectra enables the evaluation of reorganizational energies for the vertical MLCT transitions from component bandwidths and from apparent vibronic progressions. The observed bandwidths are about half of the widths expected in the limit of no metal-ligand mixing. The excited state electron exchange energy is estimated from the inferred reorganizational energies and the ambient Stokes shifts.

2. Transition metal-transition metal electron-transfer emission. Electron-transfer luminescences have been found in a simple class of covalently linked, Cr^{III}-CN-Ru^{II}, transition metal complexes at 77K in a DMSO/H_2O glass. These emissions are broad, structureless and centered at about 850 nm. The emission lifetimes are on the order of 1 μs, and increase 19-30 fold upon perdeuteration of coordinated am(m)ines. The properties of the electron-transfer excited states are consistent with an inverted region, spin forbidden, transition metal-to-transition metal, electron transfer emission process.

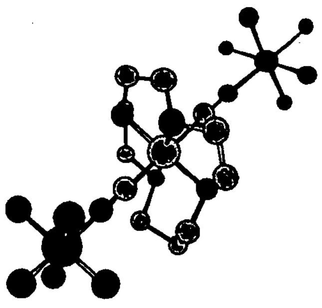
3. Vibronic coupling in CN-bridged complexes. Local, ground state Ru^{II}(NC$^-$)M^{III} vibronic coupling in *cis*- and *trans*-(NC$^-$)M^{III}(CN$^-$)-bridged Ru^{II}/Ru^{III} complexes (M an aliphatic macrocyclic ligand complex) generallly "interferes" with the Ru^{II}/Ru^{III} electronic coupling in the sense that the intervalence coupling is independent of the donor-bridging ligand, Ru^{II}M^{III} coupling, contrary to expectation based on simple superexchange models. This "interference" effect is relaxed when the Ru^{II}/Ru^{III} electron transfer excited state and the Ru^{II}/M^{III} "MLCT" excited state are nearly degenerate.

4. Face-to-face, halide bridged macrocyclic ligand complexes. Halo-bridged dicopper(II), dinickel(II) and dicobalt(III) complexes of α,α'-bis (5,7-dimethyl-1,4,8,11-tetraazacyclotetradecane-6-yl)-o-xylene have been synthesized and characterized. X-ray structures were obtained of complexes in which two copper(II) ions are axially bridged by a bromine or a chlorine. Each Cu complex displays a cofacial ring arrangement. The chloride-bridged complex had barely resolved differential pulse polarographic waves ($\Delta E_{1/2} \sim 28$ mV). The magnetic susceptibility results below 20 K follow Curie-Weiss behavior indicating that the magnetic interaction between the two Cu centers is weakly antiferromagnetic; $J \leq -1$ cm^{-1}. The x-ray structure of the halide-free dinickel(II) had the macrocyclic complexes rotated and stacked parallel to the o-xylene ring. The halide-bridged [L(Ni)$_2$X]$^{3+}$ complexes exhibited two Ni^{II}/Ni^{II} CV waves separated 300-600 mV. A bridging-ligand mediated, σ-linked superexchange model is being used to treat the magnetic and electron transfer coupling in the halide-bridged complexes. It is inferred that bridging halide mediated, dσ/pσ/dσ metal-metal coupling significantly alters the chemical properties of the bimetallic complexes only when the donor and acceptor orbitals are coaxial with the bridging ligand. Polypyridyl ruthenium(II) complexes covalently linked to monometal nickel(II) and copper(II) complexes of this tetraazamacrocylic ligand have been synthesized and photochemically characterized.

dpp LUMO



[L(Cu)$_2$Br]$^{3+}$



[{Cr([14]aneN$_4$)}(CNRu(NH$_3$)$_5$)$_2$]$^{5+}$

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ELECTROABSORPTION STUDIES OF THE MLCT TRANSITION IN TRANSITION METAL COMPLEXES

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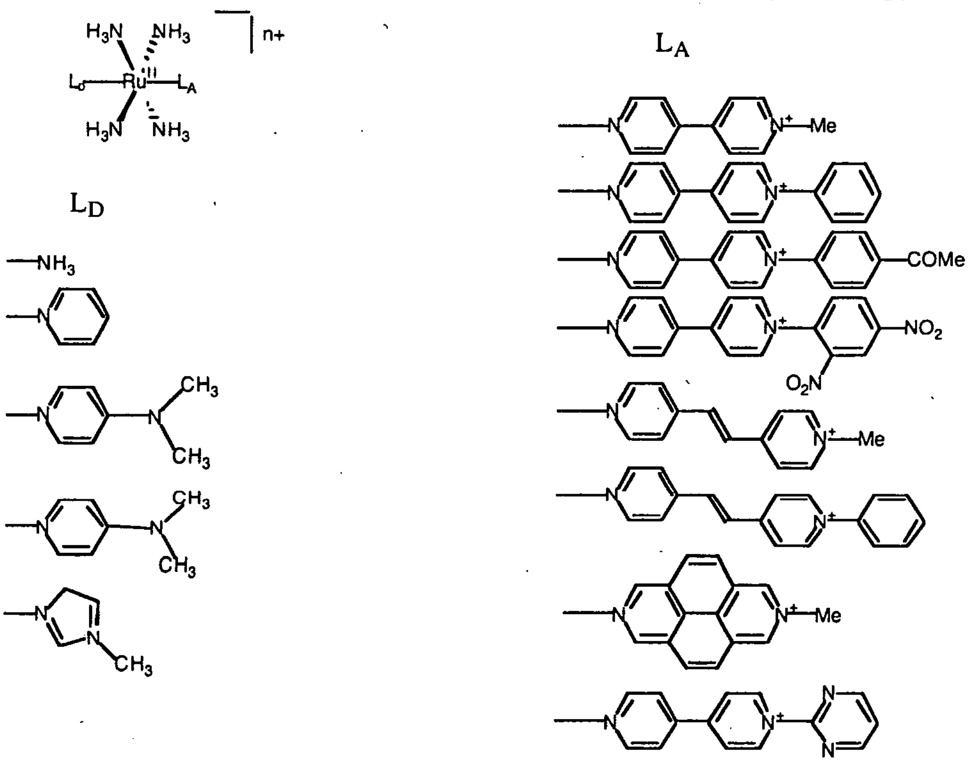
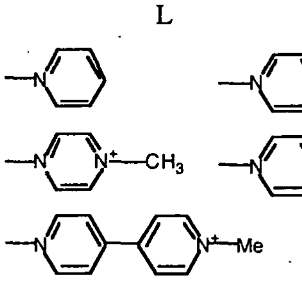
Fundamental understanding of charge-transfer processes requires a detailed knowledge of how the electron density changes when a molecule undergoes a transition between two electronic states. We have investigated a number of different systems by electroabsorption (Stark) spectroscopy in order to obtain information about the electronic redistribution in charge-transfer transitions.

A series of 20 ruthenium(II) complexes $L_D(NH_3)_4Ru^{II}L_A{}^{n+}$, where L_A and L_D are an acceptor and donor ligand shown below, has been studied by Stark spectroscopy. All of these complexes display intense metal-to-ligand charge-transfer (MLCT) absorptions in the visible region. The absorptions arise from the promotion of a metal d electron to the π^* orbital of the L_A ligand. Stark spectroscopic studies have determined the adiabatic and diabatic dipole-moment changes ($\Delta\mu_{12}$, $\Delta\mu_{ab}$), transition moments (μ_{12}) and electronic coupling (H_{ab}) for the excitations. The transition dipole moments generally increase with the electron accepting strength of L_A, most notably on replacing an *N*-methyl with a *N*-



phenyl substituent. The $\Delta\mu_{12}$ values are large ($\approx$ 14–21 D) and generally increase with the size of L_A. Comparison of experimental and calculated diabatic dipole-moment changes suggests that the orbital(s) that receive the MLCT electron are delocalized only over the first two aryl rings of L_A. ZINDO calculations on the pentaammines predict the dipole properties with reasonable accuracy, and also indicate that the low lying π^* orbitals span only the first two rings of L_A. The complexes have been shown to exhibit large molecular static first hyperpolarizabilities β_0 by hyper-Rayleigh scattering (HRS) at 298 K. β_0 values calculated from the dipole-moment changes measured by Stark spectroscopy using the two-state model are in good agreement with the HRS scattering values. Thus the Stark results confirm the unusually large magnitudes of β_0 in these complexes and also that *N*-arylation enhances β_0. The increases in β_0 are generally associated with decreases in the MLCT energy and increases in both μ_{12} and $\Delta\mu_{12}$. (with B. J. Coe[*] and J. A. Harris[*])

The effect of solvent on the MLCT transition in a series of $(CN)_5Fe^{II}L^{n-}$ complexes, where L is an aromatic ligand, has also been studied. The MLCT transition energy in these systems is sensitive to solvent, for example, in the 4,4-bipyridine complex the transition energy changes by > 50 % with solvent. The MLCT band shifts to higher energy in protic or acceptor solvents while in aprotic or low acceptor solvents the band moves to lower energy. These shifts suggest the possibility of tuning the electronic coupling between the metal center and the acceptor ligand by changing the solvent. The MLCT Stark spectra of $(CN)_5Fe^{II}L^{n-}$ complexes have been investigated for the acceptor ligands shown at left in three solvents that form glasses at 77 K. The dipole-moment changes, transition dipole-moments and absorption band maxima for the MLCT absorption of the complexes have been determined. The absorbance maxima in fluid solution and in frozen glass are not very different for most of the complexes, suggesting that the solvation of the complexes is similar in the two media. The maxima for the complexes shift $\approx$ 100 nm on going from 10M LiCl/water to 1:1 PrCN/2-MeTHF.



The dipole-moment changes determined for the pentacyanoiron(II) complexes are significantly larger than those observed for the corresponding pentaammineruthenium(II) complexes with the diabatic dipole-moment changes approaching the values expected for the transfer of one electron from the iron to the center of the aromatic ligand. For the complex with L = N-methylpyrazinium the values of $\Delta\mu_{12}$ vary with solvent from 2.0 to 0.3 eÅ while the values of $\Delta\mu_{ab}$ remains constant at $\approx$ 1.1 eÅ. The results are discussed in terms of the changes in the electronic coupling and the energies of the ground and excited states. (with J. A. Olabe[+] and A. R. Parise[+])

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Posters

Poster # 1

DEPENDENCE OF EXCITED STATE STRUCTURE IN PHENYLENE-ETHYNYLENE DENDRIMERS ON SIZE: IMPLICATIONS FOR ENERGY TRANSFER AND LIGHT HARVESTING

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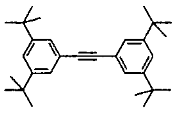
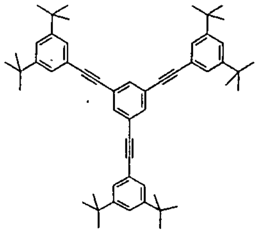
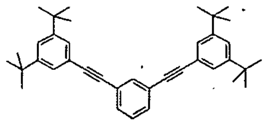
The phenylene-ethynylene dendrimers first synthesized by Moore and coworkers have continued to attract interest as potential artificial light-harvesting systems. These molecules are built up using diphenylacetylene (DPA) moieties. Most estimates of the energy transfer rates have assumed that each DPA branch of the dendrimer acts as an individual chromophore, and that these chromophores interact via dipole-dipole mechanism. Energy transfer through the dendrimer is the result of either incoherent Forster transfer or weak exciton coupling. Both types of models assume that the properties of the fundamental DPA chromophore do not change as the dendrimer increases in size.

In order to test this assumption that the dendrimer is merely the sum of its weakly interacting parts, we have synthesized the series of tert-butyl substituted phenylene ethynylene shown in the figure. The goal was to determine whether the meta-substitution had a measurable effect on the absorbing and emitting states in these molecules. Comparison of the steady-state spectroscopic properties of these and larger dendrimers shows that while the absorption shape hardly changes as the size of the diphenylacetylene network increases, the emission undergoes a large shift and shape change. This evolution of the emission spectrum saturates at D4 – larger dendrimers have similar spectral shapes and fluorescence properties. After lowering the temperature to 4 K to freeze out thermally-activated nonradiative relaxation processes, a comparison of DPA, W3, and D4 reveals that the fluorescence yield of DPA is >50% with a lifetime of 0.8 ns, while D4 has a quantum yield of 25% and a lifetime of 16 ns. A Strickler-Berg analysis, combined with fluorescence anisotropy, shows that while in DPA the absorbing and emitting states are the same, in D4 the emitting state is different from that which dominates the absorption spectrum. This result is consistent with what has been observed in branched poly-phenylene molecules, and is attributed to energy shifting of the low-lying ^1L_a and ^1L_b excited states. Thus the lowest energy excited state in the branched dendrimers, which presumably dominates the energy transfer dynamics, is different from the localized excited state that initially absorbs the photon. The practical implications of this change in excited state structure for energy transfer through the dendrimer will be discussed.


t-butyl-DPA


D-4


W-3

MAPPING ELECTRON DENSITIES IN PORPHYRINS FROM HIGH RESOLUTION X-RAY DATA

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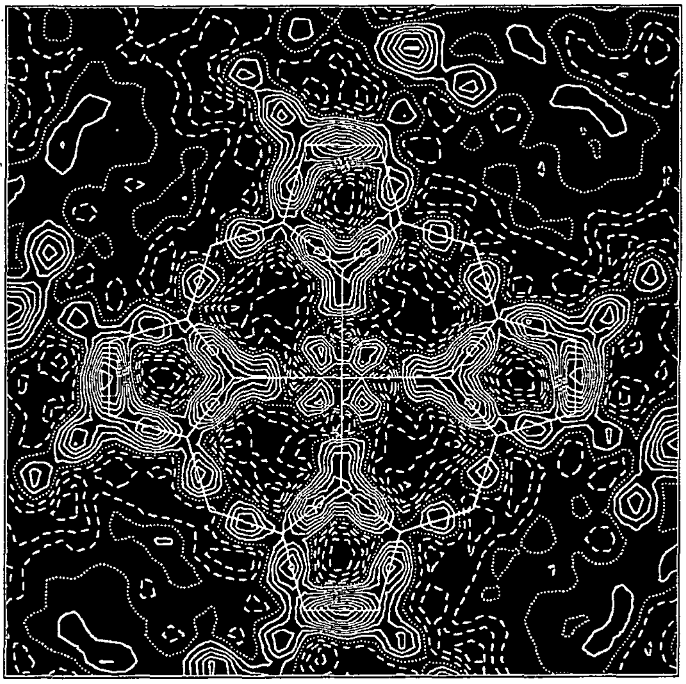
Determining electron density distributions from high resolution crystallographic data is a powerful analytical tool for understanding chemical bonding. When applied to porphyrins, such studies can provide insight into the nature of π bonding in the porphyrin, bonding between the central metal and axial ligands, distribution of electrons in the metal d-orbitals and porphyrin π-system, oxidation state of the metal, charge on the metal and porphyrin, and the electronic ground state of the metal. This technique requires carefully measured, high quality, symmetry-averaged X-ray data. Use of synchrotron radiation has several fundamental advantages over conventional X-ray methods for these determinations. Among them are: 1) the highly intense X-ray beam eliminating the need for large crystals, 2) capability for fast data collection on area detectors at 20K minimizing crystal decomposition and enabling high data redundancy, 3) short wavelengths (0.643Å or 0.394Å) for maximizing resolution. Results of the electron density mapping on a porphyrin and a porphyrin radical from data collected at the National Synchrotron Light Source will be presented.



Electron density map in the plane of the nitrogens for Ni(II)octaethylporphyrin. Each contour is 0.05 electrons. The zero contour is dotted and negative contours are dashed.

CHARACTERIZATION OF CAROTENOID AND CHLOROPHYLL PHOTOOXIDATION IN PHOTOSYSTEM II

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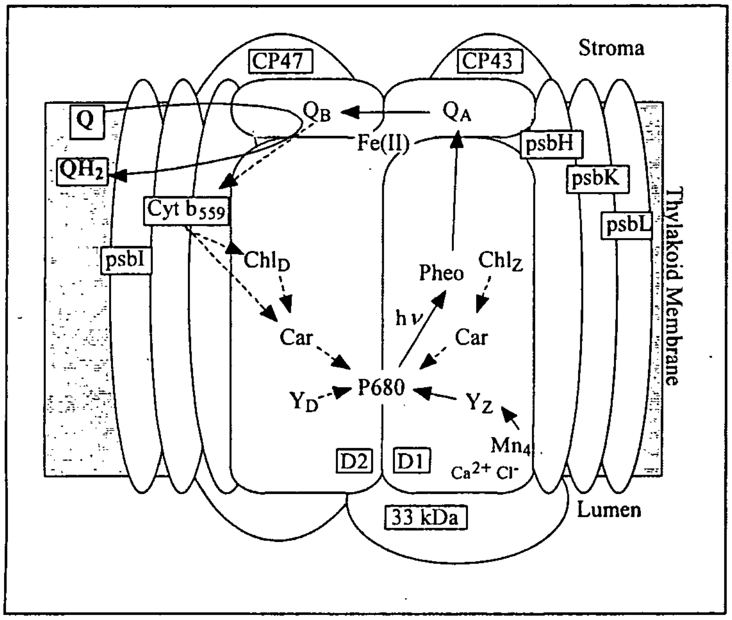
The photochemical reactions of photosystem II (PSII) leading to the oxidation of water involve the primary electron donors Mn_4 and Y_Z. PS II is unique among photosynthetic reaction centers in having secondary electron donors that compete with the primary electron donors for reduction of $P680^+$ (see Figure). The secondary electron donors are photooxidized in high yield under conditions, such as low temperature, in which electron donation from the O_2-evolving complex is inhibited. Although spectroscopic signatures of the oxidation of the individual secondary electron donors have been identified, their locations within PSII, the exact electron-transfer sequence(s) involving them and their function are still uncertain. We have characterized the photooxidation of the redox-active accessory chlorophylls and β-carotene (Car) by near-IR absorbance and EPR spectroscopies in Mn-depleted PSII over a range of cryogenic temperatures from 30 to 120 K in both *Synechocystis* PSII core complexes and spinach PSII membranes.[1] The following key observations were made: 1) Chl_Z^+ and Car^+ have significantly different stabilities with Car^+ decaying much faster; and 2) Car^+ decays by recombination with Q_A^- and not by Chl_Z oxidation, with multiphasic kinetics that indicate at least two populations of Car^+; and 3) in spinach PSII membranes, Car^+ decays mainly by recombination with Q_A^-, but also partly by hole transfer, forming a 850 nm Chl cation radical. More recently, measurements have also been made on O_2-evolving PSII complexes from both spinach and cyanobacteria. In O_2-evolving PSII, additional Chl cation radicals are formed, which are not observed in Mn-depleted PSII, and the stability of Car^+/Q_A^- is significantly decreased. These results provide insight into the alternate electron-donation pathways to $P680^+$.



Structural model of photosystem II showing the primary and secondary electron-transfer pathways. The secondary electron-transfer pathways involve β-carotene (Car), the accessory chlorophyll a's (Chl_Z in the D1 subunit and Chl_D in the D2 subunit) and cytochrome b_{559} (Cyt b_{559}).

1) Tracewell, C. A.; Cua, A.; Stewart, D. H.; Bocian, D. F.; Brudvig, G. W. *Biochemistry* **2001**, *40*, 193-203.

EXCITED STATE STRUCTURES OF METALLOPORPHYRINS IN DISORDERED AND ORIENTED MEDIA: POTENTIAL APPLICATIONS OF OPTICAL POLARIZATION SELECTED X-RAY ABSORPTION SPECTROSCOPY (OPS-XAS)

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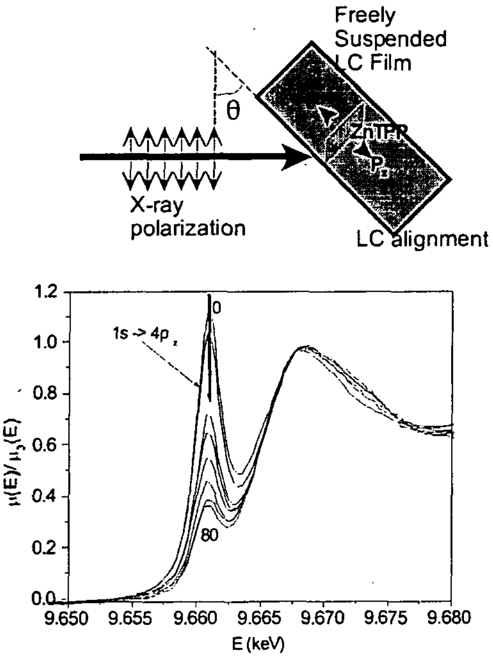
Metalloporphyrins and their analogs are building blocks for the machinery of natural and artificial photosynthesis that are carried out by photoinduced electron and energy transfer processes where the excited states are reactants. Therefore, knowing the structures of the excited states of these metalloporphyrins is important in understanding these photochemical and photophysical reactions. Using laser pulse pump, X-ray pulse probe X-ray absorption spectroscopy (LPXP-XAS) developed in our laboratory, we have captured excited state structures of triplet zinc tetraphenylporphyrin (ZnTPP) and copper(II) tetraphenylporphyrin (CuTPP) in toluene solutions. LPXP-XAS can be applied to other metal-containing molecules, such as metal sites in photosynthetic reaction center proteins and organometallic complexes, to detect transient structural changes induced by light.

Moreover, linearly polarized laser light selectively excites molecules with a preferred orientation. Thus, probing structural changes in molecules along a particular chemical bond could be realized by taking advantage of linearly polarized X-rays and the laser light, because electronic transitions induced by both lights follow dipolar transition selection rules, and the probabilities for both transitions are proportional to $|\cos\varphi^2|$, where φ is the angle between the transition dipole and the polarization of the X-ray or laser light. Liquid crystal (4'-octyl-4-biphenyl-carbonitrile,OBCN) provides an oriented medium for ZnTPP and Fe(III)TPP-Cl in freely suspended films, where the porphyrin planes are oriented perpendicular to the film, as determined by polarized XAS (Fig. 1). In these model systems, a characteristic peak originating from 1s to $4p_z$ transition varies in intensity as a function of θ, the angle between the film plane and the X-ray polarization direction. Therefore, by adjusting the relative orientation between the polarization directions of the pump laser light and the probe X-ray, the structural change along a particular bond that is aligned with the polarization of the X-ray can be selectively probed. Theoretical calculations on the model systems will be presented and the experimental feasibilities of OPS-XAS will be discussed.



PHOTOELECTROCHEMISTRY OF NANOSCALE TiO_2-DNA HYBRID MATERIAL

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Chemistry Division, Argonne National Laboratory, Argonne IL 60439

In this project we are developing electrochemical techniques for investigating photoinduced electron transfer across a nanoscale metal oxide semiconductor – biomolecule interface. Control of this interfacial electron transfer is fundamental to the goal of achieving hybrid materials that combine the chemical reactivity of the nanoscale inorganic oxide with biomolecular selectivity and molecular recognition.

In the first step, we are developing photo-electrochemical techniques to directly detect DNA hybridization and DNA-protein interactions, utilizing the stable photoinduced charge separation in dopamine sensitized TiO_2 nanoparticles (< 20 nm)[1].

Twenty-five base long DNA strains were linked to titania nanoparticles via the dopamine sensitizer, while the rest of the nanoparticle surface was protected[2]. The photoinduced signal of sample DNA hybridization with the immobilized strains was measured by different electrochemical methods: square wave voltammetry, AC voltammetry and impedance spectroscopy.

This photo-electrochemical approach to detect DNA hybridization is free from the inherent problems of the currently commercially available fluorescent DNA systems, and has several further advantages, such as the ability to detect single base mismatches. Since the electrochemical hybridization signal is obtained only under illumination, no extra care need be taken to avoid stray signals entering the detection system. The photo-electrochemical cell itself may be designed so that it can be serially produced by standard microfabrication technology and be incorporated into DNA array systems.

1. Rajh, T.; Chen, L.X.; Lukas, K.; Liu, T.; Thurnauer, M. C.; Tiede, D. M.: Surface restructuring of nanoparticles: an efficient route for ligand-metal oxide cross talk. Submitted.

2. Rajh, T.; Paunescu, T.; Wiederrecht, G.; Roitman, D.; Hancock, W.; Kuekes, P.; Woloschak, G.; Thurnauer, M. C.: Extended charge separation in TiO_2 nanoparticles linked to DNA-oligonucleotides. Submitted.

Poster #

THE PLATINUM DIIMINE CHROMOPHORE FOR PHOTOINDUCED CHARGE SEPARATION: DYADS, TRIADS, SOLVENT EFFECTS AND BUILDING BLOCKS

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The use of platinum diimine chromophores in systems for light-driven energy-storing reactions requires their connection to donors and acceptors for photo-induced charge separation. For Pt(diimine)$(C\equiv CAr)_2$ complexes, the emissive excited state is a ^{3}(metal-to-diimine) charge transfer, and both oxidative and reductive quenching have been observed. During the past several years, efforts to incorporate Pt(diimine)$(C\equiv CAr)_2$ into larger structures have led to the formation and study of a donor-chromophore-acceptor (D-C-A) triad containing an arylacetylide-linked phenothiazine (PTZ) as the donor and a diimine-attached nitrophenyl moiety as the acceptor. In the triad, the luminescence of the Pt diimine excited state is completely quenched, and transient absorption spectroscopy has revealed a charge separated species of relatively short duration in dichloromethane, DMF and THF solutions. At low temperature in frozen glass media, however, the triad exhibits structured luminescence characteristic of a metal-diimine charge transfer state. For related D-C dyads with either PTZ or trifluoromethylphenothiazine (TPZ), the extent of quenching is strongly affected by solvent (the TPZ donor is *ca.* 150 mV harder to oxidize than PTZ). The D-C dyad Pt(dbbpy)$(C\equiv C\text{-p-}C_6H_4CH_2\text{-PTZ})_2$ (dbbpy = di-t-butylbipyridine) is greatly quenched in MeCN and CH_2Cl_2 but is quenched only slightly in ethyl acetate and not at all in toluene relative to a model compound without the PTZ donor. A similar effect is seen for the corresponding TPZ dyad.

In efforts to develop better functionality for dyad and triad construction, Pt(diimine)$(C\equiv C\text{-p-}C_6H_4CHO)_2$ complexes have been synthesized and found to exhibit long-lived ^{3}MLCT emission. The bathophen (4,7-diphenylphenanthroline) derivative, the structure of which has been determined crystallographically, readily undergoes Schiff base condensation and imine reduction to form new D-C dyads which will be described. Use of 4-ethynylbenzaldehyde as a linker to the acceptor side of the Pt(diimine) chromophore is also under exploration.

Since Pt dppz complexes (dppz = dipyridophenazine) had been reported to bind to DNA intercalatively, a study was undertaken to see whether dppz and other diimine bis (acetylide) systems could act as photo-reductants for electron transfer in DNA. Initial efforts to prepare water soluble Girard derivatives of Pt(dppz)$(C\equiv C\text{-p-}C_6H_4CHO)_2$ proved unsuccessful because of solubility limitations during synthesis. In order to better assess the feasibility of using Pt diimine complexes for the unique role of electron donor to DNA, a series of quenching experiments was performed using Pt(phen)$(C\equiv C\text{-}p\text{-}C_6H_4CHO)_2$ and the 4-TBDMS-protected DNA nucleosides (A, T, C, G) as quenchers. It was found that all bases except T serve to quench the Pt(diimine) excited state and exhibit good Stern-Volmer behavior. The fastest rates of quenching occur with G and A which are the most easily oxidized bases. The rate of quenching with C is approximately an order of magnitude slower ($k_q = \sim 10^7$) while quenching by T is not observed even at high quencher concentrations. Given that G and A are the most easily oxidized bases while C and T are the most easily reduced bases, quenching undoubtedly proceeds through a *reductive* quenching mechanism involving base oxidation. The study thus shows that the Pt(diimine)(arylacetylide)$_2$ complexes are insufficiently strong photo-reductants to probe charge transfer through DNA by electron, rather than hole, injection.

CHARGE CARRIER DYNAMICS IN NANOCRYSTALLINE INDIUM PHOSPHIDE QUANTUM DOTS

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Femtosecond transient absorption spectroscopy has been used to study charge separation and cooling dynamics in colloidal indium phosphide (InP) quantum dots (QDs). Following photogeneration of an exciton with energy above the first interband transition, relaxation to the lowest exciton level occurs on the timescale of ~ 0.25 ps to 1 ps. While electron energy relaxation is inhibited due to the large spacing ($> 7\ \hbar\omega_{LO}$) between adjacent conduction band levels, energy relaxation via an Auger-like scattering process permits the electron to transfer its excess energy to the hole, which in turn cools via phonon scattering through the denser manifold of valence band states. Etched QDs show evidence of rapid carrier cooling, which we ascribe to efficient passivation of surface-related states and the concomitant confinement of charge carriers to the QD interior (permitting the Auger-like cooling). In contrast, samples that facilitate fast charge separation due to surface-related states inhibit the Auger-like scattering, thereby slowing the carrier cooling. We compare the transient absorption dynamics for InP QD samples with differing surface chemistries and find that the presence of reducing agents on the nanoparticle surface affects electron cooling dynamics. Using the three-pulse pump-probe technique, we investigate the dependence of electronic relaxation dynamics on variations in the QD surface chemistry. Results suggest that the introduction of surface trapping molecules slows electron cooling considerably, but does not produce the long cooling times that a complete phonon bottleneck would yield.

Poster #

SUPRAMOLECULAR SELF-ASSEMBLY OF A FUNCTIONALIZED FLUORINATED ZINC PORPHYRIN INTO A TWO-DIMENSIONAL NETWORK

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The crucial roles of porphyrins in photosynthetic light harvesting and electron transfer, and as catalysts in a wide variety of enzymatic reactions have naturally led to intense efforts that seek to duplicate the biological processes, and more recently, to fabricate synthetic arrays with an equally wide range of potential applications to materials chemistry as photonic devices, conductive polymers, chemical sensors, and molecular wires. Ideally, such arrays would self-assemble and their targeted properties achieved by synthetically modifying the porphyrins and/or changing the metal in metalloporphyrins. Crystal-engineering strategies for the rational design of self-assembled metalloporphyrin materials have made judicious use of 5,10,15,20-tetraphenyl porphyrins (TPPs) and related chromophores to construct rigid supramolecular networks. However, it has been more difficult to construct extended coordination arrays with ZnTPP building blocks because of the low affinity of the Zn ion for hexacoordination.

We have thus turned to an amine-functionalized, fluorinated Zn porphyrin, Zn(II) 5, 10,15,20-tetrakis(4-n-propylamino-2,3,5,6-tetrafluorophenyl)porphyrin, 1, as a tecton for supramolecular assembly for the following reasons: a)Zn-5,10,15,20-tetrakis(pentafluorophenyl)porphyrin (ZnTPPF20) is readily synthesized and reacts with n-propylamine in one step and in high yield to form 1; b)Zn porphyrins bearing multiple electron-withdrawing groups tend to form hexacoordinated complexes, unlike the general preference for pentacoordination found in less electron-deficient porphyrins; c)Fluorinated porphyrins exhibit both ground and excited state properties that differ from those typically observed in TPPs, and which arise from the fact that the peripheral fluorines change the highest occupied molecular orbital of the chromophores from a_{2u}, normally found in TPPs, to a_{1u} with a concomitant redistribution of electron density that affects optical, redox, radical and excited state properties. We report here crystallographic results which demonstrate that 1 self-assembles to form a supramolecular, 2-dimensional array in which the Zn ion is indeed hexacoordinated by the amine nitrogens of its two nearest neighbors, and in which each porphyrin is linked to four orthogonally aligned nearest neighbors.

ZnTPPF20 also reacts readily with alkoxide and thiol nucleophiles to yield the equivalents of 1 with OR and SR functions at the para phenyl positions. As well, the same regioselectivity is observed in the reaction of the nonplanar β-octabromo-TPPF20 with n-propylamine. (Recall that nonplanar porphyrins exhibit significantly altered (photo)physical and chemical properties.) The nonplanar, and oxygen or sulfur functionalized porphyrins may thus provide facile entry into new supramolecular arrays whose properties are further modulated by the nonplanarity of the chromophores or by the oxygen and sulfur ligation.

PHOTOCHEMICAL AND PHOTOPHYSICAL PROPERTIES OF Re\Ru DYADS

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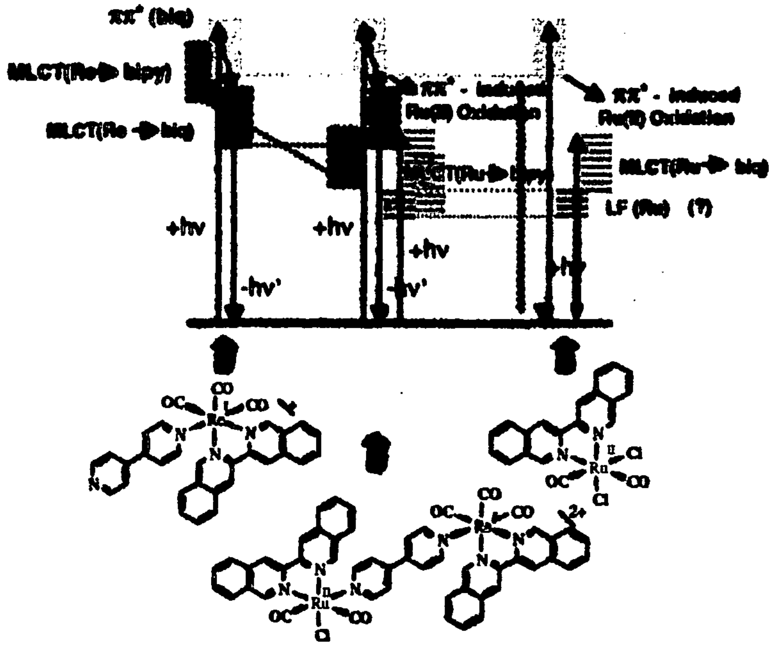
Radiation Laboratory
Notre Dame, IN 46556

Re^{I}\Ru^{II} dyads, either as pendants in macromolecules or as a repeating units in a polymer, are being evaluated as catalysts in the light-induced CO_2 reduction. In this work, the photochemical and photophysical properties of (biq)Re^{I}(bipy)Ru^{II}(biq)$^{2+}$, shown in the figure, were investigated and compared with those of the related monometallic complexes (biq)Re^{I}(bipy)$^{+}$ and Ru^{II}(biq). The Re to biq MLCT excited states of the dyad and (biq)Re^{I}(bipy)$^{+}$ have similar lifetimes and reactivities. By contrast, excited states of the Ru^{II}(biq) fragment in the dyad or the Ru^{II}(biq) are very short lived. Excitation of Ru^{II}(biq) and (biq)Re^{I}(bipy)Ru^{II}(biq)$^{2+}$at wavelengths of the biq ligand $\pi - \pi^*$ transitions resulted in the oxidation of Ru(II) to Ru(III). Based on the spectroscopy of the complexes and the kinetics of photochemically induced redox reactions, values of the self exchange rate constant for the Re(II)\Re(I) couples are $10^8 < k < 10^9$ M^{-1} s^{-1}. The Ru^{II}(biq) fragment appears to be a good, photochemically nonintrusive bridge for attachment of the Re chromophore to macromolecules.



(biq)Re^{I}(bipy)$^{+}$ Re^{I}(bipy)Ru^{II}(biq)$^{2+}$ Ru^{II}(biq)

PREPARATION OF SMALL BAND GAP COLLOIDAL QUANTUM DOTS FOR IMPACT IONIZATION STUDIES

Sue Ferrere, Pingrong Yu and Arthur J. Nozik

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When a semiconductor absorbs photon energy in excess of its band gap, typically one electron-hole pair is generated and the excess energy is dissipated via phonon emission. However, at very large excitation energies (2-3 x E_g), impact ionization may occur, whereby the photogenerated electron collides with a valence band electron to produce a second electron-hole pair. Thus, the quantum yield can be greater than one, as two electrons are yielded from one incident photon. Consideration of this phenomenon can significantly increase the theoretical maximum conversion efficiency for solar cell devices.

The investigation of impact ionization was fairly active more than thirty years ago. However, there is very little recent work in the area, and optical measurement of the phenomenon has not been reported. Previous studies were on a limited number of single crystal materials and measured photocurrent output as a function of incident photon energy in p-n devices. Our laboratory recently demonstrated impact ionization in single crystal germanium using transient absorption.

Impact ionization may be enhanced in quantum dots, and colloidal quantum dots befit spectroscopic measurements. We are investigating impact ionization in small band gap quantum dots, because of the experimental constraint of needing large excess excitation energies, and to provide relevance to solar conversion. Currently, the materials under study include InAs, PbS, and Ge quantum dots. The synthesis and characterization of these materials will be described, and recent results for the spectroscopic examination of impact ionization will be presented.

RELATION BETWEEN PARTICLE COORDINATION NUMBER AND POROSITY IN NANOPARTICLE FILMS: IMPLICATIONS FOR DYE-SENSITIZED SOLAR CELLS

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Understanding quantitatively the relation between film porosity and the coordination number of individual particles in mesoporous nanostructured films is important for gaining a comprehensive knowledge of the morphological factors that can affect photocarrier transport and recombination in dye sensitized solar cells. We have developed a computational method based on the random packing of spheres to simulate the morphology and local structure of mesoporous nanoparticle TiO_2 films. It is shown that the physical resemblance of the simulated film to the SEM image is remarkably close. The distribution of pore sizes in the film that is predicted by the simulations is found to be in excellent agreement with N_2 desorption data. The relation between the most probable pore size in a film and the average particle size is discussed. Analyses of the radial distribution function vs the radial distance from the center of a particle in a film reveal that outside of the first shell the spatial distribution of particles is essentially random. A strong relation between film porosity and the average coordination number of the nanoparticles is found. When the film porosity increases from 40 to 80%, the average coordination number of a particle decreases from about 6.6 to 2.8. The coordination number of random structured films is compared with that of several basic monatomic crystal structures at the same porosity. For example, a simple cubic structure has a relative porosity (void volume) of 48% and a coordination number of 6. At the same porosity, the simulated structures have an average particle coordination number of 5.3. The data also show that there is a significant fraction of particles with coordination numbers below and above the average coordination number. A simple analytical relationship between coordination number and porosity is found. At film porosities typically present in nanocrystalline TiO_2 films used in dye-sensitized solar cells, the value found for the average coordination number of a particle indicates that the nanostructured film is highly branched. The effect of such a highly branched particle structure on electron transport is discussed.

Poster # 1

THE ACTIVE SITE OF H_2O_2 IN Ti SILICATE MOLECULAR SIEVE

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Following our recent in-situ FT-infrared detection of HCO_2H upon UV irradiation of Ti centers in T silicalite sieve (TS-1) loaded with CO_2 gas and using CH_3OH as donor, we have now been able to observe the 2-electron reduction product of CO_2 in the Ti silicate when using H_2O as electron source. However, the fate of the concurrent water oxidation product, H_2O_2, could not be discerned from this experiment. We have just completed an FT-IR study of the interaction of H_2O_2 in TS-1 that led to the first direct observation of the active peroxide species formed in the solvent-free sieve. TS-1 is a microporous crystalline silicate with a 3-dimensional network of channels with 5.5A diameter.

Upon loading of aqueous hydrogen peroxide into TS-1 sieve and complete removal of the solvent by evacuation, a thermally stable hydroperoxo species was detected by FT-IR spectroscopy with an OO stretch at 837 cm^{-1} (^{18}O, 793 cm^{-1}) and a broad OH band at 3400 cm^{-1}. This indicated the formation of a TiOOH moiety, most probably with side-on configuration because a concurrent decrease of a band at 960 cm^{-1} characteristic for tetrahedrally coordinated Ti centers is observed. The decrease is consistent with an expected expansion of the Ti coordination sphere upon formation $TiOOH(\eta^2)$. $TiOOH(\eta^2)$ has been predicted as the most stable product of H_2O_2 interaction with framework Ti by several theoretical works. Irradiation in the visible or at 355 nm led to efficient dissociation to oxygen and Ti-OH (^{16}O, 3676 cm^{-1}; ^{18}O, 3665 cm^{-1}). The photoprocess can be understood by the electronic nature of the UV-visible absorption that gives rise to the yellow color of the TiOOH group; absorption of a photon by the LMCT state results in the excitation of an electron from the $\pi^*(OO)$ HOMO orbital to a vacant d_e orbital of Ti, thus creating a transient electron distribution approximately described by reduced Ti^{+III} and a superoxo moiety. The $d_e(Ti)$ orbital is coupled to the energetically close $\sigma^*(OO)$ orbital, thus facilitating disproportionation of the transient superoxo group by O expulsion and Ti-OH formation. A substantial fraction of the titanol groups were found to recondense with the adjacent Si-OH group to form a Ti-O-Si bridge and H_2O. Hence, the fate of H_2O_2 in Ti silicalite sieve under irradiation at wavelengths shorter than 500 nm is disproportionation to oxygen and H_2O.

In a series of experiments with adsorbed ethylene or propylene gas, we have in addition demonstrated that TiOOH is the long-sought after active site of olefin epoxidation by H_2O_2 in TS-1 sieve.

1. W. Lin and H. Frei. Photochemical and FT-IR Probing of the Active Site of Hydrogen Peroxide in Ti Silicalite Sieve. *J. Am. Chem. Soc.*, submitted.

RIGID LIGANDS FOR ELECTRON TRANSFER STUDIES AT SEMICONDUCTOR NANOPARTICLE INTERFACES

Wei Zhang,[1] Wei Qian,[1] Dong Wang[1], Elena Galoppini[1] and Gerald J. Meyer[2]

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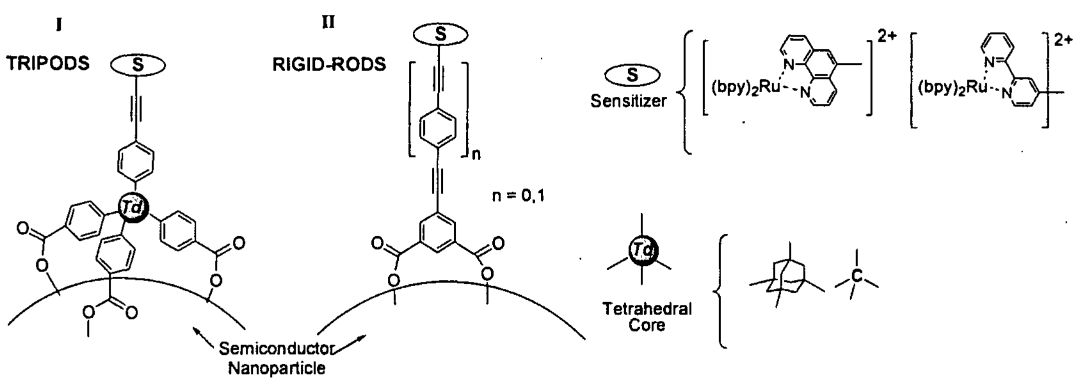
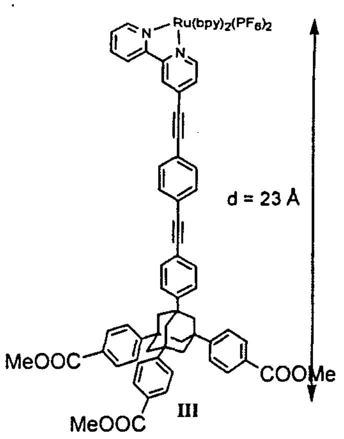
[2] Chemistry Department, Johns Hopkins University, Baltimore, MD 21218

The covalent attachment of redox- and photo-active molecules to semiconductor surfaces is an important step toward the development of molecular devices, including solar cells. Several studies have demonstrated that excited states remote to the semiconductor surface can efficiently inject electrons into TiO_2. To study these weakly coupled systems, as well as other aspects of electron injection processes at sensitizer-nanoparticles interfaces, we have prepared a series of tripodal and rigid-rod linkers substituted with Ru^{II} polypyridyl complexes, having general structure **I** and **II**.



The excited state and redox properties of tripodal sensitizers **I** in acetonitrile solution and bound to nanocrystalline TiO_2 or ZrO_2 mesoporous films have been studied. Efficient and rapid ($k_{inj} > 10^8\ s^{-1}$) excited state electron injection was observed for **I**/TiO_2. The kinetics for excited state decay were exponential in solution and non-exponential when bound to ZrO_2 or TiO_2. The recombination of the injected electron with the oxidized Ru^{III} center was well described by a second-order kinetic model with rate constants that are independent from the sensitizer. The synthesis of rigid-rod sensitizers **II**, their absorption spectra, emission spectra, and electrochemical properties have been studied in solutions. Preliminary results for the preparation of solar cells from **I** and **II**, and the synthesis of longer rods such as **III** will be discussed.



Poster # 1

PROPERTIES OF SINGLE-WALL CARBON NANOTUBE/INDIUM PHOSPHIDE QUANTUM DOT COMPOSITES

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Quantum Dot/Single-Wall Nanotube composites were formed using purified, laser grown carbon single-wall nanotubes (SWNTs) and indium phosphide quantum dots (QDs) that were synthesized by reaction between $InCl_3$ and $P(SiMe_3)_3$. The individual nanoscale building blocks were added together in pyridine. Transmission electron microscopy revealed that QDs had decorated much of the available surfaces of the SWNT bundles. Linear chains of QDs were observed at some locations, indicating a tendency for the QDs to self-assemble with the bundle surfaces acting as a template. Chains of 3-6 QDs were measured to have a center-to-center separation distance of ~ 70 Å, indicating a QD-QD edge separation of ~30 Å for the ~40 Å-diameter QDs. Raman and photoluminescence spectroscopies were used to investigate the degree of electronic coupling between the QDs and the SWNTs. The Raman G-band mode of the SWNTs was superimposed on a broad emission peak and shifted to lower frequency relative to the position of the G-band in pure SWNTs. The origin of the emission peak is uncertain at this time, but will be discussed at the meeting. The time dependence of the charge generation and relaxation processes in pure SWNTs was investigated using transient absorption spectroscopy. Purified SWNT samples were dispersed into polymers and both the time and energy dependence of the absorption was investigated. Photoinduced absorption as well as bleaching was observed at energies consistent with features in the UV-visible absorption data. Although the date is preliminary, features of the transient absorption spectrum are reminiscent of the behavior we have observed for InP QDs. For example, derivative-like features may be associated with carrier-induced Stark effect shifting of electronic transitions. Time dependent measurements at selected energies indicate the presence of at least two relaxation time constants. A short-lived, sub-picosecond component is observed, as well as a longer-lived component that persists for at least 100 ps.

CONJUGATION OF SELF-ASSEMBLING PROTEINS TO CdSe/ZnS QUANTUM DOTS

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Our objective is to design engineered systems of protein scaffolds capable of positioning quantum dots in predicable and precise arrays. Such systems would permit close range energy transfer studies to be conducted with considerably less uncertainty than currently afforded by quantum dots randomly embedded in polymer matrices. CdSe/ZnS quantum dots were purified by gel permeation chromatography in toluene and then made water-soluble by treatment with several surfactants, including mercaptopropionic acid. Aqueous high performance size exclusion chromatography indicated that at pHs above pH 7, these species are monodisperse and probably colloidal. Dockerin proteins from *C. thermocellum* have been modified genetically for chemical conjugation to the water-soluble quantum dots. Several strategies to obtain stable and active quantum dots were investigated and will be presented, including ionic interaction, chemical crosslinking, and disulphide engineering.

MECHANISTIC STUDIES OF THE WATER OXIDATION CATALYST $cis,cis\text{-}[(bpy)_2Ru(OH_2)]_2O^{4+}$

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Investigations of the mechanism of O_2 formation from water by μ-oxo bridged ruthenium dimers have been severely hampered by the inability to prepare in pure form the highest oxidation states of the complexes. This technical problem was surmounted by utilizing a high surface area columnar-flow carbon fiber electrode for constant potential electrolysis. This instrumentation has enabled us to access all of the formal oxidation states between Ru_2(III,III) and Ru_2(V,V). The cumulative results of resonance Raman (RR) and optical spectrophotoelectrochemical measurements and redox titrations of effluent solutions have led to the following major conclusions:

(1) progressive oxidation (in strongly acidic triflic acid environments) occurs through the sequence: {3,3} → {3,4} → {4,4} → {5,5}, where the {4,5} ion is apparently unstable with respect to disproportionation.

(2) optical spectral of the {4,4} and {5,5} ions are nearly identical, but these ions are clearly distinguishable by RR, since only {5,5} displays strong 818 cm^{-1} bands attributable to coordinated ruthenyl oxo atoms (ν(Ru=O)).

(3) Of the various detectable oxidation states, only {5,5} is kinetically competent to be the O_2-evolving species, i.e., decays rapidly enough to account for the measured steady-state O_2 evolution rates.

Isotope-labeling studies have been used to describe several features of the reaction mechanism. The labilities of the cis-coordinated oxo ligands were determined by incubating ^{18}O-substituted complexes in normal H_2O for timed periods, then rapidly oxidizing the samples to the {5,5} state with Ce^{4+} and measureing by RR the relative areas of the ν(Ru=O) modes at 780 cm^{-1} (O^{18}) and 818 cm^{-1} (O^{16}). The only species undergoing detectable substitution was the {3,3} ion, whose water exchange rate constant (7×10^{-3} s^{-1}) was 10^3-10^5 fold greater than that normally observed for simple monomeric ruthenium(III) complexes. This labilization can be attributed to strong σ-donation from the $-ORu(OH_2)(bpy)_2^+$ unit. Isotopic substitution at the bridging O, detectable by shifts in the Ru-O-Ru symmetric stretching (ν_s) modes, did not occur even during catalytic turnover. Thus, the bridging O plays no direct role in O_2 formation. Small downfield shifts in ν_s(Ru-O-Ru) were observed in D_2O, suggesting that the bridging O may function in catalysis by H-bonding solvent water, thereby promoting nucleophilic attack of the coordinated ruthenyl oxo groups. The rate of decomposition of {5,5} was nearly identical in D_2O and H_2O, however, indicating that O-H stretching is not extensive within the transition-state complex.

Low-temperature EPR spectra of frozen {5,5} solutions gave a unique relatively narrow axial $g = 2$ signal as a minor component. This signal, whose relative intensity depended quadratically upon the catalyst concentration, exhibited a 6-line hyperfine component comprising ~20% of the total intensity. These properties suggest that it may be a π-radical cation, formed by one-electron oxidation of the bpy ligand. Its potential role in catalysis is under investigation.

ENERGETICS OF SELF-ASSEMBLY OF A REDOX PHOTOACTIVE POLYPEPTIDE

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Despite the large number of investigations of artificial photosynthetic systems, there has been scant attention paid to the mechanisms of self-assembly of arrays of chromophores, electron donor-acceptor partners, and the molecular scaffolding that provides a template for such systems. For the construction of assemblies that are non-covalent linkages of light harvesting and redox components, there is a dependence on electrostatic, van der Waals, dipolar, and hydrophobic forces that may be at work in holding arrays in place, as with the natural photosynthetic system. In a previous communication (*J. Am. Chem. Soc.*, **2000**, *122*, 388), we reported the characterization of a 22-residue polypeptide (called TT1P) that was capped at the N-terminal with the 4-(1-pyrenyl)butanoic acid (PBA) chromophore. The system was shown to form dimers (coiled coils) of α-helixes and to evolve into higher order aggregates in water as a function of concentration ('bundles' of helices up to octamer size). These helix aggregates displayed formation of a 'special pair' of pyrene chromophores and multi-step photoinduced electron transfer, when docked with a viologen electron acceptor.

We have studied further the steps of self-assembly of the TT1P system by investigation of the appropriate equilibria, and have factored the energetic contributions of several important interactions. Using an NMR method for study of the model compound, PBA, the free energy of association of the pyrene chromophore in water was determined ($\Delta G = -2.9$ kcal/mol). Following changes in circular dichroism that are due to peptide association, the free energy of coil-coil interaction for the TT1P polypeptide, absent the pyrene chromophore, was obtained ($\Delta G = -7.0$ kcal/mol). Using a fluorescence method, the association of the TT1P peptide itself, monomer–dimer, was determined ($\Delta G = -10$ kcal/mol). With these procedures, it could be established that the interaction of the pyrene chromophores provides some of the driving force for formation of the peptide-peptide twin-helix dimer. Also, it was noted that the larger component of the free energy of association is that expected for interaction of helices at their surfaces (e.g., hydrophobic associations as in the 'leucine zipper' motif). It was further concluded that the chromophore interactions and peptide-peptide affinities do not act together cooperatively (they simply sum). This approach to the dissection of driving forces for non-covalent self-assembly will be informative in the evolutionary development of 'synthetic proteins' for artificial photosynthesis.

Poster # 18

PHOTOINDUCED TRANSFORMATIONS OF SEMICONDUCTOR-METAL NANOCOMPOSITES

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The construction of two- and three-dimensional nanoassemblies of photoactive molecules bound to metal and semiconductor nanoparticles provides new ways to improve photoinduced charge separation in light energy harvesting systems. Basic understanding of the photoinduced processes in semiconductor-metal nanocomposites is important for improving the performance of semiconductor-based nanoassemblies. Of particular interest are the TiO_2-noble metal nanostructures that enhance the efficiency of photocatalytic systems and photoelectrochemical cells.

Metal nanoparticles deposited on a semiconductor surface undergo Fermi level equilibration as photogenerated electrons accumulate within the metal layer. The effect of Fermi level equilibration is predominantly seen when the metal deposits consists of small particles or a thin shell around the semiconductor core. Unlike the bulk films, metal nanoparticles do not exhibit ohmic contact with semiconductor surface; instead, they retain the charge before transferring them to the redox species present in solution. Photoinduced electron accumulation in metal-capped TiO_2 and ZnO nanoparticles are being probed to understand the factors that control Fermi level equilibration.

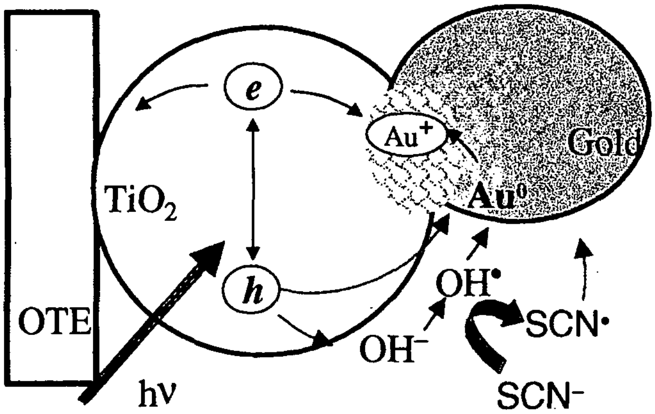

Figure 1. Oxidation of the metal at the semiconductor interface and its impact on overall photocatalytic process

When TiO_2/Au films or core/shell particles were subjected to long-term UV irradiation, oxidation of Au^0 by the photogenerated holes and oxidizing radicals (e.g., $^\bullet OH$ and $(SCN)_2^{-\bullet}$) to form Au^+/Au^{3+} ions is observed. These oxidized metal ions in turn diffuse into TiO_2 and act as charge recombination centers (Figure 1). We have further investigated the oxidation of the Au^0 at UV-irradiated TiO_2 interface using core-shell type semiconductor-metal nanoparticles, which were synthesized by reducing $[AuCl_4]^-$ on the surface of preformed TiO_2 colloids. An equilibrium between $[Au^{3+}]$ and $[Au^0]$ was found to dictate the overall efficiency of hole transfer process. Careful control of the Au^{3+}/Au^0 can yield nearly 40% enhancement in the efficiency of thiocyanate oxidation. Details on the role of metal and metal ion in dictating overall photocatalytic activity of metal-semiconductor nanocomposites will be presented.

PHOTOIONIZATION OF 10-METHYLPHENOTHIAZINE, N,N,N,N′-TETRAMETHYLBENZIDINE AND PYRENE IN Cr-AlMCM-41 MOLECULAR SIEVES

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Photoionization of 10-methylphenothiazine (PC_1); N,N,N′,N′-tetramethylbenzidine (TMB) and pyrene (Py) impregnated into mesoporous AlMCM-41 ion-exchanged with Cr(III), as an electron acceptor, to give Cr-AlMCM-41 was investigated. Cation radicals ($PC_1^{+\cdot}$, $TMB^{+\cdot}$, $Py^{+\cdot}$) are produced by 320 nm light at room temperature and characterized by electron spin resonance (ESR) and UV-VIS diffuse reflectance spectroscopy. The chromium ion concentration was varied from Si/Cr = 52 to 121. Cr-AlMCM-41 with the intermediate concentration of Si/Cr = 80 exhibits the greatest electron acceptor ability and shows the highest photoionization efficiency

photoionized. The photoionization efficiency also depends on the type of photoionizable molecule impregnated into mesoporous Cr-AlMCM-41 with PC_1 being the most efficiently photoionized. The calcination temperature used before impregnation controls the oxidation state of chromium ions to Cr^{3+} or Cr^{5+}/Cr^{6+} which also affects the photoionization efficiency. Cr-AlMCM-41 with Cr^{5+} gives about four times higher photoionization efficiency than with Cr^{3+}. Cr-AlMCM-41 is shown to be a promising heterogeneous host for the efficient formation of photoinduced cation radicals to achieve long-lived charge separation in solid state systems.

Poster # 2

LIGHT-DRIVEN CHARGE TRANSFER IN FACE-TO-FACE DONOR-SPACER-ACCEPTOR SUPRAMOLECULAR SYSTEMS

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The objective of this project is to investigate photoinduced electron transfer 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 electron transfer 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. The dynamics of photoinduced electron transfer processes in which the linker chromophore serves as an electron acceptor and one or more nucleobase as an electron donor is investigated by means of femtosecond time resolved transient absorption spectroscopy and nanosecond time resolved fluorescence spectroscopy. Our results for the period 1996-2001 have been summarized in review articles.[1]

During the past year we have continued work on both single step tunneling processes and hole migration in DNA. Our studies of the distance dependence of photoinduced charge separation dynamics in DNA are consistent with a superexchange or tunneling mechanism, for which the distance dependence can be described by $k_{cs} = k_0 e^{-\beta R}$, where R is the distance between the excited state acceptor (A) and nucleobase donor (D) and β is determined by the nature of the bridge and its coupling with D and A. Tunneling theory predicts that the magnitude of β is determined by donor-bridge-acceptor energetics (by the injection energy, or more precisely, the tunneling energy gap). New experiments have provided the first experimental evidence for the dependence of β on the tunneling energy gap.[2]

Oxidative strand cleavage in DNA is known to occur over long distances from the initial point of charge injection via a multistep hole transport process in which the hole migrates between G or GG shallow hole traps. We have reported the use of transient absorption spectroscopy and kinetic modeling to determine the rate constants for forward and return electron transfer between G and GG or GGG sites in hairpins, thereby providing the equilibrium constant and free energy for hole transport. The methodology has now been employed to determine the hole transport parameters for G to the deep hole trap Z and for G to GG across AA vs. A, across T vs. A, and for inter-versus intrastrand transport in hairpins **5-7** and related systems.[3]

(1) (a) Lewis, F. D.; Letsinger, R. L.; Wasielewski, M. R. *Acc. Chem. Res.* **2001**, *34*, 159-170. (b)Lewis, F. D.; Wu, Y. *J. Photochem. Photobiol. C: Rev.* **2001**, *2*, 1-16.

(2) Lewis, F. D.; Liu, J.; Weigel, W.; Rettig, W.; Kurnikov, I. V.; Beratan, D. N. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, under review.

(3) (a) Lewis, F. D.; Liu, J.; Liu, X.; Zuo, X.; Hayes, R. T.; Wasielewski, M. R. *Angew. Chem. Int. Ed.* **2002**, *41*, 1026-1028. (b)Lewis, F. D.; Zuo, X.; Liu, J.; Hayes, R. T.; Wasielewski, M. R. *J. Am. Chem. Soc.* **2002**, *124*, ASAP.

Poster # 21

DRIVING FORCE AND REORGANIZATION ENERGY DEPENDANT INTERFACIAL CHARGE TRANSFER AT ZINC OXIDE/LIQUID INTERFACE

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Despite much attention, there remain few examples of reliable measurements of interfacial charge transfer rate constants across semiconductor liquid junctions. In this work we are investigating electron transfer reactions at the ZnO/liquid interface in terms of driving force and reorganization energy. We have shown that ZnO in contact with various redox couples in aqueous solution exhibits a first-order kinetic dependence in surface electron concentration. However, only a few ZnO/liquid contacts, such as $ZnO/Fe(CN)_6^{3-/4-}$ and $ZnO/Co(bpy)_3^{3+/2+}$, additionally had a first order kinetic dependence in acceptor concentration. The trisbipyridinecobalt(III/II) redox couple is one example of a one-electron, non adsorbing redox couple with a well-defined reorganization energy (λ) and allowed us to obtain a reliable maximum rate constant (k_{et}) of 1×10^{-17} cm^4 sec^{-1}. This value for $k_{et,max}$ is in good agreement with the generally accepted value of 1×10^{-16} cm^4 sec^{-1} 1×10^{-18} cm^4 sec^{-1}.

Water is not a practical solvent for the investigation of the driving force dependence in the inverted region, however, since redox couples with a very positive redox potential ($E^{\circ\prime}$) will oxidize water. In order to overcome this limitation, we extended our study to non-aqueous solvents, specifically acetonitrile. Previous reports by Spittler *et al.* on ZnO microelectrodes in contact with several ferrocenes in acetonitrile indicate ideal kinetic behavior that we hoped to exploit in determining the driving force dependence. Electron transfer with our samples did not show a first order dependence in either acceptor concentration or surface electron concentration. Instead, we believe parallel reactions via surface states to be present which we were not able to passivate in non-aqueous solvents. In addition, shifts in the flat band potential were evident which we were not able to stabilize.

We will now return our focus to the driving force and reorganization dependence of electron-transfer reactions at the ZnO/water interface. In order to determine the driving force dependence, we have synthesized various $Os(L)_2L'_2{}^{3+/2+}$ (L = bpy, dmbpy; L' = imidazole, methylimidazole) compounds whose $E^{\circ\prime}$ we can tune with different electron withdrawing ligands, L. These compounds are all one electron, outer-sphere redox couples with approximately the same reorganization energy which make them ideal for this study. In addition to the low-λ redox couple, $Os(bpy)_2L_2{}^{3+/2+}$, and the high-λ redox couple, $Co(bpy)_3^{3+/2+}$, we will synthesize $Ru(sar)^{3+/2+}$ and $Ru(tacn)_2^{3+,2+}$, which have the same $E^{\circ\prime}$ but intermediate λ's. This will allow us to determine the reorganization energy dependence.

We have also focused significant effort on preparing nanometer-spaced electrodes to directly allow investigation of electron tunneling through solvents and through molecules that bridge the interelectrode gap region. In addition to gap-narrowing experiments via electroplating, we have investigated the fabrication of electron tunneling junctions by means of electromigration. We fabricated gold, palladium, and platinum nanowires with and without a chromium or titanium adhesion layer by electron beam lithography on various substrates ranging from silicon oxide to silicon nitride and silicon nitride membranes. Electromigration was carried out at liquid helium temperature in high vacuum. After breakage, electron-tunneling curves were collected in high vacuum at temperatures ranging from liquid helium to room temperature. Finally, we have prepared metal nanowires (diameter < 20 nm) that form a cross pattern. These nanowires are formed by electrochemically filling nano-sized pores in a polymer membrane with gold (or any other metal). After the gold wires are released from the polymer membrane they can be conveniently deposited on a substrate by means of a spin coater. Individual wires can be located with an AFM and contacted by electron beam writing and evaporation. Crossed wires are obtained by spinning a second layer of nanowires.

Poster # 22

pH DEPENDENCE OF ULTRAFAST INTERFACIAL ELECTRON TRANSFER IN DYE-SENSITIZED METAL OXIDE NANOCRYSTALLINE THIN FILMS

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Interfacial electron transfer dynamics between sensitizer molecules and semiconductor nanoparticles is of intense interest because of its fundamental importance and relevance to solar energy conversion. We reported previously that electron injection dynamics in dye sensitized metal oxide thin films depend critically on the nature of semiconductor and the electronic coupling between sensitizer molecules and semiconductor.

In this paper we report a recent study on the **dependence of injection rate on pH of solution.** In the nonadiabatic limit, the injection rate from adorbate excited state to semiconductor should increase with the difference of excited state redox potential and conduction band edge due to the increasing density of accepting states in semiconductor at higher energy above conduction band edge. The free energy difference can be adjusted by pH of the solution as the conduction band edge of metal oxides such as TiO_2 is raised by –60 mV per pH unit. As a result, non-adiabatic injection rate to a semiconductor should decrease with increasing pH for given adsorbate redox potential. We tested this prediction in a series of $Re(dcbpy(CH_2))Cl(CO)_3$ [ReCl] sensitized TiO_2 thin films in solutions of pH=2 to 8. In this system, injection is slow and on the non-adiabatic limit, due to reduced coupling introduced by the CH_2 spacer group. We found that injection rate decreases when the pH of solution increases. The observed trend agrees qualitatively with the theoretical prediction. We examined the injection dynamics of $Ru(dcbpy)_2(X)_2$ [X_2=2SCN, 2CN and dcbpy] sensitized TiO_2 at pH=2 to 8. While the apparent rate of the <100 fs component remains unchanged, a slow component become more pronounced and its rate become slower with increasing pH. We suggest that this behavior is a plausible explanation of the previous reported dye and sample dependence of the slow injection component observed in Ru dye sensitized TiO_2.

Fig. 1 Electron injection dynamics in $Ru(dcbpy)_3$ sensitized TiO_2 at different pH

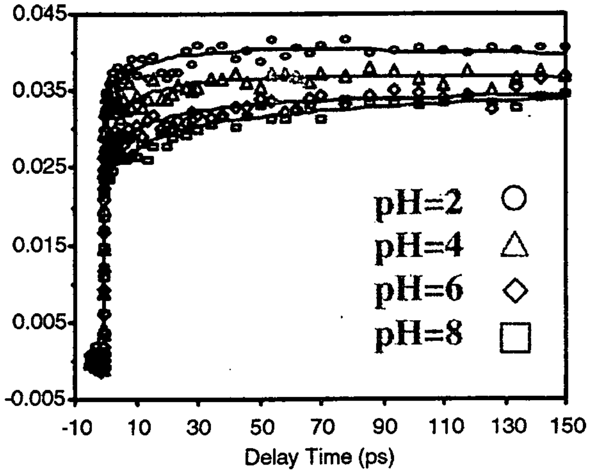
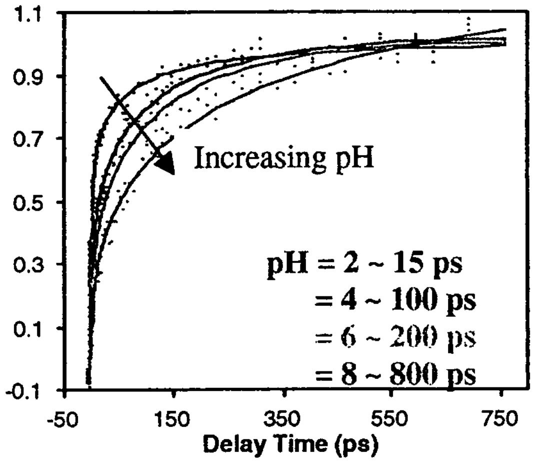


Fig. 2. Electron injection dynamics in ReCl dye sensitized TiO2 at different pH



AROMATIC EXCIMERS AS ELECTRON DONORS IN PHOTOINDUCED CHARGE TRANSFER PROCESSES

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π-π interactions in dimers of porphyrins and aromatic molecules play important roles in photoinduced electron transfer in chemical and biological systems. This is exemplified most notably by the special pair of the photosynthetic reaction center from the purple bacterium Rhodopseudomonas viridis. As part of our studies of aromatic-aromatic interactions, we have been carrying out a concerted theoretical and experimental study of the ground-state equilibrium geometry and excited-state dynamics of aromatic clusters and diarylalkanes, generated or cooled by supersonic expansion. These studies have shown that the photoionization of the species proceeds very efficiently through the formation and ionization of singlet excimers. The important precursor role of the singlet excimer in photoionization can be attributed to the conformational similarity between the excimer and the corresponding dimer cation that leads to a large Franck-Condon factor for photoionization of the excimer.

Because of the conformational dependence of excimer formation, the efficiency of the excimer-mediated photoionization is strongly dependent on the relative orientation of the two chromophores involved in the excimer formation. Thus, the efficiency of one color two-photon ionization is much greater for the naphthalene tetramer with a pair of molecules in dimer-like arrangement than for the naphthalene trimer with cyclic C_{3h} geometry. Moreover, the two-color ionization threshold is significantly lower for the tetramer that forms an excimer from the S_1 state with low excess vibrational energies than the trimer, which does not. Similarly, the efficiency of the photoionization is much greater, and the ionization threshold lower, for the trans-gauche (tg) conformer of 1,3-diphenylpropane, which readily forms an excimer, than for the trans-trans (tt) and gauche-gauche (gg) conformers that do not. Comparison of the temporal characteristic of excimer formation (and decay) with that of the time-resolved photoionization confirms the occurrence of the excimer-mediated photoionization in bichromophoric molecules.

If the cofacial excimer is a good electron donor, as the excimer-mediated photoionization of the aromatic clusters and diarylalkanes demonstrates, it is natural to ask why the special pair of the photosynthetic reaction center does not have a cofacial arrangement of the two-bacteriochlorophyll moieties. There may be a very good reason for this: A cofacial bacteriochlorophyll dimer cannot be electronically excited by energy transfer from the antenna bacteriochlorophylls as the $S_1 \leftarrow S_0$ absorption to the allowed exciton component (i.e., higher-energy excitonic level) would have S_1 electronic energy greater than that of the antenna bacteriochlorophyll. A large lateral shift of one moiety with respect to the other is therefore needed to render the allowed $S_1 \leftarrow S_0$ transition (Q_y band) of lower energy than the $S_1 \leftarrow S_0$ transition of antenna bacteriochlorophyll. It is possible therefore that the slip-parallel dimer structure of the special pair, with a large lateral displacement of the monomers, is nature's compromise between the head-to-tail coplanar dimer structure that maximizes the intensity and red shift the Q_y band, and the cofacial (or near-cofacial) dimer structure that maximizes the stability of the dimer cation.

SYNTHESIS AND EXCITED-STATE ENERGY-TRANSFER DYNAMICS OF LINEAR LIGHT-HARVESTING RODS

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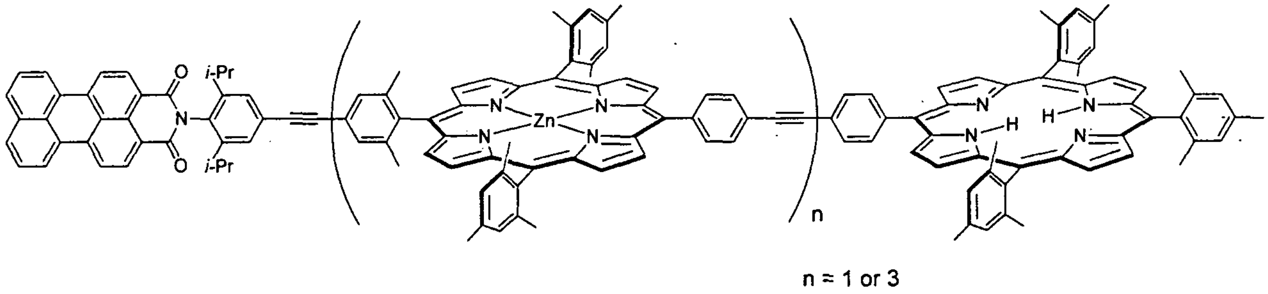
My long-term goal is to be able to create, in a rational manner and with modest effort, arrays comprised of >100 porphyrinic pigments that collect solar radiation and funnel energy to one site in the array with quantum efficiency >95%. Toward this goal, we have been examining various types of multi-porphyrin arrays. One type of array of particular interest is a linear rod, wherein excitation can be introduced with some selectivity at one end (input) and the flow of excited-state energy can be monitored along the length of the rod.

We describe the stepwise synthesis of four light-harvesting rods. Each rod consists of an input unit, transmission element, and output unit. The input unit consists of a boron-dipyrrin dye or a perylene-monoimide dye (linked either at the *N*-imide- or the C9-position); the transmission element consists of one or three zinc porphyrins (n = 1 or 3) affording short or long rods, respectively; and the output unit consists of a free base (Fb) porphyrin. The components in the arrays are joined in a linear architecture via diarylethyne linkers (an ethynylphenyl linker is attached to the C9-linked perylene). The two weakly coupled perylene-based rods are shown below.

The rods have been examined by static absorption, static fluorescence, and time-resolved absorption spectroscopy. Each rod (with the exception of the C9-linked perylene rod) exhibits a visible absorption spectrum that is the sum of the spectra of the component parts, indicating relatively weak electronic coupling between the components. Excitation of each rod at the wavelength where the input unit absorbs preferentially (typically 480-520 nm) results in emission almost exclusively from the Fb porphyrin. The static emission and time-resolved data indicate that the overall rate constants and quantum efficiencies for end-to-end (i.e., input to output) energy transfer are as follows: perylene-(*N*-imide)-linked short rod, $(33\ \text{ps})^{-1}$ and >99%; perylene-(C9)-linked short rod, $(26\ \text{ps})^{-1}$ and >99%; boron-dipyrrin-based long rod, $(190\ \text{ps})^{-1}$ and 81%; perylene-(*N*-imide)-linked long rod, $(175\ \text{ps})^{-1}$ and 86%. These studies provide a foundation for contemplating the design and synthesis of longer and more elaborate rods for light-harvesting applications.



NEW PORPHYRIN COMPLEXES: HYDROGEN-BONDING TO PYRROL NITROGENS

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The most widely studied primary interactions of porphyrins, including protonation and metal complex formation, involve the acid-base character of the central aza nitrogens. Such derivatives provide a wide range of properties, particularly with regard to spectra, redox levels and potentials, which may be tailored to various applications.For example, protonated porphyrin dications have very different spectra, are more easily photoreduced and less easily photoxidized than the corresponding free bases.

In this connection, we have identified new porphyrin complexes, formed by specific hydrogen-bonding of donors to the aza nitrogens. Such species, which have thus far hardly been studied, are of intrinsic interest in porphyrin chemistry, and may offer further possibilities for application. We may also expect that their properties will fall generally between those of the neutral and fully protonated forms of the parent

Spectrophotometric titrations of a series of porphyrins (OEP; tetra-meso-alkyl; tetra-meso-phenyls) were carried out in methylene chloride. Trifluoroacetic acid (TFA, $pK_a = 0.52$) and hexa-fluoro-isopentanol (HFIPA, $pK_a = 9.3$) were mainly used as protonating or H-bonding agents, respectively. TFA addition gave new spectra with excellent isosbestic points, corresponding to dication formation in all cases. However, both mono- and di-H-bonded complexes were found for the less basic porphyrins. In the special case of N-methyl-TPP, where the mono-cation is a very weak base, only the mono-H-bond complex with HFIPA is found, while tetra-meso-CN-PP does not bond at all

Throughout the series, systematic shifts in peak locations and intensities caused by protonation can be correlated with smaller changes caused by H-bonding. *That is , the spectra of the H-bonded porphyrins are intermediate between those of the free base and the dication.* In particular, vibronic analysis shows that the overall conversion from 4-banded to 2-banded spectra in dication formation can be related to increasing "compression", with increasing porphyrin basicity, of the gap between “X” and “Y” spectral components upon H-bonding.

Triplet-triplet spectra and initial studies on photoreduction of these H-bonded species will also be discussed.

Poster # 2

MODELING SOLVENT-CONTROLLED ELECTRON TRANSFER

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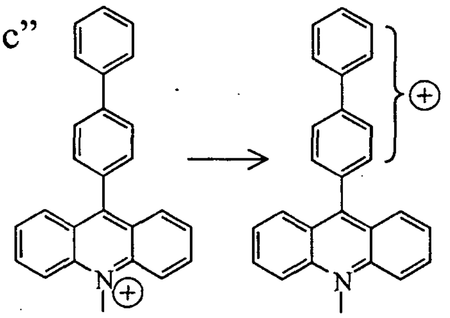
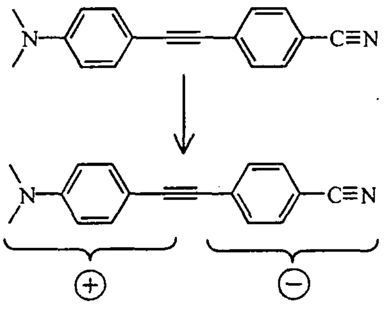
We will discuss simple models for the solvent-dependent kinetics of ultrafast electron transfer in the three systems illustrated below. Experimental results for all three reactions indicate that electron transfer is controlled by the dynamics of solvent polarization[1-3]. We have attempted to understand the nature of this solvent control using models in which reaction occurs on a 1-dimensional adiabatic reaction coordinate consisting entirely of solvent motion. Reaction surfaces are assumed to result from the mixing of two diabatic states with a coordinate independent coupling. The solvent-dependent characteristics of these surfaces are derived from a combination of electronic structure calculations and empirical information. Dynamics are modeled using a generalized Langevin equation (GLE) with solvent inertial characteristics and time-dependent friction derived from previous measurements on non-reactive solutes[4]. This type of modeling provides a satisfying description of the dynamics observed in some (BPAc) but not all of these systems (HRD) and reasons for these differences will be discussed.

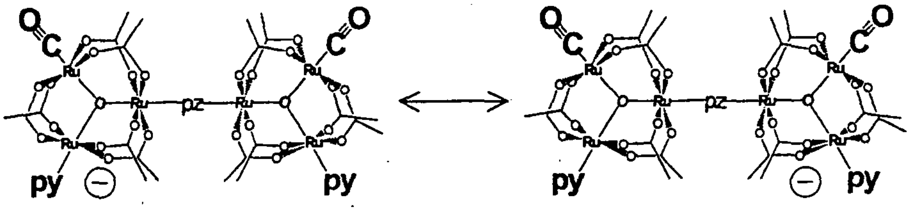
"BPAc"



"DTN"



"HRD"



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1. M. L. Horng, K. Dahl, G. I. Jones, and M. Maroncelli, *Chem. Phys. Lett.* **315,** 363-370 (1999).
2. J. A. Gardecki, Ph. D. Thesis, The Pennsylvania State University, 1999.
3. C. Londergan, J. Salsman, Ronco, R. J. Sadus, L. Dolkas, and C. P. Kubiak, *J. Am. Chem. Soc.* **2002,** in press (2002).
4. M. L. Horng, J. A. Gardecki, A. Papazyan, and M. Maroncelli, *J. Phys. Chem.* **99,** 17311-17337 (1995).

ULTRAFAST DYNAMICS IN ASYMMETRIC METAL POLYPYRIDYL COMPLEXES

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Our group is continuing to explore the ultrafast dynamics of inorganic charge-transfer complexes. Previous work has focused on several aspects of excited-state evolution such as the time scale for triplet state formation[1a] as well as the role of solvent in charge localization.[1b] Owing to the interest in employing low-symmetry molecules for use in various photovoltaic applications, we are now expanding our effort to the study of excited-state processes in asymmetric complexes.

Electronic Asymmetry. We have prepared and characterized a series of complexes based on two substituted bipyridines: 4,4'-dimethyl-2,2'-bipyridine (dmb) and 4,4'-diethylamino-2,2'-bipyridine (dea).[2] As illustrated in Figure 1, when bound to Ru^{II} these two ligands exhibit energetically disparate charge-transfer features in the visible. Mixed-ligand complexes of the general form $[Ru(bpy')_x(bpy'')_{3-x}]^{2+}$ (x = 1,2) therefore possess features of both MLCT manifolds such that selective excitation into each ligand is possible. Preliminary studies have focused on variable-pump/variable-probe studies of the tris-homoleptic complexes as a prelude to work on the more complicated C_2 symmetry analogs. Unlike ground-state recovery dynamics, which typically are invariant to either the pump or probe wavelength used, we find that excited-state evolution on ultrafast time scales exhibits a pronounced dependence on these experimental parameters (e.g., Figure 2). Details of the ultrafast electronic absorption measurements we have carried out on all of the complexes in this series will be presented.

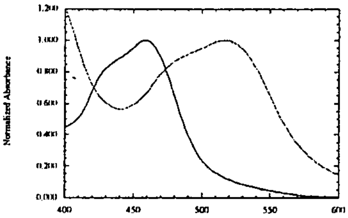

Figure 1. Ground-state absorption spectra for $[Ru(dmb)_3]^{2+}$ (black), and $[Ru(dea)_3]^{2+}$ (red) in CH_3CN solution.

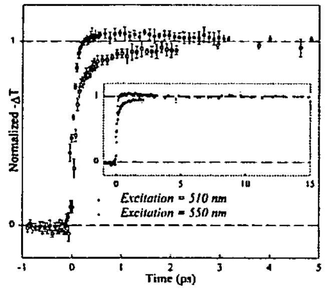

Figure 2. Femtosecond time-resolved differential absorption data for $[Ru(dea)_3]^{2+}$ at λ_{probe} = 570nm following ~120fs excitation at the wavelengths indicated.

Vibrational Relaxation. Since the emissive quantum yields of most inorganic chromophores are quite small, non-radiative relaxation plays a dominant role in the excited-state dynamics of such complexes. Therefore, in addition to electronic state dynamics, we are developing asymmetric chemical systems that will allow us to examine the dissipation of vibrational energy in the course of excited-state evolution. The probe ligand is 4,4'-dicyano-2,2'-bipyridine (dcnbpy), where the CN group provides an optical handle for monitoring vibrational dynamics on the picosecond-to-femtosecond time scale. Progress toward the synthesis of the desired compounds, as well as preliminary static and nanosecond time-resolved spectroscopic data, will be described.

1.) a) Damrauer, N.H.; Cerullo, G.; Yeh, A.; Boussie, T.R.; Shank, C.V.; McCusker, J.K. *Science* **1997**, *275*, 54. b) Yeh, A.; Shank, C.V.; McCusker, J.K. *Science* **2000**, *289*, 935.
2.) Curtright, A.E.; McCusker, J.K. *J. Phys. Chem. A* **1999**, *103*, 7032.

SIZE DEPENDENT PROPERTIES OF CORE-SHELL METALLIC NANOPARTICLES

Z. Mark Zhang[1, 2], Tomohiro Shibata[3], Bruce Bunker[3], Dan Gezelter[2] and Dan Meisel[1, 2].
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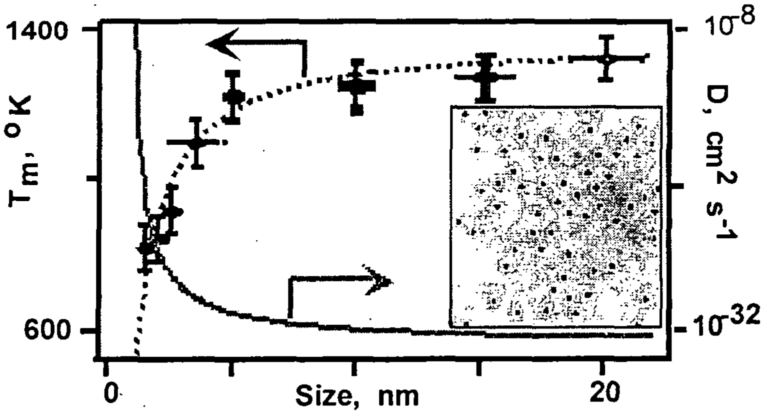
The intense interest in metallic nanoparticles, including their potential use in photochemical energy conversion strategies, prompted us to study the size dependence of some of their thermodynamic properties. We developed radiolytic methodologies to synthesize narrow size distribution of metallic particles of variable sizes. We used a similar approach to synthesize core-shell structures of bimetallic nanoparticles and of silica shells encapsulating metallic cores. We used these particles to determine the size dependence of the melting temperature and diffusion coefficient of the atoms in the particle.

Classical thermodynamic considerations predict depression of the melting temperature of small particles relative to the bulk. This results from the enormous excess surface free energy as the size of the crystallite decreases and was previously observed for semiconductor particles. We developed a simple method to determine the melting point of silica encapsulated metallic particles. The figure here shows a micrograph of the core-shell Au in silica particles. Using differential thermal calorimetry we obtained the dependence of the melting temperature of the particles on their size. Assuming that the diffusion at melting is independent of the temperature, and thus of size, and that the activation energy for diffusion is proportional to the number of bonds that need to be broken, we can extract the dependence of the diffusion coefficient of Au in the particle on size. This is also shown in the figure above.



Size dependence of the melting temperature (left axis) and diffusion coefficient (right axis) of silica encapsulated gold particles. The insert shows the core-shell AU/SiO$_2$ particles.

We then studied the stability of the core-shell structure of Au/Ag particles using EXAFS spectroscopy. The fraction of near neighbors to Au that are Ag is independent of the thickness of the Ag shell for large particles (≥10 nm). Yet, this fraction increases as the particle size decreases. For the small particles the metals spontaneously alloy at ambient temperature and in aqueous suspensions. The increase in the diffusion coefficient determined above with decreasing size could in principle explain this observation. However, quantitative examination of the diffusion using these coefficients shows that the alloying at room temperature will still be too slow. In order to explain the experimental observations we invoked the presence of defect vacancies at the bimetallic interface. Molecular dynamic simulations revealed extremely strong dependence of the rate of alloying on these vacancies.

TUNING CONDUCTION BAND ENERGETICS IN DYE-SENSITIZED NANOCRYSTALLINE SOLAR CELLS

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It is well known that the energetic position of the conduction band edge, E_{cb}, of single crystal metal oxide semiconductors can be tuned with pH in aqueous solution. Much less is known about conduction band tuning in non-aqueous solution or with nanocrystalline materials. We have developed methods for tuning E_{cb} in anatase TiO_2 nanocrystals (with protons and other potential determining cations) relative to the formal reduction potentials of surface bound Ru(II), Os(II), and Re(I) polypyridyl metal-to-ligand charge transfer (MLCT) sensitizers. These studies provide insights into mechanistic models of dye-sensitization and may provide a general approach for optimization of efficiencies in regenerative solar cells.

When E_{cb} lies above (toward the vacuum level) the excited state reduction potential of a molecular sensitizer, interfacial electron injection is absent and the sensitizer excited states are observed. Interestingly, excited state decay of long-lived MLCT excited states were well described by competing unimolecular and bimolecular excited state reactions. We have developed models that allow us to quantify the fraction of excited states that decay through each pathway as a function of irradiance, surface concentration, and excited state lifetime. The bimolecular pathway has been proposed to proceed by energy-transfer migration between the ground and excited states of adjacent, surface-attached sensitizers that leads to excited-state – excited-state reactions. Direct evidence for this now exists. In some cases, it has been possible to tune E_{cb} above the first reduction potential of the sensitizer. In these cases, the molecular sensitizers act as a traps for electrons injected from hot vibrational excited states. Trapping can lead to charge separated states that store over 2 eV of free energy for hundreds of seconds.

Titrations with potential-determining cations promotes excited state electron injection into the anatase particles. The injection efficiency is cation dependent and appears to increase with the size-to-charge ratio of the cation. At high cation concentrations the injection yield can be unity and always occurs with a rate constant $> 10^8\ s^{-1}$. Recombination of the injected electron with the oxidized dye is found to be a second-order kinetic process. The abstracted rate constants are independent of the ionic strength (and hence E_{cb} position) and the nature of the sensitizer. The data are consistent with a model where charge recombination is rate limited by diffusion of the injected electron and the oxidized dye. The cation driven electron injection processes are reversible and the resultant changes in the sensitizer photoluminescence have been exploited for cation sensors.

Potential determining cations control the power conversion efficiency in regenerative dye-sensitized solar cells. In general, high concentrations of cations increase the photocurrent efficiency and decrease the open circuit photovoltage. Therefore, an optimal cation concentration, and hence E_{cb} position, exists for light-to-electrical power conversion and this condition is expected to be dependent on the identity of the molecular sensitizer. Experiments designed to test this expectation are underway.

Poster # 30

ELECTRONIC COUPLING IN SOLID FILMS OF InP QUANTUM DOTS

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Close-packed arrays of inorganically and organically passivated InP quantum dots (QDs) were investigated using absorption and photoluminescence (PL) spectroscopies. We synthesized complex heterostructures of InP nanocrystals that consist of sintered close-packed arrays of core(InP)/shell($GaInP_2$ or ZnSe) composites in order to find the best configuration in which charge dissociation of excitons and charge separation occur. In QDs, electrons and holes are confined and can be separated upon dissociation of the initial created exciton. The binding energy of the exciton (0.122 meV for 42-Å InP QDs) is much greater than the available thermal energy at room temperature. We have studied the effect of interdot distance, QD size, the barrier height of QDs, and the bandgap offset between core QDs and the surrounding matrix array and analyzed the possibilities of interdot tunneling of a single carrier between dots. We recently incorporated colloidally prepared InP QDs arranged in a close-packed array into a larger bandgap $GaInP_2$ thin film by metal organic vapor phase epitaxy technique and found that in this composite structure the confinement energies are dramatically reduced.

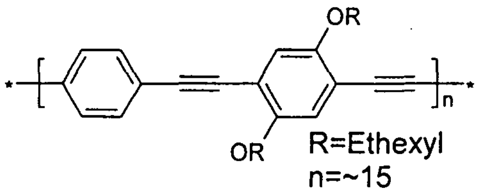
Our studies show that excitons in InP QDs formed upon absorption of light can also be dissociated by trapping electrons into energetically favorable defect states, leaving behind the delocalized hole in the core. In that case, the separation of the surface-trapped electrons and holes occurs at lower energy than separation of carriers confined in the core. The nature of electron- and hole-trapped states in colloidal InP QDs and their presence on the surface can be controlled by chemical passivation of the QDs. Semiconductor materials that grow as a shell on QDs eliminate both the anionic and cationic uncoordinated bonds on the QD surface. This raises the possibility to fabricate composite QDs with specific properties of surrounding matrix to achieve exciton delocalization in illuminated QDs.

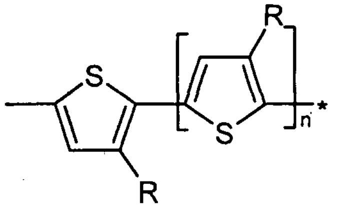
Poster # 31

LONG CONJUGATED MOLECULES: MOLECULAR WIRES FOR SOLAR ENERGY CONVERSION?

John Miller,[a] Norihiko Takeda,[a] Alsion Funston,[a] James Wishart,[a] Andrew Cook,[a] Kirk Schanze [b] and Eric Silverman[b]
[a]Chemistry Department Brookhaven National Laboratory and [b]Chemistry Department, University of Florida

The premise of this project is that new strategies for capture of solar energy may arise from development of long, conjugated molecules that can act as "molecular wires". We use the term molecular wire to indicate a very thin (~ 1 nm or less) and long (2-200 nm) molecule that may transport charge rapidly and efficiently over its entire length. For these conjugated molecules bandgaps are usually >> 1 eV so their intrinsic conductivities are low, and become high only when a charge is injected. Most such "wires" are therefore semiconductors, not metals. Examples of such wires under study are:





We argue that the semiconductor nature of the wires is possibly appropriate for creating molecular electronics, where there has been much discussion of their use, and highly appropriate for solar energy conversion. It is plausible that the development of molecular wires, spurred by electronics, could actually find more use in energy conversion processes.

This work investigates the transport in materials that may act as molecular wires and the factors affecting the transport, attaching electrons or holes using electron pulses from the LEAF accelerator at BNL. Optical absorption spectra for the wires with a single charge have strong bands in both the visible and near IR that imply strong delocalization of the charges. The spectra are compared to those produced by chemical oxidation or reduction where possible. The accelerator experiments also enable measurement of rates of bimolecucular attachment of electrons or holes to the wires. Under construction is a wire with a pendant "sink" groups that is expected to capture a charge attached to the wire. Measurement of the time for transfer to the sink is expected to either reveal the rate of transport within the wire or establish a lower limit for that rate. If the wires behave as expected then transport will be extremely fast. The poster will also describe special methods under development at the LEAF accelerator to enable measurement of very fast transport processes.

Poster # 3

MODELLING LONG-RANGE THERMAL AND OPTICAL CHARGE TRANSFER (ELECTRON AND/OR HOLE): RESULTS FROM THEORY AND COMPUTATION

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The goal of this program is the elucidation of theoretical issues fundamental to a class of processes of central importance in modern chemical science-namely, charge transport events in which charge carriers (here, electrons and holes) migrate between localized donor and acceptor sites in molecular systems, or between "contacts" in more general types of conducting junctions. Theory and computation are combined in broad-based mechanistic analysis of such charge transport (both thermal and optical) in extended molecular assemblies comprised of organic and organometallic units. Key energetic and electronic quantities such as activation energies and entropies, and electron coupling elements and transition moments, are evaluated using unified models for electronic and nuclear motion (exploiting continuum and molecular-level approaches, as needed), thereby enabling a self consistent account of thermal and optical charge transport dynamics and kinetics.

Electronic structure is based on Self Consistent Field (SCF) or Configuration Interaction (CI) calculations (using ab initio or semiempirical Hamiltonians). A framework for evaluating donor/acceptor (D/A) electronic coupling in a fully flexible manner (for arbitrary nuclear coordinates, thus obviating the constraints of approaches limited to Hartree-Fock theory or requiring the use of artificial external "forces" to achieve "resonance") is provided by the Generalized Mulliken Hush (GMH) formulation of diabatic states, coupling, effective D/A separation (R_{DA}) and energetics.

While effective 1-particle (mean field) models like Hartree-Fock theory are often of at least semi-quantitative use in formulating the states, energy gaps, and matrix elements controlling charge transport, 1-electron constructs like HOMO/LUMO gaps may often give poor results, and in the general case, especially for photoinitiated processes in electronically excited states, explicit attention must be given to charge and state-specific many-electron effects such as state-specific polarizability, which can have appreciable influence on redox energetics.

Relative propensities for electron tunneling over a range of several nanometers were evaluated and analyzed for a range of organic spacers (S) linked covalently to terminal ferrocenyl donor (D) and acceptor (A) groups. Based on all-valence-electron orbital calculations, sensitivity of tunneling was determined quantitatively with respect to chemical substitution (on both D, S, and A units), molecular conformation (oligomer torsion angles), electronic spacer type (saturated vs unsaturated) and length (number of spacer units), donor electronic state type (of crucial importance for quasi-degenerate transition metal complexes), and charge carrier type (electron vs hole). Direct calculation of crucial energy gaps separating the D/A and S manifolds indicate major contributions from both carrier types.

The recent investigation of the apparently anomalous attenuation factor ($\beta > 1.5 Å^{-1}$) for photoinitiated hole injection into DNA duplexes modified by protonated 9-amino-6-chloro-2-methoxyacridine (X^+) led to the conclusion that in addition to the electronic coupling, the activation energy must also be distance-dependent. Combination of new experimental and theoretical studies have now verified this postulate. Direct measurements of the activation energies for a series of (X^+)-modified DNA duplexes have sampled a range of donor-acceptor distances (4-11 Å), and detailed calculations based on classical and semiclassical rate constant models have provided a self-consistent account of the driving forces and reorganization energies controlling the kinetics. The resulting changes in thermal activation energy may be attributed to a distance-dependent reorganization energy (with Michel-Beyerle, Technical University of Munich).

Poster # 33

PHOTOSYNTHETIC MOLECULAR WIRES

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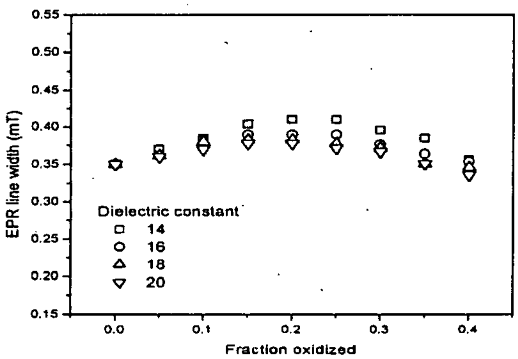
Light harvesting complex 1 (LH1) of purple photosynthetic bacteria is a self-assembled circular protein complex containing bacteriochlorophyll that is used by nature to harvest solar energy. LH1 complexes exhibit the following useful features for the construction of solar devices: 1. LH1 self assembles from small membrane spanning polypeptides and bacteriochlorophyll. 2. LH1 complexes self assemble into highly ordered two-dimensional arrays. 3. Upon "dark" chemical oxidation of LH1, unpaired electrons are created that rapidly migrate along the array of bacteriochlorophylls as if the assembly were a molecular wire.

The electron transfer properties of LH1 have been characterized by EPR studies. Most intriguing in these natural systems is the dramatic difference in the EPR behavior upon going from liquid solution to solid solution. To model the effect of electron transfer on the EPR of these LH1 complexes, free energy heterogeneity and coulomb repulsion have now been included. The figure (calculated EPR line widths vs. fraction oxidized for LH1 of *B. viridis*) illustrates the electron transfer model that includes coulomb repulsion for the room temperature case where energy heterogeneity is not important. Not surprisingly, the time-versus-distance for electron transfer between adjacent bacteriochlorophyll molecules in LH1 complexes is found to be typical of electron transfer in alpha-helical proteins[1,2]. Interestingly, the EPR of these LH1 complexes indicates that differences in electron transfer properties exist between natural and artificial light harvesting systems[3,4]. Implications for natural and artificial solar-harvesting complexes will be presented.



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SURFACE RESTRUCTURING OF METAL OXIDE PARTICLES: AN EFFICIENT ROUTE FOR NANOPARTICLE-BIOMOLECULE CROSSTALK

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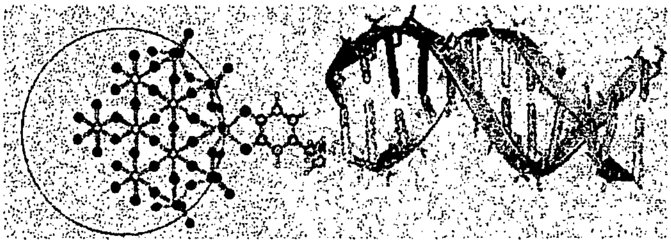
Surface modification of nanocrystalline metal oxide particles with enediol ligands was found to result in altered optical properties of nanoparticles. Upon surface modification the semiconductor absorption band shifts to the red, as compared to unmodified nanocrystallites. The optical shift is correlated with the dipole moment of the ligands at the particle surface, and decreases with the ligand size. The binding was found to be exclusively characteristic of colloids in the nanocrystalline domain (<20nm). X-ray absorption near edge structure (XANES) measurements indicate that in this size domain the surface metal atoms adjust their coordination environment to form under-coordinated sites. These under-coordinated defect sites are the source of novel enhanced and selective reactivity of the nanoparticle toward bidentate ligand binding as observed using IR spectroscopy. Enediol ligands have the optimal geometry for chelating surface Ti atoms resulting in their five-membered ring coordination that then results in restored stable geometry of surface metal atoms. The binding of enediol ligands is enhanced due to the stability gained from adsorption-induced restructuring of the nanoparticle surface. Consistent behavior was found for the three different nanocrystalline metal oxide systems: TiO_2, Fe_2O_3 and ZrO_2.



Combining chemical reactivity of metal oxides with molecular recognition of biomolecules (DNA)

The unique binding of enediol ligands was used to covalently attach biomolecules such as DNA to the metal oxide nanoparticles. The tight electronic coupling establishes efficient crosstalk between the biomolecule and metal oxide surfaces. The nanoparticle serves as a reporter of the bio-molecular state and can carry out photocatalytic functions. The DNA oligonucleotides build the site recognition properties into the hybrid system, allowing localization of nanoparticles at desired sites and can be used as a means for self-organization. Light induced extended charge separation in these systems was found to occur in double stranded DNA linked to the TiO_2 nanoparticle, while charge separation does not extend beyond the dopamine linker when single stranded DNA is linked to the TiO_2 nanoparticle. Light driven chemistry in systems having varied enediol ligands allows for time- and frequency-addressable active functions. The role of sequential electron transfer and electrochemical parameters, and how they affect the charge separation distances was studied by attaching oligonucleotides with a different nucleobase sequence. EPR was used to probe the molecular environment of paramagnetic intermediates formed during photoinduced charge separation in hybrid systems. The methods for electronic coupling of nanoparticles to proteins are being developed.

STRUCTURAL CONSEQUENCES OF OXIDATION IN NONPLANAR CHROMOPHORES. MOLECULAR STRUCTURES OF A Co(II)PORPHYRIN, ITS Co(II) π CATION RADICAL AND Co(III) CATION AT 20K

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The increasing crystallographic evidence that porphyrin derivatives often adopt nonplanar conformations in photosynthetic reaction centers and many heme proteins has prompted the synthesis of conformationally designed porphyrins in order to model and assess the physical and chemical consequences of the distortions observed *in vivo*.

High precision molecular structures of nonplanar cobalt porphyrins in different oxidation states yield the following results that illustrate the stereochemical consequences of electron transfer.

1) Oxidation of the porphyrin macrocycle results in only minor changes in bond distances (0.01Å or less), consistent with the extensive delocalization of the unpaired electron in the π cation radical.
2) Axial ligands, imidazoles for example, convert the Co(II) radical to a Co(III) cation.
3) Oxidation of the saddle-shaped macrocycle induces additional conformational distortions but oxidation to Co(III) does not.
4) Formation of the π radical does not lead to the pseudo Jahn-Teller bond alternation often observed in π cation radicals, and indicates that the two highest occupied molecular orbitals in the present case are sufficiently separated in energy so as not to lead to the orbital mixing believed to cause the Jahn-Teller distortion.
5) The saddle-shaped Co(II) π radical is diamagnetic at low temperatures because of antiferromagnetic coupling between the unpaired electrons on the Co(II) ($S=1/2$) and on the porphyrin which is symmetry allowed in nonplanar porphyrin radicals incorporating paramagnetic metals.

EXCITATION ENERGY DEPENDENCE OF CHARGE CARRIER RELAXATION AND PHOTOLUMINESCENCE IN COLLOIDAL InP QUANTUM DOTS

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Olga I. Mićić, and Arthur J. Nozik
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Colloidal quantum dots offer great potential as candidates for charge transporters and light absorbers in photovoltaic solar cells. These materials are prepared in solution and are thus amenable to the armory of chemical synthesis methodologies to tune and improve their electronic properties as well as their processability. As they can be processed from solution, it opens up the opportunity to prepare photovoltaic solar cells that are both efficient and relatively cheap to manufacture.

This presentation will focus on the electronic properties of colloidal quantum dots made from the III-V semiconductor, indium phosphide, InP, in addition to the II-VI material cadmium selenide, CdSe, both with and without a zinc sulphide shell. The band gap of these materials is dependent upon the size of the dots and therefore they can be tuned to optimize absorption of the solar spectrum. Alternatively, there is an opportunity to use the restricted carrier relaxation mechanisms in these quantum-confined systems to utilize photons absorbed at energies higher than the band gap. Two such examples are the extraction of the absorbed energy from the hot carriers prior to relaxation or the enhancement of intra-dot, impact ionization to increase the number of carriers per absorbed photon. To examine these processes in more detail requires knowledge of the excited state properties of the quantum dots and the relationship to their chemical make-up, particularly the nature of the surface. It is this topic that is focused on here.

Femtosecond transient absorption spectroscopy has been used together with time-integrated photoluminescence (PL) measurements to study charge carrier relaxation in colloidal InP quantum dots (QDs). Measurements of band-edge photoinduced bleaching as well as PL intensity measurements indicate that the fraction of charge carriers relaxing to the band edge states depends on excitation wavelength, with a markedly reduced relaxation efficiency observed for excitation well above the absorption edge. The results concur with previous research on CdSe and InP QDs, and suggest that with increasing excitation energy there arise relaxation pathways involving surface or external energy states exhibiting reduced radiative efficiency. Such highly-excited carriers are either inhibited or deviated from reaching the band edge states. Excitation intensity-dependent measurements indicate that those charge carriers that contribute to the band edge absorption bleaching also contribute proportionally to the time-integrated PL spectrum.

Poster # 37

SOLVATOCHROMISM AND PREFERENTIAL SOLVATION OF INTRALIGAND CHARGE TRANSFER EXCITED STATES OF Zn(II) TERPYRIDYL SUBSTITUTED PHENYLENE VINYLENE OLIGOMERS

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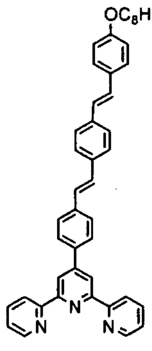
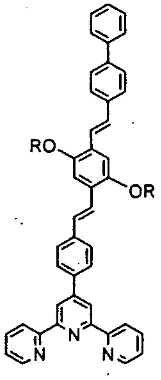
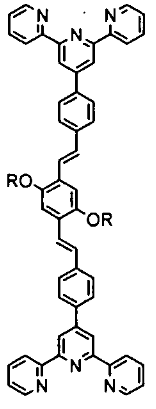
Recently we have investigated the photophysical behavior of Ru(II) diimine complexes of terpyridyl substituted phenylene vinylene containing ligands (below). The Ru(II) → tpy(π*) MLCT state of $[Ru(tpy)_2]^{2+}$ is very short lived (< 1 ns) in room temperature solution, but the analogous Ru(II) complexes of the phenylene vinylene containing ligands have long lived (> 10 μs) excited state lifetimes that can be used for photoredox chemistry. It is known that distyrylbenzene and derivatives have triplet excited states with energies of 14,500 cm^{-1} ± 300 cm^{-1}, significantly lower than the energy expected for the Ru(II)→ tpy (π*) MLCT state. Thus, the long lived excited state of the Ru(II) tpy complexes with phenylene vinylene substituents could be assigned as a ligand localized triplet (^{3}IL). However, the complexes exhibit weak, broad, luminescence with a maximum of 780 ± 20 nm (E_{00} ~ 13,500 cm^{-1}) and transient absorption spectra of the complexes differ considerably from the ligand spectra. These facts suggested the potential involvement of another state and led us to investigate the photophysical behavior of the $[Zn(II)(L)_2]^{2+}$ complexes of the distyryl benzene ligands t-2v-OR and t-2v-Ph, complexes lacking MLCT transitions.



t-2v-OR



t-2v-Ph



t-2v-t

The complexes were prepared in $CHCl_3$ solution by reaction with $Zn(OAc)_2$ at room temperature. Both the t-2v-OR and t-2v-Ph complexes exhibit strong yellow fluorescence (τ < 2 ns) in $CHCl_3$ at room temperature. The emission spectra lack structure and the maxima of both complexes are strongly solvatochromic; for $[Zn(t\text{-}2v\text{-}2)_2]^{2+}$ the maximum ranges from 580 nm in $CHCl_3$ to 640 nm in CH_3CN. The behavior is consistent with luminescence from a charge transfer excited state and we have tentatively assigned the emissive state as alkoxy to Zn(II)terpyridyl (π*) intraligand-charge transfer state (ILCT). An interesting aspect of the behavior of the complexes is that the emission observed in mixed solvents (i.e. $CHCl_3/CH_3CN$) suggests preferential solvation of the ILCT state. Details of the excited state solvation process will be discussed in the poster.

Poster # 38

A HIGH PRESSURE SPECTRAL HOLE BURNING STUDY OF CORRELATION BETWEEN ENERGY DISORDER AND EXCITONIC COUPLINGS IN THE LH 2 COMPLEX FROM *RHODOPSEUDOMONAS ACIDOPHILA*

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Low temperature (5 K) non-photochemical hole burning and absorption spectroscopies were used to study the effects of high pressure (up to 1015 MPa) on excitonic coupling energies and energy disorder in the light-harvesting complex 2 (LH 2) from *Rhodopseudomonas Acidophila* (strain 10050). The pressure dependences of the widths and positions of the B850 and B870 (lowest exciton level of the B850 ring) bands were determined. The results show, for the first time, that these parameters are linearly correlated (common scaling law), consistent with recent theoretical predictions (Jang et al. *J. Phys. Chem.* B 2001, 105, 6655). Excitonic calculations for the B850 ring of bacteriochlorophyll *a* molecules were performed in the nearest dimer-dimer coupling approximation (Wu et al. *J. Phys. Chem.* B 1997, 101, 7654) with E_{1+} diagonal energy disorder. Such a symmetry is known to dictate the response of the B870 level (absorption bandwidth, displacement (ΔE) from the B850 band maximum) to either diagonal or off-diagonal energy disorder. The results reveal that the pressure dependences of nearest neighbor coupling energies and the width of the distribution function for energy disorder are positively correlated, both increasing with pressure. Importantly, an effective pressure dependent excitonic Hamiltonian for the B850 ring was obtained. This Hamiltonian was used to show that mixing of the upper excitonic levels of the B850 ring in close proximity to the B800 levels is too weak to account for the additional (other than B800→B850 energy transfer) decay channel of the B800 band. A simple combinatorial model for intra-B800 band downward energy transfer is presented that qualitatively explains all available low temperature data on the additional decay channel.

VIBRATIONAL DYNAMICS IN PHOTOINDUCED ELECTRON TRANSFER

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The main objective of the prior funding period was to study how vibrational states (geometry distortions) are involved in photoinduced electron transfer rates.

We have re-examined our earlier report of electron transfer (ET) in the radical pair $[Co(Cp)_2|V(CO)_6]$ using ultrafast infrared transient absorption spectroscopy. The radical pair is created by ultrafast charge-transfer excitation of an ion pair in the visible charge-transfer band. We observe two electron-transfer components of ~ 700 fs and ~ 5 ps by transient IR with 75 fs resolution. The two ET lifetimes are attributed to the presence of two ion-pair contact geometries with absorption origins different by about 1250 ± 350 cm^{-1}. The ~ 700 fs ET lifetime depends on the vibrational quantum state of the nontotally symmetric CO stretch in the $V(CO)_6$ radical, where the lifetime decreases by ~ 10% for the first vibrational quantum and ~ 45% for the second quantum. There is no quantum effect for the second ion-pair geometry with a 5 ps ET lifetime. Standard ET rate models cannot explain the rate dependence for a nontotally symmetric mode, and we assign it as a breakdown of the Condon approximation. We also find that the intramolecular vibrational redistribution time (IVR) to transfer vibrational energy from the totally symmetric CO stretch to the nontotally symmetric stretch is less than 75 fs for a 1-quantum IVR process. An apparent change in the ET kinetics occurs when charge-transfer excitation wavelengths decrease from 800 and 700 nm to 620 and 555 nm. At the higher energies all quantum levels show a 200 fs rise time, which is unexpected for the zero quantum level. We assign this effect to the onset of sufficient internal vibrational energy in low-frequency vibrations to cause geometric interconversion between energetically similar Jahn–Teller geometries in the $V(CO)_6$ radical. The rise time reflects the time for the $V(CO)_6$ radical species to assume a stable geometry by vibrational relaxation to the solvent. The hypothesis of two ion-pair geometries leading to different ET rates is supported by the transient absorbance data, where the relative amplitudes of the two rate components change with excitation frequency. Further examination of the charge-transfer band via time-dependent Raman analysis and Franck–Condon calculations confirms that two absorptions could exist under the single broad band.

Recent work on methyl quinolinium cation and the $V(CO)_6$ anion will be reported at the meeting, along with theoretical calculations on this system.

Poster # 4

DESIGN AND SYNTHESIS OF CHROMOPHORE-CORED DENDRIMERS FOR PHOTOINDUCED CHARGE SEPARATION

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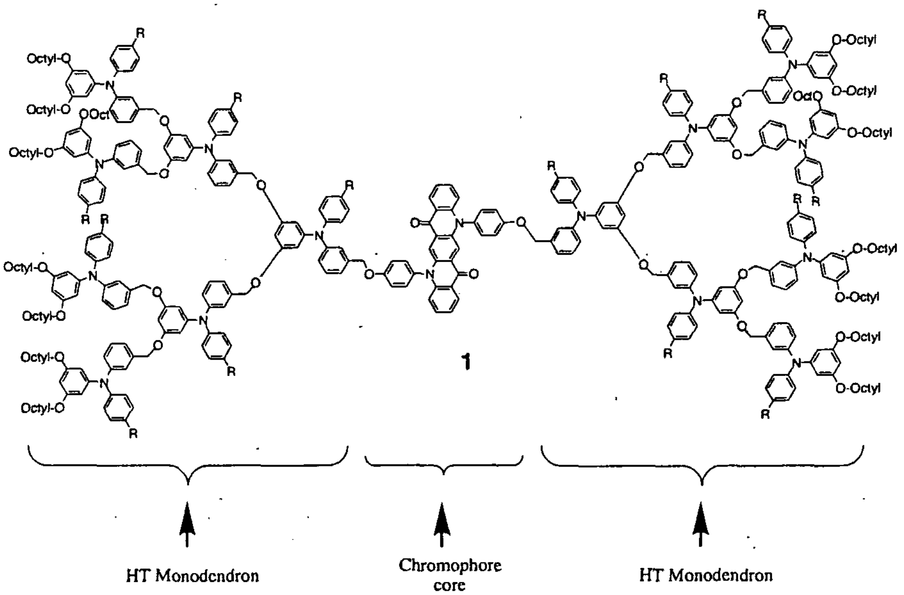
Nature's energy harvesting devices are based on the relative spatial organization of the functional units to direct the charge migrations. The unique macromolecular architecture of dendrimers presents new avenues to control the spatial placement of functional moieties and thus control electronic motions within a macromolecule. Therefore, opportunities to design molecular-scale devices and carry out fundamental studies on the factors that affect light initiated processes such as photoinduced charge migrations are available. Compared to their linear chain counterparts that afford control in one dimension, dendrimers present more compact spatial arrangements in higher dimensions. Also, note that the construction of a linear molecule with four different donors, a chromophore core, and four different acceptors will require nearly the same amount of synthetic effort as a dendrimer with the similar variations. However, in this case, the dendrimer will have a total of thirty charge transport (CT) units, whereas the linear analogs will have a total of only eight CT units. Moreover, as the charge separates from the core to the periphery, the number densities of the CT units double with each layer of the dendrimer. Therefore, the charge separation could be expected to be more favorable in the compact three-dimensional dendritic macromolecules than their one-dimensional linear counterparts.



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In this project, dendrimers have been designed and synthesized that contain a chromophore core and two hole-transporting (HT) dendrons. The hole-transporting dendrons are triarylamine based and the chromophore core is based on quinacridone. An example of the synthesized dendrimer is shown by the structure 1. In order to investigate whether these dendritic architectures indeed provide advantages for photoinduced charge separation, the corresponding linear analogs of the chromophore cored dendrimers have been synthesized. In order to further facilitate charge migrations, dendrimers with built-in energy gradients have also been synthesized. In the poster, the design, syntheses and preliminary photophysical studies of these dendrimers will be outlined.

Poster # 41

PHOTOPHYSICS AND ELECTRON TRANSFER DYNAMICS IN PORPHYRYL(ETHYNYLENE)-BRIDGED DONOR-ACCEPTOR ARRAYS

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We have shown that conjugation expansion of the porphyrin core through *meso*-arylethynyl groups imparts a number of distinctive electronic properties to the metallomacrocycle. These effects derive from the fact that the significant steric interactions existing between a conventional *meso*-aryl ring's *ortho* substituents and the porphyrin β-hydrogen atoms, that normally effect a large dihedral angle between the planes of the two aromatic systems, have been removed.

In contrast to the overwhelming majority of donor-spacer-acceptor (D-Sp-A) systems in which D, Sp, and A are electronically distinct, relatively little is known regarding the photophysics and electron transfer (ET) dynamics of D-Sp-A assemblies in which strong electronic coupling mixes D, Sp, and A electronic states effectively. Initial efforts examining ET reactions involving electronically delocalized excited and charge-separated (CS) states have focused on a series of D-Sp-A systems that utilize a 5-arylethynyl or 5,15-di(arylethynyl)-substituted porphyrin core with peripherally attached pyromellitic diimide (PI) and 1,8;4,5-naphthalenediimide (NI) electron acceptors (Figure 1).

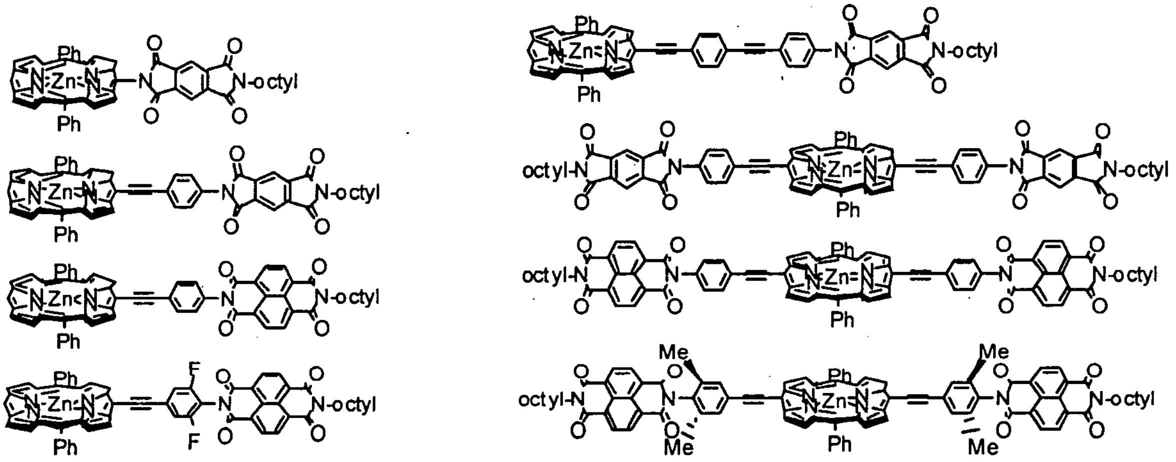

Figure1. A family of rigid D-Sp-A structures designed to probe the extent to which the cyllindrically š-symmetric ethyne impacts electronic delocalization and D-A coupling within the electronically excited and charge-separated states.

Extensive solvent dependent studies of the photoinduced CS and thermal CR ET reactions of these species using pump-probe transient absorption spectroscopic methods, coupled with EPR experiments, potentiometric studies, and electronic structure calculations suggest that the CS states of the compounds that feature arylethynyl moieties bridging the (porphinato)zinc(II) (PZn) and NI/PI units manifest highly delocalized cation radicals. The nature of the relaxed CS states in these arylethynyl-bridged PZn-PI/NI assemblies highlight the importance of stabilizing Coulombic interactions; Marcus-Levich-Jortner analysis of the dynamical data suggest that the effective edge-to-edge D-A distance in these CS states differs little from that defined by the directly-linked PZn-PI complex shown in Figure 1.

Poster # 4

PULSED HIGH-FREQUENCY EPR STUDY ON THE LOCATION AND FUNCTION OF THE CAROTENOID AND CHLOROPHYLL CATION RADICALS IN PHOTOSYSTEM II

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In Photosystem II (PS II), chlorophyll, β-carotene, and cytochrome b_{559} are alternate electron donors that may be involved in a photoprotection mechanism. In our previous study we described the use of high-field EPR spectroscopy to characterize the low-temperature photooxidation of chlorophyll z (Chl_Z) and carotenoid (Car) cofactors in PS II. The EPR signals of the individual species, previously not resolved at X-band frequency (9 GHz), have been resolved at higher frequency, D-band (130 GHz), in deuterated *Synechococcus lividus* PS II. Deuteration of PS II results in significant narrowing of the EPR lines, yielding well-resolved EPR spectra of the Car^+ and Chl_Z^+ radicals at 130 GHz. Our results prove that both the carotenoid and chlorophyll radicals are generated in PS II following illuminations at temperatures from 6-190 K and that they both participate in the photoprotection electron transfer reaction. This study also establishes the feasibility of using deuteration and high-field EPR to resolve previously unresolvable cofactor signals in PS II. Based on previous results, in the present study high-frequency pulsed EPR spectroscopy has been used to measure the location of the carotenoid relative to other PS II cofactors. Several X-ray crystal structures of the PS II protein are available now. Nevertheless, the location of the Car molecule is not established. In order to find a location of Car^+ relative to Chl_Z^+, whose position is known from X-ray data, we measure spin-lattice relaxation rates of these radicals in Mn-depleted samples with high- and low-spin Fe present in PS II. The low-spin Fe (S=0) has been produced by cyanide treatment of the Mn-depleted PS II sample. The analysis of the enhancement of the Car^+ and Chl_Z^+ relaxation rates in the presence of high-spin Fe (S=2) allows us to determine the distance between Fe and Car by using the X-ray diffraction data on the Fe-Chl distance. The location of the carotenoid and the scheme of the photoprotection electron transfer reaction in PS II are discussed in the poster.

Poster # 43

THE THEORY OF ELECTRON TRANSFER REACTIONS: WHAT MAY BE MISSING?

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The basic theory for electron transfer (ET) rate constants, as originally developed by Marcus and extended to some degree by many other researchers, has enjoyed a great deal of success for nearly fifty years. However, in the past decade or so increasingly complex ET systems have been probed by increasingly more accurate experimental techniques. Furthermore, larger and more ambitious computer simulations of ET reaction have been carried out. A general picture emerging from these efforts is that the original theory and its most common generalizations may well be missing one or more key features. In particular, the full effects of electronic polarizability (of both the ET complex and the solvent), electronic delocalization, conformational effects on the donor-acceptor electronic couplings, and nuclear quantum effects are not fully incorporated into the standard theoretical framework. In this poster, results will be presented which serve to illustrate the potential magnitude of these various effects, in some cases *qualitatively* modifying the theoretical picture (e.g., the effects of polarizability and it impact on the famous Marcus "law of intersecting parabolas.") A generalized three-parameter model for ET will be described which allows us to quantify many of these effects in terms of simple, calculable (and measurable) parameters. The generalized model is based on the Hamiltonian for a two-state ET complex linearly coupled to a collective solvation mode with different force constants in the initial and final states. The exact analytical solution for the ET free energy surfaces for this model leads to Marcus-like curves which are parabolic close to their minima but linear far from their minima positions. A theory will also be described for the ET free energy surfaces of charge transfer reactions in electronically delocalized systems, which are common, e.g., in cases involving large electronic overlap between the donor and acceptor species.

Results on the electronic structure of semiconductor/electrolyte interface systems will also be reported based on the Car-Parrinello first-principles molecular dynamics method (CPMD). The CPMD simulation of the InP-water interface has been carried out for the first time, revealing the importance of both electronic delocalization and polarization effects, and thereby again highlighting overall theme of this presentation.

Poster # 44

CHARGE TRANSPORT IN PHOTOFUNCTIONAL NANOPARTICLES SELF-ASSEMBLED FROM ZINC 5,10,15,20-TETRAKIS(PERYLENEDIIMIDE)PORPHYRIN BUILDING BLOCKS

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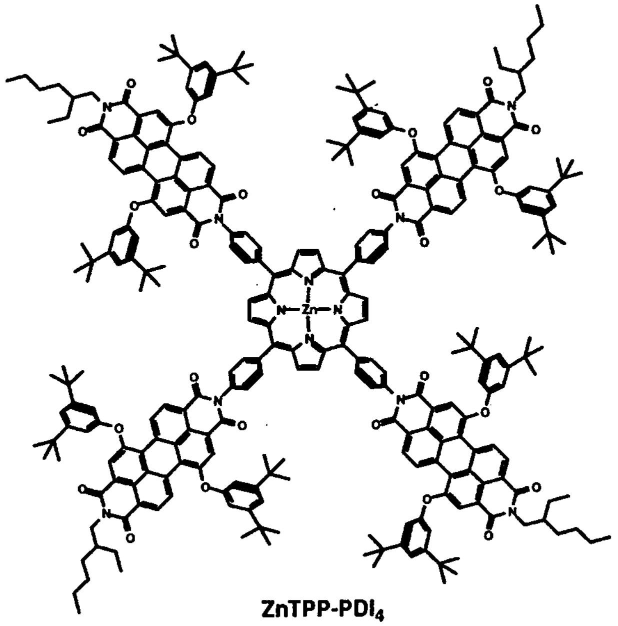
Molecules designed to carry out photochemical energy conversion typically employ several sequential electron transfers, as do photosynthetic proteins. Yet, these molecules typically do not achieve the extensive charge transport characteristic of semiconductor devices. We have prepared a large molecule in which four perylene-3,4:9,10-tetracarboxydiimide (PDI) molecules that both collect photons and accept electrons are attached to a central zinc 5,10,15,20-tetraphenylporphyrin (ZnTPP) electron donor. This molecule self-assembles into ordered nanoparticles both in solution and in the solid state driven by van der Waals stacking of the PDI molecules. The optical spectra of the $(ZnTPP\text{-}PDI_4)_n$ nanoparticles strongly support the proposed structure depicted schematically in Figure 1. The PDI molecules most likely stack directly on top of one another in register, presumably at a van der Waals contact distance of about 3.5 Å, while the ZnTPP molecules occupy sites in every other layer with an interlayer Zn-Zn distance of about 7 Å. Photoexcitation of the nanoparticles results in quantitative charge separation in 3.2 ps to form $ZnTPP^+$ PDI^- radical ion pairs in which the radical anion rapidly migrates to PDI molecules as much as 4 nm away as evidenced by magnetic field effects on the yield of the PDI triplet state that results from radical ion pair recombination. These nanoparticles exhibit charge transport properties that combine important features from both photosynthetic and semiconductor photoconversion systems.



ZnTPP-PDI$_4$

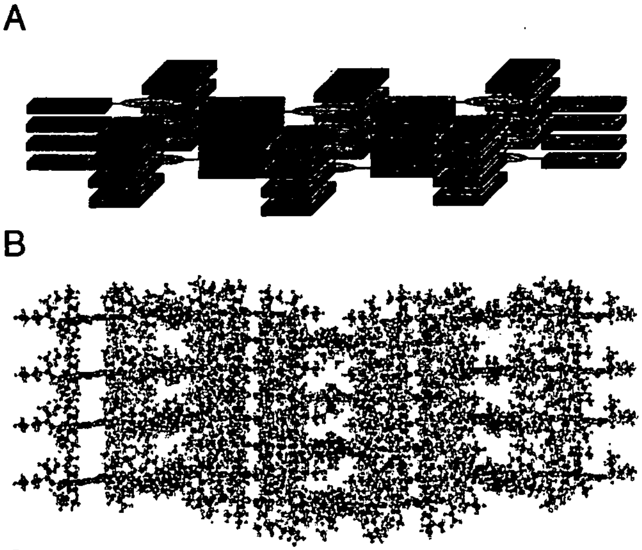


Figure 1. A) Cartoon of the structure of self-assembled $(ZnTPP\text{-}PDI_4)_{12}$ nanoparticles. B) side view of the energy-minimized structure of $(ZnTPP\text{-}PDI_4)_{12}$ nanoparticles determined using MM+ force field calculations.

Poster # 45

PHOTOINDUCED CHARGE SEPARATION REACTIONS OF J-AGGREGATES BOUND TO SILVER AND GOLD NANOPARTICLE COLLOIDS

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J-aggregates are characterized by a red shifted and sharp absorption band relative to the monomer band, a result of exciton delocalization over the molecular building blocks of the aggregate. In addition to their use as photographic sensitizers, the large oscillator strength and fast electronic response of J-aggregates are of interest in many fields, such as modeling energy transfer in photosynthetic reaction center antenna and solar photochemical energy conversion. Since organics frequently possess enhanced optical properties on metal surfaces, the exciton dynamics of J-aggregates near bulk metal surfaces have been explored. In general, coupling of the exciton to the plasmon of the metal leads to ultrafast quenching of the exciton and its fluorescence. Very recently, however, the J-aggregation of cyanine dyes on the surface of noble metal nanoparticle colloids was reported. This offers a unique opportunity to study the interaction of molecular J-aggregates with the larger near-field enhancements and modulated electrochemical properties of metallic colloidal nanoparticles when compared to bulk metal surfaces. Transient spectroscopies are used to show that photoexcitation of the plasmon in Ag nanoparticles coated with J-aggregates leads to exciton dynamics that are much different than for J-aggregate monolayers on bulk metal surfaces. Specifically, charge separated states with a lifetime of ~300 ps between the J-aggregate and Ag colloid are formed (Figure 1).[1] The reduction of the Ag nanoparticles is shown to be a multi-electron process. Control experiments using gold nanoparticles with a plasmon resonance energy below that of the J-aggregate absorption band are also described. Finally, near-field scanning optical microscopy experiments are performed to ascertain the plasmon damping due to J-aggregates on the surface of the nanoparticles.[2]

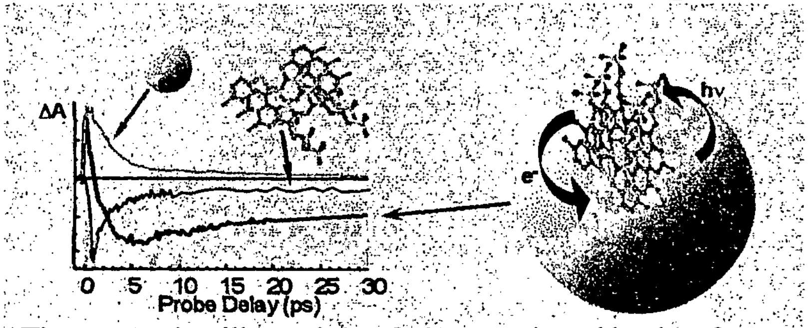

Figure 1. An illustration of the transient kinetics for J-aggregate coated metal nanoparticles undergoing photoinduced charge separation.

References

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Poster # 46

COMPUTATIONAL STUDIES OF CATECHOL AND WATER INTERACTIONS WITH TITANIUM OXIDE NANOPARTICLES

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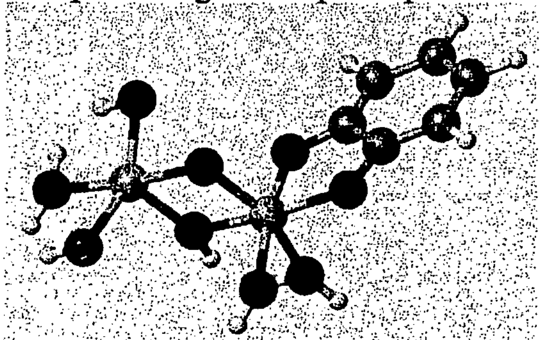
Anatase nanoparticles show a large red shift of about 1.6 eV in the optical spectra when their surface is modified by catechol. Suggested explanation involves under-coordinated corner defects having Ti=O double bonds, which are reactive towards these ligands and result in bidentate dissociative bonding. Previous EPR studies suggest a charge transfer mechanism with the ligand acting as the donor site and the conduction band of TiO_2 acting as the acceptor. In contrast, only a small red shift of 0.4 eV occurs for catechol binding to large nanoparticles.

To elucidate the nature of the large red shift, the interaction of catechol and water with titanium oxide nanoparticles was investigated using *ab initio* molecular orbital theory and density functional theory. Hydrogen terminated TiO_2 clusters were used to model the surface of anatase nanoparticles. The calculations indicate that catechol reacts with a Ti=O defect site on the surface to form a bidentate structure that is favored over dissociative or molecular adsorption on the (101) anatase surface. The adsorption of catechol at the defect site leads to a much larger red shift in the TiO_2 excitation energy than dissociative or molecular adsorption on the (101) anatase surface. This is consistent with recent experimental results on titania nanoparticles.

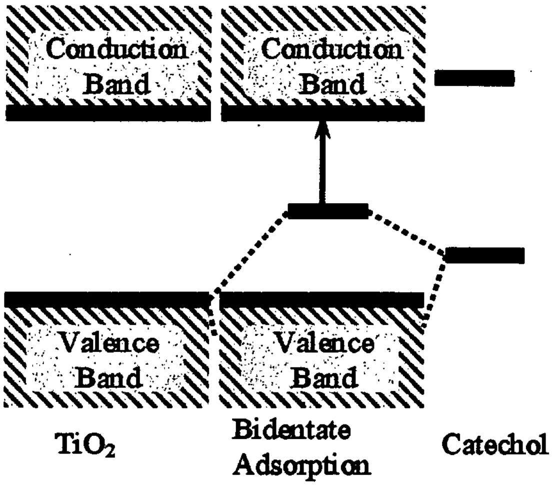
The excitation occurs from a molecular orbital primarily associated with catechol carbon atoms to a molecular orbital mostly on titanium and corresponds to a charge transfer from the catechol to the TiO_2 cluster.

The calculations on water adsorption indicates that it can also add at Ti=O sites on small TiO_2 nanoparticles. Molecular adsorption on the (101) anatase surface is more favorable than dissociative adsorption for an isolated water molecule.

Future studies will concentrate on a wider range of adsorbed species, including biomolecules, larger cluster models for titania, improved description of surface relaxation, simultaneous presence of adsorbed organic species and water on the surface, dependence of adsorption energies and optical spectra on surface structure and coverage.



Bidentatively adsorbed catechol geometry at the corner site and schematic illustration of the corresponding electronic structure.



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