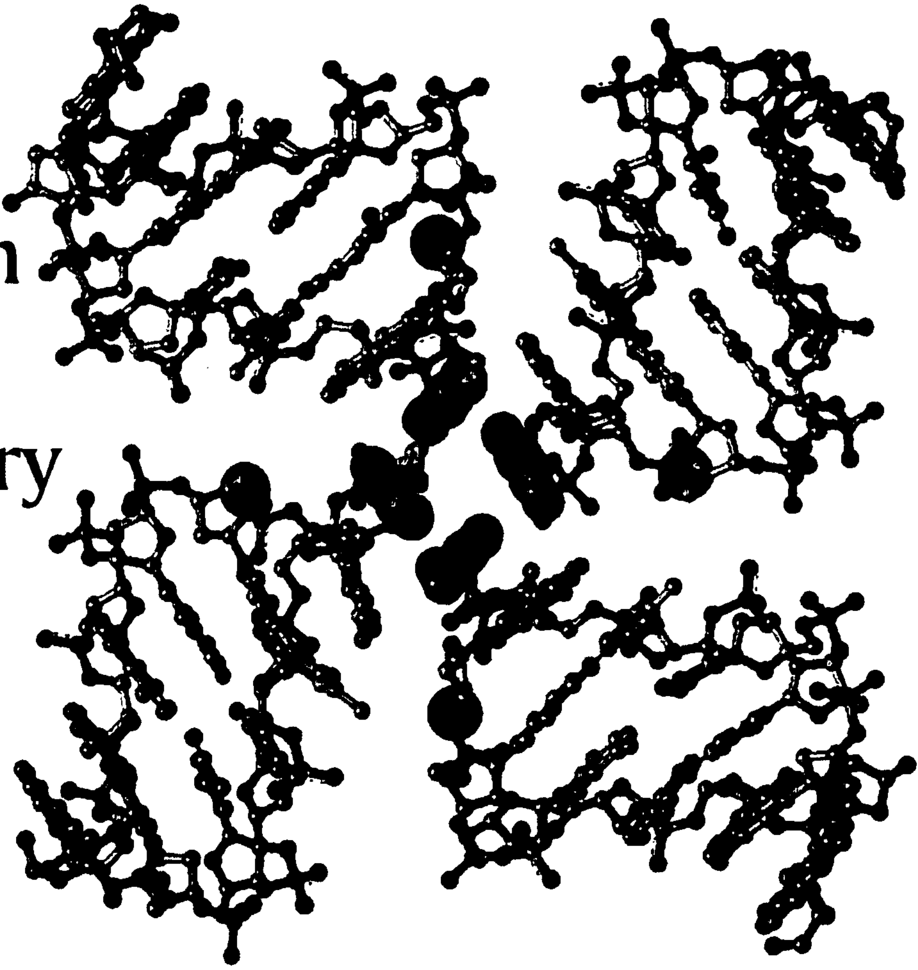
Proceedings of the Twenty-Fourth DOE Solar Photochemistry Research Conference



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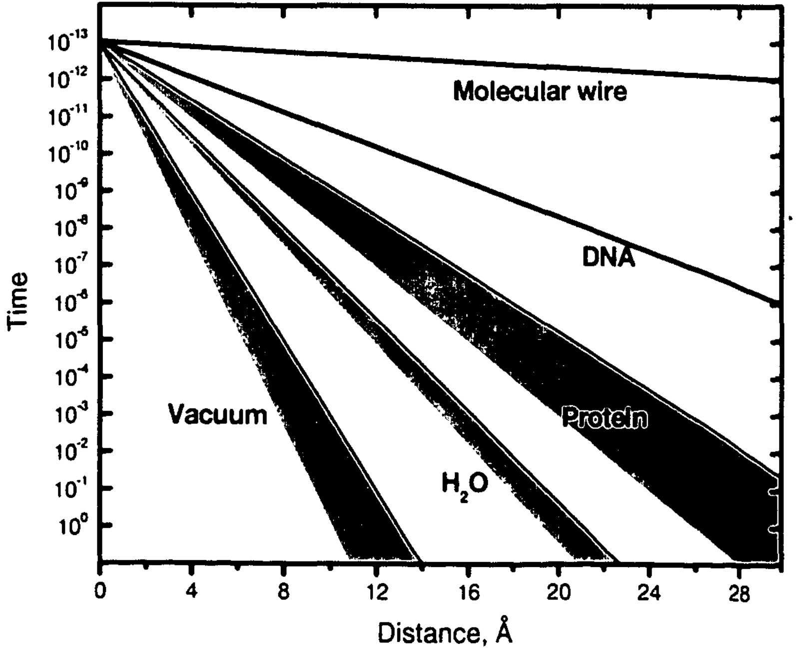

Held at
Granlibakken Conference Center
Tahoe City, California
June 3-7, 2001

Cover Graphics

The figure at the top shows the asymmetric unit in the crystal structure of a stilbenediether-linked DNA hairpin used in studies of photoinduced electron transfer in DNA. There are four hairpins in each unit. The "pinwheel-like" arrangement of the stilbene moieties is visible in the center (green), and Sr^{2+} ions, which are added to help in the crystallization, are magenta. The plot at the bottom shows that the distance dependence of electron transfer dynamics in DNA is intermediate between that of a molecular wire and a protein. (Yansheng Wu and Frederick D. Lewis, Northwestern University)

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FOREWORD

The 24th Department of Energy (DOE) Solar Photochemistry Research Conference is being held June 3-7, 2001, at the Granlibakken Conference Center in Tahoe City, California. The meeting is sponsored by the Chemical Sciences, Geosciences and Biosciences Division, Office of Basic Energy Sciences.

The annual conference brings together grantees and contractors of the Chemical Sciences, Geosciences and Biosciences Division who are engaged in fundamental research on solar photochemical energy conversion. The conference affords a singular opportunity for coordination of the program, by fostering collaboration, cooperation, and exchange of information on recently completed work, research in progress, and future plans. The synergy that is achieved involving investigators from diverse disciplines is a strength of the program.

Solar photochemical energy conversion is a long-range option for meeting the world's energy needs. It offers an alternative to solid state, semiconductor photovoltaic cells. In the DOE solar photochemistry research program, molecule-based biomimetic systems and photoelectrochemical methods are explored with the goal of providing the knowledge base needed for future technologies in conversion of light energy to chemical energy. Biophysical studies on photosynthetic antennas and reaction centers provide molecular design criteria for efficient light collection and charge separation in model systems. Studies on electron and energy transfer in the condensed phase explore fundamental concepts in charge separation. Inorganic and organic photochemical studies provide information on new chromophores, donor-acceptor molecular assemblies, and photocatalytic cycles. Photochemical reactions are investigated in nanoscale heterogeneous environments, such as zeolites, inorganic multilayer films, dendrimers, silica gel, and liposomes. Photoelectrochemical energy conversion is explored in fundamental studies of the semiconductor/liquid interface, colloidal semiconductors, and dye-sensitized solar cells.

The program features topical sessions on photosynthetic antenna complexes and synthetic light-harvesting arrays; porphyrins, carbon nanotubes, and nanoparticles; electron transfer and charge separation; charge separation in organized assemblies; photoelectrochemistry; and photochemical reduction of CO_2. Our special guest lecturer is Professor Martin Head-Gordon of Lawrence Berkeley National Laboratory who will discuss theoretical calculations on excited states of large molecules. In this volume may be found the program, abstracts of the 29 formal presentations, 42 poster abstracts, and an address list for the 86 participants.

Special thanks are due to John Otvos and Marilyn Taylor, formerly of the Calvin research group, who emerged yet again from retirement to run this conference, and to Bill Parson and his staff at Granlibakken for their gracious hospitality. Andreene Witt of the Oak Ridge Institute of Science and Education is gratefully acknowledged for preparation of this volume. The success of the conference, notwithstanding, is due to all of the participants for sharing their expertise and experience in pursuit of common research goals.

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

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Program

24th DOE SOLAR PHOTOCHEMISTRY RESEARCH CONFERENCE

June 3-7, 2001

Granlibakken Conference Center
Lake Tahoe, California

PROGRAM

Sunday, June 3

4:00 - 9:00 p.m.	Registration
5:00 - 10:00 p.m.	Welcoming Reception
6:00 - 7:30 p.m.	Buffet Dinner, Granhall

Monday Morning, June 4

7:30 - 8:30 a.m.	Breakfast, Granhall
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
9:00 a.m.	**Plenary Lecture.** Electronic Structure Calculations on Excited States of Large Molecules: Theory and Recent Applications **Martin Head-Gordon**, Lawrence Berkeley National Laboratory
10:00 a.m.	Coffee Break, Garden Deck

SESSION II
Light-Harvesting Arrays
Gerald J. Small, Chairman

10:30 a.m.	Towards the Rational Design of Synthetic Light-Harvesting Arrays **Jonathan S. Lindsey**, North Carolina State University
11:00 a.m.	Photosynthetic Light Harvesting and Its Regulation **Graham R. Fleming**, Lawrence Berkeley National Laboratory

11:30 a.m. Exploring Photosynthetic Proteins with EPR and X-Rays
James R. Norris, Jr., University of Chicago

12:00 a.m. Lunch, Garden Deck

Monday Afternoon, June 4

SESSION III

Porphyrins, Nanotubes and Nanoparticles

Ana L. Moore, Chairman

1:30 p.m. Structure-Function Designs of Photosynthetic and Catalytic Porphyrins
Jack Fajer, Brookhaven National Laboratory

2:00 p.m. Resonance Raman Studies of Single Wall Carbon Nanotube Structure and Electronic Properties
Louis Brus, Columbia University

2:30 p.m. Size Dependent Structural Dynamics in Nanostructures
Dan Meisel, Radiation Laboratory, University of Notre Dame

Monday Evening, June 4

5:00 p.m. Social Hour, Garden Deck
6:00 p.m. Dinner, Granhall

7:30 p.m. Posters (Odd numbers), Pavilion

Tuesday Morning, June 5

SESSION IV

Electron Transfer and Charge Separation

Joseph T. Hupp, Chairman

8:30 a.m. New Theoretical Perspectives on Electron Transfer
Gregory A. Voth, University of Utah

9:00 a.m. Interaction of Aromatic Hydrocarbon Triplet States with MLCT States: A Way around the Energy Gap Law
Russell H. Schmehl, Tulane University

9:30 a.m. Intramolecular Charge-Transfer Interactions and Their Involvement in Highly Efficient Photoinduced Charge Separation
C. Michael Elliott, Colorado State University

10:00 a.m. Coffee Break

10:20 a.m. Mapping Electronic Coupling between Radical Ion Pairs within Covalent Donor-Acceptor Molecules Using Magnetic Fields
Michael R. Wasielewski, Northwestern University

10:50 a.m. Light-Driven Charge Transfer in Face-to-Face Donor-Spacer-Acceptor Supramolecular Systems
Frederick D. Lewis, Northwestern University

11:20 a.m. Vibrational Dynamics in Photoinduced Electron Transfer
Kenneth G. Spears, Northwestern University

11:50 a.m. Polar Solvation, Friction, and Electron Transfer
Mark Maroncelli, Pennsylvania State University

Tuesday Evening, June 5

5:00 p.m. Social Hour, Garden Deck
6:00 p.m. Dinner, Granhall

SESSION V

Charge Separation in Organized Assemblies

Thomas E. Mallouk, Chairman

7:30 p.m. Closed Bilayer Membranes as Control Elements in Complex Photoinitiated Redox Systems
James K. Hurst, Washington State University

8:00 p.m. Photoinduced Charge Separation in Microheterogeneous Media
Larry Kevan, University of Houston

8:30 p.m. Spectroscopic and Photophysical Studies of Polypyridine Complexes of Divalent Ruthenium in Solution and Entrapped in Zeolite-Y
James R. Kincaid, Marquette University

Wednesday Morning, June 6

SESSION VI
Photoelectrochemistry
Arthur J. Nozik, Chairman

8:30 a.m. Electron Transport and Interfacial Phenomena in Dye-Sensitized Nanocrystalline TiO_2 Solar Cells
Arthur J. Frank, National Renewable Energy Laboratory

9:00 a.m. Excited State Charge Transfer at Nanocrystalline Semiconductor Interfaces
Gerald J. Meyer, Johns Hopkins University

9:30 a.m. Ultrafast Electron Injection Dynamics in Dye Sensitized Nanocrystalline Semiconductor Thin Films
Tim Lian, Emory University

10:00 a.m. Coffee Break

10:30 a.m. Time-Resolved Studies of Organic Dye Molecules Bound to Titanium Dioxide Particles: Effect of Particle Size and Structure
Gregory V. Hartland, University of Notre Dame

11:00 a.m. Metal-Semiconductor Composites. Photoinduced Transformations in Gold Capped TiO_2 Nanostructures
Prashant V. Kamat, Radiation Laboratory, University of Notre Dame

11:30 a.m. Early Stages of Photoinduced Charge Separation in Surface Modified Metal Oxide Nanoparticles
Tijana Rajh, Argonne National Laboratory

Wednesday Evening, June 6

5:00 p.m. Social Hour, Garden Deck
6:00 p.m. Dinner, Granhall

SESSION VII
Photoelectrochemistry
Krishnan Rajeshwar, Chairman

7:15 p.m. Synthesis of Extremely Small InP Nanocrystals and Electronic Coupling in Their Close-Packed Solid Arrays
Olga I. Mićić, National Renewable Energy Laboratory

7:45 p.m. Energetics and Dynamics of Electron Transfer across Chemically Modified InP/Liquid Junctions
Nathan S. Lewis, California Institute of Technology

8:15 p.m. Posters (Even numbers), Pavilion

Thursday Morning, June 7

SESSION VIII
Carbon Dioxide Photoreduction
Richard Eisenberg, Chairman

8:30 a.m. Photochemistry in Framework Transition Metal Sieves
Heinz Frei, Lawrence Berkeley National Laboratory

9:00 a.m. Redox Reactions of Metalloporphyrins in Catalyzed Reduction of Carbon Dioxide
Pedatsur Neta, National Institute of Standards and Technology

9:30 a.m. Coffee Break

10:00 a.m Transition Metal Complexes in Photoconversion
Carol Creutz, Brookhaven National Laboratory

10:30 a.m. Carbon Dioxide Utilization: Photochemical Conversion and a Replacement Feedstock for Isocyanate Synthesis
Clifford P. Kubiak, University of California, San Diego

11:00 a.m. Closing Remarks
Mary E. Gress, U.S. Department of Energy

Monday Morning

Session I

Plenary Session

ELECTRONIC STRUCTURE CALCULATIONS ON EXCITED STATES OF LARGE MOLECULES: THEORY AND RECENT APPLICATIONS

Martin Head-Gordon
Department of Chemistry, University of California, Berkeley, and,
Chemical Sciences Division, Lawrence Berkeley National Laboratory,
Berkeley, CA 94720

Today, electronic structure calculations are an indispensable supplement to experimental studies on the structure and reactivity of molecules in their ground states. For excited states, the development of suitable general-purpose computational methods has lagged significantly behind. The purpose of this talk is to summarize the status of excited state methods that can be applied to large molecules (say with 10 to 50 non-hydrogen atoms), and to describe some recent chemical applications from my group using these methods.

The only first principles theoretical methods that can be applied to systems of the target size are those based on a 1-electron treatment of electronic structure. To begin with, I shall describe the development of one-electron excited state methods within molecular orbital theory. This results in the single excitation configuration interaction (CIS) method [1], and the time-dependent Hartree-Fock (TDHF) method [2]. These methods yield a qualitatively correct description of low-lying excited states that are describable as (linear combinations of) single electron promotions from the ground state. Much like Hartree-Fock theory for the ground state, the neglect of electron correlations precludes attaining high accuracy for vertical excitation energies, but excited state structures and vibrational frequencies are predicted with useful precision [3].

Density functional theory (DFT) provides an alternative, formally exact one-electron description of the ground state through Kohn-Sham theory. Even though we must be content with approximate exchange correlation potentials in practice, their accuracy is a usually a significant improvement over Hartree-Fock theory. There is a sound formal basis for excited state density functional theory, based on time-dependent response theory, which can also be exact in principle [4]. This time-dependent density functional theory (TDDFT) is an analog of TDHF where the response matrix is dressed with the effect of electron correlation. A Tamm-Dancoff approximation [5] yields a density functional analog of CIS. An adiabatic approximation is necessary to make these excited state density functional theories feasible in practice.

The accuracy of TDDFT calculations with approximate exchange-correlation functionals will be discussed for different types of molecules, and different classes of excited states. Remarkable improvements in accuracy for vertical excitation energies relative to CIS and TDHF are found for many low-lying valence excited states. An accuracy of +/- 0.3 eV is often observed. However, some quite serious systematic problems exist with present-day functionals. Rydberg excited states are not correctly described, and similar deficiencies sometimes exist with charge-transfer excited states. With standard functionals, the entire spectrum above the Rydberg threshold is potentially contaminated. Therefore it is important to be aware of these deficiencies when performing TDDFT calculations!

Turning from excited state theories and generalities about their performance to specific chemical applications, I shall discuss 3 specific studies that have been recently undertaken in my group. First, as a relatively small system, I shall describe calculations of the low-lying excited states of substituted peroxy radicals. There has been interest in the phenyl peroxy radical because experiments showed that it exhibits an absorption in the visible. This is in dramatic contrast to the corresponding vinyl peroxy radical which only absorbs in the UV, or alkyl peroxy radicals. TDDFT is able to correctly predict the substituent effects on peroxy excitation energies, which is encouraging. Furthermore, based on examination of the calculations, we are able to extract a simple and satisfying qualitative picture of the origin of the substituent effects.

The second area of application is to calculations of excited states of unsaturated hydrocarbon cations [6]. These species arise in combustion chemistry (as intermediates in sooting flames), and may also be present in the interstellar medium, where researchers have speculated that they may be wholly or partly responsible for the so-called diffuse interstellar bands. I shall describe calculations that complement experimental data for some systems that have recently been studied in the laboratory (for example, $C_{10}H_9^+$, and $C_{30}H_{16}^+$), where TDDFT can assist in assigning observed bands. Additionally I shall present some calculations on systems that have not yet been studies experimentally, where TDDFT calculations can make potentially useful predictions.

The third area is a collaborative application (with the Fleming group, Berkeley) to study low-lying excited states in the carotenoids involved in photosynthetic energy transfer. I shall discuss the description of low-lying bright and dark states in polyenes by TDDFT versus molecular orbital methods [7]. Having established what level of accuracy we can expect, we then examine TDDFT calculations on carotenoids in light harvesting complex II of purple bacteria, and their implications for excitation energy transfer. This is a very challenging application because of the mixing of nearly degenerate bright and dark states due to the non-planar geometry of the polyene chain. Nevertheless, using the calculations as input to a simple model for energy transfer appears to yield excitation energy transfer times that are similar to recent experimental measurements.

[1] "Towards a Systematic Molecular Orbital Theory for Excited States", J.B.Foresman, M.Head-Gordon, J.A.Pople and M.J.Frisch, J. Phys. Chem. 96, 137-149 (1992).

[2] "Time-dependent Hartree-Fock theory for molecules", A. D. McLachlan and M. A. Ball, Rev. Mod. Phys. 844 (1964).

[3] "Analytical Second Derivatives for Electronic Excited States using the Single Excitation Configuration Interaction Method: Theory and Application to Benzo[a]pyrene and Chalcone", D.Maurice and M.Head-Gordon, Mol. Phys. 96, 1533-1541 (1999).

[4] "Density functional theory for time-dependent systems", E. Runge and E. K. U. Gross, Phys. Rev. Lett. 52, 997 (1984).

[5] "Time-dependent Density Functional Theory within the Tamm-Dancoff Approximation", S.Hirata and M.Head-Gordon, Chem. Phys. Lett. 314, 291-299 (1999)

[6] "Time-dependent Density Functional Study of the Electronic Excitation Energies of Polycyclic Aromatic Hydrocarbon Radical Cations of Napthalene, Anthracene, Pyrene and Perylene", S.Hirata, T.J.Lee, and M.Head-Gordon, J. Chem. Phys. 111, 8904-8912 (1999).

[7] "Excitation Energies from Time-Dependent Density Functional Theory for Linear Polyene Oligomers: Butadiene to Decapentaene", C.-P.Hsu, S.Hirata and M.Head-Gordon, J. Phys. Chem. A 105, 451-458 (2001).

Monday Morning

Session II

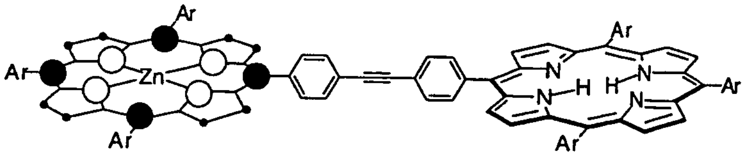
Light-Harvesting Arrays

TOWARDS THE RATIONAL DESIGN OF SYNTHETIC LIGHT-HARVESTING ARRAYS

Jonathan S. Lindsey, and the groups of D. F. Bocian and D. Holten
Department of Chemistry, North Carolina State University, Raleigh, NC 27695-8204

My long-term goal is to be able to create, in a rational manner and with modest effort, arrays comprised of large numbers of porphyrinic pigments that collect solar radiation and funnel energy to one site in the array with quantum efficiency >95%. Toward this goal, we have developed a building block approach for preparing covalently-linked multiporphyrin arrays that transfer singlet excited-state energy in a controlled manner. We also have synthesized and prepared an extensive family of dyads, so that we can (1) understand the mechanism of energy transfer, and (2) use this knowledge to design large multiporphyrin arrays with improved energy-transfer properties.

Our typical dyad architecture encompasses a Zn porphyrin and a free base (Fb) porphyrin with a covalent linker at the *meso*-positions, as shown below for ZnFbU. The dominant mechanism of energy transfer involves a through-bond process mediated by the diphenylethyne linker. We found that the rate of transfer depends on the electronic composition of the frontier molecular orbitals as well as the site of linker connection. ZnFbU, for example, has the a_{2u} HOMO and gives a fast rate. A dyad with identical distance, orientation, energetics, and site of linker connection but an a_{1u} HOMO gives a much slower rate (see Osuka's dimer below). The a_{1u} HOMO has a node at the meso position, which is the site of linker connection. Confirmation of this phenomenon has come from synthesis and characterization of a variety of ZnFb dyads: moving the linker to the β-position in a system with an a_{2u} HOMO gives a slower rate; moving the linker to the β-position in a system with an a_{1u} HOMO gives a faster rate.



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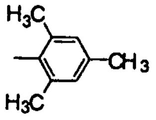
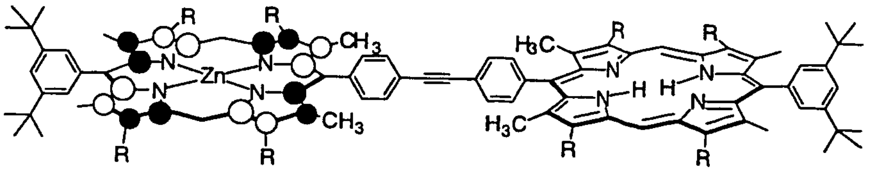


$a_{2u}(\pi)$ HOMO **ZnFbU** $k_{trans} = (24\ ps)^{-1}$



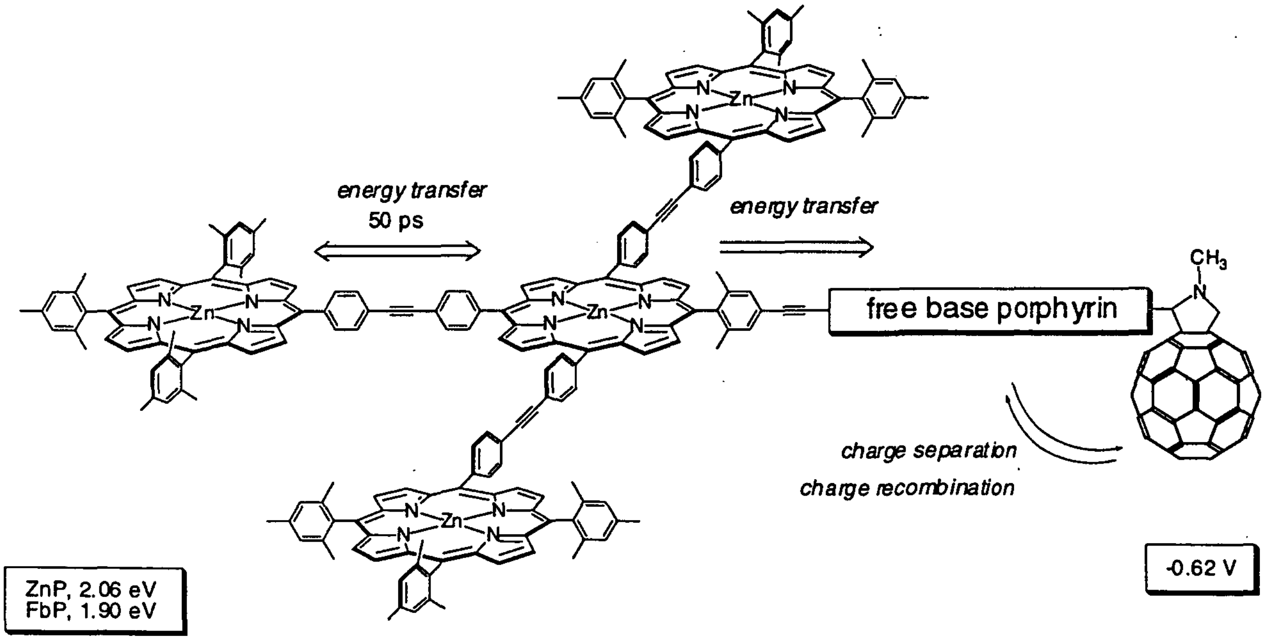
$R = C_6H_{13}$

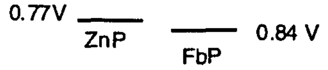
$a_{1u}(\pi)$ HOMO **Osuka's dimer** $k_{trans} = (417\ ps)^{-1}$

Are the rate differences observed in dyads manifest in larger arrays? An opportunity to examine this issue arose in a collaboration with the Arizona State group (Devens Gust, Ana Moore, Tom Moore). Our groups prepared the antenna-reaction center complexes shown below.

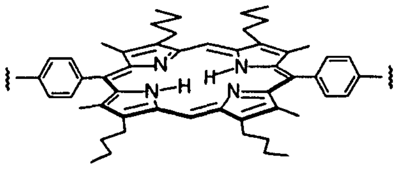
In the system containing the β-substituted free base (Fb) porphyrin, the rate of energy transfer from Zn to Fb porphyrin was ~(240 ps)$^{-1}$. Upon use of a meso-substituted Fb porphyrin, the rate was (32 ps)$^{-1}$. This 7.6-fold rate enhancement is attributed to the better orbital matching of the meso-substituted Fb and Zn porphyrins, which have a_{2u} HOMOs, versus the β-substituted porphyrin, which has an a_{1u} HOMO. The faster rate is essential for efficient funneling of energy from antenna to reaction center. The minimum conclusion from this work is that the factors observed to affect the rates of energy transfer in dimers do carry over to much larger arrays.

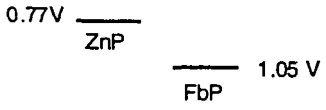
Integrated Antenna-Reaction Center Complexes (ASU/NCSU)



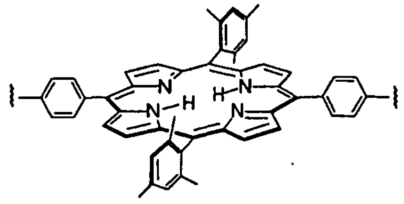


energy transfer	244 ps
charge separation	3 ps
charge recombination	1,330 ps
quantum yield of CSS	70%





energy transfer	32 ps
charge separation	25 ps
charge recombination	240,000 ps
quantum yield of CSS	90%



We are now using this knowledge about rational design in concert with new synthetic strategies to prepare large light-harvesting arrays. The arrays contain a variety of pigments (perylene, porphyrin, chlorin, phthalocyanine, etc.) to adequately cover the solar spectrum.

DOE publications 1999-present

(1) "An Artificial Photosynthetic Antenna-Reaction Center Complex," Kuciauskas, D.; Liddell, P. A.; Johnson, T. E.; Weghorn, S. J.; Lindsey, J. S.; Moore, A. L.; Moore, T. A.; Gust, D. *J. Am. Chem. Soc.* **1999,** *121*, 8604-8614.

(2) "Synthesis and Properties of Star-Shaped Multiporphyrin-Phthalocyanine Light-Harvesting Arrays," Li, J.; Diers, J. R.; Seth, J.; Yang, S. I.; Bocian, D. F.; Holten, D.; Lindsey, J. S. *J. Org. Chem.* **1999,** *64*, 9090-9100.

(3) "Convergent Synthesis of Light-Harvesting Arrays Composed of Eight Porphyrins and One Phthalocyanine," Li, J.; Lindsey, J. S. *J. Org. Chem.* **1999,** *64*, 9101-9108.

(4) "A Tightly Coupled Linear Array of Perylene, Bis(porphyrin), and Phthalocyanine Units that Functions as a Photoinduced Energy-Transfer Cascade," Miller, M. A.; Lammi, R. K.; Prathapan, S.; Holten, D.; Lindsey, J. S. *J. Org. Chem.* **2000,** *65*, 6634-6649.

(5) "Efficient Energy Transfer and Electron Transfer in an Artificial Photosynthetic Antenna-Reaction Center Complex," Kodis, G.; Liddell, P. A.; de la Garza, L.; Clausen, P. C.; Lindsey, J. S.; Moore, A. L.; Moore, T. A.; Gust, D. *J. Phys. Chem.* submitted.

(6) "Synthesis and Properties of Weakly Coupled Multiporphyrin Light-Harvesting Arrays and Hole-Storage Reservoirs," del Rosario Benites, M.; Johnson, T. E.; Weghorn, S.; Yu, L.; Polisetti, D. R.; Diers, J. R.; Yang, S. I.; Kim, D.; Bocian, D. F.; Holten, D.; Lindsey, J. S. *J. Mater. Chem.* submitted.

PHOTOSYNTHETIC LIGHT HARVESTING AND ITS REGULATION

Graham R. Fleming, Gregory Scholes, Xanthipe Jordinades, Mino Yang, Cherri Hsu,
Ritesh Agarwal, Peter Walla, Kaoru Ohta, and Patty Linden

Physical Biosciences Division, Lawrence Berkeley National Laboratory
and
Department of Chemistry, University of California, Berkeley

Our efforts to understand the primary steps in photosynthesis have focused on two main areas over the past two years: developing an understanding of energy transfer in systems with confined molecular geometries, with multiple donors and/or acceptors, and characterizing and developing new nonlinear optical techniques for the study of such systems.

In confined molecular aggregates, standard ideas relating optical spectra to Coulombic coupling between donors and acceptors fail badly. A spectacular example involves excitation energy transfer from the 'forbidden' S_1 states of carotenoid molecules to chlorophyll (or bacteriochlorophyll) molecules in photosynthetic complexes. In such systems, the rate calculated by the standard Forster approach would be zero, but in fact we have measured rates of the order of $10^{12}\,s^{-1}$. Our measurements are based on direct two photon excitation of the car S_1 state and are the first to definitively show S_1 to Q_y energy transfer. The two photon spectroscopy also allowed the spectrum of the S_1 state to be measured in the protein complex for the first time. To understand the origin of the electronic coupling we have used time dependent density functional theory (in collaboration with Martin Head-Gordon). Two factors are critical: the spatial symmetry breaking inherent in the structure, and the mixing of the strongly allowed S_2 state with S_1 as a result of the distortion of the natural carotenoid from a planar configuration.

We next extended these symmetry-breaking ideas to the bacterial photosynthetic reaction center where the rates of energy transfer had long been mysterious. We are able to obtain quantitative agreement for the native RC and for several mutants with radically altered energy transfer rates. Energetic disorder plays a minor role in the RC, but a major role in the light harvesting 2 complex. Here energy transfer from B800 to B850 can be thought of as a single donor coupling to a manifold of acceptors.

The dynamics within strongly coupled groups of chromophores, such as B850 of LH2 or B875 of LH1, requires a more sophisticated approach. We have developed a multi-level Redfield approach that allows calculation of linear and non-linear optical signals. The approach incorporates the influence of exchange narrowing, exciton relaxation, disorder, and the excitation and probing spectra. This method successfully describes our photon echo peak shift data for LH2 and LH1 and gives new insight into the motion of excitation energy in the bacterial light harvesting system.

Publications (1999-2001)

1. Three Pulse Echo Peak Shift Measurements and *ab initio* Excited State Calculations of Bacterial Light Harvesting Function. G.D. Scholes, I.R. Gould, J-Y. Yu, G.R. Fleming. *Ultrafast Phenomena XI, Springer,* 658-662 (1998).

2. Fluorescence Upconversion and *ab initio* Studies of the Light Harvesting Function of Carotenoids in Bacterial Light Harvesting Antenna, B.P. Krueger, G.D. Scholes, I.R. Gould, and G.R. Fleming. *Ultrafast Phenomena XI, Springer*, 666-668 (1998).

3. On the Mechanism of Light Harvesting in Photosynthetic Purple Bacteria: B800 to B850 Energy Transfer, G.D. Scholes and G. R. Fleming. *J. Phys. Chem.*, **B104**, 1854-1868 (2000).

4. Two Photon Excitation Spectrum of LHC II and Fluorescence Upconversion After One- and Two-Photon Excitation of the Carotenoids, P. J. Walla, J. Yom, B. P. Krueger, and G. R. Fleming. *J. Phys. Chem. B*, **104**, 19, 4799-4806 (2000).

5. The Mechanism of Energy Transfer in the Bacterial Photosynthetic Reaction Center, X. J. Jordanides, G. D. Scholes and G. R. Fleming. *J. Phys. Chem. B.*, **105**, 1652-1669 (2001).

6. Adapting the Forster Theory of Energy Transfer for Modelling Dynamics in Aggregated Molecular Assemblies, G. D. Scholes, X. J. Jordanides, and G. R. Fleming, *J. Phys. Chem. B.*, **105**, 1640-1651 (2001).

7. Excitation Energy Transfer in Condensed Media, C-P. Hsu, T. Head Gordon and G. R. Fleming, *J. Chem. Phys.*, **114**, 3065-3072 (2001).

8. Femtosecond Dynamics of the Forbidden Carotenoid S_1 State in Light-Harvesting Complexes of Purple Bacteria Observed After Two-Photon Excitation, P. J. Walla, P. A. Linden, G. D. Scholes and G. R. Fleming. *Proc National Acad Sci USA*. **97(20)**, 10808-10813 (2000).

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EXPLORING PHOTOSYNTHETIC PROTEINS WITH EPR AND X-RAYS

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Tremendous advances have been made in understanding how the individual parts of nature's solar energy machinery work. In purple photosynthetic bacteria, a ring composed of light-harvesting protein (LH–I) surrounds an inner photosynthetic reaction–center protein (RC), forming one of nature's most fundamental and essential biochemical complexes. In this core complex, light energy drives the chemistry responsible for the organism's existence. Considerably less is understood about how such core complexes self-assemble. The ability to control the detailed self–assembly of the photosynthetic apparatus is key to practical applications utilizing principles based on the natural process of photosynthesis. In this research, the working elements of photosynthetic core complexes are forced to self-assemble into thin sheets, one and two molecular layers thick or into three–dimensional single crystals. How the active components self-assemble and function in these thin films or three–dimensional crystals is being examined by transmission electron microscopy (TEM), electron paramagnetic resonance (EPR) and by Laue x–ray diffraction.

In one aspect of the project, the long–range integrity of LH–I complexes in solid solution, liquid solution and membranes is explored using EPR. Electron spin migration represents a unique tool for examining various aspects of the integrity and assembly of photosynthetic complexes. EPR spectra of the chemically oxidized antenna complexes of purple bacteria *Rhodobacter sphaeroides* and *Blastochloris* (formerly *Rhodopseudomonas*) *viridis* have been measured. The observed EPR line widths are less than the width of the monomeric bacteriochlorophyll (BChl) cation, which indicates that the spins (holes) in the complexes are delocalized over several molecules. At room temperature, the line width appears independent of the oxidant concentration. A Monte–Carlo model that simulates diffusive, stepwise, electron transfer and spin exchange between adjacent BChl cation sites in circular molecular arrays is assumed. Within the framework of this approach, the experimental EPR line widths as illustrated by the horizontal lines in Figure 1 are consistent with electron transfer rate constants of 0.5 ns^{-1} and 1.5 ns^{-1} for *Rb. sphaeroides* and *B. viridis*, respectively.

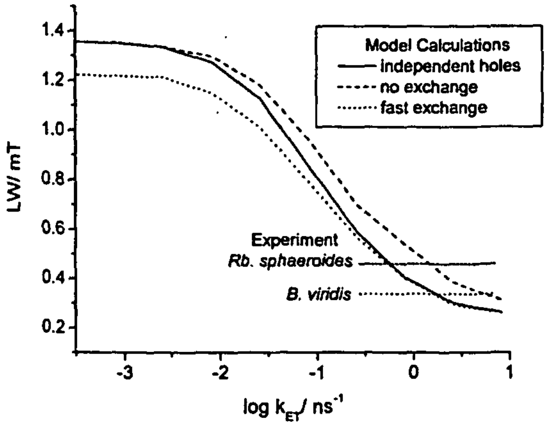

Figure 1. Comparison of calculated and experimental EPR line widths for oxidized LH–I complexes as a function of ET rate.

In LH–I complexes of *Rb. sphaeroides* at low temperature, the EPR spectral lines are broader than at 300 K, but narrower than that for the monomeric BChl cation. The reduced line width indicates that spins (holes) remain delocalized at low temperatures among several BChl molecules although spin dynamics is slower than at room temperature. In contrast to room temperature measurements, the line width drastically depends on the concentration of BChl cations at low temperatures. To explain this dependence on the fraction of oxidized BChls, a heterogeneous distribution of BChl oxidation potentials is assumed in the frozen samples of LH–I complexes. The Monte–Carlo model for simulating spin dynamics is extended to include heterogeneous electron transfer. For calculating the EPR line width, an algorithm based on the Kubo approach is employed. With this heterogeneous model, the simulated EPR line widths now depend on the oxidant concentration in agreement with experiment. The roles of electron transfer and spin exchange are modeled in Figure 1. Future experiments are planned to coordinate the EPR line widths with TEM studies of two dimensionally ordered membrane complexes of intact photosynthetic core complexes as well as core complexes without RCs.

Secondary electron transfer in the photosynthetic reaction center is distinctive in its use of a mobile quinone (Q_B) as an electron carrier. Recent experiments of others have suggested that electron transfer is coupled to a structural rearrangement at the active site of Q_B binding. In principle, such a structural rearrangement could be directly observed by a time-resolved x–ray diffraction study of a single crystal of the RCs of *B. viridis*. In a second aspect of the project, using the University of Chicago CARS facility of the Advanced Photon Source at Argonne National, we have acquired a 73 microsecond Laue x–ray diffraction data set of the RC of *B. viridis* in the dark. A typical Laue diffraction pattern with resolution between 2.5 to 3.0 Å is shown in Figure 2. Preliminary data and analysis will be presented. One of the CARS synchrotron beam lines is designed to follow photochemically induced structural changes. Our recent experiments indicate that monitoring the movement of the mobile Q_B is possible at CARS. Thus, future experiments are planned to measure photoinduced structural changes of the RC of *B. viridis* using Laue x–ray diffraction.

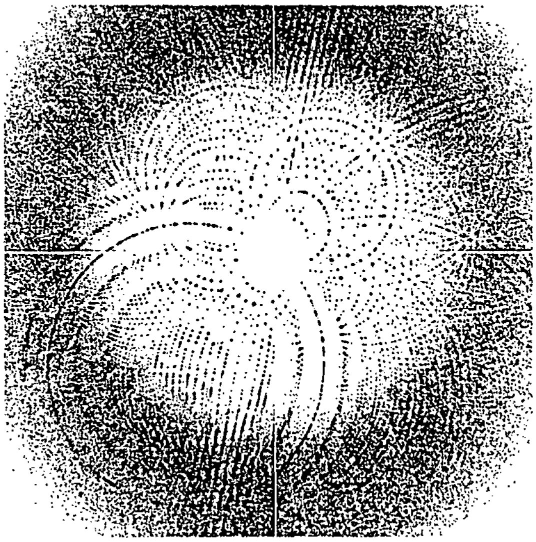

Figure 2. Laue diffraction pattern from a single crystal of the RC of B. viridis.

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Monday Afternoon

Session III

Porphyrins, Nanotubes and Nanoparticles

STRUCTURE-FUNCTION DESIGNS OF PHOTOSYNTHETIC AND CATALYTIC PORPHYRINS

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Porphyrins are Nature's choice catalysts. They carry out a remarkable spectrum of bioenergetic reactions ranging from photosynthetic energy transduction to generation of ammonia, regiospecific oxygen transfer (hydroxylations and epoxidations), and conversion of carbon dioxide to hydrocarbons. This program seeks to unveil the chemistry common to these multifaceted (photo)catalytic reactions mediated by porphyrins *in vivo*, and aims to develop tailored, synthetic porphyrins that duplicate the selectivity and efficiency of porphyrin–based solar energy conversion and catalysis. The present thrust of the work focuses on the structure-function relationships that determine the photophysical and chemical properties *in vivo*, work prompted by the mounting crystallographic evidence of considerable porphyrin skeletal flexibility and distortions in photosynthetic light-harvesting and reaction center proteins, as well as in an increasing number of heme proteins. Molecular engineering of synthetic porphyrins, such as the introduction of bulky or multiple peripheral substituents, yields new classes of nonplanar porphyrins with significantly altered optical, redox, magnetic, free radical and excited state properties. In addition, because the *in vivo* protein microenvironment consisting of axial ligands, hydrogen bonding and nearby residues forms the scaffolding that induces the distortions of the porphyrinic chromophores and prosthetic groups observed crystallographically, we have extended the work to construct primitive, *in vitro* protein frameworks to assess the potential structural effects of axial ligands, hydrogen bonds and nearby residues. The cumulative results for the synthetic models can be summarized as follows: 1) Distortions destabilize the highest occupied molecular orbital (HOMO) and render the molecules easier to oxidize. Because the HOMO is affected more than the LUMO, optical spectra also red-shift. 2) The nonplanar molecules exhibit significantly shortened singlet excited state lifetimes. These results, based on an increasing body of photodynamic data, support the evolving concept that photoinduced conformational changes underlie the significantly perturbed photophysical properties of nonplanar porphyrins because the distorted chromophores can access multiple conformational landscapes which are separated by only small energy barriers, multiple landscapes which are often already evident crystallographically in the ground state. 3) In combination with axial ligation, the conformations of nonplanar metalloporphyrins can be used to control sites of oxidation (metal vs. porphyrin), spin states, orbital occupancy, as well as ferro- or antiferromagnetic coupling in porphyrin radicals incorporating paramagnetic metals. (See poster by Renner et al.) 4) Axial ligation, hydrogen bonding and interactions with nearby groups also induce multiple conformations which, in turn, result in altered photophysical and chemical properties, see above. In particular, conformational changes that accompany hydrogen bonding with nearby "residues" suggest that point mutations in photosynthetic reaction centers may not be structurally innocent. 5) The distorted porphyrins can be oxidized to "stable" π cation radicals whose structures can be determined to high precision using synchrotron-based microcrystallography, results which map both the electronic and structural consequences of electron transfer. (See poster by Barkigia et al.) The conformationally designed synthetic porphyrins and their quasi-protein interactions thus not only begin to document the consequences of the skeletal distortions observed *in vivo* but also provide new classes of biomimetic chromophores and catalysts with tuneable and controllable photophysical and chemical properties. (Work done in collaboration with D. Holten, Washington University, D. Mansuy, Université Paris V, B. Robinson, Miravant Medical Technologies, K. Mobius and M. O. Senge, Free University of Berlin, and K. M. Smith, University of California at Davis.)

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RESONANCE RAMAN STUDIES OF SINGLE WALL CARBON NANOTUBE STRUCTURE AND ELECTRONIC PROPERTIES

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Carbon nanotubes are simply a special family of very large aromatic molecules with pi electron delocalization, and electronic structure that can be quantitatively calculated with the simple Huckel theory. Yet as we study these tubes more deeply, it becomes apparent that they are a unique hybrid of molecular and solid state properties because of their 1D band structure. The fact that both metallic and semiconducting wires exist implies that, beyond being simply wires, the tubes also can be made into devices, such as metal/semiconductor diodes, if we learn how to control the covalent chemical bonding at the junction between two different structural types. From one perspective, these tubes are all surface, with no interior atoms and the pi electron current flowing on the surface. Thus the electron properties will be very sensitive to surface adsorption and charge donation. In order to study these properties we have developed methods to obtain the resonance Raman spectra of single (or just a few) tubes with good signal to noise.

Raman scattering from individual single-wall carbon nanotube (SWNT) bundles was measured using confocal optical microscopy with 632 nm laser excitation. The Raman scattering from carbon-carbon double bond stretches in metallic SWNTs shows a Fano lineshape that depends sensitively on adsorbed oxidizing molecules. Tangential mode Raman lines of HNO_3-treated SWNTs exhibited different line shapes from those of H_2SO_4/H_2O_2 treated SWNTs. However, the line shapes became identical after high power laser irradiation, which heats the bundle to ~750 K based on measurement of the breathing mode Stokes to anti-Stokes Raman intensity ratio. Thermal annealing of both samples at 873 K caused the same change in Raman spectra as with laser irradiation, which is attributed to degassing of oxidizing adsorbates. A mechanism of charge transfer between carbon nanotubes and adsorbate molecules is proposed to explain the large change in Raman scattering from metallic SWNTs. The Fano lineshape results from coherent interference between vibrational and electronic Raman scattering. The line shape changes with oxidation as the Fermi level shifts.

It becomes possible to assign structure to nanotubes by examination of Raman spectra from thin bundles containing just a few SWNT. These spectra exhibit new characteristics absent in the ensemble Raman measurements. A large variation in the radial breathing mode (RBM) Stokes to anti-Stokes Raman intensity ratio was observed for different metallic tubes, and can be understood with a simple resonant Raman analysis. An (n, m) structural assignment for many tubes at 632 nm laser excitation, was tentatively achieved based on the RBM frequency, and the Stokes to anti-Stokes Raman ratio. The (9,9) armchair tube fits the simple model poorly. The varying relative intensities of different components observed in the tangential G-band Raman modes provide convincing evidence for a recently predicted chirality dependence of Raman scattering. A new Raman feature at 1417 cm^{-1} was assigned to achiral tubes.

While this talk will focus on SWNTs , we have also studied semiconductor nanocrystals, and Surface Enhanced Raman Scattering SERS from Ag nanocrystals, as part of the DOE Basic Energy Sciences program. In order to explore the relationship between local electromagnetic fields and the large SERS enhancement that enables the observation of single molecule Raman spectra, we measure both resonant Rayleigh scattering spectra and Raman spectra from single Ag particles. Our apparatus combines the techniques of dark-field optical microscopy for resonant Rayleigh measurements, and grazing incidence Raman spectroscopy. Atomic force microscopy (AFM) measurements show that the Ag nanoparticles that yield surface-enhanced Raman scattering (SERS) of single molecules of Rhodamine (R6G) are all compact aggregates consisting of a minimum of two individual particles. Comparison of 514.5 nm and 632.8 nm excitation shows that the single molecule R6G signal is significantly higher when the excitation wavelength is resonant with the absorption band of R6G and suggests that the Raman excitation spectrum follows the absorption profile for R6G. We have also observed a superlinear power dependence of the SERS signal which we tentatively assign to polarizability optical trapping at the junction. We are presently studying the Raman spectra of single rigid linker molecules in synthetic dimers of 50 nm Ag particles, and building an experiment for study of electromagnetic field enhancement between two particles in an AFM optical apparatus.

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SIZE DEPENDENT STRUCTURAL DYNAMICS IN NANOSTRUCTURES

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Scope: Increased sophistication in the use of nanoparticles in solar-photochemical schemes requires synthetic methodologies to control the size and size distribution of composite particles. In such composites structural parameters may depend on the size of the particle size. The large excess surface free energy of the small particles is expected to lead to phase transitions at reduced temperatures, increased diffusion coefficients, changes in inter-atomic distances and variation of collective properties relative to their bulk values. These changes are also expected to alter electronic structures and thus optical and spectroscopic parameters. We focus in this report on the synthesis of composite core-shell particles and their characterization and utilization. We developed radiolytic methods to generate metallic (mono- and bimetallic) core-shell nanoparticles. We observed that small bimetallic core-shell particles spontaneously alloy at ambient temperature and in aqueous suspensions. In contrast, larger particles of the same materials maintain sharp core-shell boundary essentially indefinitely. We utilize metallic-core insulator-shell particles to encapsulate fluorescent probes that report on the local environment within the nano-shells. We also study the effects of solid particles in aqueous suspensions on yields of radiolysis products in an effort to understand radiocatalytic processes, analogous to photocatalysis.

Radiolytic Synthesis of Metallic Nanoparticles: We developed a general methodology for the synthesis of metallic nanoparticles from the corresponding aqueous salts using radiolysis under reductive conditions. The synthesis takes advantage of the difference between the redox potentials of different complexes of the reduced metal. The size distribution of the obtained particles narrows as the size increases. A mechanism for focusing the size distribution has been developed. Making use of this mechanism we use this approach to either increase the size or deposit a shell of another metal on the core. Analogous chemical methodologies for similar metallic and semiconductor particles were reported but we prefer to use the radiolytic approach because the fine control that it provides over the steady state concentration of reduced metal seeds. It is the competition between generation of new seeds and increased growth of the existing particles that determines the width of the size distribution. The particles synthesized using this technique were used in the studies described below as well as in other structural studies. They were also deposited on atomically flat supports using layer-by-layer deposition approaches and their optical properties as a function of the number of layers and of the surrounding medium were determined.

Size Dependent Structure of Metallic Nanoparticles: We initiated a study of the dependence of the structure of metallic particles obtained by the synthesis described above. Here we report preliminary results on the effect of size on two properties: dependence of the inter-atomic distances on the size and alloying of bimetallic particles of small sizes. Both were determined using the XAFS technique at the MRCAT of Argonne's APS. We demonstrate these effects on Au_{core}-Ag_{shell} composite particles. Because of the extreme similarities between these two metals it is essentially impossible to determine these parameters using any other technique. Contraction of the inter-atomic distance is theoretically predicted and was previously observed for particles deposited on solid supports. We observe the same contraction in the aqueous suspension, indicating that the contraction is independent of the medium.

The synthetic approach guaranties initial formation of core-shell structures. Indeed, for large (20 nm) particles the results show clear phase boundaries between the core and the shell. However, small particles show increased penetration of one metal into the other (see Figure 1). Several reasons for this size-dependent interpenetrating were considered. It is concluded that diffusion or melting of the particles cannot be the cause for the mixing if the diffusion coefficients and the melting temperatures are similar to their values in the bulk. Note that the melting temperatures of Au and Ag are in the vicinity of 1000 °C and all the experiments described above were conducted at room temperature (and in suspension).

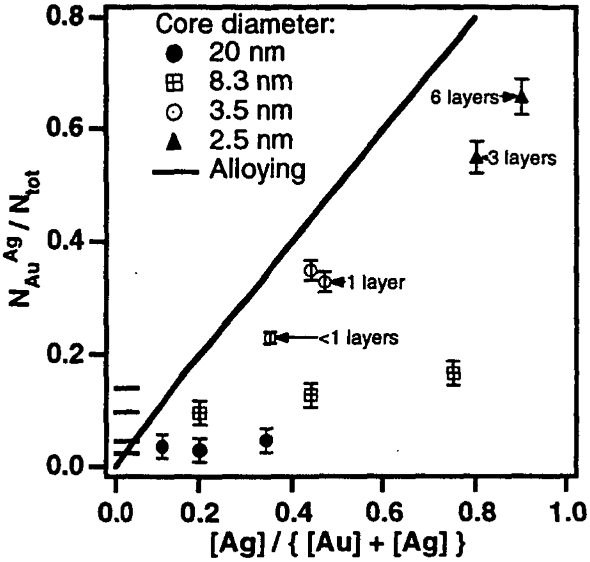

Figure 1: Size dependent alloying of Au_{core}-Ag_{shell} particles. Plotted is the fraction of Ag atoms around Au vs. the stoichiometry of particles of various sizes. Complete alloying will follow the diagonal line. Complete segregation will follow the small right-hand horizontal lines for the 20 to 2.5 nm (from bottom up) particles.

Encapsulation in Nano-shells: In an attempt to demonstrate the utility of core-shell structures we synthesized nano-shells of silica using the silica on gold (or CdS) core-shell synthesis followed by dissolution of the core (in collaboration with Dr. J. Norris' group at the University of Chicago). Fluorescent dyes (fluorescein, $Ru(bpy)_3^{2+}$, Eu(III)) were encapsulated within the shell and varying the porosity and density of the shell controlled the accessibility of species in the external medium to the interior of the shell.

Radiation Induced Interfacial Charge Transfer: In analogy to photocatalysis, charge carriers were generated in wide-band semiconductors using ionizing radiation. It was shown that charge carriers could cross the interface into the aqueous phase leading to increased yields of water decomposition. These effects strongly depend on the material and the availability of redox traps at the interface. These effects will not be further discussed here.

Future Plans: Studies of the effect of size on structural properties will continue. Various bimetallic combinations will be tested to determine the dependence of inter-diffusion on the size of the partners. The effect of partial mixing on optical spectra will be studied. Charge transfer across insulating shells and the dependence of its rate on shell thickness will be measured.

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Tuesday Morning

Session IV

Electron Transfer and Charge Separation

NEW THEORETICAL PERSPECTIVES ON ELECTRON TRANSFER

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The long term goal of this project is an accurate theoretical and computational description of electron transfer (ET) processes, including ET across semiconductor-electrolyte interfaces. This research effort thus involves the implementation of realistic Molecular Dynamics (MD) methods within a theoretical ET context broad enough to include nonlinear phenomena not described in the standard theory.

A New Theoretical Model for Electron Transfer

A new three-parameter model [1] for electron transfer (ET) in condensed phases has been developed based on the Hamiltonian for a two-state solute linearly coupled to a collective, classical 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. Importantly, *the model provides an analytical framework to map physical phenomena conflicting with the standard Marcus-Hush two-parameter model of ET*, These phenomena include nonlinear solvation, ET in polarizable charge-transfer complexes, and configurational flexibility of the donor-acceptor system. *The theory leads to a significant modification of the energy gap law for ET reactions.*

A new theory has also been developed for the ET free energy surfaces of charge transfer reactions in electronically *delocalized* systems [2, 3]. The latter kind of situation is common, e.g., in systems involving large electronic overlap of the donor and acceptor species. The free energy surfaces are found to depend on reorganization parameters invariant to electronic delocalization and on an electronic delocalization parameter. The theory was also used to modify the bandshape analysis of optical spectra to include the dependence of optical observables on the chromophore transition dipole. The optical Stokes shift depends strongly on the delocalization parameter, deviating downwards from twice the adiabatic reorganization energy with electronic delocalization. By contrast, the Stokes shift is a rising function of solvent polarity for localized systems. A novel inverted solvent dependence develops for delocalized complexes: The Stokes shift decreases with solvent polarity. The spectrum of permissible solvent fluctuations is limited from the low-energy side, thus inducing a narrowing of the emission optical bands compared to the absorption bands.

First-Principles Molecular Dynamics Studies

The electronic structure of semiconductor/electrolyte interface systems [4] has also been studied using the Car-Parrinello first-principles molecular dynamics method (CPMD). The CPMD method is based on a plane-wave basis set approach and density functional theory. The *ab initio* simulation of a stable reconstructed hydrogen-terminated indium phosphide InP(100) lattice, as well as the InP-water interface, both using Becke-Lee-Yang-Parr (BLYP) density functionals, has been carried out. In these simulations, the importance of both electronic delocalization and polarization effects [5], as described above in the general ET model, is revealed.

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INTERACTION OF AROMATIC HYDROCARBON TRIPLET STATES WITH MLCT STATES: A WAY AROUND THE ENERGY GAP LAW

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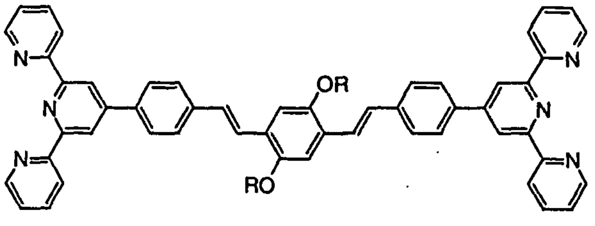
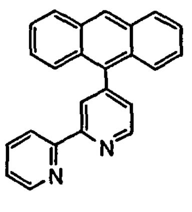
Since the 1970's it has been known that coordinated ligands having low energy triplet excited states could be sensitized by metal-to-ligand charge transfer excited states. Most aromatic hydrocarbons have large energy gaps between their singlet and triplet excited states and there are a significant group of molecules that do not absorb light in the visible but have triplet excited states at or lower than the energy of the ^{3}MLCT states of most Ru(II), Os(II) and Re(I) complexes with diimine ligands. The $^3(\pi-\pi*)$ states of aromatic hydrocarbons are only weakly coupled to the singlet manifold and often have lifetimes in excess of 100 μs in deoxygenated solutions. In the early 1990's, Rodgers and coworkers[1] clearly illustrated that reversible energy transfer between ^{3}MLCT and $^3(\pi-\pi*)$ states is possible for a Ru(II) diimine complex covalently linked to pyrene; the complex had a lifetime at least an order of magnitude longer than the parent Ru(II) diimine and, as shown later by Sasse,[2] exhibited photoredox behavior characteristic of the ^{3}MLCT state. Later, our group and others illustrated that the effect of lengthening the excited state lifetime of Ru(II) diimine complexes could be enhanced through synthetic elaboration. This approach to extending the excited state lifetime of metal diimine complexes can be used to circumvent the effect of increasing non-radiative relaxation with decreasing excited state energy of the ^{3}MLCT state (energy gap law).

The intent of this work is to show (1) intra-ligand charge transfer ^{3}ILCT excited states are observed in some complexes of this type, (2) even Ru(II) complexes known to have very short lived ^{3}MLCT states can be used to sensitize long lived $^3(\pi-\pi*)$ states of aromatic hydrocarbons and (3) the concept can be extended to Os(II) diimine complexes, which have very low energy ^{3}MLCT states strongly spin-orbit coupled to the singlet manifold.

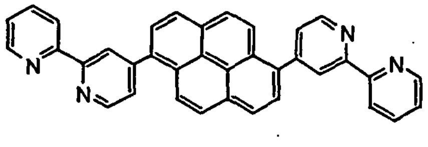
Our objective in this work has been to prepare ligands capable of strong electronic interaction between the metal complex localized charge transfer (MLCT) excited states and the $^3(\pi-\pi*)$ state (IL) of the aromatic hydrocarbon moiety. The ligands to be discussed in this work are shown below.



t-pvpvp-t



An-bpy



b-pyr-b

The ligands t-pvpvp-t and An-bpy were prepared in our labs and b-pyr-b was obtained as part of a collaboration with Dr. Frédéric Fages of the Université de Bordeaux.

We have prepared the complex $\{[(tpy)Ru]_2(t\text{-}pvpvp\text{-}t)\}(PF_6)_4$ and examined its redox and photophysical behavior in solution. While the complex does not emit, it exhibits excited state absorbtion throughout the visible with a lifetime of 8 μs. Most Ru(II) terpyridyl complexes have very short lived ^{3}MLCT states; in this case we believe the excited state may be a ligand localized triplet $^3(\pi-\pi^*)$ state (^{3}IL); we are examining the free energy dependence of quenching of the excited species with both triplet quenchers and electron donors and acceptors to determine the excited state energy and the excited state redox properties. We have also prepared oligomers of the t-pvpvp-t ligand with Fe(II) and have found that the resulting deep purple product has a positive transient absorbance in the visible with a lifetime of 50 ns; we are examining the photophysical behavior in greater detail and are attempting to make simple derivatives that can be fully characterized.

Using the ligand An-bpy we have prepared a series of Os(II) diimine complexes that contain the ligand. Since the anthracene $^3(\pi-\pi^*)$ state and the Os(dπ)-bpy(π*) ^{3}MLCT states are close in energy, the possibility exists to prepare complexes exhibiting reversible energy transfer between the two states and produce, in effect, a long lived ^{3}MLCT state. The anthracene ^{3}IL state is higher than the ^{3}MLCT state in $[(bpy)_2Os(An\text{-}bpy)](PF_6)_2$ by 800-1000 cm^{-1} and no interaction between the states is observed. However, in $[(An\text{-}bpy)_2Os(CO)(Br)](PF_6)$, an emission is observed in 77K glasses that appears to originate from a ^{3}MLCT state and has a lifetime of several hundred microseconds. The same complex is nonemissive in solution at room temperature, but has a transient absorption characteristic of the anthracene triplet and a lifetime of 8 μs. It is not clear whether the energy transfer is reversible in this case, although the energy gap between the ^{3}IL and the ^{3}MCLT states is very likely no more than a few hundred wavenumbers. We have prepared the complex $K[(An\text{-}tpy)Os(CN)_3]$ and are in the process of examining the solvent dependence of the photophysical behavior. It should be possible to tune the energy gap between the ^{3}IL and ^{3}MCLT states since the ^{3}IL energy for anthracene is known to be solvent independent and the ^{3}MLCT energy exhibits large changes with solvent.

As an extension of earlier work on the photophysics of $[(bpy)_2Ru(bpy\text{-}pyr)](PF_6)_2$ (bpy-pyr = 4-(1-pyrenyl)-2,2'-bipyridine), Rubpy-pyr, we have examined a bimetallic complex of the bis-bipyridylpyrene derivative b-pyr-b shown above, $\{[(bpy)_2Ru]_2(b\text{-}pyr\text{-}b)\}(PF_6)_4$. The bimetallic complex emits at 670 nm in CH_3CN (30 nm to the red of Rubpy-pyr) and has a biexponential decay with short and long components of 1.8 and 100 μs. The complex has an excited state absorption spectrum that is unlike the ^{3}MLCT state of related complexes and the ^{3}IL state ($^3(\pi-\pi^*)$) of the associated pyrene. This and other spectral evidence, have led us to assign the emissive excited state as a pyrene to bipyridine intra-ligand charge transfer (^{3}ILCT) state. We are in the process of exploring the photoredox reactivity of this and related complexes.

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INTRAMOLECULAR CHARGE-TRANSFER INTERACTIONS AND THEIR INVOLVEMENT IN HIGHLY EFFICIENT PHOTOINDUCED CHARGE SEPARATION

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Nearly unity quantum efficiencies for the photoinduced generation of long-lived ($\geq$ 200 ns) charge separated states (CSS) have been observed in a series of donor-chromophore-acceptor (D-C^{2+}-A^{2+}) assemblies. Under appropriate conditions, CSS are formed with $\Phi_{CS} \approx 86\%$ and can store 50% of the incident photon energy at λ_{max} of the chromophore. Moreover, high efficiencies are also possible from related bimolecular systems consisting of free donor molecules and chromophore-acceptor diads (C^{2+}-A^{2+}; D).

In these assemblies the donor is an N-alkylated phenothiazine (PTZ), the chromophore is a trisdiimine complex of ruthenium(II) and the acceptor moiety is either a viologen or diquat. In the cases of D-C^{2+}-A^{2+} triads, the donor and acceptor are each appended to separate bipyridine ligands of the chromophore via flexible polymethylene chains; the diads have similar structures with only an acceptor being appended to one ligand.

The origins of the exceptional quantum efficiencies lie in the confluence of several factors. First, a charge-transfer interaction occurs between the donor and the chromophore. This interaction brings the donor into close contact with the chromophore but it does not significantly perturb the chromophore's ground-state energetics. Second, the quenching of the photogenerated ^{3}MLCT state of the chromophore by electron transfer to the attached acceptor occurs with virtually 100% efficiency. This is true irrespective of the presence or absence of the donor. In the total absence of a PTZ donor (i.e., either attached or in solution), the photogenerated species undergo back electron transfer at a rate greater than or equal to its rate of formation. However, within the donor-chromophore charge transfer complex, the oxidation of the donor occurs significantly faster than back electron transfer from the reduced acceptor. Furthermore, once the donor is oxidized, the donor-chromophore interaction ceases and they separate,. The CSS formed from D-C^{2+}-A^{2+} triads have magnetic-field dependent lifetimes that are typically a few hundred nanoseconds. In the bimolecular case, depending on the conditions, the charge-separated products can persist for milliseconds.

The success of these systems at separating charge in large part lies in their structural flexibility. The ability of the donor and chromophore to undergo the charge-transfer interaction and to physically separate subsequent to donor oxidation, are both key features. Presently, we are investigating new ways these types of charge-transfer interactions might be exploited to effect photoinduced charge separation. Of particular interest to us is the concept of using these interactions to self-assemble the components of a charge separation system.

Finally, as mentioned above, with D-C^{2+}-A^{2+} triads the CSS lifetimes are magnetic field dependent. The radical ions that constitute the CSS are formed with triplet spin multiplicity and, consequently, their energy is field dependent. This, in turn, results in a significant increase in the CSS lifetime (at least a factor of X 10) for the outer Zeeman components. Studies of the influence of spin-orbit coupling on these lifetimes are underway.

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MAPPING ELECTRONIC COUPLING BETWEEN RADICAL ION PAIRS WITHIN COVALENT DONOR-ACCEPTOR MOLECULES USING MAGNETIC FIELDS

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Efficient photoinduced charge separation within electron donor-acceptor molecules requires reasonably strong electronic coupling between the photoexcited donor and the acceptor. However, the radical ion pair product state requires weak electronic coupling between the radical ions to maintain a long-lived charge separated state. Weak electronic coupling in the product state can be achieved by employing discrete, multiple electron transfer steps in a manner analogous to photosynthesis, or by using a donor-bridge-acceptor molecule in which the electronic states of the bridge provide strong donor-acceptor coupling in the initial state and weak coupling in the product state. One of the most important issues that arises in designing molecular systems to photochemically separate and store charge efficiently is how molecular structure controls the electronic coupling between the donor, bridge, and acceptor molecules. The spin-spin exchange interaction in the radical ion pair product, $2J$ can be used to provide a reasonable estimate for the matrix element, V for electron transfer leading to charge recombination. Yet, the vast majority of radical ion pairs photochemically generated within covalently linked donor-acceptor molecules have values of $2J$ that are much too large to be measured by magnetic resonance techniques.

We have developed a series of donor-acceptor molecules in which $2J$ is sufficiently small to be measured directly using magnetic field effects on the yields of the molecular triplet state of the acceptor, which results from radical pair intersystem crossing (RP-ISC) in the radical ion pair product followed by radical ion pair recombination. These molecules, illustrated in Figure 1, are similar in structure to the donor-acceptor system in which we made the first observation of the RP-ISC mechanism leading to a spin-polarized molecular triplet in a covalent system.

In molecule A excitation of the ANI donor molecule results in electron transfer to the NI acceptor in $\tau = 0.8$ ns. The resultant radical ion pair undergoes RP-ISC and lives for $\tau = 120$ ns before recombining to yield the triplet state of NI. Within the initially formed radical ion pair, the charge (and spin) density of the radical cation is concentrated on the nitrogen atom of the piperidine, while the charge (and spin) density of the NI radical anion is distributed mainly on the oxygen atoms of NI. This results in a radical ion pair in which the average distance between the two radicals within the pair is 12.7 Å. In molecules B the initial photochemical reaction is

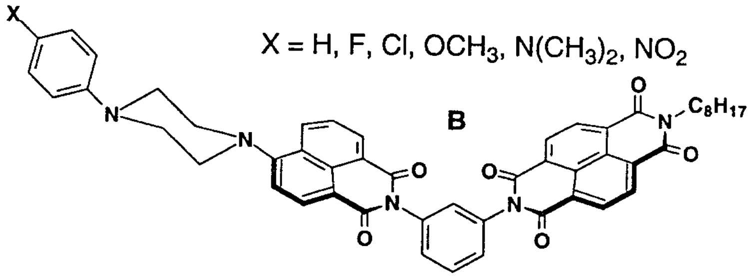

Figure 1

oxidation of the para-substituted aniline by the lowest excited singlet state of ANI with $\tau \approx 10$ ps followed by thermal electron transfer ($\tau \approx 0.5$ ns) from ANI^- to NI. This two step charge separation places the radical ion pairs at a longer distance, ≈ 20 Å. The degree of delocalization of charge (and spin) density onto the aniline, and therefore the average distance between the radical ion pairs is modulated by the para-substituent. The rates of charge recombination and yields of ^{3*}NI were monitored by transient absorption spectroscopy as a function of magnetic field, Figure 2.

The ^{3*}NI yield data clearly show resonances as a function of magnetic field for several of the molecules. The positions of these resonances directly give $2J$ for the radical ion pairs. These values of $2J$ can be plotted as a function of the distance, r between the centroid of the spin distributions of the two radicals that comprise the pair. Plotting the data in the form $\ln(2J)$ vs. r yields a slope equal to –1.5. Since $2J$ is directly proportional to V^2, this slope suggests that the recombination rates in these molecules obey an exponential distance dependence with $\beta = 0.75$. In addition, using the measured values of V^2, and the semi-classical Marcus-Jortner expression for the electron transfer rate, the predicted charge recombination rates agree with the measured rates. This work shows that the ability to directly measure the electronic couplings as a function of molecular structure by an independent means, such as the spin-spin exchange coupling can provide insights into the often subtle structural features that can result in long-lived radical ion pairs.

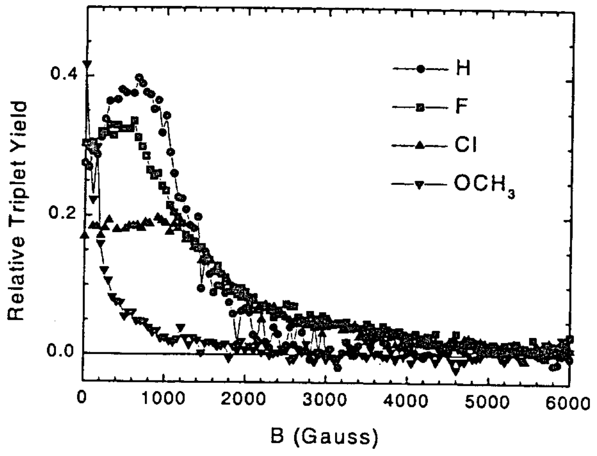

Figure 2. Relative triplet yield upon radical ion pair recombination as a function of magnetic field.

Our future work centers on furthering our understanding of long distance charge separation and storage in complex molecules and nanostructures. The role of molecular structure in dictating electron transfer rates will be explored using donor-bridge-acceptor molecules in which the bridge can act as an electron carrier. This involves both conjugated bridge structures and π-stacked arrangements of chromophores. In the former case we will continue to study conjugated oligomers, while in the latter case we have developed a series of structures that self-assemble into molecular stacks that can be used as charge transport agents. Another important issue that we will address is the role of solvent in controlling charge transport. We are particularly interested in liquid crystals as ordered media that can be used to control charge transport rates. We will be examining fundamental differences in the interaction of liquid crystal solvents with molecules that undergo charge shift as well as charge separation reactions. Our earlier work has indicated that liquid crystals exert strong and important dynamical control over electron transfer reactions. These properties can be used to control long-lived charge separation and storage.

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

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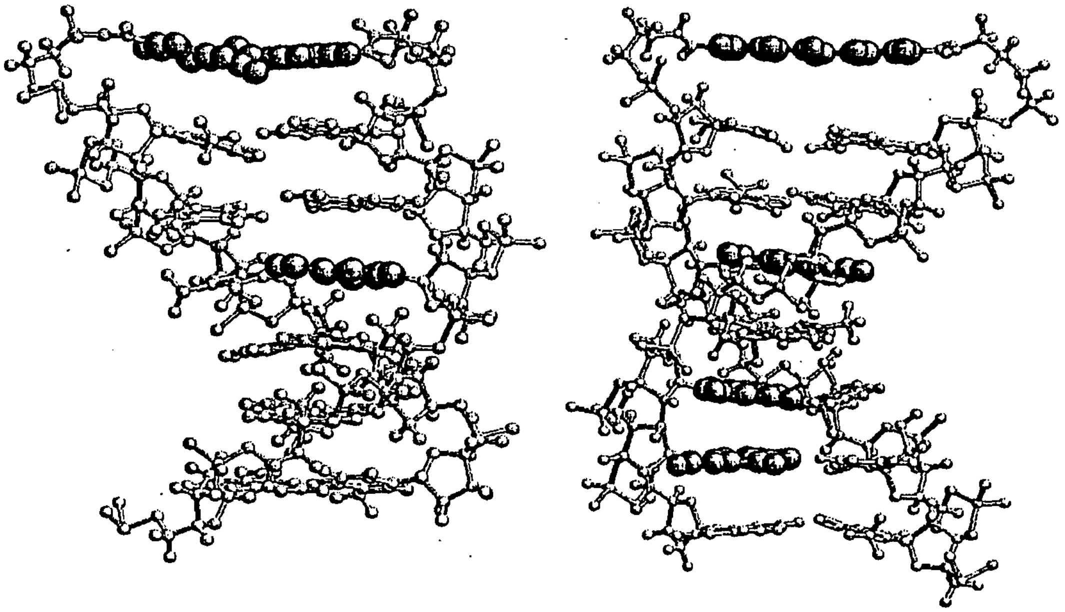
The objective of this project is to investigate photoinduced electron transfer in supramolecular systems which possess an electron donor and acceptor separated by aromatic spacers having a face-to-face or π-stacked geometric relationship. The π-stacked base pairs in duplex DNA possess such a geometry 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 an organic or metal complex 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.



During the past year we have completed major studies of the distance and driving force dependence of photoinduced electron transfer in DNA. We have also initiated an investigation of hole transport dynamics in DNA. The results of these studies have been summarized in a recent article published in *Accounts of Chemical Research.* Our studies of the distance dependence of photoinduced charge separation in DNA are consistent with a superexchange or tunneling mechanism, for which the distance dependence can be described by eq 1,

$$k_{cs} = k_o e^{-\beta R} \qquad (1)$$

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. The value of $\beta \sim 0.7$ $Å^{-1}$ that we reported in 1997 has been confirmed by subsequent studies in our lab and by others, including the leading proponent of the "molecular wire" theory. Thus there now seems to be general agreement that DNA is a better medium for electron transfer than are sigma-bonded bridges, but that it does not function as a wire.

The driving force dependence of electron transfer has also been investigated by varying the reduction potential of the excited state acceptor and the oxidation potential of the donor nucleobase. The rate constants for both charge separation and charge recombination processes have been determined by means of sub-picosecond time-resolved transient absorption spectroscopy and the results analyzed using quantum mechanical Marcus theory. This analysis provides intimate details about electron transfer processes in DNA including the distance dependence of the electronic coupling between the acceptor and nucleobase donor and the solvent and nuclear reorganization energies. The distance dependence of the rate constant depends primarily upon changes in the electronic coupling rather that the nuclear or solvent reorganization energies.

The dynamics of electron transfer processes involving G, GG, and GGG sequences as the electron donors and singlet stilbene-4,4'-dicarboxamide as the electron acceptor have been investigated in hairpin-forming bis(oligonucleotide) conjugates.[5,6] The stilbene serves as a linker connecting two complementary oligonucleotide strands which form the hairpin stem. The rate constants for charge separation and charge recombination for G, GG, and GGG sequences are similar, suggesting that the oxidation potentials of these sequences are also similar. Rate constants for forward and return hole transport from a single G to a GG or GGG sequence have also been determined. The ratio of forward and return rates provides equilibrium rate constants from which free energy changes of 0.052 and 0.022 eV, respectively, for hole transfer from G to GG and GG to GGG are determined. These free energy differences are much smaller than previously reported calculated values, but are in good agreement with a available experimental data. Relative rate constants for oxidative strand cleavage at G, GG, and GGG sequences calculated from our equilibrium data and literature strand cleavage data decrease with increasing charge delocalization. Our kinetic data is being used extensively by theoreticians who seek to model electron transfer and charge transport processes in DNA.

We are currently studying electron transfer processes in duplex and triplex DNA which possess both an electron donor and electron acceptor linker placed at opposite ends of a short stack of based paired nucleotides. The formation and decay of both the acceptor anion radical and donor cation radical can be observed in such systems. Preliminary studies of the dynamics of these processes have provided results that are consistent with our earlier studies which employed nucleobases as electron donors. The electronic interaction between the donor and acceptor chromophores can also be observed by means of the exciton chirality method.

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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. Specific objectives were sought in several major areas and significant progress has been made in all areas.

One objective was to study strongly coupled donor-acceptor molecules to understand delocalized excited state relaxation dynamics, which is the first time bimetallic Class III mixed-valence molecules have been studied with time resolved methods. These studies showed the power of time-resolved methods by revealing a strong low frequency coherence feature in the transient intermediate states that is assigned to an exceptionally low frequency vibronic coupling, via non-totally symmetric vibrations, to cause non-radiative relaxation. Such a mechanism is likely in many inorganic complexes and compounds, perhaps even in semiconductor sensitization dyes, and it is of general importance in understanding excited state relaxation. A study by Raman spectroscopy on a related complex with Ni atoms, that is not in the Class III limit, was also accomplished as part of this work.

Another objective was to complete molecular modeling of an ion pair complex using Density Functional Theory (DFT) for good electronic and vibrational properties and solvation models. This extensive modeling effort was supported with resonance Raman spectra, and the models made absolute predictions of ET rates. The models showed that vibrational quantum effects on ET rate in the IR active CO stretching mode requires an Intramolecular Vibrational Relaxation (IVR) into IR active vibrations from the optically pumped totally symmetric vibrations. One suggestion from this work was that the origin of any quantum effect in the IR mode has to be due to a breakdown in the Condon approximation. This work preceded the new experimental work (see below) where an ultrafast component of ET was detected with a vibrational quantum effect in the IR modes. It also demonstrates the utility of sophisticated quantum computational modeling and rate modeling in both formulating and interpreting experiments.

A related objective of the modeling was to examine if Franck-Condon contributions to the rate constant for ET were being over-simplified to the point of obscuring key mechanistic information. We have been able to show, in a *very general way* that ET in the exothermic domain requires a much better understanding of vibrations in molecules. In particular, fairly modest structural changes between electronic states can give *3 or more orders of magnitude increase in inverted region ET rates, and these effects have been totally unanticipated by prior work.* The coupling of vibrations called the Duschinsky effect is the core reason for the effect, and it had never been analyzed for consequences on ET rates. Several new effects arise from this work showing that even modest mixing of low and high frequency totally symmetric modes, as well as non-totally symmetric modes, are very important. This result will change our concept of absolute ET rates and how they can be affected by molecular structure and bonding. In addition, the concept of vibrational reorganization energy needs to be redefined since it can become dependent on the mixing of vibrations in some cases.

Another objective was to re-examine our prior experiments on solutions of ion pairs with femtosecond transient infrared spectroscopy. This work demonstrates a more complex behavior than we previously expected, and more experiments are required to refine our tentative understanding of the observations. The experiment optically excites an ion pair to a radical pair, and we observe transient infrared on the populations of the metal carbonyl, $V(CO)_6$, in the radical pair. The results show that there is an ultrafast ET (~450 fs with a small quantum effect) as well as the longer ET process measured previously (~5 ps) and a very small component from diffusion/reformation of the radical pair over a long time. The yield of the ultrafast component increases with larger quantum numbers and it has a moderate quantum effect of about 20% per increase per quantum of population in the IR active CO stretching mode, which is unexpected from standard ET models. The prior data with picosecond equipment couldn't resolve the ultrafast component or the long component due to noise, and with the yield correlation that we have now found we can understand why prior work gave decays that appeared to have a quantum effect on the ps time scale. We also found an IVR process converting totally symmetric CO vibrations to IR transitions that is <75 fs. Another unusual effect for the higher energy excitation wavelengths is that a risetime appears in the ultrafast decay. We currently hypothesize that this is a measure of the time to stabilize geometric inter-conversions of the $V(CO)_6$ radical. The initial carbonyl radical is a Jahn-Teller distorted molecule which appears to sample many conformations when enough excess energy is present in low frequency vibrations. The specific reason for two fast components in the ET rate is not yet clear. We hypothesize that the one of the ET rates is due to movement in the radical pair causing a small relative rotation of the radical pair to a different electronic overlap, and thereby changing the ET transfer time ten-fold.

DOE Supported Publications (1999-2001)

"Models For Quantum Effects in Electron Transfer: Co(Cp)2+|V(CO)6– ", K. G. Spears and Hairong Shang, *J. Phys. Chem. A, v104, 2668-2680, 2000*

"Resonance Raman and Semi-Empirical Electronic Structure Studies of an Odd-Electron Di-Nickel Tetraiminoethylenedimacrocycle Complex", G.M. Sando, A. Ray, L.O. Spreer, K.G. Spears, J.T. Hupp, *Inorganic Chemistry, v39, 3911-3914, 2000*

"Ab Initio Computation of the Duschinsky Mixing of Vibrations and Non-Linear Effects", G.M. Sando and K.G. Spears, in press *J. Physical Chemistry A*

"Large Electron Transfer Rate Effects from the Duschinsky Mixing of Vibrations", G.M. Sando, K.G. Spears, J.T. Hupp, P.T. Ruhoff, in press *J. Physical Chemistry A*

"Vibrational Coherence Due to Promoting Mode Activity in the Relaxation Dynamics of the Class III Mixed-Valence Molecule [Ru2TIEDCl4]+ ", T.W. Marin, B.J. Homoelle, K.G. Spears, J.T. Hupp, L.O. Spreer, accepted by J. Phys. Chem.

"Ultrafast Electron Transfer with Vibrational Quantum State Dependence", T.W. Marin, B.J. Homoelle and K.G. Spears, submitted to J. Phys. Chem.

POLAR SOLVATION, FRICTION, AND ELECTRON TRANSFER

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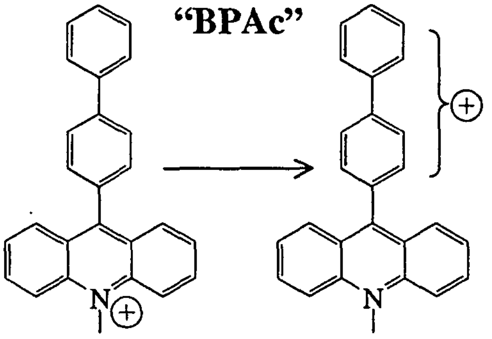
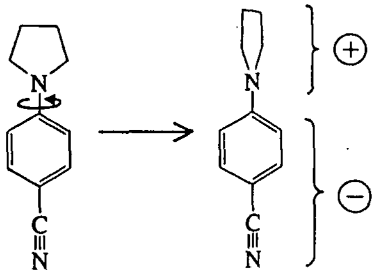
Overview: Our DOE sponsored research has focused on polar solvation, its time dependence, its relationship to the friction experienced by charged and dipolar species in solution. Our past work has helped to establish a solid foundation for understanding and modeling the phenomenon of polar solvation dynamics. Our more recent work focuses on how this dynamical aspect of solvation, the non-instantaneous response of a solvent to solute charge redistribution, leads to friction on processes such as rotational and vibrational relaxation and on charge transfer processes in polar solvents. In the case of electron transfer, solvent reorganization can dominate the reaction coordinate, meaning that most of the nuclear motion occurring during the electron transfer event is motion of solvent molecules. We have been measuring the rates of ultrafast electron transfer reactions and attempting to model these rates and the time-dependent spectra of the reacting systems in terms of what we know about polar solvent dynamics.

Recent Studies: For the past few years we have been collecting steady-state and time-resolved data on the three intramolecular electron transfer reactions depicted below. In all three of these systems, electronic excitation first leads to a locally excited ("LE") state, a state having a charge distribution similar to that of the ground state. Electron transfer then takes place on a picosecond time scale, which produces a charge-transfer ("CT") state via either a charge-shift (BPAc) or a charge separation (PYRBN and DTN). In all three reactions both the LE and CT states are fluorescent, which enables detailed study of the charge-transfer kinetics using time-resolved emission spectroscopy on ps and fs time scales.

"BPAc"



"PYRBN"



"DTN"

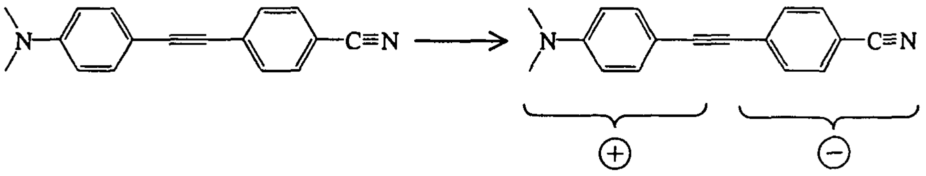
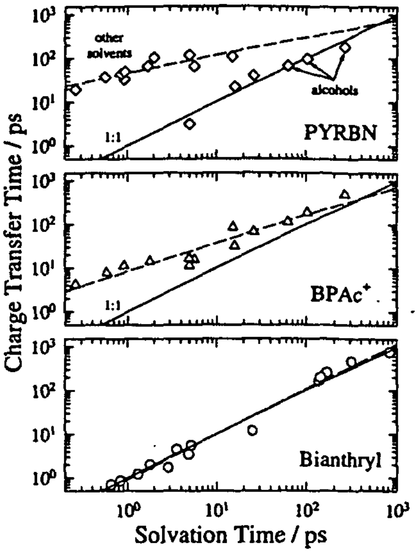


Fig. 1: LE→CT vs. Solvation Times



We have measured steady-state spectra, decay kinetics, and complete time-resolved emission spectra of these three systems under a wide variety conditions. Our goal is to relate the charge-transfer dynamics observed to the time-scales of solvent motions. At the crudest level, we can simply compare (average) times measured for these reactions with average solvation times measured using a non-reactive probe like coumarin 153[1]. Figure 1 shows such a comparison for two of the reactions of interest together with older data on the similar LE→CT reaction in bianthyl. All data here are for reactions at room-temperature in a collection of representative polar solvents. The bianthryl data, from the work of Barbara's group[2], is included because it displays the clearest connection to solvation dynamics of any reaction studied to date. In bianthryl, the time for the LE→CT conversion is simply equal to the solvation time (solid line). Such behavior is expected for barrierless reactions in which solvent coordinates dominate the reaction coordinate. These conditions are not met in most reactions. (In fact, no other reaction has yet been demonstrated to possess such a simple connection to solvation dynamics!) More typical are the data for BPAc and PYRBN. At least in nonassociated solvents, the latter reactions are much slower than solvation, suggesting the presence of a non-negligible reaction barrier. In addition, intramolecular coordinates (such as the internal twisting indicated for PYRBN) may play an essential role in these reactions, rendering the connection to solvation times less direct. Nevertheless, Fig. 1 reveals an obvious relationship between reaction and solvation times, especially in the BPAc case. To understand the meaning of this relationship requires a quantitative understanding of the solution-phase (free) energy surfaces on which these reactions take place.

Most of our current efforts have therefore concentrated on developing such surfaces for BPAc, DTN, PYRBN, and related molecules using electronic structure calculations and continuum solvation models. Our first goal is to be able to quantitatively predict the solvent dependence of experimental steady-state spectra using either one- (solvent only) or two- (solvent + 1 intramolecular mode) dimensional surfaces. We can then explore to what extent the basic kinetics as well as the detailed time-resolved emission spectra measured in these systems can be related to dynamics on such surfaces, with friction (at least in one dimension) dictated by the solvation response known from independent experiments. Success with these studies will provide a much deeper understanding of solvent participation in charge transfer processes in polar solvents. My talk will describe the progress we have made toward this end.

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Tuesday Evening

Session V

Charge Separation in Organized Assemblies

CLOSED BILAYER MEMBRANES AS CONTROL ELEMENTS IN COMPLEX PHOTOINITIATED REDOX SYSTEMS

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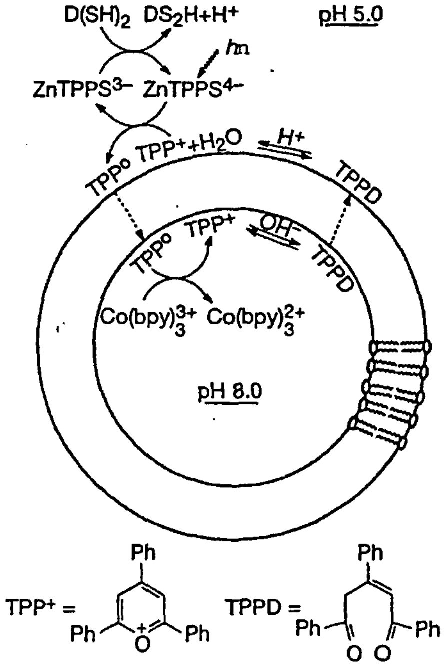
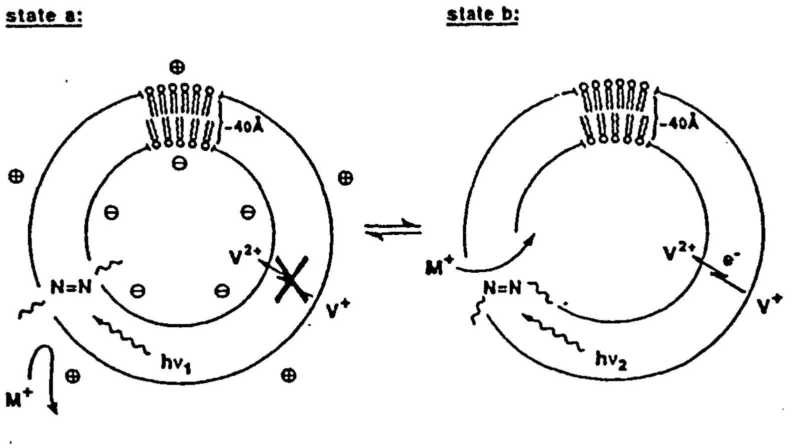
Our research is directed at understanding how the aqueous/organic interface and compartmentation in closed bilayer membranes can be used to modify reactivity in integrated chemical systems. Emphasis is placed upon reactions germane to solar photoconversion and related emerging technologies. To date, our work has focused primarily upon using closed membranes to effect efficient long-lived charge separation attending photoinitiated oxidation-reduction. Additionally, we have been investigating mechanisms of water oxidation catalyzed by dinuclear ruthenium μ-oxo ions since development of this catalytic capability is crucial to obtaining practical water photolysis systems. Our experimental designs are based upon "minimalist" strategies--i.e., use of simple compounds with reliance upon supramolecular self-assembly to minimize the number of components/reaction steps required to achieve a desired level of control.

Highly charged membranes can be very effective at preventing charge recombination following photoinitiated electron transfer when one of the primary products is adsorbed and the other is repelled from the membrane interface. Well-described examples from our research include the photosensitized one-electron reductions of viologen, 4-cyanopyridinium, and pyrylium ions by ZnTPPS^{4-}, all of which occur in the presence of anionic dihexadecyl phosphate vesicles with overall quantum yields approaching unity and organic radical/porphyrin π-cation primary product lifetimes of 1-100 ms. The neutral cyanopyridinium and pyrylium radicals, as well as the doubly-reduced viologen diradical, very rapidly permeate the membrane bilayer and can reduce electron acceptors that have been occluded within the inner aqueous phase of the vesicle. In these asymmetrically organized systems, stable photoinitiated charge separation is achieved; the mediating ion performs the dual functions of oxidative quencher of the photoexcited sensitizer and transmembrane electron carrier. However, to be useful in practical systems for bulk photolysis, the quencher/electron carrier must be capable of rapidly diffusing across the membrane in both its oxidation states. This requires that both oxidation states be formally neutral. We have been examining by transient spectroscopy the reaction behavior of two types of quenchers that are potentially capable of meeting this requirement, specifically, N-carbalkoxy derivatives of 4-cyanopyridinium ions and pyrylium ions. In the former



case, the presence of the weak acid substituent allows the ion to act as an electron/proton cotransporter. Additionally, the basic form of the oxidized species is able to form an internal zwitterion, which formally neutral and therefore somewhat membrane-permeable. By undergoing reversible ring-opening hydrolysis to the corresponding neutral 1,5-diketone, the pyrylium ion can function as a cyclic electron/OH^- antiporter (Figure 1). We have demonstrated that both of these types of quencher/carriers are capable of multiple (10-100) cycles of electron transport in photoinitiated reactions; for the pyrylium ion, reaction was limited by the amount of electron acceptor that could be occluded within the vesicle. Further, thiopyrylium analogs can also function as photosensitizers in these assemblies, thus obviating the need for a separate quencher/carrier. Ongoing research is involved with examining the capabilities of these assemblies for continuous photoproduction of H_2; in these systems, the occluded sacrifical electon acceptor has been replaced by colloidal Pt.

We have also been developing membrane-based photogated redox systems by incorporating both amphiphilic photoisomerizable molecules and electrogenic electron transport chains into the bilayers; the concept (Figure 2) is that, following rapid polarization of the membrane by the redox chain, electron transport becomes limited by the rate of charge-compensating electrolyte leakage across the membrane. The electron transport rate can then be modulated if photoisomerization of the second dopant alters the electrolyte leak rate, e.g., by disturbing the alkyl chain packing in the hydrocarbon phase of the membrane. Initial studies utilized molecules that undergo cis-trans photoisomerization (azobenzenes, stilbenes); although conversion to the cis form increased K^+ leak rates $\leq$10-fold in a dose-dependent manner, numerous experimental difficulties were encountered, the most significant being that trans →cis photoconversion of the stilbene was irreversible and the azobenzene cross-reacted with all the viologen radicals that were investigated. More promising results have recently been obtained with compounds containing spiro carbon centers (spirooxazines, spiropyrans) that undergo photochemically reversible ring opening-closing photoisomerization reactions to generate more polar and spatially larger merocyanine forms of the dye. Spiro→mero conversion caused an equivalent discrimination in K^+ leak rates at 1/100th the dopant levels of the cis-trans compounds, indicating very effective modulation of electrolyte leakage. However, contrary to expectations, the spiro form caused the greater leak rate. Transient spectroscopy revealed that, upon isomerization, the initially formed merocyanine relocated from the membrane interior to the aqueous/organic interface, reducing the extent of perturbation of membrane structure. Preliminary studies with a phenanthroline-based $Ru(bpy)_2^{2+}$-coordinated spirooxazine suggest that both electron transport and ion-gating functions can be combined in a single molecule. Photoreduction of electron acceptors in the membrane hydrocarbon phase is enhanced when the membrane-bound $Ru(bpy)_2$-coordinated spirooxazine is in its merocyanine form.



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(9) R. F. Khairutdinov & JKH: "Photocontrol of Ion Permeation through Bilayer Membranes using an Amphiphilic Spiropyran" manuscript submitted (*Langmuir*).

PHOTOINDUCED CHARGE SEPARATION IN MICROHETEROGENEOUS MEDIA

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Scope

Novel solid state systems are being developed to achieve very long-lived photoinduced charge separation of incorporated, easily photoionized molecules. The solid state hosts are porous oxide materials with channels of molecular size from about 10 Å to several hundred Angstroms so that they can incorporate large photoionizable molecules. In addition, a redox active center involving a transition metal ion which can act as an electron acceptor center is built into the oxide framework in a substitutional site or is positioned by electrostatic interactions.

The product of molecular photoionization is a paramagnetic radical cation that is stabilized within the pores or channels of suitable oxide materials. The environment and photoyield of this paramagnetic cation can be studied by electron spin resonance and in more detail by a pulsed electron spin resonance method known as electron spin echo spectrometry in which weak nuclear modulation of nearby magnetic nuclei like aluminium or phosphorus is detected.

Initial successful work in this area was carried out on layered zirconium phosphates, microporous silicoaluminophosphates and aluminophosphates, aluminosilicate zeolites including a new synthesis of clinoptilolite and the ETS-10 and ETS-4 titanosilicates. Of these, the silicoaluminophosphate or SAPO materials seem most promising with incorporated transition metal ions by both synthesis and by ion exchange. Electron spin echo modulation was used to demonstrate the synthetic incorporation of metal ions like Ni(II) which can be reduced to paramagnetic Ni(I) in framework sites of SAPO-n materials where n denotes a particular structure type. Photoionizable molecules have included tetramethylbenzidine, alkylporphyrins and alkylphenothiazines, but the alkylphenothiazines with alkyl chain lengths from 1 to 16 carbons seem most versatile for modifying the size of the photoactive molecule and also undergo simple one-photon photoionization in contrast to porphyrins. The photoionization efficiency has been found to depend on the SAPO channel size, the metal ion electron acceptor and the size of the photoionizable molecule. The photoproduced alkylphenothiazine cation has been found to be stable at room temperature for several hours or more so very long-lived charge separation is indeed achievable in these solid state systems.

Microporous silicoaluminophosphates have channel sizes up to about 18 Å. To incorporate larger photoionizable molecules, mesoporous silica and aluminosilica materials denoted as hexagonal MCM-41, cubic MCM-48 and large hexagonal SBA-15 materials are also being studied. These materials have pore sizes up to several hundred Angstroms but much less is known about methods to incorporate in them a variety of transition metal ions by direct synthesis or by ion exchange.

Among the transition metal ions investigated as electron acceptors in these solid state materials Ni(II), Ti(IV) and V(V) are particularly effective. These ions can be incorporated into framework positions by direct synthesis in SAPO materials although the ease and amount of incorporation does vary with the particular SAPO structure selected. Ti(IV) and V(V) can also be synthetically incorporated, with more synthetic difficulty, into MCM-41 mesoporous silica materials, but Ni(II) is synthetically incorporated to only a small degree in these materials. The photoyield enhancement and its dependence on the concentration of the incorporated metal ion give indirect evidence that these ions do act as built-in electron acceptors in these solid state materials. However, only for V(V) do we see direct evidence by the electron spin resonance (ESR) observation of paramagnetic V(IV) formation after photoexcitation. Although there is some overlap between the ESR spectrum of the radical cation of the incorporated photoionizable molecule and that of the expected paramagnetic Ti(III) or Ni(I), we have not been able to definitely detect Ti(III) or Ni(I) formation thus far. The $g_{\parallel}$ feature that we search for is perhaps too weak to detect. Further research is required to better understand the role and mechanism of specific transition metal ions on the clear enhancement of the photoefficiency.

These new molecular/solid state microporous/mesoporous systems with built-in electron acceptors offer new potential for creating photoactive systems with long-lived charge separation. The solid state nature implies a robust material. The variable dimensions of the mesoporous MCM-41, MCM-48 and SBA-15 silica and aluminosilica tube materials, and the microporous silicoaluminophosphate materials offer control for optimally locating the photoionizable molecules. The incorporation of magnetic nuclei like aluminum and especially phosphorus into these materials enables rather detailed structural delineation by electron spin echo detection of the nuclear modulation.

Future Plans

Future work will focus more on the photoionization of alkylphenothiazines and alkylpyrenes in mesoporous silica and aluminosilica materials. Also, continued efforts will be made to better understand the factors that determine which transition metal ions most enhance the photoefficiency and why and how this is affected by the host material structure. With certain metal ions, significant dark reactions occur and this does not seem to be simply related to the solution reduction potentials. To optimize the photoreactions, the dark reaction must be minimized.

Finally, we will explore mesoporous silicoaluminophosphates for which we have developed a new synthesis with recently further improved thermal stability. These new mesoporous SAPO materials offer the advantage of doing P-31 electron spin echo modulation to more incisively determine the metal ion locations, and how this relates to their photoefficiency.

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SPECTROSCOPIC AND PHOTOPHYSICAL STUDIES OF POLYPYRIDINE COMPLEXES OF DIVALENT RUTHENIUM IN SOLUTION AND ENTRAPPED IN ZEOLITE-Y

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The general long-term objectives of this research program are the development and characterization of molecular species, and assemblies of such species, which capture solar energy and facilitate its conversion to usable forms of chemical energy. While major efforts in the recent past were devoted to the successful development of effective synthetic strategies for the construction of multi-component assemblies based on zeolite-Y supports, which exhibit impressive photo-catalytic properties relative to less organized systems, current attention is being focused on improving spectroscopic methods to elucidate the molecular and electronic structure of the individual components of such assemblies. To accomplish these current goals, several powerful spectroscopic probes of ground- and excited-state structure are being employed at the present time, including resonance Raman and time-resolved resonance Raman spectroscopic techniques, as well as diffuse reflectance and time-resolved luminescence methods.

Extending initial work that described the preparation and characterization of zeolite-based ("adjacent cage") organized assemblies (1) and documented increases in net charge-separation efficiency relative to less organized systems (2), efforts were made to provide a more detailed interpretation of the complicated lifetime decay curves exhibited by such assemblies by undertaking extensive studies on a series of zeolite materials which contained increasing amounts of entrapped $Ru(bpy)_3^{2+}$, wherein the percentage of complexes involved in adjacent cage pairs and higher aggregates can be calculated on a purely statistical basis (3). The results of this systematic study provided firm evidence for the existence of several different decay pathways associated with the adjacent cage pairs, with characteristic lifetimes being consistent with those derived from studies of the synthetically engineered adjacent cage assemblies referenced above.

More recently, this synthetic strategy has been employed to produce assemblies containing a more stable donor so as to permit direct spectroscopic confirmation of electron transfer quenching of the oxidized primary sensitizer by the adjacent cage donor component (4). Finally, while photo-physical and spectroscopic studies provide strong support for the efficiency of adjacent cage dyad formation, a synthetic strategy was recently employed to provide more direct evidence. Specifically, studies were carried out for the zeolite- entrapped $Ru(bpy)_2(pypz)^{2+}$ complex (pypz is pyridylpyrazine), wherein the primary complex contains a single reactive peripheral N-donor group. Following formation of the $Ru(bpy)_2(pypz)^{2+}/Ru(bpy)_3^{2+}$adjacent cage dyad by the standard procedure, application of a second treatment with the reactive $(H_2O)Ru(NH_3)_5^{2+}$ complex, yielded no evidence for reaction with the peripheral N-donor. These results convincingly document the high efficiency of adjacent cage dyad formation, confirming the fact that, upon detachment from the primary complex, the secondary complex does not migrate to more remote cages, but is trapped in the cage adjacent to the primary complex, $Ru(bpy)_2(pypz)^{2+}$, in this case shielding the latter from further reaction with the pentammine reagent (5).

In the search for synthetic complexes which mimic the oxygen evolving complex of natural systems, most interest has turned to the oxo-dimeric complex, $(H_2O)(bpy)_2Ru$-O-

$Ru(bpy)_2(H_2O)^{4+}$, discovered and characterized by Meyer and coworkers (6 and references therein) and intensively studied by Hurst's group (7 and references therein). Prompted by the documented effectiveness of resonance Raman (RR) spectroscopy as a probe of various oxidized forms of this complex, as reported by Hurst and coworkers (7), newer methods of time-resolved RR spectroscopy, involving novel and efficient mixing devices, are currently being employed in our laboratory in attempts to generate and structurally characterize fleeting intermediates which may arise during the catalytic oxidation of water, using Ce^{4+} as the oxidant. In related work being conducted in collaboration with Professor Dutta's group, it has been noted that aqueous suspensions of zeolite samples loaded with varying amounts of $Ru(bpy)_2(H_2O)_2^{2+}$ form brightly colored (blue-green) zeolite-entrapped complexes upon bubbling O_2 at temperatures near boiling. Studies in our laboratory have confirmed that only colorless products are formed at low loading levels, with the yield of colored products increasing with increasing loading levels. Efforts are currently underway to isolate and characterize these colored, apparently oligomeric, oxidation products.

Finally, given the fact that there is an ever-increasing number of reports of heterogeneous (entrapped or adsorbed) catalytic systems involving assemblies based on monomeric or dimeric polypyridine complexes of divalent ruthenium, coupled with the fact that RR and time-resolved RR are potentially among the most effective techniques to characterize the ground and excited states of such systems, it seems important to further develop a reliable interpretational framework for the observed spectral parameters of such systems. In order to do so, efforts are currently underway in studying the RR and TR3 spectra of dimeric complexes involving several different bridging ligands in an attempt to establish the spectral sensitivity to subtle alterations in ground and excited state electronic structure arising from internal or environmental perturbations.

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Wednesday Morning

Session VI

Photoelectrochemistry

ELECTRON TRANSPORT AND INTERFACIAL PHENOMENA IN DYE-SENSITIZED NANOCRYSTALLINE TiO_2 SOLAR CELLS

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This research is directed toward understanding the underlying processes governing the performance of dye-sensitized nanocrystalline TiO_2 solar cells. Major issues recently addressed include the mechanism and kinetics of electron transport and recombination, the separability of the ion and electron diffusion process, the electrical potential distribution in the cell, the location of charge separation, and the mechanism for the photopotential. Some specific recent achievements are summarized below.

Photopotential mechanism. The mechanism creating the photovoltage of the cell is under debate. Several years ago, we reported, based on the analyses of intensity-modulated photovoltage spectroscopy measurements, that the photovoltage in the dye-sensitized solar cells originates from the buildup of photoinjected electrons in the bulk of the TiO_2 film, which causes the Fermi level of the TCO back contact (TCO: transparent conducting oxide) to rise with respect to the solution redox potential. Recently, a p-n junction model was introduced to challenge this notion. In the p-n junction model, the Fermi level of the TCO contact rises as a result of compensation of the dark electrical potential drop at the TCO/TiO_2 interface, owing to the buildup of photoinjected charge at the TCO/TiO_2 interface. Electrical impedance spectroscopy (EIS) studies were carried to identify the loci of charge buildup in the photoelectrode and its relation to the photovoltage of the cell. Analyses of EIS and other data showed that the buildup of photoinjected electrons in the TiO_2 film causes both an increase of the photovoltage and the decrease of the dark electrical drop across the TCO/TiO_2 interface. Furthermore, these studies showed that the kinetic limiting process in these cells occur at the TiO_2/electrolyte interface (as a result of recombination) instead of at the TCO/TiO_2 interface.

Low photocurrent conversion efficiency (IPCE). Under bright sunlight (AM 1.5), high-efficiency dye-sensitized nanocrystalline TiO_2 solar cells can supply a current density above 18 mA/cm^2 at a voltage of about 0.5 V. However, most cells deliver a current density much less than 18 mA/cm^2. A low photocurrent density indicates a low IPCE in the spectral region, where the dye absorbs strongly. The IPCE is determined by the light absorption efficiency of the dye, the electron injection efficiency, and the efficiency of collecting the injected electrons at the back contact. It is difficult experimentally to determine, especially as a function of applied bias, which of the three efficiencies limit the IPCE. Toward identifying the limiting efficiency, an analytical expression was developed and its prediction of the relation between the time constants for charge collection and recombination and the charge-collection efficiency and IPCE was verified. As the applied bias is varied from short-circuit to open-circuit conditions at one-sun illumination intensity, recombination becomes faster, the collection of electrons becomes slower, and the IPCE decreases. The drop off of IPCE correlates with the decline of the charge-collection efficiency.

Inseparability of electron-ion motion. Photocurrent transient studies demonstrate that electron transport is coupled to ion motion in the electrolyte. The significance of such "ambipolar diffusion" is that the rate of electron transport, and thus cell efficiency, may become limited by ion motion in electrolytes containing low ion concentrations. This study also resolves a controversy about whether the measured current in the external circuit is in response to the motion of photoinjected electrons in TiO_2 films (a displacement current) or to the arrival of electrons at the collecting electrode (an arrival current). Contrary to most solid-state devices, only electrons that arrive at the collector contribute to the measured photocurrent in dye-sensitized solar cells.

Nonlinear electron transport kinetics. With increasing light intensity, electron transport in dye-sensitized solar cells becomes faster. The increased transport rate is shown to depend on the buildup of photoinjected electrons in the film. In the absence of recombination (at short circuit), a power law dependence of the short-circuit J_{sc} on the number of electrons Q in the film is observed: $J_{sc} \propto Q^m$, where m $\approx$ 2.64. An equivalent relation between the time constant for electron collection, determined by intensity-modulated photocurrent spectroscopy (IMPS), and J_{sc} has been observed by others. The light intensity I ($I \propto J_{sc}$) dependence of Q implies that the electron-transport rate depends nonlinearly on the steady-state population of electrons in the film. To understand the cause of the observed nonlinear behavior, we developed an analytical model that assumes that electrons, during their transit through the film, undergo multiple trapping/detrapping events, involving an exponential trap-state distribution. The electron-population profile in the conduction band as a function of light intensity was calculated by solving the continuity equation. The charge in trap states was calculated from the exponential trap-state distribution and knowledge of the Fermi level in the dark and in the light. These considerations yield the following expression: $J_{sc} \propto Q^{\frac{m_c}{kT}}$, where $Q = J_{sc}\tau_{IMPS}$ is the total number of electrons in the film $Q \approx Q_t$ (Q_t denotes the number of trapped electrons) and the parameter m_c describes the steepness of the trap-state distribution curve. This expression is identical in form to the experimentally observed one, implying that the exponential dependence of trap states on energy is the likely cause for the observed nonlinearity or power-law dependence of short-circuit current on the number of electrons in the film.

Electron transport dynamics. A random-walk approach was developed to model the electron-transport dynamics in dye-sensitized TiO_2 solar cells within a multiple trapping framework, and the predicted results were verified by transient photocurrent measurements. The model considers the trap-state energy distribution, the mobility of free electrons, the light intensity, the absorption coefficient for the probe light, the film thickness, and whether a cell is illuminated from its front side or backside. The studies suggest that nonthermalized electron transport is important in dye-sensitized solar cells under normal operating conditions. Failure to account for the presence of nonthermalized electrons is shown to be the main limitation of current transport theories.

Cell development. Cells with solar conversion efficiency of up to 9.46% at AM 1.5 were fabricated. A semi-automated procedure is being developed for depositing nanoporous films.

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EXCITED STATE CHARGE TRANSFER AT NANOCRYSTALLINE SEMICONDUCTOR INTERFACES

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The objective of this research is to provide models of surface mediated photochemical processes relevant to dye-sensitized solar cells. By firmly establishing mechanistic details of the molecular-semiconductor interface we will tune photo-responses through the sensitizer, semiconductor, and environment. Summaries of some recent studies are presented below.

Tuning conduction band energies in anatase titanium dioxide nanocrystallites. It is well known that the conduction band edge position 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. Here we are investigating methods for controlling the energetic position of the acceptor states in anatase nanocrystals (with pH and other potential determining cations) relative to the formal reduction potentials of Ru(II), Os(II), and Re(I) polypyridyl sensitizers. These studies are important in the development of mechanistic models and may provide a general approach for optimization of open-circuit photovoltages measured in regenerative solar cells. We recently identified conditions where the quantum yield for interfacial excited state electron injection can be reversibly tuned from zero to unity simply by controlling the ionic strength of an external acetonitrile solution. The metal-to-ligand charge transfer (MLCT) excited states of $Ru(dcb)(bpy)_2^{2+}$, where dcb is 4,4'-$(COOH)_2$-2,2'-bipyridine, are observed in neat acetonitrile and fast interfacial electron transfer in 1.0 M $LiClO_4$. In ongoing work, we have pre-treated TiO_2 nanocrystallites with acid or base prior to sensitization studies. We find that the surface acidity alters the nature of the sensitizer-surface linkage, the kinetics for surface binding, the interfacial electron injection yield, and the redox properties of the surface bound sensitizer. Furthermore, we find that a pH ~ 2 pretreatment optimizes the light-to-electrical energy conversion properties of TiO_2 sensitized with $Ru(dcb)(bpy)_2^{2+}$in a regenerative solar cell consisting of 0.5 M LiI/0.05 M I_2 in acetonitrile. The generality of these results and the expected correlation of conduction band edge energies and excited state reduction potentials will be evaluated in the future.

MLCT excited states bound to semiconductors. Little information exists on the nature of molecular excited states bound to semiconductor surface. This is due to the fact that electron injection into the semiconductor generally results in short-lived excited states and weak photoluminescence, PL, that are experimentally difficult to rigorously quantify. In fact, most reported PL measurements of semiconductor-bound MLCT excited states have been made as an indirect method for estimating electron injection rate constants. The recent discovery of methods for shifting the energetic position of the conduction band above (toward the vacuum level) the excited state reduction potentials of the sensitizer described previously, have allowed the characterization of semiconductor-bound molecular excited states in considerable detail. Interestingly excited state decay of long-lived MLCT excited states was well described by competing unimolecular and bimolecular excited state reactions. While relatively narrow distributions of rate constants may exist, we have found no reason to resort to dispersive kinetic models. The bimolecular pathway has been proposed to proceed by excited-state – excited-state encounters that occurs by energy-transfer migration between the ground and excited states of adjacent, surface-attached sensitizers. Direct evidence for lateral intermolecular energy transfer cross the nanocrystalline surface from $Ru(dcb)(bpy)_2^{2+*}/TiO_2$ to $Os(dcb)(bpy)_2^{2+}/TiO_2$ is observed with a quantum yield near unity. We find that the short-lived Os MLCT excited state, $\tau = 50$ ns, decay exponentially on the surface. This result suggests that excited state energy transfer can be used to probe the distance between and the relative orientation of molecular sensitizers. These studies are planned for the near future.

Supramolecular sensitizers. A final area of focus, involves bimetallic coordination compounds as sensitizers designed to probe electronic coupling and interfacial electron transfer. Two novel Ru(II)-Rh(III) polypyridine dyads, containing carboxylic function as the Rh(III) unity, $Rh(dcb)_2$-(BL)-$Ru(dmp)_2$ and $Rh(dcb)_2$-(BL)-$Ru(bpy)_2$ (dmp is 4,7-dimethyl-1,10-phenanthroline; BL is 1,2-bis[4-(4'-methyl-2,2'-bipyridyl)]ethane] were synthesized and bound to nanocrystalline TiO_2. The energetics of this assembly were designed such that the Rh acceptor levels lie between the acceptor states in the semiconductor and the Ru MLCT excited state. Light excitation results in an unprecedented electron "hopping" from the Ru chromophore to the Rh unit to the semiconductor nanocrystallite. This work provides an example of how the principles of stepwise charge separation, originally developed in the field of supramolecular photochemistry, can be applied to solid-state materials. The systems studied were designed as proof-of-principle heterotriads, without any pretension to compete with the sensitizers commonly used in regenerative solar cells. In fact, the photocurrent efficiency is rather low, mainly because of low charge injection yields. Nevertheless, they demonstrate a strategy to slow down recombination of the injected electron and oxidized sensitizer.

In a related project we have utilized the bimetallic sensitizer $[Ru(dcb)_2(Cl)$-bpa-$Os(bpy)_2(Cl)](PF_6)_2$, abbreviated Ru-bpa-Os, where dcb is 4,4'-$(COOH)_2$-2,2'-bipyridine and bpa is 1,2-bis(4-pyridyl)ethane, for interfacial electron transfer studies. Either 417 nm or 532.5 nm light excitation of a TiO_2|Ru-bpa-Os material immersed in a 1.0 M $LiClO_4$ acetonitrile bath at 25 °C results in rapid interfacial electron transfer and intramolecular electron transfer to ultimately form an interfacial charge separated state with an electron in TiO_2 and an oxidized Os(III) center, abbreviated $TiO_2(e^-)$|Ru-bpa-Os(III). This same state can also be generated after selective excitation of the Os(II) moiety with 683 nm light. The rates of intramolecular and interfacial electron transfer are fast, $k > 10^8$ s^{-1}, while interfacial charge recombination, $TiO_2(e^-)$|Ru-bpa-Os(III) → TiO_2|Ru-bpa-Os, requires milliseconds for completion. The results show a general strategy for promoting rapid intramolecular electron transfer (Os(II) → Ru(III)) after interfacial electron injection and provide another example of remote electron injection from the Os → bpy MLCT state. In future work, we will replace the bridging bpa ligand with 4,4'-bipyridine and pyrazine to control the electronic coupling between the two metal centers and will replace the chloro ligands with other non-chromophoric ligands to tune the driving forces for electron transfer.

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ULTRAFAST ELECTRON INJECTION DYNAMICS IN DYE SENSITIZED NANOCRYSTALLINE SEMICONDUCTOR THIN FILMS

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The objective of our DOE funded research is to understand electron transfer dynamics between semiconductor nanoparticles and molecular adsorbates. This knowledge is essential to many semiconductor nanoparticle based devices and processes, including photocatalytic waste degradation and dye sensitized solar cells.

In recent years, ultrafast interfacial ET in solid/liquid interface has been a subject of intense interest. There have been many reports of interfacial ET rates with widely varying rates from < 100 fs to ns. Comparison between different studies and with theory has been difficult because of varying conditions and molecules used. It is still not understood what parameters control the interfacial ET rate. In most previous studies, electronic spectral change of the adsorbates was monitored to obtain ET rate. It is often hard to avoid spectral overlap between ground, excited and oxidized form of large dye molecules used for these studies. As a result, there has not been any systematic study of this process and the dependence of ET rate on various parameters of the adsorbate, semiconductor and their interaction has not been examined.

Our approach to this problem is to develop a technique that allows systematic study of ET in various dye-sensitized semiconductors. Using femtosecond infrared (transient-absorption) spectroscopy, we directly monitor the IR absorption of injected electrons in semiconductor nanomaterials and the vibrational spectral change of adsorbates. The main accomplishments of our research in the past two and half years are two-fold: 1) We have demonstrated that femtosecond IR can be used to systematically study electron transfer dynamics in any dye-sensitized semiconductor thin films.; and 2) We have studied ET in a few Ru dye sensitized metal oxide thin films and gained preliminary and qualitative understanding of the dependence of interfacial ET on semiconductors, adsorbates, and their interaction. The main findings are the following:

Two-state electron injection in Ru dye sensitized TiO_2 thin film: For $Ru(dcbpy)_2(SCN)_2$ [Ru N3] sensitized TiO_2 thin films, 400 nm excitation leads to broad featureless transient mid-IR absorption in the < 1 ns time scale. This absorption signal was assigned to injected electrons based on our previous work. Electron injection kinetics from Ru N3 excited state to TiO_2 were dominated by a fast component with a time constant of about 50 fs and a slower component. The amplitude and time of the slow component was sensitive to sample conditions. The observed biphasic electron injection dynamics in Ru N3-sensitized TiO_2 can be accounted for by a two-state electron injection model. The fast injection component occurs from vibrational excited state of the adsorbate and is in competition with intramolecular vibrational energy relaxation process. The slow injection occurs from vibrationally relaxed excited state. The partition between these pathways and time scale of the slow component depend critically the energetic of the adsorbates and their position relative to the conduction band of TiO_2. Similar biphasics injection kinetics were observe in other Ru dye sensitized TiO_2. The validity of the model was tested by comparing injection kinetics in different Ru dyes, pH, solvent and excitation wavelengths.

Dependence of injection rate on semiconductor. To find out the dependence of ET rate on semiconductors,, we are investigating injection rate of Ru N3 on a series of semiconductors. In a previous study we found a dominating < 100 fs injection component on TiO_2 but ~ 100 ps injection on ZnO. We have extended this comparison to SnO_2, in which a ~ 4ps (stretched exponential) was observed. We attributed ultrafast injection in TiO_2 to the d-orbital nature of its conduction band, which gives rise to higher density of states and stronger coupling with electron donating orbitals of the adsorbate. We propose to further test this hypothesis in more semiconductor materials in the future

Dependence of injection rate on electronic coupling. The dependence of injection rate on electronic coupling was investigated in TiO_2 films sensitized by a series of Re(CO)3Cl(Ln) dyes (Ln are dcbpy ligands with n=0,1, and 3 CH_2 spacers) These dyes have systematically varied electronic coupling with the adsorbate. We found that ET rate decreased with electronic coupling as expected from ET theory, but the quantitative dependence requires more studies in the future.

Dependence of injection rate on the energetics of the adsorbate. Non-adiabatic ET theory predicts that injection rate to a semiconductor should increases with adsorbate redox potential. We tested this prediction in a series of Ru dyes sensitized SnO_2 thin films. In deed, we found that injection rate increases when the adsorbate excited state energy lies further above the conduction band. The observed trend agrees qualitatively with the theoretical prediction. We are continuing this experiment in a series dyes with bigger change of redox potential.

Dependence of injection rate on solution pH. The free energy difference for interfacial ET can also 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 $Re(dcbpy(CH_2))Cl(CO)_3$ sensitized TiO_2 thin films in solutions of pH=2 to 8. We found that injection rate decreases when the pH of solution increases. The observed trend agrees qualitatively with the theoretical prediction. We are continuing this experiment in a series dyes with bigger change of pH and in more metal oxide materials (SnO_2 and ZnO).

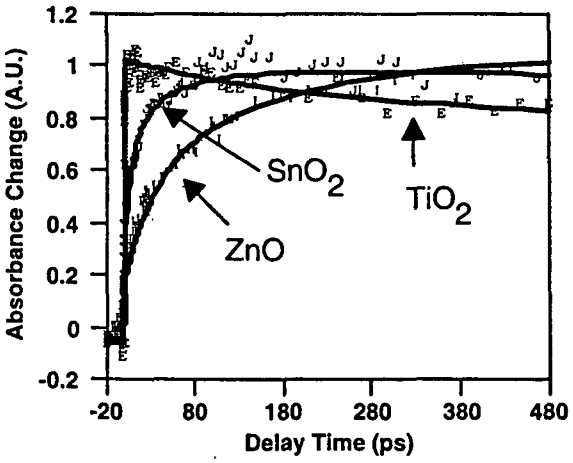

Fig. 1. Comparison of electron injection dynamics in Ru N3 sensitized TiO_2, SnO_2 and ZnO thin film

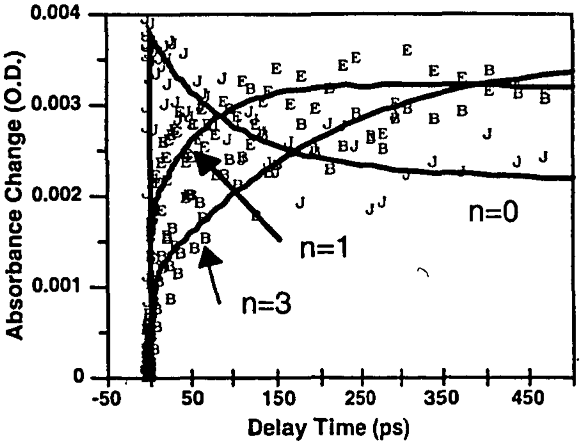

Fig. 2. Dependenc of Electron injection rate on the number of CH_2 units inn ReCOn sensitized TiO_2 thin films

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TIME-RESOLVED STUDIES OF ORGANIC DYES MOLECULES BOUND TO TITANIUM DIOXIDE PARTICLES: EFFECT OF PARTICLE SIZE AND STRUCTURE

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In this talk I will present the results from time-resolved experiments that are designed to probe electron transfer between titanium dioxide particles and adsorbed dye molecules. In these experiments the dye molecule is excited by an ultrafast (ca. 200 fs) laser pulse and the formation and decay of the dye radical cation is monitored with a near-IR probe laser pulse. Our results primarily pertain to the semiconductor-to-dye back electron transfer reaction. The issues addressed are how factors such as the crystal structure of the particles (anatase versus amorphous), the size of the particles, and their surface potential affect the rate of the back electron reaction. The differences in rate for the different crystal structures are due to differences in the coupling between the dye molecules and the semiconductor particles. Experiments with different isomers of anthracene carboxylic acid bound to titanium dioxide and zirconium dioxide will also be presented. In this case differences in the back electron transfer rate are attributed to differences in the driving force for electron transfer, due to the different redox potentials of the dye molecules (and the different conduction band energies of the semiconductor). Our time-resolved experiments also show that the size of the semiconductor particles has no affect on the semiconductor-to-molecule electron transfer rate. Specifically, anatase TiO_2 particles in the 4 nm to 40 nm size range have identical back electron transfer times. These results imply that the electrons are rapidly trapped into sites adjacent to the dye radical cation.

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METAL–SEMICONDUCTOR COMPOSITES. PHOTOINDUCED TRANSFORMATIONS IN GOLD CAPPED TiO_2 NANOSTRUCTURES

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A major goal of designing composite systems is to tailor the photoelectrochemical properties or to tune the sensing properties of the semiconductor nanomaterials. A series of semiconductor-semiconductor or semiconductor-metal composite nanoparticles have been shown to facilitate charge rectification following bandgap illumination (Figure 1). Of particular interest are the semiconductor-metal composite films that play an important role in improving the performance of photocatalytic systems and photoelectrochemical cells. For example, deposition of a noble metal on semiconductor nanoparticles is beneficial for maximizing the efficiency of photocatalytic water splitting reactions.

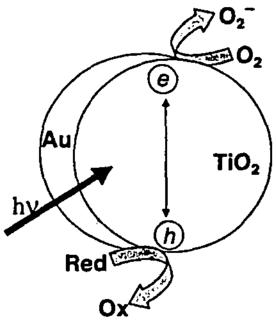

Figure 1. Improving the charge separation in a semiconductor-metal composite Nanoparticle

TiO_2@Au Nanoparticles. Core-shell type semiconductor-metal nanoparticles have been synthesized by the reduction of $[AuCl_4]^-$ on the surface of preformed TiO_2 colloids in aqueous media. The concentration of the TiO_2 core directly influences the particle size (10 to 50 nm diameter) and the stability of these core-shell composite nanoparticles. Aggregation effects were observed at a TiO_2:Au ratio of 0.25:1. When excited with 532 nm laser pulse these aggregates undergo fusion to form bigger multicore TiO_2–gold shell composite nanoparticles. The process of melting and fusion occurred with a rate constant of $1.25 \times 10^9\ s^{-1}$. The role of metal shell in promoting photocatalytic oxidation has also been probed using thiocyanate oxidation at the semiconductor interface. Nearly 40% enhancement in the oxidation efficiency is seen with TiO_2nanoparticles capped with low concentrations of the gold.

Nanostructured Films. In order to utilize semiconductor/metal nanocomposites for photocatalytic and photoelectrochemical applications we have immobilized the two nanoclusters by sequential deposition on conducting glass electrodes. Thin films of TiO_2 cast on conducting glass plates (OTE) were immersed in gold nanoparticle suspension and subjected to a dc electric field of 100 V. The pink coloration of the film along with the presence of a surface plasmon absorption band at 546 nm confirmed the deposition of gold nanoparticles on the TiO_2 films.

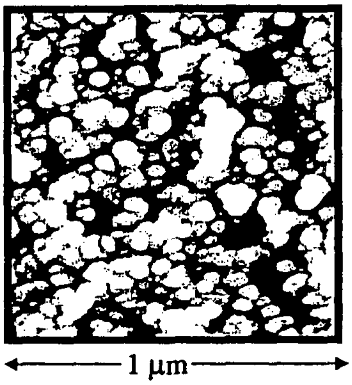

Figure 2. AFM image of gold nanoparticles deposited on OTE/TiO_2 film

The AFM image shown in Figure 2 demonstrates the usefulness of electrophoretic deposition in assembling Au nanoparticles as a 3-dimensional network on nanostructured semiconductor films. Although these metal nanoparticles are deposited as packed arrays, the interparticle interaction between the metal nanoparticles is expected to be minimal. The gold nanoparticles deposited on TiO_2 films show the characteristic plasmon band with minimal aggregation effects. Whereas outer layers of gold nanoparticles may be less important in modifying the properties of TiO_2 film, the first one or two layers of gold nanoparticles are expected to introduce most of the changes in the performance of the semiconductor film. The deposition of metal nanoparticles on TiO_2 films improved the photocurrent generation and induced a shift in the apparent flat band potential. A 3-fold enhancement in the photoconversion efficiency was observed with Au-TiO_2 composite films as compared to native TiO_2 films. Improved photoelectrochemical performance of semiconductor-metal composite film is attributed to the presence of metal deposits, which promote interfacial charge transfer kinetics.

Future Studies. Because of large surface/volume ratio, the metal nanoparticles exhibit significant photoactivity and/or undergo oxidation at the semiconductor interface. Questions still remain regarding the stability of the semiconductor-metal interfaces during photoelectrochemical operation. The oxidation of the noble metals such as Au not only destroys the TiO_2/metal interface but also creates new electron-hole recombination centers. Whereas modification of the semiconductor surface with metal nanoparticles is advantageous to promote charge transfer process at the interface, it is important to tackle the problems associated with metal oxidation at the semiconductor/metal interface. In order to address these issues, we will prepare semiconductor-metal nanoparticles in aqueous media and investigate the radical attack and interfacial charge transfer dynamics using laser flash photolysis and pulse radiolysis. Mechanistic and kinetic information gained in these studies will enable us to optimize the core-shell geometry of metal-semiconductor nanoparticles for light energy harvesting applications. We will also modify nanostructured TiO_2 films with Au, Pt, Ir nanoparticles using an electrophoretic approach and probe their effectiveness and size dependence in photoelectrochemical and photocatalytic applications.

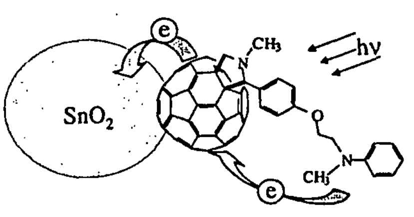

Figure 3 Strategy for harvesting light energy using semiconductor-dyad assembly

A feasible approach to utilize the photoinduced charge separation in a sensitizer-bridge-donor dyad (e.g., fullerene-aniline dyad) molecule would be to transfer the electron from the anion moiety into a semiconductor nanoparticle (Figure 3) and utilize these electrons for photocurrent generation. The C_{60}-aniline dyad cluster films when cast on nanostructured SnO_2 films are found in our laboratory to be photoelectrochemically active and to generate photocurrent (up to 0.2 mA/cm^2) under visible light excitation. The methodology of casting high surface area sensitizer films on electrode surfaces will be investigated to utilize sensitizer-bridge-donor type dyad molecules efficiently in light energy conversion devices such as solar cells.

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EARLY STAGES OF PHOTOINDUCED CHARGE SEPARATION IN SURFACE MODIFIED METAL OXIDE NANOPARTICLES

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Surface modification of nanocrystalline metal oxide particles with ortho dihydroxyl enediol ligands was found to result in altered optical properties of small particles. Upon surface modification the onset of absorption shifts to the red, as compared to unmodified nanocrystallites (Fig.1). Consistent behavior was found for the three different nanocrystalline systems (ZrO_2, TiO_2 and Fe_2O_3) with different crystalline structures, band gaps and Fermi level positions. The binding was found to be exclusively characteristic of colloids in the nanocrystalline domain (<20nm). The structure of the surface modifier nanoparticles was determined by FTIR spectroscopy confirming bidentate binding. In nanocrystalline TiO_2 this binding results in the formation of a five membered ring around surface Ti atoms, a favorable conformation of bond angles and distances for the octahedral coordination of surface Ti atoms. In order to correlate the surface structure and the origin of unique functions that we have observed in photocatalysis on nanoparticulate TiO_2, we have investigated the effect of particle size on the coordination of surface Ti atoms using Ti K-edge XAS (X-ray Absorption Spectroscopy). As the particles become smaller than 20nm, the coordination environment of Ti surface sites changes from sixfold-coordinated (octahedral) into fivefold-coordinated(square-pyramidal). These different under-coordinated defect sites are the source of enhanced and selective reactivity of nanoparticles, resulting in bindings that are the consequence of adsorption induced restructuring of the nanoparticle surface. XAS reveals that surface modification with ascorbic acid restores the pre-edge features of octahedrally coordinated Ti in the anatase crystal environment. This indicates that bidentate binding of ascorbic acid helps to reestablish the octahedral coordination of the nanocrystalline surface, relaxing the surface Ti atoms to their original anatase environment. The binding of surface modifiers therefore becomes significantly enhanced due to the stability gained from adsorption induced restructuring of the particle surface. Similar results were obtained for nanocrystalline Fe_2O_3 and ZrO_2.

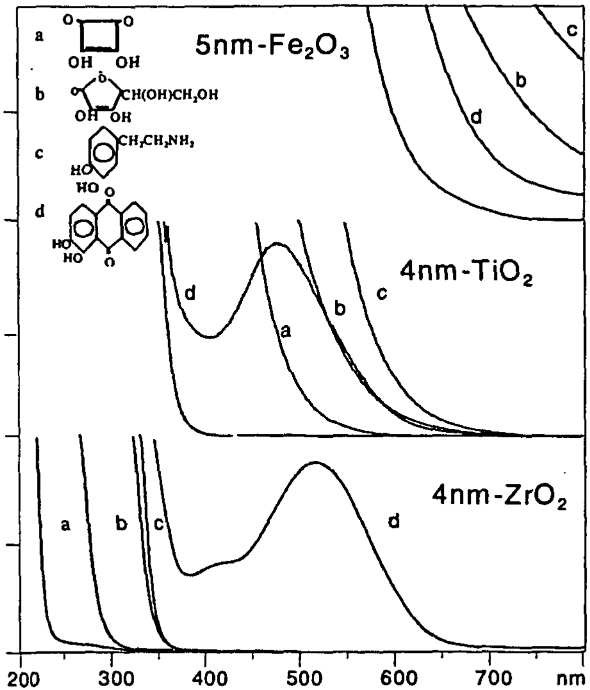

Figure 1 Optical properties of different metal oxide nanocrystallites surface modified with different enediole ligands, a-d.

It was found using electron paramagnetic resonance (EPR) that, as with organic charge transfer superconductors, these novel nanocrystallites operate with a charge-transfer mechanism. Importantly, this mechanism is distinctively different from dye sensitization of large band gap semiconductors. The EPR spectra were consistent with hole trapping on the surface modifier and electron trapping on metal oxide particles. In nanocrystalline TiO_2 we have shown charge pairs are instantaneously separated into two phases, the holes on the donating organic

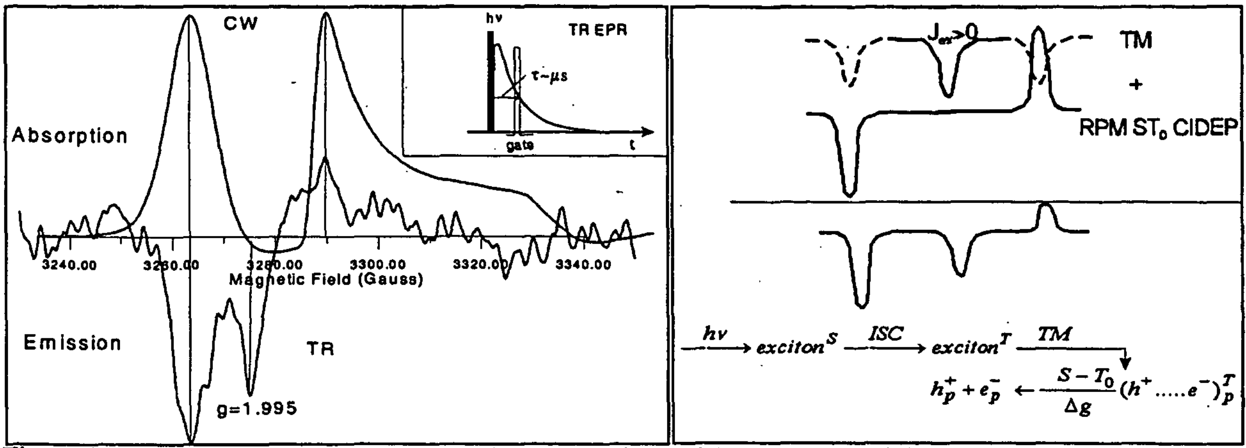

Figure 2 Comparison between integrated continuous light-induced (upper trace) and time-resolved pulsed laser-induced (lower trace) EPR spectra from 4nmTiO_2 modified with ascorbate. The lower trace was obtained with a 550 nm laser (laser intensity 10 mJ per pulse, 10 ns pulse duration), 1 μs after the laser pulse. Right section shows how triplet and radical pair mechanism of CIDEP in addition to fast exchange can contribute to the observed polarized spectrum.

modifier and the electrons in the conduction band of TiO_2. Full understanding and simulation of the events that take place in the early stages of charge separation is necessary for the design and optimization of an efficient artificial photosynthetic system. The initial spin population in photogenerated radicals that are precursors of fully charge separated states were investigated using time resolved direct detection (TRDD) EPR. Both steady-state and time-resolved EPR experiments reveal that photoinduced charge separation yields interacting electron/hole radical pairs with Chemically Induced Dynamic Electron Polarization (CIDEP) and EPR spectral features indicative of a range of dynamic properties. Features of Radical Pair Model (RPM) and Triplet Model (TM) CIDEP are observed in time-resolved experiments (fig 2). Evidence of a fast exchange in the radical pair is indicated by the presence of a central line at the midpoint of electron and hole resonances, an intermediate that was not observed in steady state measurements. The observation of this signal at $g_{ave}=(g_h+g_e)/2$ indicates that the origin of the signal comes from a strongly interacting delocalized precursor that experiences the influence from both environments, Ti d-orbitals and carbon centered π orbitals of the organic modifier. Excess emission via TM is consistent with triplet character of this exciton precursor of the observed electron-hole radical pairs and may account for the prolonged life of electron hole pairs in nanocrystalline TiO_2.

A subset of electron-hole radical pairs that survives in the millisecond regime at 4.2 K exhibits spin features characteristic of Correlated Radical Pair Polarization (CRPP). In these EPR spectra each transition is split into a doublet of absorptive and emissive lines. The A/E/A/E pattern of the photogenerated EPR signal reflects the existence of a weak interaction between photogenerated holes and electrons. These spectra indicate that upon localization of electrons onto Ti(III) centers, their interaction with holes localized on the organic modifier becomes weaker but still correlates the behavior of holes at the surface modifier and electrons in the TiO_2 lattice. This nonexcitonic interaction is manifest by observation of characteristic spin correlated radial pair electron spin polarization (CRPP), a signature for stabilized charge separation natural photosynthetic systems. We speculate that the triplet character of the surviving charge pairs may be both an indicator and a cause of the longer-lived charge separation. Similar spectra were obtained upon surface modification with other enediol ligands. Work in progress is focusing on the role of sequential electron transfer and electrochemical parameters on charge separation distances and spin polarization parameters when different biomolecules are attached to the appendant amino groups of surface modifiers.

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T. Rajh, O. G. Poluektov and M. C. Thurnauer
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Wednesday Evening

Session VII

Photoelectrochemistry

ENERGETICS AND DYNAMICS OF ELECTRON TRANSFER ACROSS CHEMICALLY MODIFIED INP/LIQUID JUNCTIONS

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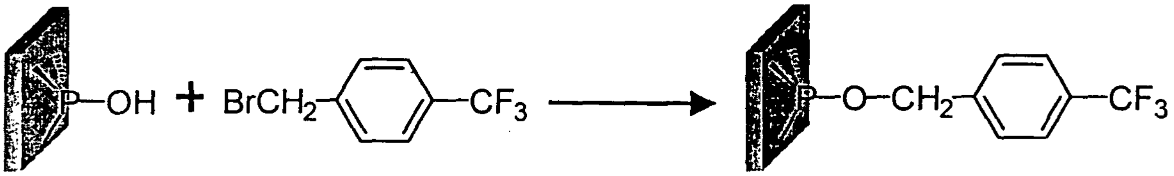
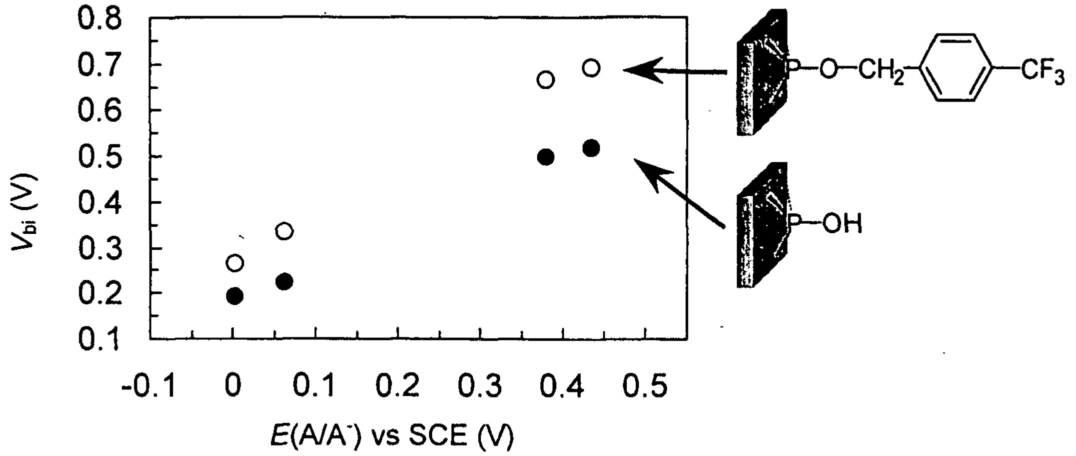
An extensive body of literature has been published describing techniques for chemically modifying semiconductor surfaces with organic reagents. However, the effects of these chemical transformations on the electrical properties of the underlying semiconductor are largely unknown and will likely determine/limit the application of these chemistries. Specifically, methods that introduce significant levels of electrical defects on the surface or compromise interfacial charge-transfer properties of the semiconductor are undesirable. We recently reported synthetic routes that allow attachment of a variety of functional groups to etched single-crystal InP surfaces. Benzyl halides, alkyl halides, silyl halides, and esters reacted readily with InP to yield covalently attached overlayers on the semiconductor surface. X-ray photoelectron spectroscopy revealed that the functionalization chemistry was consistent with the reactivity of surficial hydroxyl groups and monolayer coverages could be obtained:



The surface recombination velocity for InP modified with benzyl groups was reported to have a similarly low value (100 cm^{-1}) as that of the unmodified surface indicating that attachment of the organic overlayer was achieved with out compromising the electrical properties of the InP. We now report on the energetics and dynamics of interfacial electron transfer of these modified n-InP surfaces in contact with CH_3CN/THF electrolytes of varying electrochemical potential.

Interfacial electron-transfer rate constants were measured with steady-state current density vs potential techniques on n-InP/CH_3CN/THF-1,1'-dimethylferrocene$^{+/0}$ and n-InP/CH_3CN/THF-decamethylferrocene$^{+/0}$ contacts with both pristine and $-CH_2C_6H_4CF_3$ modified InP (111)B electrodes. In all cases bimolecular kinetic behavior was observed that was first order in the concentration of acceptors in the solution and first order in the concentration of electrons at the semiconductor surface. The measured charge-transfer rate constants, k_{ct}, for these systems were $\approx 10^{-16}$ - 10^{-18} cm^4 s^{-1} with the lower values corresponding to the chemically modified surfaces.

Differential capacitance vs potential measurements were used to determine the energetics of the charge-transfer process and to determine the surface electron concentration as a function of applied potential. For both the modified and pristine surfaces, the potential drop across the semiconductor space charge region scales linearly with the Nernst potential of the electrolyte indicating ideal behavior for these semiconductor/liquid junctions. The built in voltages obtained for the modified InP/liquid interfaces were 70 - 120 mV larger than those for the etched surfaces indicating that the band edges shift to higher energies with modification:



This shift in band edges is consistent with the proposed reaction scheme involving surface hydroxyl groups rather than alkylation of phosphorus lone pairs as previously proposed.

Future work will take advantage of the InP functionalization chemistry in the construction and characterization of well-defined metal-insulator-semiconductor (MIS) devices. The molecular level control provided by our InP chemistry will allow us to introduce electrically nondefective insulating layers and circumvent the problem of fermi level pinning associated with n-InP/metal junctions. The thickness of the organic insulating layer will be controlled by introducing alkyl chains of various lengths. Once the organic films are in place, metals of different work functions will be deposited by evaporation and/or electrodeposition to yield MIS structures. In the proposed devices electronic tunneling will occur through the organic film physically separating the semiconductor and metal. With current density vs potential measurements, the electronic coupling between the conduction band of InP and electrons in the metal will be probed as a function of the thickness of the insulating layer, the work function of the metal, and temperature. With our developments in InP surface chemistry, we should be able to manipulate, at the molecular level, the structure and function of these technologically important MIS devices.

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SYNTHESIS OF EXTREMELY SMALL InP NANOCRYSTALS AND ELECTRONIC COUPLING IN THEIR CLOSE-PACKED SOLID ARRAYS

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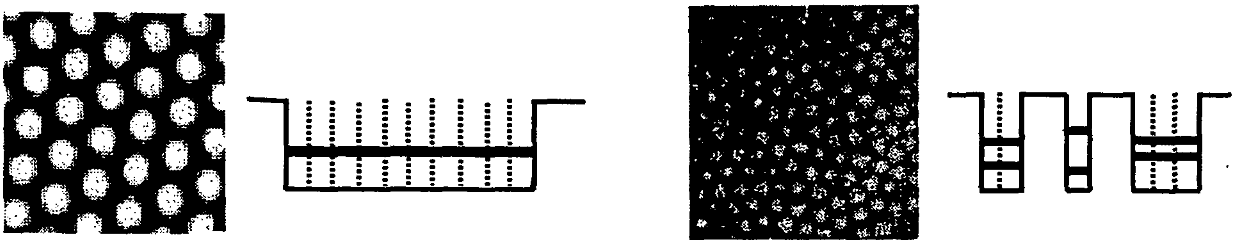
In order for quantum dot (QD) arrays to be useful in photon conversion devices, it is essential that the charge carriers that are photogenerated in the QDs can move through the array with good mobility. This requires good electronic coupling between QDs in the array. Transport studies of the close-packed arrays prepared with colloidal semiconductor QDs show that excitons formed by illumination are confined to individual QDs as a result of small overlap integral values between neighboring QDs. In colloidally-prepared QD arrays, the semiconductor QD cores are surrounded with organic ligands that behave as an insulator and create a large potential barrier between the QDs. Quantum mechanical coupling becomes only important when the potential barrier between dots is small and the inter-dot distance is short. It is important to find configurations in which electrons and holes are delocalized and extend out to the surrounding matrix. This work reports a study of electron delocalization in two QD configurations: (i) solid close-packed array of extremely small InP QDs with short inter-dot distances and (ii) core/shell QDs in which core InP QDs are overcoated with another semiconductor that forms a small potential barrier such that charge carriers extend outside the boundary of the core QDs.

Synthesis of extremely small InP QDs and solid close-packed arrays of these dots. Very recently we synthesized extremely small colloidal InP quantum dots (QDs) with diameters ranging from 15 to 23 Å in order to study optical properties of solid close-packed arrays of dots. To our knowledge, extremely small InP QDs with diameters below 25 Å have not yet been synthesized. For the synthesis of extremely small colloidal InP QDs we used the same starting reactants as for large QDs: indium salts and $P(SiMe_3)_3$[tris-(trimethylsilyl)phosphine]. A protic reagent, such as MeOH, was added to stop the growth of the QDs. The isolated QDs in dilute solution exhibit pronounced discrete absorption spectra, indicating a narrow size distribution with first exciton peaks in the range from 2.5 to 3.0 eV.

One of the most important objectives in the field of semiconducting nanostructures is to form superstructures of QDs that consist of QD arrays that may be ordered or disordered. We recently fabricated ordered arrays of larger InP nanocrystals (diameter > 25 Å) by self-organization upon slow evaporation of the colloidal solution. Transport studies of the close-packed arrays did not indicate the formation of conduction bands, and the solid close-packed array behaved as an insulator. This is connected with the fact that delocalization and band formation are very sensitive to the electronic properties of the quantum dots and the surrounding matrix.

For close-packed QD solids, a reduced bandgap should be expected if the electron or hole wave function extends outside the boundary of the individual QDs, resulting in inter-QD electronic coupling. In that case, absorption spectra can give information about the electronic structure of close-packed QD arrays, and these data will be less sensitive to trapped charge in surface states compared to conductivity and emission measurements.

Electron coupling between dots in close-packed solid films. We studied the optical properties of close-packed arrays of dots with small diameter and found that the absorption spectra of the close-packed solid films shift toward lower energies. Close-packed arrays produced from these dots showed a large red shift of the excitonic peaks in the absorption spectra when the inter-dot distance is very short. We adjusted the inter-dot distance by varying the length of the linear alkylamine molecule that was used as the colloidal stabilizer. For smaller QDs and shorter inter-dot distances (< 10 Å), the shift becomes larger and reaches hundreds of meV. In that case, new electron (and hole) states develop in the close-packed array. The spacing between single-dot electronic levels is reduced and results in the appearance of lower-energy band states. Figure 1 summarizes the simple coupling schemes between QDs for ordered superlattice arrays and for disordered arrys. For the former case, this effect is similar to the formation of minibands in a one-dimensional superlattice of quantum wells.



Perfect superlattice:

Disordered film:

Figure 1. Coupling in perfect superlattice and disordered film.

Core/shell QDs. Another parameter controlling electron transport is the potential barrier (bandgap offset) between dots and their matrix. We also tried to vary the barrier height of InP QDs to increase overlap integral values between neighboring QDs and enhance electron delocalization over the entire QD by preparation of core/shell QD structures [InP(core)/ZnCdSe$_2$(shell) QDs]. Our results show that lattice matching permits growth of ZnCdSe$_2$ concentric epilayer shells up to 50 Å in thickness on InP core quantum dots; the bandgap was shifted to lower energy. The electron is delocalized in this core/shell QD structure over the entire QD whereas the hole is localized within the core.

The studies described above are begining to reveal the importance of the potential barrier (bandgap offset) between dots and their matrix, and the energy required to dissociate an exciton and place the electron in one dot and hole in another dot, in order to induce conductivity and delocalization. Our future work will specifically address these matrix effects on delocalization of charge carriers in close-packed arrays.

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FOREWORD

The 24th Department of Energy (DOE) Solar Photochemistry Research Conference is being held June 3-7, 2001, at the Granlibakken Conference Center in Tahoe City, California. The meeting is sponsored by the Chemical Sciences, Geosciences and Biosciences Division, Office of Basic Energy Sciences.

The annual conference brings together grantees and contractors of the Chemical Sciences, Geosciences and Biosciences Division who are engaged in fundamental research on solar photochemical energy conversion. The conference affords a singular opportunity for coordination of the program, by fostering collaboration, cooperation, and exchange of information on recently completed work, research in progress, and future plans. The synergy that is achieved involving investigators from diverse disciplines is a strength of the program.

Solar photochemical energy conversion is a long-range option for meeting the world's energy needs. It offers an alternative to solid state, semiconductor photovoltaic cells. In the DOE solar photochemistry research program, molecule-based biomimetic systems and photoelectrochemical methods are explored with the goal of providing the knowledge base needed for future technologies in conversion of light energy to chemical energy. Biophysical studies on photosynthetic antennas and reaction centers provide molecular design criteria for efficient light collection and charge separation in model systems. Studies on electron and energy transfer in the condensed phase explore fundamental concepts in charge separation. Inorganic and organic photochemical studies provide information on new chromophores, donor-acceptor molecular assemblies, and photocatalytic cycles. Photochemical reactions are investigated in nanoscale heterogeneous environments, such as zeolites, inorganic multilayer films, dendrimers, silica gel, and liposomes. Photoelectrochemical energy conversion is explored in fundamental studies of the semiconductor/liquid interface, colloidal semiconductors, and dye-sensitized solar cells.

The program features topical sessions on photosynthetic antenna complexes and synthetic light-harvesting arrays; porphyrins, carbon nanotubes, and nanoparticles; electron transfer and charge separation; charge separation in organized assemblies; photoelectrochemistry; and photochemical reduction of CO_2. Our special guest lecturer is Professor Martin Head-Gordon of Lawrence Berkeley National Laboratory who will discuss theoretical calculations on excited states of large molecules. In this volume may be found the program, abstracts of the 29 formal presentations, 42 poster abstracts, and an address list for the 86 participants.

Special thanks are due to John Otvos and Marilyn Taylor, formerly of the Calvin research group, who emerged yet again from retirement to run this conference, and to Bill Parson and his staff at Granlibakken for their gracious hospitality. Andreene Witt of the Oak Ridge Institute of Science and Education is gratefully acknowledged for preparation of this volume. The success of the conference, notwithstanding, is due to all of the participants for sharing their expertise and experience in pursuit of common research goals.

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

Thursday Morning

Session VIII

Carbon Dioxide Photoreduction

PHOTOCHEMISTRY IN FRAMEWORK TRANSITION METAL SIEVES

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A major obstacle towards progress in visible light-driven synthesis of everyday chemicals and fuels is the lack of photoreactors with robust chromophores and redox centers of appropriate wavelength response and redox energetics. We are exploring the constrained environment of microporous solids, combined with the unique photoredox properties of framework transition metals for accomplishing demanding photosynthetic transformations relevant to the manufacture of industrial chemicals and for fuel synthesis. Our recent effort has focussed on exploring the reactivity of excited framework metal centers at the gas-micropore interface using small molecules as chemical probes and time-resolved FT-IR spectroscopy for detecting and identifying transient redox intermediates. In a parallel effort, we have established the primary products of CO_2 and CO photoreduction by UV light in framework Ti silicate sieve, and begun to explore visible light-absorbing redox centers in these materials.

Time-resolved FT-IR study of LMCT-induced photoredox chemistry of O_2 and CH_3OH in $FeAlPO_4$ sieve

Excited ligand-to-metal charge-transfer states of framework metals have a favorable electron distribution for initiating electron transfer chemistry of adsorbed reactants. Essential for designing photochemical synthesis in transition metal sieves is knowledge of the redox potential of such LMCT-excited centers and a detailed mechanistic understanding of how the adsorbed reactants interact with the framework redox sites. Taking O_2 as acceptor and CH_3OH as donor, we have elucidated the photoredox chemistry at the $Fe^{+III}\text{-}O^{-II} \rightarrow Fe^{+II}\text{-}O^{-I}$ LMCT transition of framework Fe centers in the large pore $FeAlPO_4$-5 sieve. In-situ monitoring of the $CH_3OH + O_2$ photoreaction (and ^{13}C, ^{18}O, or D labeled reactants) by static FT-IR spectroscopy revealed the 4-electron transfer products HCO_2H (HCO_2^-) and H_2O as the only observed species even at temperatures as low as 173 K. A comprehensive time-resolved study of the reaction by step-scan and rapid-scan FT-infrared spectroscopy, details of which are presented in the poster by Y.H. Yeom, showed HO_2CH_2OH as the main 2-electron transfer intermediate. It rearranges in 4 seconds to HCO_2^- and H_2O (250 K), and is formed within microseconds after photo-initiation of the redox reaction. The latter result implies that transient HO_2CH_2OH originates from direct combination of HOO and CH_2OH radicals, the expected one-electron transfer intermediates formed from O_2^- and CH_3OH^+. The finding constitutes the most conclusive evidence yet of direct electron transfer from transient Fe^{+II} to O_2. Since E° of O_2 is -0.3 V (and rather independent of the surrounding medium), it suggests that the reduction potential of Fe centers at the gas-micropore interface lies at least half a Volt more negative than the conduction band edge of dense phase Fe_2O_3 particles. This reflects most likely the less stable tetrahedral coordination into which Fe centers are forced by the aluminophosphate framework. The finding that photo-reduced metal centers at the gas-micropore interface are substantially stronger reductants than the conduction band electrons of the corresponding semiconductor material reveals an important advantage of microporous framework materials for conducting demanding photoreductions.

Our recent detection of the first small transient radicals in a microporous solid by step-scan FT-IR spectroscopy has revealed surprisingly long lifetimes of tens to hundreds of microseconds, even at room temperature (CH_3CO, HCO). While conducting these studies, we have established methods for recording transients of irreversible reactions in static samples with a time resolution as high as 10 nanoseconds. This has opened up the search, now underway, for HOO and CH_2OH radicals of the $CH_3OH + O_2$ system in $FeAlPO_4$ sieve, and a method to determine how these one-electron transfer products interact with the metal centers.

Mechanistic study of CO_2 photoreduction in Ti silicalite sieve

Understanding of the elementary steps of UV light-induced reduction of LMCT-excited Ti centers in framework substituted Ti silicalite (TS-1) is expected to furnish crucial insights for the selection of new framework metals and pore structures suitable for CO_2 activation with longer wavelength photons. However, the mechanism of CO_2 photoreduction in Ti containing molecular sieves remains unknown as no in-situ monitoring of such reactions has thus far been attempted. We have conducted a FT-IR spectroscopic study of the photoreduction of CO_2 in TS-1 sieve using CH_3OH as electron source. Methanol was chosen as donor because the 2-electron transfer reaction of CO_2 and CH_3OH involves endoergicities that, in principle, render the reaction accessible by visible light. TS-1, synthesized and characterized in our laboratory (including characterization by XANES spectroscopy at the ALS) was loaded with CO_2 and CH_3OH gas, and photo-reaction initiated by 266 nm excitation of the Ti^{+IV}-O^{+II} -> Ti^{+III}-O^{-I} LMCT transition. Infrared difference spectroscopy revealed growth of HCO_2H, CO and HCO_2CH_3. No reaction was observed in neat silicalite sieve, which confirms that the Ti centers are acting as chromophores and redox initiators. The origin of the products was elucidated by photolysis experiments with $C^{18}O_2$, $^{13}CO_2$, and $^{13}CH_3OH$. Carbon monoxide was found to originate from CO_2, but the induction behavior of its growth indicates that it is produced by secondary photolysis of HCO_2H. We conclude that CO_2 photoreduction at LMCT-excited framework Ti centers results in single photon-induced 2-electron reduction of CO_2 to HCO_2H, and not CO, as previously speculated by other groups. Concurrently, CH_3OH is oxidized to $CH_2{=}O$, which undergoes Tishchenko dimerization to yield HCO_2CH_3. The key result of this study is that C-H bond formation occurs in the initial steps of the photoactivation of CO_2 at the gas-solid interface, and O atom abstraction does not take place. The result constitutes the first insight into the primary steps of CO_2 photoreduction in a Ti molecular sieve.

Visible light absorbing redox centers in Ti silicalite sieve

Hydrogen peroxide is a possible donor for CO_2 photoactivation under visible light as reduction to formic acid involves an endoergicity of 39 kcal mol^{-1}. H_2O_2 loaded into TS-1 gives rise to a LMCT absorption with a tail extending beyond 500 nm and a maximum between 350 and 400 nm depending on experimental conditions. We have begun to investigate the photochemical properties of this visible LMCT absorption and established that it is very efficiently photobleached under concurrent decrease of an infrared band at 837 cm^{-1}. The chromophore is attributed to a cyclic TiOO (peroxide) moiety of framework Ti formed by the reaction of adsorbed H_2O_2 with framework $(O\text{-})_3Ti\text{-}OH$ centers. Experiments with the goal of determining the redox properties of the excited LMCT state of the TiOO moiety are in progress.

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REDOX REACTIONS OF METALLOPORPHYRINS IN CATALYZED REDUCTION OF CARBON DIOXIDE

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The role of highly reduced metalloporphyrins (MP) and related metal complexes as catalysts for reduction of carbon dioxide in homogeneous solutions is studied. In early experiments we studied the stepwise reduction of iron and cobalt porphyrins by photochemical and radiation chemical methods, using the water soluble complexes of TSPP (meso-tetrakis(4-sulfonatophenyl)porphyrin) and the three isomeric TMPyP (meso-tetrakis(N-methyl-X-pyridinium)porphyrin) and the water insoluble TPP (tetraphenylporphyrin) and its phenyl-substituted derivatives. All the metalloporphyrins were reduced to $M^{II}P$ and then to $[M^{I}P]^-$ (the peripheral charges of the water soluble porphyrins are neglected in this notation), but further reduction was necessary before the complex reacted with CO_2. The reactive species were identified as $[M^0P]^{2-}$. Catalyzed photochemical reduction of CO_2 to CO and formate was confirmed with FeP and CoP in acetonitrile or dimethylformamide solutions containing triethylamine (TEA).

The photochemical yield was increased by adding p-terphenyl (TP) as a sensitizer. This compound forms an excited state that is rapidly quenched by TEA to produce the radical anion, $TP^{\bullet-}$, which can reduce the metalloporphyrins to their $[M^0P]^{2-}$ state. The rate constants for these reactions, determined by pulse radiolysis, were essentially diffusion-controlled, close to 1×10^{10} L mol^{-1} s^{-1} for both $M^{II}P$ and $[M^{I}P]^-$. Direct reaction of $TP^{\bullet-}$ with CO_2 is very slow.

Photoreduction of CO_2 catalyzed by metalloporphyrins was accompanied by hydrogenation and degradation of the macrocycle, a side reaction that limits the catalytic process. Therefore, we examined related complexes that may exhibit a higher catalytic activity or higher longevity and also tested whether a catalytic process takes place with the metal ions released from the porphyrin when the macrocycle is decomposed.

Experiments in the same medium (organic solvent, amine, p-terphenyl, CO_2) using Fe and Co salts instead of their porphyrin complexes indicated that ferrous ions in this medium formed complexes with the amines, were reduced by the $TP^{\bullet-}$ radical anions, and catalyzed reduction of CO_2 until competitive binding of CO limited the process. On the other hand, cobalt ions did not catalyze the reduction of CO_2 in this medium.

As to macrocyclic complexes other than porphyrins, we examined phthalocyanines and corrins and have begun experiments with corroles. Phthalocyanines have a more highly aromatic structure and are known to be more resistant to degradation, corrins and corroles have a smaller macrocycle cavity (missing one meso bridge) but corrins have only 6 double bonds, i.e. the macrocycle is more saturated than that in corroles (10 double bonds) or porphyrins (11 double bonds).

Cobalt and iron phthalocyanines ($M^{II}Pc$) were reduced to $[M^{I}Pc]^-$, which did not react with CO_2. Reduction of $[Co^{I}Pc]^-$ formed a product which was characterized as the radical anion, $[\mathrm{Co^{I}Pc^{\bullet -}}]^{2-}$, on the basis of its absorption spectra in the visible and IR regions. This species was stable under dry anaerobic conditions and reacted rapidly with CO_2. Catalytic formation of CO and formate was confirmed in photochemical experiments. To study the mechanism of the CO_2 reduction, an attempt was made to produce the reactive species within a short pulse and to follow its subsequent reaction with CO_2. The mono-reduced species formed from $[\mathrm{Co^{I}Pc}]^{-}$ was unstable under pulse radiolysis conditions but was longer-lived under laser flash photolysis conditions. Therefore, we utilized the latter technique (with E. Fujita and B. Brunschwig) to examine the reaction of this species with CO_2. The results indicate that the interaction of this species with CO_2 is either too weak or too slow to detect in these experiments, where a competing reaction with protons predominates and is unpreventable in such an experiment. This conclusion of weak CO_2 binding to the doubly reduced $[\mathrm{Co^{I}Pc^{\bullet -}}]^{2-}$ complex is in contrast with earlier observations of strong CO_2 binding to Co(I) complexes of flexible (saturated) macrocycles like cyclam. The extended π-system of the phthalocyanine can better accommodate negative charge donated from the reduced metal center, which reduces the charge on the metal that can be back donated to the CO_2. Furthermore, the relatively rigid planar structure of the phthalocyanine and the consequently weaker axial ligation leads to the weak binding of CO_2. The photochemical formation of CO suggests that such binding does take place, but this binding does not compete favorably with the protonation reaction leading to hydrogenation of the macrocycle.

Similar studies with cobalt corrins showed that these complexes are far more efficient than cobalt porphyrins or phthalocyanines in catalyzing the photoreduction of CO_2 under identical conditions and that the corrins persisted in solutions to provide much higher total yields of CO and formate. These finding may be explained by the more flexible structure of the corrin macrocycle, due to the smaller number of double bonds, which permits stronger binding of CO_2. Nevertheless, this process also reached an eventual plateau, due to degradation and competitive CO binding, as in the case of the metalloporphyrins.

Studies with iron and cobalt corroles were undertaken because this macrocycle has been shown to stabilize the higher metal oxidation states and it was speculated that reduction of CO_2 might be effected by the M(I)P rather than M(0)P and that M(I)P will be less susceptible than M(0)P to protonation on the macrocycle. This speculation was based on the behavior of the oxidation products, while the reduction products have not been studied before. Therefore, we began a careful examination of the reduction products of iron and cobalt corroles by photochemical and electrochemical methods (with Z. Gross and E. Fujita). The results indicate that Fe(I) and possibly Co(I) corroles react with CO_2 and produce CO. Further experiments are underway.

Preliminary experiments were carried out on the photoreduction of CO. Photolysis of ferrous ions in MeCN/TEA/TP/CO solutions led to consumption of CO. Another avenue being explored is the insertion of CO into hydridorhodium porphyrins. Photolysis of CO-saturated $\mathrm{Rh^{III}}$-porphyrin solutions containing TEA and TP produced $\mathrm{Rh^{I}}$-porphyrins and in the presence of acetic acid it produced the hydride ($\mathrm{HRh^{III}P}$). Further photolysis led to consumption of CO. The products and mechanism are under study.

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TRANSITION METAL COMPLEXES IN PHOTOCONVERSION

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Homogeneous Reduction of Water and Carbon Dioxide at Metal Centers. Photogeneration of fuels from aqueous media is attractive, because water provides an inexpensive source of both protons and electrons, along with the environmentally benign co-product O_2. We have used pulse radiolysis, photochemistry, and a range of spectroscopic and analytical techniques to carry out mechanistic studies of aqueous systems that provide insight into some of the reactions and species that can be involved in using transition metal complexes as catalysts for homogeneous generation of H_2 from water and reduction of carbon dioxide to methanol.

Metal hydride complexes can deliver hydrogen to a carbon substrate as a proton, a hydrogen atom, or as a hydride anion. We have used pulse radiolysis of aqueous solutions of the hydride complexes $(C_5H_4CO_2H)WL(CO)_2H$ (L = CO, PMe_3) to study H-atom transfer from the metal hydride to saturated carbon radicals. Reactions of the hydride complexes with the carbon-centered radical for tert-butanol and the α-hydroxy radicals from ethanol and 2-propanol radicals ranged from $(0.9 \text{ to } 4.8) \times 10^8$ and $(0.3 \text{ to } 0.6) \times 10^8\ M^{-1}\ s^{-1}$ for $(C_5H_4CO_2)(CO)_3WH^-$ and $(C_5H_4CO_2)(PMe_3)(CO)_2WH^-$, respectively. While the transition-metal based hydrogen atom self-exchange process is rapid ($>10^6\ M^{-1}s^{-1}$ at 25 °C), the carbon-centered process is not. Thus these rate constants, recorded for highly exoergic reactions, illustrate the difficulty of pursuing reduction strategies in which the intermediate carbon fragments are not stabilized through bonding to a transition-metal center.

The hydride complex $(C_5H_4CO_2H)(CO)_3WH^-$ is reduced by e_{aq}^- ($k = 1.2 \times 10^{10}\ M^{-1}s^{-1}$). The only transient observed is the metal radical, which was observed to dimerize with $k = 2.4 \times 10^9\ M^{-1}\ s^{-1}$. The lifetime of the primary reduction product $(C_5H_4CO_2H)(CO)_3WH^{2-}$ is thus very short ($<10^{-7}$s) and formation and release of H_2 from this transient must occur on the same time scale. A dihydride/dihydrogen intermediate is strongly implicated.

Potential Intermediates in *CO_2-Reduction Systems.* Of importance to carbon dioxide reduction by more than two equivalents is the reactivity of complexes in which the carbon ligand is progressively more reduced:
CoL(**CO_2**), Co(**CO**), CoL(**CHO**) or CoL(**$CH(OH)_2$**), CoL(**CH_2OH**), CoL(**CH_3**).
The hydroxymethyl complex was prepared by addition of the photogenerated CH_2OH radical to the cobalt(II) macrocycle *meso*-CoL^{2+} (L = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene) in 0.1 M perchloric acid and characterized by x-ray crystallographic studies of its crystals and spectroscopic characterization of

solutions and solid. Acidic aqueous solutions are fairly stable and the complex decomposes, with formaldehyde elimination, by a base-catalyzed pathway. The products of this stage are the hydride complex, meso-CoL(H)$^{2+}$, and CH_2O. In subsequent stages, *meso*-CoL^{2+} and H_2 form via a pathway second order in the hydride complex and inverse first order in hydrogen ion. This rate law is consistent with reduction of the hydride by the cobalt(I) complex to yield CoL(H)$^{+}$ which then adds a proton to form a dihydride/dihydrogen complex from which H_2 is released. Thus, as for the tungsten hydrides (above), hydrogen formation occurs by electron transfer to a metal hydride, followed by protonation, H_2 formation and release.

Mixed Valence Systems in the Crossover Regime. Understanding and modeling of charge transfer spectra and electron transfer rates are profoundly intertwined. The electronic coupling between donor and acceptor sites determines whether a reaction is nonadiabatic or adiabatic and can, in addition, lead to significant stabilization of the donor-acceptor pair. Moderate to strong electronic coupling can be probed through the charge transfer spectrum of the donor acceptor pair and very strong electronic coupling can be probed through thermodynamic studies of the system. In recent work we have examined a series of mixed valence ruthenium complexes, for example $(NH_3)_5$Ru-bridge-Ru$(NH_3)_5$ in which donor D = Ru(II) and acceptor A = Ru(III). Using a two-state model as a framework, we have probed the Class II (moderate electronic coupling H_{ab}) to Class III (delocalized system, $H_{ab} > \lambda/2$) transition.

Within the two-state model,[1] the following are predicted for a symmetric species: The Class II to III transition occurs when $H_{ab} = \lambda/2$. The charge transfer transition occurs at $h\nu_{max} = \lambda$ for Class II systems (double minimum), regardless of the magnitude of H_{ab}. Although the splitting of the ground-excited state curves increases with H_{ab}, this is splitting is exactly offset by the reactant and product minima moving closer together. The experimental quantity $\Gamma = 1 - (\Delta\nu_{1/2})/(2310\nu_{max})^{1/2}$, where $\Delta\nu_{1/2}$ is the full width at half intensity at ν_{max}, provides a useful measure of the extent of electronic delocalization. Γ is zero for a very weakly interacting system and 0.50 for a system at the Class II/III transition. For a homologous series of mixed-valence dimers, Γ increases linearly with H_{ab} estimated from thermodynamic parameters of the systems.

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CARBON DIOXIDE UTILIZATION: PHOTOCHEMICAL CONVERSION AND A REPLACEMENT FEEDSTOCK FOR ISOCYANATE SYNTHESIS

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Photochemical splitting of carbon dioxide to carbon monoxide and oxygen is a conceptually simple means of recycling carbon since CO can be used both in fuel cells and as a feedstock in the manufacturing of liquid fuels and specialty chemicals. The key to Part I of this project is the design of multi-electron inorganic catalysts that catalyze the reduction of CO_2 to CO extremely close to the thermodynamic potential for this process.

The 48 e- *triangulo* trinickel cluster cations $[Ni_3(\mu_3\text{-}CNR)(\mu_3\text{-}I)(\mu\text{-}dppm)_3]^+$ (R = alkyl, aryl; dppm = $Ph_2PCH_2PPh_2$) undergo reversible reduction to neutral, 49 e- species that in turn reduce CO_2 to a mixture of CO and CO_3^{2-} in anhydrous solvents. Reduction potentials for these compounds fall in a narrow range of -1.08 V to -1.18 V vs. SCE. Clusters with reduction potentials at the more cathodic end of the range catalyze the reductive disproportionation of CO_2 to CO and CO_3^{2-} at rates that are slow, but measurable by CV. The rates of electrochemical reduction of CO_2 by these nickel clusters are limited by the fact that these clusters operate by single electron redox cycles, while CO_2 reduction is a two electron process. Chemical modification of the face-capping isocyanide ligands allows the introduction of a "reservoir" for an additional electron, potentially enabling the clusters to function as two-electron catalysts. Specifically, several new trinuclear nickel clusters of the form $[Ni_3(CNR)(I)(dppm)_3]^+$, where dppm = $Ph_2PCH_2PPh_2$ and CNR = 4-pyridylisocyanide or 4-pyridylmethylisocyanide and their *N*-substituted derivatives, were synthesized and fully characterized, and their reduction potentials determined by cyclic voltammetry (CV). Electrophilic attack at the ring nitrogen atom in $[Ni_3(CN(CH_2)_nC_5H_4N)(I)(dppm)_3]^+$ (n = 0, 1) has been employed to prepare the dicationic clusters $[Ni_3(CN(CH_2)_nC_5H_4N\text{-}E)(I)(dppm)_3]^{2+}$ (n = 0, 1; E = Me, Re(bpy)$(CO)_3$) in which the pyridinium or Re centers can act as the electron "reservoir." These clusters are not significantly more active in CO_2 reduction than the best 1e- catalysts. This appears to be a result of the more anodic reduction potentials for the dicationic clusters.

An alternative strategy developed for formation of 2e- catalysts entails linking two trinickel clusters via a diisocyanide bridge. In these cases, there is essentially no electronic communication between the two linked clusters, as determined by EPR spectroscopy and CV. Several such dimers-of-trimers are thermodynamically competent to reduce CO_2 to CO and CO_3^{2-}, and do so when the diisocyanide linker is rigid, such as 4,4'-biphenyldiisocyanide. Surprisingly, when the linker is the flexible chain $CN(CH_2)_6NC$, C-C bond formation occurs and the reduction product is oxalate, $C_2O_4^{2-}$, rather than the expected 1:1 mixture of CO and CO_3^{2-}. This is clearly indicative of a change in mechanism. Experiments are under way to elucidate the effects of chain length, rigidity, and geometry on product selectivity.

Covalent attachment of the clusters to an electrode surface through a bifunctional isocyanide capping ligand provided additional mechanistic information. Although the tethered clusters retain their reduction potentials of *ca.* -1.2 V vs. SCE, near the optimal value for efficient CO_2 reduction, they exhibited no reactivity toward CO_2. This suggests that the active site for CO_2 reduction by the clusters is on the face containing the isocyanide ligand, which is not accessible to CO_2 when the clusters are bound to an electrode surface. This finding necessitates the synthesis of a new class of clusters having the form $[Ni_3(CNR)(X)(dppm)]^+$, where X = alkyl/arylthiolate or -selenolate, in which the clusters can be tethered to the electrode surface through the X functionality, leaving the isocyanide-capped face accessible to the bulk solution. Attempts to abstract iodide from the cluster $[Ni_3(\mu_3\text{-}I)_2(\mu\text{-dppm})_3]$ to open a face for introduction of aryl thiolate surface tethers resulted in oxidation of the cluster, with one exception. Treatment with thallium triflate in acetonitrile led instead to insertion of Tl into the Ni-I bonds on one face, and generated a symmetrically bridging TlI-capped cluster cation, $[Ni_3(\mu_3\text{-}TlI)(\mu_3\text{-}I)(\mu\text{-dppm})]^+(OTf)^-$. Development of a more general route to the desired cluster complexes is an area of current investigation.

The second focus of this project is the development of multiple bond metathesis chemistry for the synthesis of isocyanates from CO_2. Isocyanates are important industrial chemicals used mostly in the preparation of polyurethanes. Isocyanates are presently synthesized from phosgene and primary amines. The replacement of phosgene by CO_2 would significantly decrease both costs and environmental risks. Our group's earlier work has shown that both mononuclear and dinuclear nickel isocyanide complexes can react with CO_2 via O atom/NR group metathesis to form nickel carbonyl complexes and isocyanates. Besides nickel isocyanide complexes, there are numerous other isocyanide complexes that appear to have sufficiently well developed sp^2 lone pair character at nitrogen such that metathesis with CO_2 would be expected. For example, the group 6 metallocene isocyanides $Cp_2M(CNR)$ (M = Mo, W) exhibit structures with significantly bent isocyanide ligands and reactivity consistent with a lone pair at nitrogen. The chemistry of these complexes with CO_2 is under investigation.

A series of metallocene isocyanide complexes $Cp_2Mo(CNR)$ (R = *t*-Bu, 2,6-$C_6H_3Me_2$) have been synthesized by photolysis of Cp_2MoH_2 in the presence of different isocyanides. Reaction of Cp_2MoCN-*t*-Bu with 1 atm of CO_2 has been carried out. Although the multiple bond metathesis has not yet been observed, which maybe due to the steric hindrance of *t*-Bu group, we do find the high reactivity of the metal center toward electrophiles. For example, the complex Cp_2MoCN-*t*-Bu reacts with even trace amounts of acid to form molybdenocene isocyanide hydride cation. Future work will address the use of less sterically hindered isocyanide ligands such as methyl isocyanide and different reaction conditions such as liquid or super critical CO_2.

We have also examined the reaction of Aresta's complex, $Ni(PCy_3)_2CO_2$, with aza-Wittig reagents to prepare the corresponding isocyanates. In this case, the iminophosphoranes react by multiple bond metathesis with *both* coordinated and free CO_2 to form isocyanates and phosphine oxide, very rapidly. Future work will explore the use of less reactive organoimido donors such as imines or even amines, and supercritical CO_2 as both reactant and reaction medium for this promising reaction to prepare isocyantes directly from CO_2.

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Posters

SYNCHROTRON-BASED MICROCRYSTALLOGRAPHY OF PORPHYRIN RADICALS

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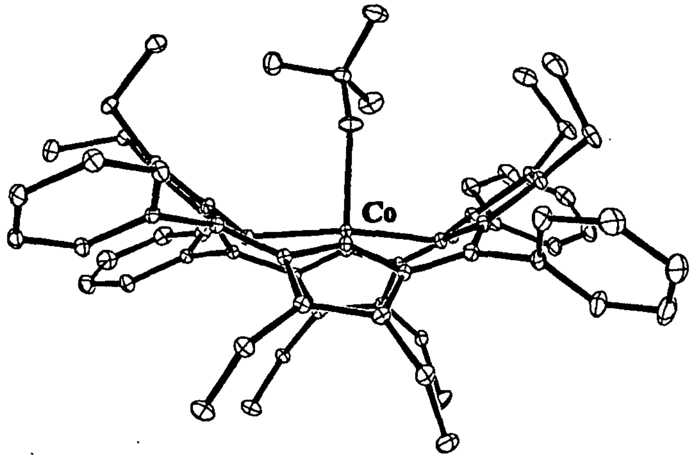
The brightness of synchrotron X-rays combined with area detectors allows short data acquisition times and the use of extremely small crystals. (Crystals of some finite size are an obvious but nontrivial requirement for crystallography.) This microcrystallography technique, using the Brookhaven National Laboratory National Synchrotron Light Source, is particularly well-suited for inherently unstable porphyrin free radicals and yields high precision data which map in detail the electronic and structural consequences of electron transfer in porphyrin models of the radicals generated in photosynthetic reaction centers and in enzymatic catalysis. Several examples of the stereochemical consequences of oxidation in porphyrin π-cation radicals (changes in the π bonding pattern and in conformations) will be presented including a $ZnOEP^{+}\bullet ClO_4^{-}$ π-π dimer, an $Fe(III)OETPP^{2+}\bullet 2ClO_4^{-}$ radical, two different $Co(II)OETPP^{+}\bullet ClO_4^{-}$ radicals, and a high spin $(py)_2Ni(II)OETPP^{+}\bullet ClO_4^{-}$ radical.

(Abbreviations used: OEP=2,3,7,8,12,13,17,18-octaethylporphyrin,OETPP=2,3,7,8,12,13,17,18-octaethyl-5,10,15,20-tetraphenylporphyrin, py=pyridine.)



Edge-on view of the molecular structure of the $Co(II)OETPP^{+}\bullet ClO_4^{-}$ π-cation radical at 20K. Thermal ellipsoids enclose 50% probability. Estimated standard deviations are 0.001Å for Co-N distances and 0.002Å for a typical C-C or C-N bond.

PHOTOINDUCED CHARGE SEPARATION IN LIQUIDS

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Long Distance Coupling of "Random" Donor-Acceptor Pairs. The separation of free radical ions in electron-donor-acceptor (**EDA**) systems of alkylbenzenes and tetracyanoethylene (**TCNE**) exhibit a remarkable wavelength dependence in dichloromethane, a medium polarity solvent. We propose that weak absorption by long-distance, unassociated or "random" **D......A** pairs (separated by ca. 1 nm or more) is mainly responsible for the free radical ion quantum yield. The ion yield may increase by as much as 100-fold on the short wavelength side of a charge transfer absorption band. The photoexcitation of ground state **EDA** complexes plays little role in this process. A model for the wavelength dependence of the free ion yield is developed for four systems in which differing degrees of **EDA** complex formation are present: 1,3,5-tri-*tert*-butylbenzene-**TCNE** in which only random pairs exist due to the bulky groups on the electron donor, and toluene-**TCNE**, 1,3,5-triethylbenzene-**TCNE** and 1,3,5-trimethylbenzene-**TCNE**. Mulliken-Hush theory is used to determine the excitation distance distribution for random pairs at different wavelengths. For each absorption distribution, free radical ion yields at different wavelengths are then calculated using Onsager's result for the ion separation probability. Encouraging agreement between the calculated yields and our experimental results is obtained with β values of about 0.8 $Å^{-1}$. So far as we are aware, this is the first time that photoexcitation of unassociated donor/acceptor pairs has been invoked as the source of separated radical ion pairs.

Fluorescence Quenching. Radical ion and fluorescence quantum yields from the geminate ion pairs formed by electron-transfer quenching of the excited acceptor, 9,10-dicyanoanthracene (DCA) by aromatic electron-donors are measured in different solvents. The effects of driving force, steric substitution and solvent polarity on free ion yields are studied. From the comparison of the effect of energetic driving force on free ion yields and fluorescence quantum yields in different solvents, especially those of medium polarity, it is concluded that free ion yields are controlled by both recombination rate constants and the separation distance distribution of the initially formed geminate radical ion pairs. In dichloromethane, the recombination and free ion formation processes are directly observed by fluorescence lifetime and transient photocurrent measurement. The results indicate that free ion formation is faster than ion recombination. This is interpreted to mean that free ions and the geminate radical ion pairs that recombine via electron transfer have different histories. The recombination theory of Hong and Noolandi is useful, but lacks realism. We still seek a more appropriate theory.

ELECTROABSORPTION SPECTROSCOPY OF $(NC)_5Fe^{II}(CN)Ti^{IV}$ COMPLEXES

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The metal-to-metal charge transfer (MMCT) transition in $(NC)_5Fe^{II}(CN)Ti^{IV}(H_2O)_5$ and $(NC)_5Fe^{II}(CN)Ti^{IV}(Cp)_2Cl$ and the metal-to-particle charge transfer (MPCT) transition for $Fe^{II}(CN)_6^{4-}$ attached to a TiO_2 nanoparticle have been examined using electroabsorption (Stark) spectroscopy.

$$(NC)_5Fe^{II}(CN)Ti^{IV}L_n \xrightarrow{h\nu} (NC)_5Fe^{III}(CN)Ti^{III}L_n$$

Ground-excited-state dipole-moment changes, transition dipole-moments and absorption band maxima of the complexes have been determined. The $Fe^{II}(CN)_6^{4-}/TiO_2$ nanoparticle system exhibits a metal-to-particle charge transfer absorption at 400 nm. The two dimers feature a new absorption band at 395 ($Ti(H_2O)_5$) and 540 ($Ti(Cp)_2Cl$) nm that are assigned as MMCT transitions. The dipole-moment changes determined for the nanoparticle system is ~ 5 eÅ which yields a one-electron transfer distance that is very close to the Fe to Ti distance calculated for a hexacyano iron complex coordinated to a surface titanium through a cyanide ligand. The dimers show a dipole moment change of ~ 3 eÅ that corresponds to a charge-transfer distance that is shorter than the Fe–CN–Ti separation. The observed dipole moment change in the nanoparticle system suggests that the MPCT transition does not promote an electron into the conduction band of the TiO_2 particle but rather into an orbital that is localized at the Ti center attached to the $Fe(CN)_6$ moiety.

CAPTURING TRANSIENT MOLECULAR STRUCTURES DURING PHOTOCHEMICAL REACTIONS USING LASER PUMP X-RAY PROBE X-RAY ABSORPTION FINE STRUCTURE (XAFS)

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The photoexcitation causes displacement of electron densities within or among molecules, which consequently leads to nuclear movements. Such nuclear displacements often occur in transient states with short lifetimes. Knowing transient molecular structures during photochemical reactions is important for understanding fundamental aspects of solar energy conversion and storage. Fast X-ray techniques provide direct probes for these transient structures. Using X-ray pulses from a third generation synchrotron source, the Advanced Photon Source (APS) at Argonne, a laser pulse pump, X-ray pulse probe XAFS technique has been developed to capture transient molecular structures in disordered media with a current time resolution of 14-ns (a sextuplet pulse-cluster). We have carried out the following recent studies:

(1) Identifying the Transient Molecular Structure of the Photodissociation Product of Nickel-tetraphenylporphyrin with Piperidine Axial Ligands (*NiTPP-*L_2) [Science, **292**, 262 (2001)] The transient molecular structure of a reaction intermediate produced by photoexcitation of NiTPP-L_2 in solution was determined by XAFS data from the APS under a special timing mode operation. The XAFS measurements confirm that photoexcitation leads to the rapid removal of both axial ligands to produce a transient square-planar intermediate, NiTPP, with a lifetime of 28 ns. The transient structure of the photodissociated intermediate is nearly identical to that of the ground state NiTPP, suggesting that the intermediate adopts the same structure as the ground state in a non-coordinating solvent before it recombines with two ligands simultaneously to form the more stable octahedrally coordinated NiTPP-L_2.

(2) Determination of the Transient MLCT State Structure of Bis(2,9-dimethyl-1,10-phenanthroline)Copper(I) $[Cu(I)(dmp)_2]^+$ The structure of the photoexcited MLCT state $Cu(I)(dmp)_2BArF$ in toluene with a 40-ns lifetime at room temperature has been captured by the pump-probe XAFS at Cu K-edge (8.979 keV). The transition edge of the excited state is shifted to a higher energy, indicating a transient Cu(II) species as a result of the electron movement from the metal to the ligands. The XANES (X-ray absorption near edge structure) spectrum of the excited state reveals the change in coordination environment from a tetrahedral geometry in the ground state to a penta-coordinated geometry. The average Cu-N bond distance in the excited state is about 0.08 Å longer than that of the ground state.

Future studies include probing transient structures in electron donor-acceptor complexes and optical polarization selected XAFS (OPS-XAFS) using the same technique with singlet X-ray pulses on a time resolution of 100-ps.

PLATINUM DIIMINE COMPLEXES AND THEIR INCORPORATION INTO DYADS AND TRIADS FOR PHOTO-INDUCED CHARGE SEPARATION

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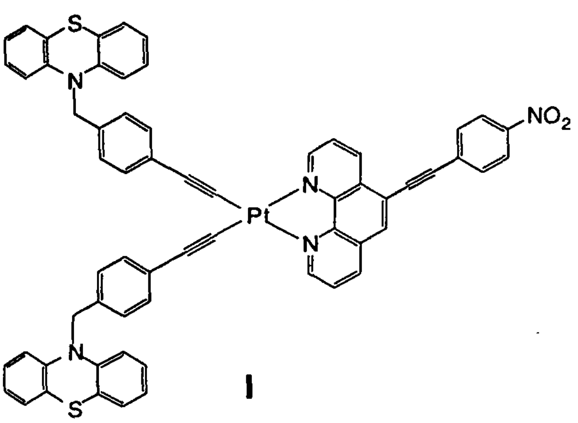
A continuing and important challenge remains the development of molecularly-based multi-component systems for light-to-chemical energy conversion. While considerable work has utilized porphyrins and d^6 diimine complexes as chromophores in these multi-component systems, less has been done with luminescent d^8 platinum(II) complexes of the formula Pt(diimine)L_2 where L_2 = dithiolate or bis(arylacetylide) and diimine = 2,2'-bipyridine, 1,10-phenanthroline or a derivative. Previously, we have demonstrated that these Pt(II) chromophores possess a long-lived charge-transfer to diimine excited state, with the directionality of the charge transfer making these systems of interest as the chromophore in multi-component constructions.



I

Recent efforts have focused on the synthesis and initial photophysical studies of molecular dyads and triads. The donor-chromophore-acceptor (D-C-A) triad **I** utilizes the Pt(diimine)(arylacetylide)$_2$ functionalized with an electron donor, phenothiazine, on the arylacetylide and an electron acceptor, nitrophenyl, on the diimine. The synthesis of **I** involves a multi-step sequence in which Pd-catalyzed Sonagashira-Hlagihara coupling reactions are used to build the connections between donor, acceptor and chromophore ligands. Chromophore emission from **I** is completely quenched and transient absorption studies of the triad reveal a charge separated state that forms within 15 ns and lives 70 ns in DMF and methylene chloride at 298 K following excitation at 405 nm. Model D-C and C-A dyads were also synthesized and their photophysical properties examined. Luminescence from these dyads is quenched completely or nearly so, but a charge separated state is not observed on the ns timescale. Efforts to synthesize a series of D-C-A triads where A corresponds to different acceptors and D is a Ru complex are in progress.

Other efforts have been directed toward the synthesis of water soluble Pt diimine(arylacetylide)$_2$ complexes for possible intercalation into DNA. Precursor complexes employing substituted 1,10-phenanthrolines and 2,2'-bipyridines as the diimine and 4-ethynylbenzaldehyde as the arylacetylide have been prepared. These complexes are emissive in acetonitrile at ambient temperature with excited state lifetimes of >100 ns. Water soluble derivatives of these complexes have been prepared by condensation with Girard's T reagent which is a hydrazide functionalized with a tetraalkylammonium salt. These dicationic products display aqueous solubility as well as enhanced solubility in polar aprotic solvents when compared to the parent compounds. Photophysical studies of these first water soluble Pt(diimine)(arylacetylide)$_2$ complexes are currently in progress.

ELECTRONIC PROCESSES IN INP QUANTUM DOTS: DYNAMICS OF CARRIER COOLING, CHARGE SEPARATION, AND CHARGE TRANSFER

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Owing to the high ratio of surface to interior atoms for colloidal quantum dots (QDs), which are typically grown to diameters of ≤ 80 Å, surface properties play an important role in determining their chemical and electronic properties. The surface becomes increasingly influential as the dot size decreases and the surface atom ratio increases. We have continued our efforts to understand the mechanics and dynamics of energy relaxation, charge separation, and charge transfer following photoexcitation of colloidal InP QDs in the size range of 30 Å to 50 Å diameter.

QDs offer promise as critical components of devices designed for solar energy conversion. Operation of such devices will depend centrally on electron energy loss mechanisms and dynamics. Research on colloidal CdSe QDs has indicated that electron-hole interactions allow electrons to cool efficiently in spite of the large intraband energy level gap separating the electronic states in the conduction band (CB). This large intra-band "gap" is the source of the postulated QD phonon bottleneck. Using sub-picosecond visible and infrared transient absorption spectroscopy, we have extended our measurements of InP QDs with adsorbed hole-scavenging molecules and with electrons injected from donors exterior to the QDs to investigate electron relaxation rates in the absence of holes. We use a technique based on dual pump pulses and a single probe pulse. An inter-bandgap pump pulse is followed by a delayed infrared pulse tuned to promote an electron from the lowest CB state to the next higher CB level. Probing the (inter)band-edge transmission versus time allows us to measure hot electron relaxation dynamics. Additionally, this technique affords us a method of studying the dynamics of carrier trapping by surface molecules, as well as the cooling rate of hot electrons injected from dye molecules.

The mechanisms of electron energy relaxation in InP and CdSe QDs were also determined by detailed measurements of the photoluminescence quantum yield as a function of excitation wavelength, particle size, capping groups, and temperature. The hypothesis that the quantum efficiency of electron relaxation to the emitting state is independent of the excitation energy is found to be violated and suggests slowed hot electron cooling. Comparison with molecular absorbers, for which Kasha's Rule for efficient relaxation is rarely violated, indicates that the excited state depopulation pathways for these QDs differ markedly from molecules.

We have begun exploration of the kinetics of electron transfer from various semiconductor QDs to nanocrystalline TiO_2. Of major importance is inter-particle distance, surface passivation of the quantum dots, interparticle binding molecules, and the degree to which inhibited hot electron cooling may affect electron transfer. The study of such systems provides insight into the relative rates of various deactivation pathways of electrons in quantum dots, and elucidates the factors necessary to make interparticle electron transfer competitive in these systems. Initial results show evidence of fast electron transfer from InP QDs to nanocrystalline TiO_2 particles.

DYNAMICS AND STRUCTURE OF MOLECULES IN MICELLES

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Fluorescence lifetime measurements of 2-ethylnaphthalene (2EN) probes in the cationic micelles tetradecyl-trimethylammonium chloride (TTAC), tetradecyl-trimethylammonium bromide (TTAB), dodecyl-trimethylammonium bromide (DTAB), and dodecyl-trimethylammonium chloride (DTAC) demonstrate the close proximity of the 2EN to the Br^- counter ions. The fluorescence lifetimes in TTAB and DTAB are much shorter than in TTAC and DTAC because of fluorescence quenching caused by the external heavy atom (Br^-) effect. These results indicate that 2EN resides to a substantial degree in the head group region of the micelles. However, detailed analysis of the fluorescence decays shows that the decays are non-exponential in TTAB and DTAB. For micelles with chloride counter ions, the fluorescence decays are single exponentials. Fluorescence measurements on non-micelle solutions with bromide ions are also single exponentials. The data were analyzed with a kinetic exchange model. The results indicate that 2EN is exchanged between the head group and core regions on a 5 to 10 ns time scale, depending on the micelle, and that at any given time ~80% and ~50% of the 2EN are found in the head group regions of the tetradecyl and dodecyl micelles, respectively.

Ultrafast optical heterodyne detected optical Kerr effect experiments reveal that orientational dynamics of 2EN heavily doped in the micelles (5, 15, and 25 2EN per micelles) have a complex time dependence that depends on the extent of doping. Heavy doping of molecules seems to modify the micelle structure, changing the orientational dynamics. The observed dynamics are distinct from those observed in liquid solution or pure 2EN.

Photoinduced intermolecular (donor/acceptor) electron transfer was studied both experimentally and theoretically for donors and acceptors located in the head group region of micelles. Fluorescence up-conversion and fluorescence yield measurements were performed to characterize photoinduced electron transfer from N,N-dimethylaniline (DMA) and N,N-dimethyl-1-naphtylamine (DMNA) to octadecylrhodamine B (ODRB) in DTAB, TTAB, and cetyl-trimethylammonium bromide (CTAB). The data were analyzed with a detailed theory that assumes a Marcus distance-dependent rate constant. The theory includes diffusion of the molecules in the head group region of the micelles. The theory also accounts for geometrical and dielectric properties of the 3-region micelle environment, and the solvent reorganization energy and free energy of transfer are calculated. Including local structure is required to fit the data, yielding some information about molecular organization in the head group region.

Ultrafast infrared vibrational echoes and vibrational pump-probe experiments were conducted on the OD stretching mode of methanol-OD in CCl_4 at concentrations that enabled the monomer and hydrogen bonded clusters to be studied. These are the first vibrational echo experiments on an alcohol and on H-bonded clusters. The experiments are examining hydrogen bond dynamics and how the dynamics change with the size of the H-bonded clusters. These initial experiments will be extended to water clusters in reverse micelles.

Poster # 7

ELECTRONIC COUPLING, ELECTRON DELOCALIZATION AND THE ELECTRON-TRANSFER PROPERTIES OF POLYPYRIDYL-RUTHENIUM MLCT EXCITED STATES

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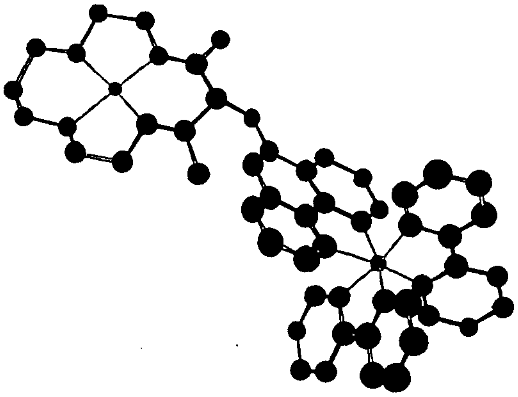
Nuclear reorganizational energies, the energy differences of electronic states and electronic coupling between donor and acceptor are widely recognized as factors that contribute to excited state electron transfer reactivity. The electronic delocalization that results when electronic coupling is very large can attenuate the reorganizational energy contributions. This is demonstrated in the marked variations in the relative intensity of vibrational fine structure in the 77 K MLCT emission spectra of a series of Ru(II)(bpy)(am[m]ine) complexes, and the observed behavior can be described with simple perturbation theory. More complicated situations arise when bpy is replaced by 2,3-bis(2-pyridyl)pyrazine (dpp), a ligand widely used in the construction of supramolecular arrays of metal complexes. Ab-initio calculations suggest that the LUMO of coordinated dpp correlates with LUMO+1 of pyrazine, not with the pyrazine LUMO. This inversion of LUMOs may account for some features of the MLCT spectroscopy of Ru-dpp complexes; e.g., two absorption bands that are close in energy and intensity in the monometallic complexes, a dominant low energy band of the dpp-bridged bimetallic complexes whose energy does not parallel the reduction potentials of the donor and acceptor and some aspects of the mixed valence absorptions may all be consequences of the metal/bridging-ligand orbital mixing. Electron transfer processes of the MLCT excited states tend to have small reorganizational barriers and often fall within the Marcus inverted region. We are beginning to capitalize on this in synthesizing bimetallic complexes in which inverted region-back electron transfer (to the ground state) is slow compared to electron transfer relaxation of the MLCT state. We are also beginning to document the extent to which inverted region electron transfer relaxation processes are facilitated by high frequency (N-H) vibrational modes that are not dominant in the vibrational fine structure.



Poster # 9

PHOTOCHEMICAL AND PHOTOPHYSICAL PROPERTIES OF fac-Re(I) TRICARBONYL COMPLEXES. A COMPARISON OF MONOMER AND POLYMER SPECIES WITH $Re^I(CO)_3phen$ CHROMOPHORES

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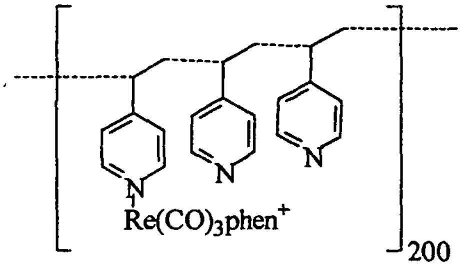
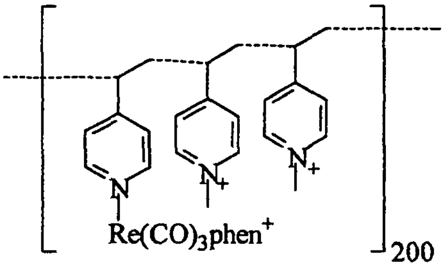
The photochemical and photophysical properties of a polymer containing nearly 200 pendant groups $Re(CO)_3(1,10\text{-phenanthroline})^+$ bonded to poly-(vinylpyridine)$_{600}$, (I), the methylated form of the polymer, i.e., with pendant N-methylpyridinium, (II), and a related monomer, $pyRe(CO)_3(1,10\text{-phenanthroline})^+$, were investigated in solution phase. In CH_3CN / H_2O mixtures, the Re(I) macromolecules behave as polyelectrolytes and their excited states oxidize electrostatically attracted ions, e.g., I^- or SO_3^{2-}, under conditions where $pyRe(CO)_3(1,10\text{-phenanthroline})^+$ does not react. Metal to ligand charge transfer excited states in (I) undergo intrastrand annihilation reactions and secondary photolysis more efficiently than in the monomer. By contrast to (I), charge separation is a process more important in (II) than the excited state annihilation.The MLCT excited states in the polymers react with methylviologen and 2,2',2"-nitrilotriethanol. These redox reactions caused intrastrand electron transfer processes with a complex kinetics. Mechanisms of the excited state annihilation and electron transfer processes in the polymer are proposed.



(I)



(II)

Poster # 10

DYE SENSITIZED SOLAR CELLS: NEW PERYLENE SENSITIZERS AND THE EFFCT OF UV ILLUMINATION ON SOLAR CELL EFFICIENCY

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The dye sensitized solar cell (DSSC) can achieve solar conversion efficiencies of 10%, and a recent analysis found the technology competitive with amorphous silicon. Although in theory there are many possible dye/semiconductor combinations, there is still only a single combination of components (TiO_2, N3 dye and I_3^-/I^- electrolyte) that actually achieves a competitive efficiency. Thus, learning to tune dyes to be more compatible with TiO_2 and vice versa - tuning the TiO_2 to be more compatible with certain dyes - is of interest. I will discuss both approaches.

We have for several years been exploring perylene derivatives as photosensitizers because they have excellent photophysical properties and are inexpensive. Our work began with perylene di- and monocarboximides (Figure 1a), and we showed they were good sensitizers for nanocrystalline tin oxide (SnO_2) but poor sensitizers of TiO_2. We have since applied a synthetic strategy of Langhals to prepare perylene sensitizers (example, Figure 1b) with properties more suitable to sensitizing nanocrystalline TiO_2. Our efforts have resulted in a second generation of perylene photosensitizers that have excellent compatibility with TiO_2. I will present synthetic details for the new sensitizers and describe their behavior in the DSSC.

We have also discovered that by illuminating a DSSC with ultraviolet (UV) light, dramatic increases in short circuit photocurrent and overall conversion efficiencies are observed (Figure 2). This technique has proved useful in optimizing a variety of sensitizers. Details of the UV effect will be discussed and results will be presented.

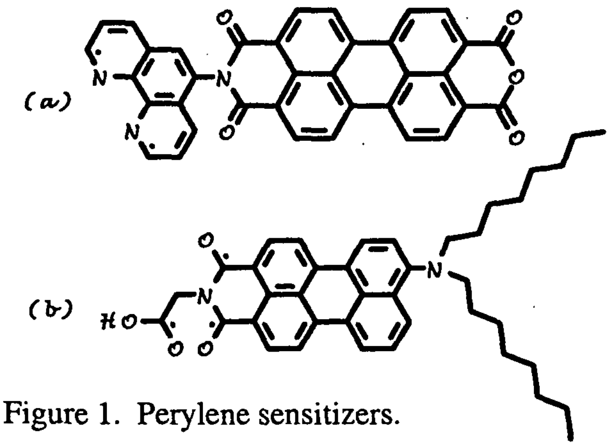

Figure 1. Perylene sensitizers.

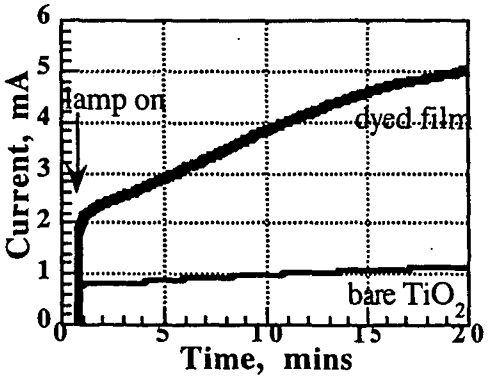

Figure 2. Current vs. time of DSSC's under UV illumination.

Poster # 11

THE EFFECT OF THE SPACER CHAIN LENGTH ON THE FLUORESCENCE INTENSITY OF 9-ALKYLFLUORENYL THIOL SELF-ASSEMBLED MONOLAYERS ON GOLD

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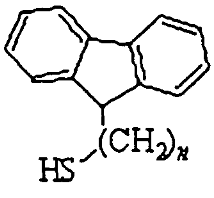
Spectral characterization indicates that 9-alkylfluorenyl thiols form well-ordered self-assembled monolayers (SAMs) on polycrystalline gold. Sessile drop contact angle measurements demonstrate the uniformity and hydrophobic nature of these tightly packed thin films. The film thicknesses, as measured by optical ellipsometry, correspond well those calculated from a model with extended alkyl chains oriented at a 30° angle to the Au surface. The films are passivating toward through-layer electron transfer from the Au surface to a soluble redox probe, $K_4Fe(CN)_6$, present in a contacting aqueous electrolyte. Grazing angle reflectance FTIR spectra show that the fluorenyl groups are fixed at a defined distance from the Au surface as determined by the varying length of the alkyl spacer disposed in an all-trans, extended conformation. Surface fluorescence bands are red-shifted and broader in these SAMs than in the component molecule's fluorescence in dilute solution. Fluorescence lifetimes for the anchored groups are bimodal, with a long-lived species corresponding to that observed in solution (~3.2 ns), and a shorter lifetime species (~260 ps) affected by metal-mediated quenching. The fluorescence intensity increases with alkyl spacer length in a monotonic fashion, with the rate of fluorescence quenching depending inversely on the distance separating the bound emissive probe from the gold surface.



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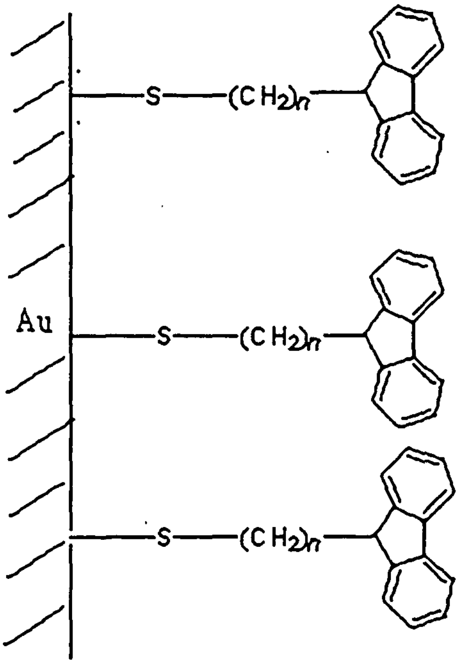

Au-1

THEORETICAL STUDIES OF ELECTRON TRANSFER AND OPTICAL SPECTROSCOPY IN COMPLEX MOLECULES

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Following is a description of progress in each area that we have been working in:

Semiconductor Clusters: We are starting to carry out density functional quantum chemical calculations of models for the cluster surface that will realistically treat capping groups, multiple layers of materials, and solvation effects. The goal is to study sites for trapping holes and electrons. Ultimately we intend to use mixed QM/MM methods (discussed below) to address this problem which will allow highly realistic modeling of the system.

Calculation of Redox Potentials of Complex Molecules in Solution: We have developed quantum chemical methods for computing redox potentials of complex molecules, including metal containing species, in solution. Initially applications to bacteriochlorophyll and bacteriopheophytin yielded good results as compared to experiment for relative redox potentials of the two species. Our current project is to carry out such calculations for several series of molecules of interest in the DOE solar photochemistry program. Once the methodology has been validated for known cases, it can be used to predict redox potentials for new molecules prior to synthesis..

Calculation of STM Images: We have used our ab initio quantum chemical technology for calculating electron transfer matrix elements to generate first principles predictions of STM images. This project has also involved significant analytical theory to understand how to take a cluster calculation and compute results relevant to the solid state system. Our initial application has been to a series of halogenated alkanes on a graphite surface studied by Flynn and coworkers. We are able to use the calculations to predict the geometry of the molecules on the surface. Application to molecules adsorbed on a TiO_2 surface is planned in collaboration with the Flynn group.

Mixed QM/MM Methods for Solids: We are beginning development of mixed QM/MM embedding methods for carrying out calculations on solids, with the principal focus on semiconductor particles. We have already developed fundamental QM/MM technology which we have successfully applied to molecules. We have also developed a way to represent the classical charge distribution from the solid efficiently in quantum chemical calculations. Our current efforts are focused on implementation of the QM/MM boundary for solid state systems and development of a self-consistent algorithm in which the localized frozen orbitals that we use to build the QM/MM interface are updated at each iteration cycle.

TRANSIENT FTIR STUDY OF RHENIUM COMPLEXES IN PHOTOCHEMICAL CO_2 REDUCTION

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The tricarbonyl rhenium complex with the general formula, *fac*-Re(α-diimine)$(CO)_3X$ (X = halide, solvent, alkyl, monodentate phosphine, CO, etc), has been shown to be a photocatalyst for the reduction of CO_2. The mono- and di-reduced species, $Re^I(bpy^{\bullet -})(CO)_3$ and $[Re(bpy)(CO)_3]^-$, respectively, are proposed as intermediates which react with CO_2.

We have used transient FTIR to study the reaction mechanism involving the mono-reduced species, which is produced either by reductive quenching of $^*Re(dmb)(CO)_3X$ (dmb = 4,4'-dimethyl-2,2'-bipyridine, X = Cl^- or solvent) or by photolysis of $Re(dmb)(CO)_3(Et)$. Transient FTIR of the excited state, $^*Re(dmb)(CO)_3X$ (X = Cl^- or solvent), shows a significant shift (20 to 80 cm^{-1}) of the CO vibrational frequencies to higher energy, which is consistent with the formation of the ^3MLCT state. The reductive quenching reactions of $^*Re(dmb)(CO)_3Cl$ and $^*Re(dmb)(CO)_3(CH_3CN)^+$ by triethylamine produce $[Re(dmb)(CO)_3Cl]^-$ and $Re^I(dmb^{\bullet -})(CO)_3$, respectively. A transient FTIR study of the photolysis of $Re(dmb)(CO)_3(Et)$ indicates clean cleavage of the Re-Et bond, forming $Re^I(dmb^{\bullet -})(CO)_3$. Under an Ar atmosphere the mono-reduced complex produces two species with bands at 1990, 1947, ~1870, and 1855 cm^{-1} and 2021, 1919, and ~1870 cm^{-1}. Comparisons with IR spectra obtained by sodium reduction of $Re(dmb)(CO)_3(OTf)$ (OTf = trifluoromethanesulfonate) suggests that the former is a $[Re(dmb)(CO)_3]_2$ dimer. Under a CO_2 atmosphere the mono-reduced complex produces the formato complex, $Re(dmb)(CO)_3(OC(O)H)$, and the carboxylate complex, $Re(dmb)(CO)_3(COOH)$. When small amounts of water are present, a yellow precipitate is obtained during the photolysis. The precipitate was identified as a bicarbonato complex, $Re(dmb)(CO)_3(OC(O)OH)$.

This study suggests that $Re^I(dmb^{\bullet -})(CO)_3$ reacts to form either a dimer ($k = 20\ M^{-1}\ s^{-1}$) or a CO_2 adduct ($k < 1\ M^{-1}\ s^{-1}$). Due to the sluggishness of these reactions very small amounts of water can intercept $Re^I(dmb^{\bullet -})(CO)_3$.

DOPING ORGANIC SEMICONDUCTORS: N-TYPE DOPING OF A LIQUID CRYSTAL PERYLENE DIIMIDE

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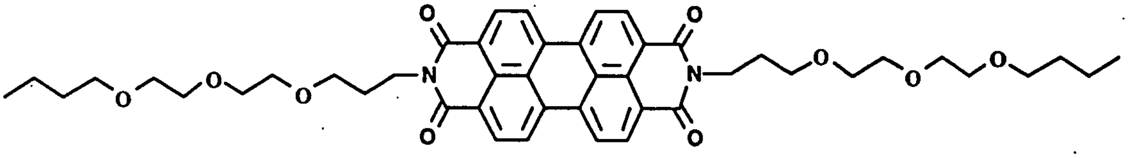
Organic semiconductors have been doped for the first time in a manner consistent with the formation of stable semiconductor junctions. The usual "dopants" in organic semiconductors are adventitious and unidentified, preventing a fundamental understanding of organic semiconductors. Worse, most "dopants" can move through the lattice, thus electrical junctions (Schottky or p-n) are neither spatially nor temporally stable. To "correctly" dope organic 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 criteria: 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 have recently synthesized the first example of this idea, shown below with its host molecule.



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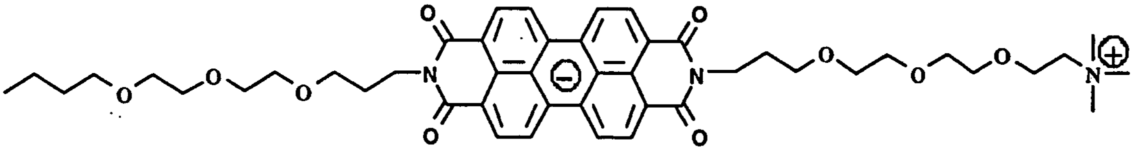

n-type dopant

Conductivity in n-doped films rises very rapidly with increasing dopant concentration. Instead of the expected linear increase, it rises faster than the square of the dopant concentration. This is evidence for the electrostatic attraction between the electron and its bound counterion and is expected to be a general feature of doped organic semiconductors.

Poster # 15

MOLECULAR ENGINEERING OF C_{60}-BASED CONJUGATED OLIGOMER ENSEMBLES; MODULATING THE COMPETITION BETWEEN PHOTOINDUCED ENERGY AND ELECTRON TRANSFER PROCESSES

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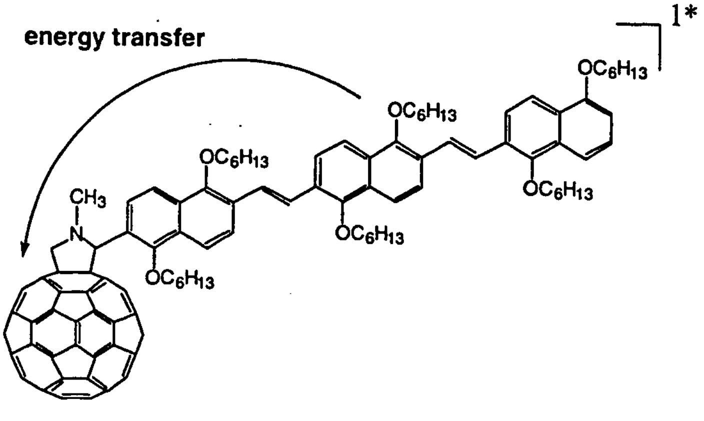
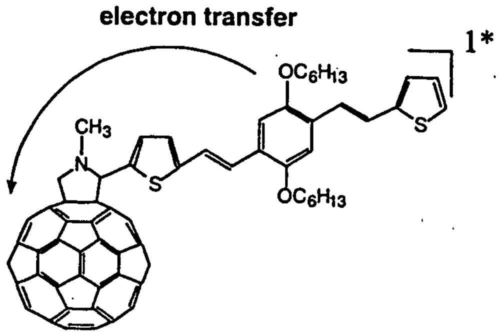
A series of soluble and strongly fluorescent C_{60}-(π-conjugated) oligomer ensembles were synthesized starting from suitably functionalized oligomers, which were prepared in a multistep synthetic procedure involving a Wittig reaction. A systematic change in the nature of the oligomeric component allowed (*i*) tailoring of the light absorbing chromophore by shifting the ground-state absorption from the ultraviolet to the visible region and (*ii*) varying of the oxidation potential of the oligomeric donor, without, however, effecting the overall solubility.

These novel photo- and electroactive species were probed by means of electrochemical and photophysical techniques. Both singlet-singlet energy transfer and intramolecular electron transfer were found to take place and to compete with each other in the overall deactivation of the photoexcited chromophore. The control over the structure of the fluorescent π-conjugated system changed the outcome of this ultrarapid deactivation: In particular, the intramolecular reaction was successfully shifted from an all-energy-transfer to an all-electron-transfer scenario. In this context, the oxidation potentials of, for example, dihexyloxynapthalene, 1,4-dihexyloxybenzene / thiophene and 1,4-dihexyloxynapthalene / thiophene moieties, ranging between 1.41 and 1.01 V *versus* SCE, helped to direct the competition between these two transfer channels. The relative energy of the charge-separated state in reference to the fullerene singlet excited state determines the nature of the photoproduct: only the energetically lowest lying state is populated in high yields. Strong electronic couplings (V) between the donor and acceptor moieties affect not only the ground state spectra, which exhibit marked red shifts, but, more importantly, give rise to ultra-fast electron and energy transfer reactions. In terms of stabilizing the product and enhancing the yield of charge separation, particular benefits were noted by attaching two fullerene cores (*i.e.*, triad), instead of just one (*i.e.*, dyad), to the oligomeric structure.





PHOTOINDUCED ELECTRON TRANSFER IN HELICAL POLYPEPTIDE *MAQUETTES*

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Investigation of synthetic photoactive polypeptide *maquettes* (e.g., helix dimers, trimers, etc.) leads to a deeper understanding of the mechanism of initial charge separation in natural photosynthesis. The present research has concentrated on characterization of helix dimers that contain N-terminal chromophores (various pyrene derivatives) having a high propensity for aggregation. Formation of a "special pair" by the principal chromophore contributes up to 30 % of the total free energy of dimerization for the polypeptide. Auxiliary electron donors are placed along peptide chains as far as 15 residues away from the N-termini. In one peptide dimer design, four positive charges are placed near the "*special pair*" (electron acceptor) terminus as an Orn^{+}–Orn^{+} (ornithine residues) sequence, while negative counter-charges are distributed along charged hydrophilic helix surfaces. The electron donor is a carbazole derivative introduced by attachment to the side chain of a synthetically modified aspargine residue. The rate constants for electron-transfer involving pyrene pairs and remotely positioned donor moieties are of the order of $10^{9}\ \mathrm{s}^{-1}$ indicating that the pathways involve "short cuts" through the helix loops. Furthermore, there is evidence for the direct role of the side chains of aromatic residues in the electronic coupling between the donor and the principal chromophore, thus, mediating the fast electron transfer processes. The electron transfer kinetics are extracted from emission and transient absorption data.

LIGHT-INDUCED CHARGE TRANSFER AND CHARGE REDISTRIBUTION: EXPERIMENTAL ASSESSMENT OF DISTANCE AND DIRECTION

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"Distance" is one of the most fundamental parameters in light-induced charge-transfer reactions. Interestingly, true CT distances (one-electron transfer distances) often differ substantially from simple geometric donor-site/acceptor-site separation distances. The true CT distance is equivalent to the dipole moment difference between initial and final electronic states, divided by the unit electronic charge. Electroabsorption spectroscopy (electronic Stark-effect spectroscopy) can be used to provide absolute measures of adiabatic transfer distances by providing absolute measures of the difference in dipole moment between ground and photo-excited electronic states. As pointed out by Newton and Cave, if CT oscillator strengths are available, the diabatic CT distance can also be determined, i.e. the hypothetical distance of charge transfer in the absence of perturbations due to initial-state/final-state electronic coupling. Our group, the Brookhaven group, and a handful of others have shown how the Stark methodology can be used to investigate electron transfer in a number of conceptually interesting model systems.

We have now combined Stark absorption and emission measurements with transient DC photoconductivity (TDCP) and traditional ground-state dipole measurements to move beyond absolute distance measurements and evaluate charge redistribution in a more general way. To accomplish this, we take advantage of the fact that TDCP (in combination with ground-state dipole moment measurements) provides scalar measures of ground-state/excited-state dipole changes while Stark techniques provide measures of vector differences. The distinction is unimportant in simple linear donor/acceptor systems, but can be tremendously important in lower-symmetry systems. We illustrate the differences with experimental examples where: a) localized "charge-transfer" occurs in a direction that is nearly orthogonal to that for overall "charge redistribution", and b) localized "charge separation" results, surprisingly, in global dipole moment contraction.

RADICAL SCAVENGING PROPERTIES AND SURFACE REACTIONS OF CAROTENOIDS

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Carotenoid radical cations have been detected in photosynthetic membranes of plants and bacteria. Carotenoids play a photoprotective role in plants and bacteria and are intrinsic components of the reaction centers and the pigment-protein complexes in photosynthetic membranes. Carotenoids can also function as scavengers of free radicals. We have employed the spin-trapping EPR technique to study the scavenging ability of several natural and synthetic carotenoids with different redox properties. The relative rates of the reactions of carotenoids with $^{\bullet}OH$, $^{\bullet}OOH$, and $^{\bullet}CH_3$ radicals generated via the Fenton reaction were determined. Three possible mechanisms were considered: addition of radicals to the polyene chain, hydrogen abstraction from the C(4) position of the cyclohexene ring and the redox process. The results show that carotenoids can serve as effective scavengers of reactive radical species and that the scavenging ability of the carotenoids increases with their oxidation potentials.

We have also measured the photo-oxidation of canthaxanthin, β-carotene and 8'-apo-β-caroten-8'-al on silica-alumina and in MCM-41, Ni-MCM-41 and Al-MCM-41. Both the ESEEM and the HYSCORE spectra of $Car^{\bullet+}$ on silica-alumina exhibited the ^{27}Al nuclei peak at 3.75 MHz. Davies ENDOR measurements of canthaxanthin radical cation on silica-alumina determined the hyperfine couplings of β-protons belonging to three different methyl groups with $a_{H1} = 2.6$ MHz, $a_{H2} = 8.6$ MHz and a_{H3} *ca* 13 MHz. The principal components of the proton hyperfine tensors estimated from HYSCORE spectra appeared to be much more anisotropic than those which were reported previously for the carotenoid β-protons in frozen $AlCl_3/CH_2Cl_2$ solution. It was found that the large anisotropy is due mostly to the α-protons. However, twisting or isomerization of the carotenoid backbone results in a substantial increase of anisotropy for some β-protons on the solid support compared to frozen solution. Formation of $Car^{\bullet+}$ within the M^{n+}-MCM-41 is due to electron transfer between incorporated carotenoids and metal ions. Detected EPR signals of Ni(I) species provide direct evidence for the reduction of Ni(II) ions by carotenoids. The presence of Ni(II) ions in Ni-MCM-41 was verified by 220 GHz EPR spectroscopy. ENDOR measurements revealed that the central C13-CH_3 and C13'-CH_3 methyl groups of both carotenoids in Al-MCM-41 are rapidly rotating, while mobility of the C9-CH_3 and C9'-CH_3 group is restricted. We propose that carotenoids are bound to the MCM-41 pore walls via the ends of the polyene chain in contrast to silica-alumina, where they have maximum interaction with the surface via the center of the polyene chain.

Carotenoids can also self-assemble on gold surfaces. The change in electron transfer rates, surface coverage, and hydrophobicity have been measured. Iodine-catalyzed R/S isomerization of the allenic carotenoid fucoxanthin proceeds by attack of $I^{\bullet}$ on C7'. Electrochemical experiments shows that the R/S isomerization of allenic carotenoids is not via radical cation or dication mechanisms as has been shown to be the case for the isomerization of the polyene chain.

QUENCHING OF PHENOL-LINKED PORPHYRINS INDUCED BY HYDROGEN-BONDING

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Rates of electron transfer may be much enhanced by associated proton displacements within the redox reaction complex. Thus, we have shown that reduction of an excited substrate by phenols is facilitated by concerted movement or transfer of the phenolic proton to an H-bonded base. An important instance of this effect occurs in photosynthesis, where tyrosine, H-bonded to histidine, participates in the electron transfer chain of System-2. To develop this further, we now study cases in which the phenol is covalently linked to the substrate.

In this connection, we have found that fluorescence of meso-4-hydroxyphenyl-substituted porphyrins is quenched by added bases in aprotic solvents. This has been studied as function of the extent of hydroxy and methoxy substitution of the phenyls, the strength and H-bonding power of the base, the solvent, and deuteration of the hydroxyl. Porphyrins used were: 5,10,15,20(4-hydroxy-3,5 -dimethoxyphenyl)P; 5,10,15,20(4-hydroxy-3-methoxyphenyl)P, and 5(4-hydroxy-3,5-dimethoxyphenyl-10,15,20-triphenyl)P, denoted respectively as (4,8), (4,4) and (1,2). Bases tested included substituted pyridines, pyridine oxides, sulfoxides and amines. SV plots derived from either intensity or lifetime measurements agreed, indicating little initial static quenching. For all bases, the ratio of rates for (4,8) to (1,2) were very close to four. Quenching of (4,8) was faster than that of (4,4) reflecting the effect of methoxy on the phenol oxidation potential. Replacement of hydroxy by methoxy completely eliminated quenching. SV constants correlated with Bronsted base strength rather than H-bonding equilibria. However, a maximum in solvent polarity dependence of the rate shows need for H-binding in the reaction complex. A positive isotope effect indicates that motion of the electron and proton is concerted in these systems.

Further work will be directed towards establishing the relative phasing of these motions.

PHOTOCHEMICAL OXYGEN EVOLUTION IN COLLOIDAL ASSEMBLIES

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An important goal of this project is to couple heterogeneous systems for photochemical charge separation with nanoparticle catalysts that can perform useful reactions, such as oxygen and hydrogen evolution. Our current efforts focus on constructing multilayer assemblies from transition metal oxide semiconductor sheets, which are sensitized by adsorbed or intercalated $Ru(bpy)_3^{2+}$ derivatives. By platinizing these composites internally, we have been able to generate hydrogen photochemically, using visible light, from aqueous iodide solutions. Flash photolysis experiments show that back electron transfer between conduction band electrons and I_3^- occurs on a timescale of milliseconds. Coupling of this system to an oxygen evolution catalyst for overall water splitting will therefore require comparable turnover rates.

We have studied 10-20 nm diameter IrO_2 colloids as potential oxygen evolution catalysts for these systems. Harriman and coworkers showed a number of years ago that IrO_2 has higher activity for oxygen evolution in $Ru(bpy)_3^{2+}$/persulfate solutions, and is more stable, than RuO_2 and other oxides. Re-investigating this system we have found that the reaction rate and turnover number obtained with these catalysts is strongly affected by their surface chemistry, which is determined by buffers and other adsorbates. The catalyst operates in a narrow window of pH (4-5), having low turnover rate at lower pH; at higher pH, the oxidized sensitizer is increasingly susceptible to nucleophilic attack by hydroxide ions. Phosphate buffer, which has historically been used to control the pH of this system, accelerates the decomposition of the oxidized sensitizer and inhibits O_2 evolution, whereas silicate-bicarbonate solutions are ideal buffers. Decomposition of $Ru(bpy)_3^{3+}$ is not kinetically competitive with oxygen evolution in Na_2SiF_6-$NaHCO_3$ buffers. Under these conditions the turnover number of the $Ru(bpy)_3^{2+}$ photosensitizer exceeds 200 Adsorption of Nafion additionally stabilizes the colloidal IrO_2 particles and increases both the turnover rate and the quantum yield for oxygen evolution (from about 40 to 70%).

Unfortunately, the turnover rate per sensitizer molecule in this sacrificial (persulfate) system is still on the order of 1 s^{-1}, which is too low for coupling to the non-sacrificial hydrogen evolving system. Bleaching-recovery experiments were performed by irradiation of $IrO_2/Ru(bpy)_3^{2+}$/persulfate solutions followed by methanol addition (to reduce $Ru(bpy)_3^{3+}$ to $Ru(bpy)_3^{2+}$) after a variable time delay. By varying the concentrations of IrO_2 and $Ru(bpy)_3^{2+}$, we determined that interfacial electron transfer between adsorbed $Ru(bpy)_3^{2+}$ and the colloid is fast compared to oxygen evolution under all conditions of steady state photolysis. Further, the absence of a D_2O/H_2O kinetic isotope effect on the oxygen evolution rate indicates that proton transfer reactions are not rate-limiting. This suggests that the rate determining step involves charge transport within the colloid, oxide ion transfer within the colloid or on its surface, or formation of the oxygen-oxygen bond.

We are currently experimenting with mixed metal oxide (Ir, Os, Ru, Pt) colloids, using a factorial design of experiment approach, in order to determine the effects of different components on the catalyst turnover rate. We have developed an optical screening method that is amenable to rapid evaluation of different colloid/buffer combinations in a 96-well plate format. Because catalyst turnover competes kinetically with decomposition of photogenerated $Ru(bpy)_3^{3+}$, the absorbance and emission of the $Ru(bpy)_3^{2+}$ sensitizer decays more slowly with good catalyst/buffer combinations than it does with bad ones under steady state photolysis conditions. We have verified that this method gives the same ranking of catalysts as do steady state oxygen evolution measurements. However, the parallel screening method permits a much larger array of photocatalysts to be evaluated in a relatively short period of time.

POLARIZED NMR SPECTRA FROM PHOTOSYNTHETIC REACTION CENTERS: MECHANISM AND NEW SYSTEMS

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Over the past year we have been simulating the polarized NMR spectra of the photosynthetic reaction center, and those of a dye sensitized cell. The numerical simulations are based on a coherent mixing mechanism with a stochastic Liouvillian formalism. A separated pair of electrons begins in a singlet state; one electron is strongly coupled to a nucleus. Coherent effects of the electrons (g tensors, and hyperfine tensor) and stochastic effects of chemical decay were included in simulating the nuclear polarization. Buildup during CW illumination, anisotropic effects of the powder ensemble sample, and magic angle spinning can be accounted for as well. These calculations predict that additional systems should be amenable to CIDNP spectroscopy, and predict that low-field NMR is preferable to high-field. We confirmed some of these predictions. Preliminary data show Photo-CIDNP signals for both PS I and PS II centers and weak signals for dye sensitized cells. In this mechanism it is of particular interest to control the electron back-reaction rates. We have also established a protocol for collecting NMR spectra of solids, liquids, and liquid crystals in a transparent electrode inside the NMR coil, with the long term aim of tuning back electron transfer rates in-situ. The home-built apparatus involves AC electric fields of 100kV p-p. The use of AC pulsed electric fields reduces sample damage substantially in comparison with DC fields. Effects of the applied fields on photochemistry are planed.

Poster # 2

FAST CHEMISTRY AT BROOKHAVEN'S LEAF ACCELERATOR

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Pavel Poliakov, James P. Kirby and Norihiko Takeda
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The Laser Electron Accelerator Facility at Brookhaven was constructed to provide short pulses of electrons for experiments in the fields of radiation chemistry and charge transfer processes relevant to energy conversion. This poster describes LEAF's present and planned capabilities and experiments underway.

LEAF ejects short pulses of electrons from a cathode by a short laser pulse and then accelerates the electrons with intense electromagnetic fields in RF cavities. The overall system response time is 7 ps in "pulse-probe" transient absorption experiments and 0.2 ns in conventional single-shot experiments with transient digitizers. Some technical details will be described including the broadening of the portion of the laser pulse used for the photocathode in order to reduce space charge.

Radiolysis with electron pulses has provided an important way to investigate charge transfer processes, but that ability has not included aromatic fluids like benzene and toluene, because few ions were known to be produced in such fluids. Experiments at LEAF find that substantial yields of ions are produced in toluene, but that the ions decay more rapidly than do ions in non-aromatic fluids such as cyclohexane. Fits to models indicate that the distribution of ion-pair distances is shortened in the aromatic fluid but also (surprisingly) that the initial yield is lower. This interesting puzzle is being investigated. The results do indicate that pulse radiolysis experiments will be applicable to electron transfer in aromatic fluids, at least at short times. Other experiments are investigating the fast dissociation anions of aryl halides, understanding of which is important to the mechanism of the Grignard reaction.

Hydrogen-bonded complexes provide methods for modular assembly of moieties for carrying out charge transfer. The complexes are also tools for investigation of proton-coupled electron transfer in which both electrons and protons move. It is important to know energetics in these complexes, but hydrogen-bonded amidinium-carboxylate complexes were found to have much larger driving forces than expected from the unsubstituted groups because the amidinium substituent is a far stronger electron-withdrawing group than expected. Pulse radiolysis experiments showed that the very weakly exoergic transfer from biphenyl anion to naphthalene in the biphenylamidinium-naphthalenecarboxylate complex becomes highly-exoergic in the opposite direction, but quantitative energetics are not available from electrochemical experiments because the reductions are irreversible. Previously electron transfer in this complex was found to be too fast for measurement. Present experiments aimed at resolving the energetics will be followed by use of LEAF's 7 ps time resolution to measure electron transfer in these complexes.

LEAF is presently a very capable tool, but its most special potential lies in the future. Two techniques are under development that may dramatically extend its capabilities. One of these will combine electron and laser pulse excitation to obtain ~ 0.1 ps time resolution. The other will obtain ultrafast data in single shots to extend LEAF's fast time resolution of scarce, valuable materials that are not now available for fast experiments.

Poster #

TRANSMEMBRANE CALCIUM ION PUMPING BY AN ARTIFICIAL PHOTOSYNTHETIC REACTION CENTER

Hebe Vanegas, Ira M. Bennett, Alex Primak, Paul A. Liddell, Ana L. Moore, Thomas A. Moore and Devens Gust
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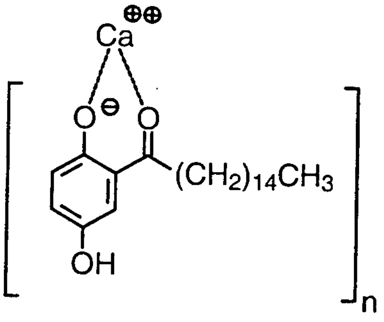
Photosynthetic solar energy harvesting begins with light absorption and conversion of excitation energy to charge separation in the reaction center. This electrochemical energy is rapidly converted to other forms that are more useful to the organism, or more easily stored. The electrochemical potential of the reaction center is converted to proton-motive force (pmf) across a lipid bilayer membrane, and this in turn is used to power the production of adenosine triphosphate (ATP). Photosynthetic organisms convert the chemical energy of ATP to other kinds of potential energy for various purposes. A large amount of ATP is used to transport calcium, sodium, potassium and other metal ions across membranes against a concentration gradient. For example, the pumping of calcium ions across membranes controls the relaxation phase of muscle function. In a contraction-relaxation cycle, about one-third of the ATP consumed is used to power transmembrane calcium transport.

In previous work, we have synthesized artificial photosynthetic reaction centers from porphyrins and electron donor and acceptor moieties and inserted them into the bilayer membranes of liposomes. Irradiation leads to transmembrane charge separation, which has been coupled to the generation of pmf through a redox loop involving a quinone proton shuttle. Insertion of ATP synthase into the membrane allows the pmf to power the synthesis of ATP.

Using these same principles, we have now designed and prepared a light-driven system that pumps calcium ions across a lipid bilayer membrane. The basis of the pump is a redox loop involving the hydroquinone shown below. The compound features a saturated chain that confers lipid solubility. NMR evidence indicates that the hydroquinone in anionic form binds calcium relatively strongly, whereas the quinone form does not. For the ion pumping experiments, liposomes containing the hydroquinone in the membrane bilayer were prepared, and a carotenoid (C) porphyrin (P) quinone (Q) triad artificial reaction center was inserted into the membrane vectorially, with the carotenoid end near the inside of the liposome. Irradiation of the liposomes with red light results in formation of C$^{\bullet+}$-P-Q$^{\bullet-}$. The hydroquinone, which carries along bound calcium from the solution outside of the liposome, diffuses across the hydrophobic membrane interior and is oxidized by the carotenoid radical cation near the interior surface, whereupon calcium is released to the liposome interior volume. The hydroquinone can be regenerated by the C-P-Q$^{\bullet-}$ radical anion after diffusion of the oxidized species back to the outer membrane surface. The calcium import may be quantified using a fluorescent, calcium-sensitive dye, or indirectly by monitoring the membrane potential generated by uncompensated ion transport. This light-driven ion pump translocates calcium into the liposome interior against a calcium concentration gradient, and generates a significant membrane potential.



LONG-RANGE THERMAL AND OPTICAL CHARGE TRANSFER (ELECTRON AND/OR HOLE): FACTORS CONTROLLING ENERGETICS AND COUPLING

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This program applies theoretical and computational techniques to elucidate the electronic and nuclear factors controlling thermal and optical electron (or hole) transfer in molecular systems. Electronic structure is based on Self Consistent Field (SCF) or Configuration Interaction (CI) calculations (using ab initio or semiempirical Hamiltonians), and effective donor/acceptor (D/A) coupling elements (H_{DA}) and separation distances (r_{DA}) are obtained from analysis of CI results in terms of the Generalized Mulliken Hush (GMH) model (Cave, Newton). Influence of polar solvent on relevant energy gaps or H_{DA} magnitudes has been modelled using various self consistent reaction field models based on realistic molecular cavities, and allowing solvent optical response based on the instantaneous or "smeared out" (mean field) solute charge distributions (developed with M. Basilevsky and I. Rostov).

Applications to intramolecular optical charge transfer in polar solvents have dealt with: (1) an acridinum acceptor linked to aromatic amine donors (with R. Cave and G. Jones); and (2) coumarin 153 (with D. Matyushov). For the acridinum systems (whose spectroscopy and charge transfer has been studied previously by Jones, Wasielewski, and Hupp, and their coworkers), the vertical adsorption and emission maxima, and the adiabatic gap, have been examined as a function of solvent polarity, allowing estimates of the differential solvation for initial and final states in the nominal "charge shift" process. Solvent-controlled non-condon behavior is also assessed. Relative to the traditional 2-state diabatic model, an extended model including D/A mixing and a flexible treatment of state-specific solute polarizability is found necessary to account for solvent-dependence of adsorption and emission line widths for C153.

The implementation of a 2-state model for analyzing charge transfer and associated non-Condon behavior requires a particular choice of the 2-state space and the model for solute polarizability (including that implicit in the 2-state quantum mechanics, and "supplementary" polarizability added explicitly to the model). A fixed 2-state space (and hence fixed diabatic states, if obtained via the GMH model), e.g., a vacuum 2-state space (as employed by Matyushov et al), is convenient for comparison of a number of solvents, but an "in situ" 2-state space for each solvent (entailing solvent-dependent diabatic states) is an alternative.

Variation of H_{DA} magnitude and distance-dependence for hole-transfer in a number of homologous donor/bridge/acceptor ($(DBA)^+$) systems has been monitored as a function of D/A type ($CH_2^{\cdot}$, a phototypical sp^2 type D/A group, vs ferrocenyl-), oligomeric B type (based on the saturated and unsaturated spacers studied experimentally by Chidsey, Feldberg, Smalley and coworkers), and chemical substitution (alkoxy) or torsional modifications of the bridge.

EFFECT OF PRESSURE ON THE ELECTRONIC BAND STRUCTURE OF InP QUANTUM DOTS

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and

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One of the very interesting theoretical predictions resulting from three-dimensional quantum confinement in semiconductors is that direct bandgap semiconductors (i.e., those with strongly allowed fundamental optical transitions requiring no phonon participation) can be converted to indirect semiconductors (i.e., those with forbidden or weakly-allowed fundamental optical transitions that require phonon participation) at much lower pressure compared to bulk semiconductors, and that the inverse transition from indirect to direct behavior may also be analogously affected.

We tested this prediction by determining the critical pressure at which InP quantum dots convert from exhibiting direct fundamental optical transitions to indirect fundamental optical transitions compared to bulk InP. These experiments were done in a high-pressure diamond anvil cell that allowed the photoluminescence (PL) to be determined at pressures ranging from atmospheric pressure to 7 GPa. The transition from direct to indirect behavior was manifested by the change of the PL intensity and the emitted PL wavelength as a function of pressure.

Comparison of the experimental results with theoretical predictions and the results of other recent literature reports will be discussed.

Poster # 26

ULTRAFAST INVESTIGATION OF THE EXCITED-STATE ENERGY MIGRATION DYNAMICS IN AN LIGHT-HARVESTING ANTENNA POLYMER BASED ON RU(II) AND OS(II) POLYPYRIDYL COMPLEXES

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The excited state energy migration dynamics in a polymeric light harvesting assembly consisting of twenty polypyridyl Ru(II) and Os(II) coordination complexes linked together through a polystyrene backbone have been studied using ultrafast laser techniques. Energy migration is initiated through the photoexcitation of the metal-to-ligand charge-transfer (MLCT) band of one of the Ru complexes. Through energy transfer processes, the Ru excited state hops from one Ru site to another, ultimately being terminated by energy transfer to a lower energy Os trap. The energy migration dynamics are followed by monitoring the Os excited state emission at 780 nm using time-correlated single-photon counting. We find that when there is an average of three Os complexes per chain, the sensitization efficiency of the lower energy Os(II) sites by photoexcited Ru complexes is greater than 95%. We have augmented our time-resolved experiments with Monte Carlo simulations. These simulations provide insight into the polymer array's structure and at the same time form the basis of a molecular-level description of the energy migration dynamics. The kinetic model combines a Monte Carlo simulation of the polymer structure with a stochastic simulation of the excited state migration. Our analysis indicates that hopping times for Ru*→Ru and Ru*→Os energy transfer are 1-3 ns and 800 ps, respectively.

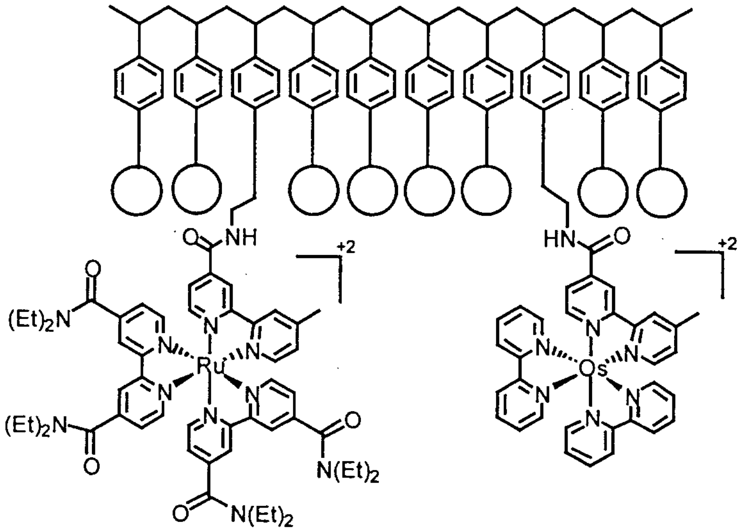

Fig. 1: Schematic diagram of PS-Ru$_{17}$Os$_3$ assembly. Open circles represent Ru(II) and Os(II) complexes that are not shown for clarity.

The excited state relaxation processes that take place within the Ru(II) and Os(II) monomer units have been investigated using femtosecond transient absorption spectroscopy. In particular we have investigated the interligand electron transfer (ILET) processes that take place within the low-lying electronic states of mixed ligand Os(II) complexes. Our experiments indicate that ILET in these systems is quite fast, with the photoexcited electron localizing on the lowest energy ligand in approximately 1 ps after excitation.

Poster #

RELATIONSHIP BETWEEN MORPHOLOGY OF SQUARAINE DYE LAYERS ON VAN DER WAALS SURFACES AND THEIR ELECTROCHEMICAL AND PHOTOELECTROCHEMICAL RESPONSE

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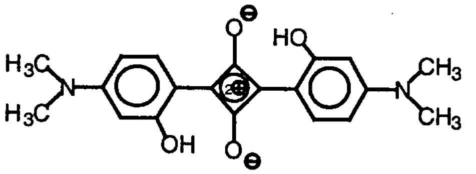
Electrochemical reactions of insoluble highly ordered squaraine (1-1OHSQ) dye layers (see structure below) adsorbed on highly oriented pyrolytic graphite (HOPG) electrodes were studied in aqueous electrolytes. Staircase cyclic voltammetry obtained in chloride electrolytes revealed hysteresis char-acterized by large peak separations (100 – 200 mV) and sharp redox peaks (fwhm 10 – 60 mV) the shape and potentials of which depended on electrolyte concentrations. A number of small stochastic reduction peaks were often observed at more negative potentials. We interpret the current spikes to be associated with the reduction of small domains or crystallites of the oxidized 1-1OHSQ layers. Peak potentials and peak shapes were also dependent on the identity of the electrolyte anion species. The results support a reaction scheme where electrolyte anions are incorporated into surface confined one-electron oxidized dye molecular layers. From the results of peak potential shifts, the preference for ion-pairing is estimated to be in the order of: $I^- > Br^- > Cl^- > SO_4^{2-} \approx ClO_4^- \approx F^-$. *Ex-situ* STM observations were performed to reveal structural changes upon electrochemical oxidation of 1-1OHSQ layers in LiCl electrolytes. Two polymorphs with different angles of the long-axis of molecules to the directions of the molecular row were observed for the oxidized samples. Both polymorphs had smaller packing densities compared to the reduced form of the dye. The positions of the anions, incorporated into the 2D structure upon oxidation of the layer, are assigned based on the STM images of the layers.



In addition, the sensitization of SnS_2 electrodes by 1-1 OHSQ and a related dye with hexyl groups and no hydroxide substitution on the phenyl rings was also studied. Absorption spectra, photosensitization spectra, photocurrent-voltage curves and AFM morphologies were all obtained on the same SnS_2 samples. We have confirmed that some dye layers have 100% quantum efficiency for the production of photocurrent. Photocurrent-voltage curves showed onsets of photocurrent well after the flatband potential and were less steep than theoretically predicted for a high photocurrent yield system. These results suggest that recombination of photogenerated carriers at low band bending is still a problem in this system.

ELECTRONIC COMMUNICATION BETWEEN ORTHOGONAL CHROMOPHORES BRIDGED BY SINGLE >C<, >Si<, >Ge< AND >Sn< ATOMS

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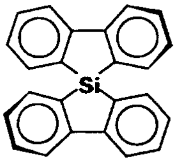
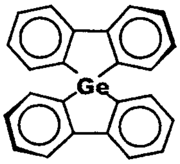
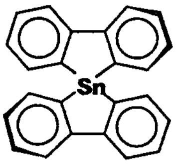
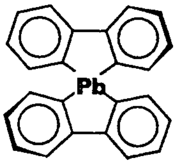
Donor-acceptor interactions in a series of rigid bichromophores bridged by the heavier analogues of carbon (Group IV) were investigated using a combination of spectroscopy, electrochemistry and computation. The objective was to probe the role of the accessible empty valence orbitals of the central heteroatoms in mediating interactions between the aromatic chromophores. The excited singlet and triplet states, as well as radical cations and anions of the molecules shown below were investigated. The strongest excited state inter-chromophore interaction was found for the silicon-bridged compound, followed by the germanium, with the tin bridge giving the most "carbon-like" behavior in most instances.









Density fuctional (DFT) calculations support the experimental findings and reveal that the contribution from the atomic orbitals of the central bridging heteroatom X to the low-lying empty molecular orbitals of the spiran are largest when X = Si, and diminish for the heavier members of group IV (see the Figure 1). This demonstrates that silicon bridges should be particularly efficient in mediating photoinduced electron transfer. Interestingly, the *p* rather than *d*-type orbitals of the heteroatom are most heavily involved in the mixing.

The contribution to the occupied orbitals (HOMO, HOMO-1) is in general very small for all investigated heteroatoms X. This suggests that the hole delocalization is in all cases caused primarily by the direct interaction between the π-orbitals of the aromatic units (spiro-conjugation). Indeed, as a result of the increasing distance between the π-electron systems, the interaction between the localized HOMO orbitals decreases steadily from 2260 cm^{-1} for X = C, to 790 cm^{-1} for Si, to 440 cm^{-1} for Ge and to 175 cm^{-1} for Sn. Thus, somewhat surprisingly, the "hole conductivity" should be highest for the original carbon-bridged compound.

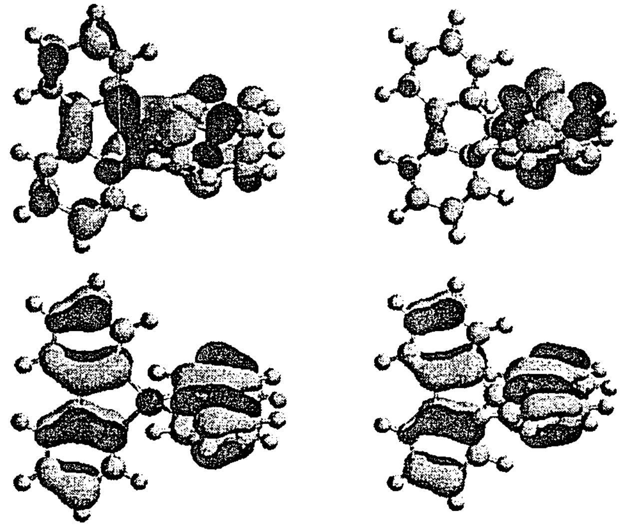


Fig. 1. Valence orbitals of the >Si< (left) and >C< (right) bridged spiran. Note the large Si contribution to the LUMO orbital (top left).

PROBING THE LOCAL DYNAMICS OF THE PHOTOSYNTHETIC BACTERIAL REACTION CENTER PROTEINS

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Many of the important functions of biological systems are connected to electron transfer (ET) reactions. These ET reactions occur in "soft" biopolymer molecules such as proteins, which experience a strong thermal motion. As was shown recently, in many biological systems ET reactions are coupled to protein dynamics.[1-5] In these cases the kinetics of the charge separation does not depend upon free energy, but is gated by conformational transitions or protonation reactions. Thus, the dynamic structure of the proteins is exploited to tune the reaction kinetics.

ET reactions in photosynthetic reaction center (RC) proteins are the first steps in the solar energy conversion processes that occur in green plants and photosynthetic bacteria. There is strong evidence from experimental and theoretical research[3-5] that electron transfer in the RC proteins is governed by conformational changes. In order to reveal the mechanism of the electron transfer processes in the photosynthetic RC proteins, a detailed study of the protein dynamics is required.

The spin label Electron Paramagnetic Resonance (EPR) approach presents a technique that is ideally suited to resolving molecular dynamics linked to the photosynthetic ET. It is highly sensitive to dynamic processes and can provide information of the global protein dynamics and local mobility of specific sites within a protein. Here we report the study of local dynamics of the spin-labeled purple photosynthetic bacterial RC protein from *Rhodobacter sphaeroides*. The protein was labeled by a specific spin label (MTSL) covalently bound to the surface cysteine residue. A multifrequency EPR approach was employed to discriminate between different dynamic modes, such as unrestricted Brownian diffusion or restricted fast libration. Relaxation effects in continuous wave and pulsed EPR spectra, recorded at X-band (9.5 GHz) and D-band (130GHz), were analyzed. Several dynamically nonequivalent sites have been observed. This might indicate the presence of different local conformations of the protein. Results demonstrate that the RC protein has a very flexible and dynamic structure. Local dynamics are revealed at a temperature as low as 100 K. These motions can be described as a very fast libration (restricted reorientational motion) with a correlation time faster than 10^{-9}s. This type of dynamical behavior is typical for conformational changes, matrix reorganization, and dynamic interactions in protein assemblies, and may govern the physiological functioning of proteins.

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TEMPLATE-DIRECTED ELECTRO- AND PHOTOELECTRO- SYNTHESIS OF SEMICONDUCTOR NANOSTRUCTURES

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Nanostructured semiconductor materials and composites are attractive for their technological uses in electronic and electrochemical devices such as nanoelectronic circuits, nano-robotics, solar cells, and chemical sensors. Three different strategies for template directed electro- and photo- electrosynthesis of semiconductor nanoparticles are introduced in this paper. First, it is shown that titania-based heterogeneous photocatalysis can be combined with underpotential deposition, for the preparation of composite or coupled semiconductors. Thus ultraviolet (UV) irradiation of titania particles in an aqueous solution of Se(IV) is shown to result in the formation of Se/TiO_2 composites. Subsequent UV irradiation of these composites in aqueous solutions containing M^{2+} ions (M = Cd, Pb) results in the underpotential deposition of the latter on the Se/TiO_2 surface, to afford MSe/TiO_2 composites. These composites are characterized by UV-visible reflectance spectroscopy, X-ray powder diffraction analysis, and X-ray photoelectron spectroscopy.

Two other strategies for electrochemically preparing semiconductor arrays are discussed, based on two contrasting template structures – one based on polystyrene spheres and the other based on porous alumina (alumite). Polystyrene sphere templates with two-dimensional (2D) periodical arrays are made from nanosized particles suspended in solution, and the void lattices are filled with precursor solutions for semiconductor deposition. Porous alumina templates, with self-organized cylindrical, uniformly sized holes ranging from 20 to 200 nm in diameter, are prepared by anodic oxidation of aluminum in acidic electrolyte, and are used for the fabrication of semiconductor one-dimensional (1D) nanowires. The two types of templates provide nanostructured semiconductor materials with structural ordering (in 1D and 2D arrays), and due to their nanometer size, their electrical and optical properties differ from those of the corresponding semiconductor bulk materials. We will present scanning electron microscopy characterization of the resultant nano-architectures.

Poster #

CONFORMATIONAL CONTROL OF OXIDATION SITES, SPIN STATES AND ORBITAL OCCUPANCY IN NICKEL PORPHYRINS

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Photosynthetic reaction centers and heme proteins can be reconstituted with nickel bacteriochlorophylls and porphyrins which serve both to modulate redox potentials and rates of electron transfer and act as spectroscopic probes. As well, current interest in the chemistry of carbon dioxide has focused attention on Factor 430,the sole biological tetrapyrrole to contain Ni. The cofactor mediates the final stages of the conversion of CO_2 to hydrocarbons in methanogenic bacteria via a catalytic cycle postulated to involve Ni(I) and Ni(III) intermediates, redox states which may require significant structural reorganization of the tetrapyrrole skeleton.

We present here results for the oxidations of planar and nonplanar Ni(II) porphyrins which illustrate the acute sensitivity of sites of oxidation (metal vs. porphyrin), spin states, and orbital occupancy to the conformation and plasticity of the porphyrin skeleton, effects likely to be imposed *in vivo* by the protein scaffolding.

1) Sterically unconstrained, planar porphyrins

"Ordinary" Ni(II) porphyrins are oxidized to Ni(II) π cation radicals which, on addition of axial ligands (L), undergo an internal electronic isomerization to $L_2Ni(III)P^+$. The ligand field strength of the axial ligands in turn determines whether the unpaired electron of the Ni(III) resides in the d_{z^2} (weak ligands such as imidazole or pyridine) or in the $d_{x^2-y^2}$ orbital (strong ligands such as cyanide). Occupancy of the latter requires a significant expansion of the Ni-N porphyrin core.

2) Nonplanar, flexible porphyrins

Distortion of the porphyrin macrocycle renders the molecule easier to oxidize. On addition of axial ligands (Im, py) to the π cation radical, the radical is retained and the Ni(II) is simply converted to a high spin Ni(II), resulting in an unusual, formally 3 spin system. Here again, the high-spin Ni(II) requires expansion of the Ni-N equatorial core.

3) Nonplanar, sterically constrained porphyrins.

Porphyrins can be conformationally designed to introduce a large energy barrier to expansion of the Ni-N core, Ni 5,10,15,20-tetra(t-butyl)porphyrin, for example. In contrast to the above results, this barrier prevents population of the $d_{x^2-y^2}$ orbital and its concomitant required core expansion such that addition of weak AND strong field ligands to the NiT(t-Bu)P π cation leads ONLY to Ni(III) with d_{z^2} occupancy which requires no expansion of the Ni-N core. Thus, porphyrins can be molecularly engineered to control the sites of oxidation and orbital occupancy with a resulting vectorial direction of the unpaired electron density, i.e. in the porphyrin plane, in the axial plane, or both.

PRIMARY CHARGE SEPARATION AND $A_0^- \rightarrow A_1$ ELECTRON TRANSFER IN PHOTOSYSTEM I REACTION CENTERS FROM *Synechocystis* sp. PCC 6803

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The charge separation $P700^*A_0 \rightarrow P700^+A_0^-$ and the subsequent electron transfer from the primary to secondary electron acceptor have been studied by subtracting absorption difference profiles for wild-type cyanobacterial photosystem I (PS I) complexes with open and closed reaction centers. The PS I kinetics were analyzed in terms of the relevant P700, $P700^+$, A_0, and A_0^- absorption spectra. The radical pair $P700^+A_0^-$ forms with 1.3 ps rise kinetics after creation of electronically excited P700*. The formation of A_1^- via electron transfer from A_0^- requires ~ 13 ps in wild-type PS I. The kinetics of the latter step are appreciably faster than previously estimated by other groups (20-50 ps).

These reaction center processes have also been studied in photosystem I complexes from several site-directed PsaB mutants targeting residues that bind P700, the accessory chlorophyll, or the primary electron acceptor A_0. For mutants that grow well enough to permit isolation of PS I trimers (H651C, H651Q, N582Q, H430N, F647Y, and F649C/G650T), the kinetics of the primary charge separation and the $A_0^- \rightarrow A_1$ electron transfer are not appreciably different from those in the wild type. This does not imply that these processes are insensitive to changes in protein environment; rather, PS I assembly and/or growth tends to be disabled in mutants that significantly perturb the reaction center cofactor arrangement.

The $A_0^- \rightarrow A_1$ electron transfer was also studied in a PS I *menB* mutant in which biosynthesis of the native phylloquinone secondary electron acceptor A_1 is inhibited. The A_1 binding site is then occupied by plastoquinone (denoted Q), which ordinarily appears elsewhere in the photosynthetic apparatus. The $A_0^- \rightarrow Q$ electron transfer in this mutant is several orders of magnitude slower than the $A_0^- \rightarrow A_1$ electron transfer in native PS I. Despite this, the whole-chain electron throughput in *menB* PS I is ~80% that in native PS I; photosynthetic function thus appears more tolerant of structural changes in the secondary acceptor than to changes in the chlorophylls that comprise P700 through A_0.

When the P700 special pair becomes oxidized into $P700^+$, it becomes converted into a chlorophyll cation, plus an uncharged monomeric chlorophyll (C690) whose 0-0 Q_y transition occurs at 690 nm. The emerging C690 absorption band broadens with 300 ns kinetics after creation of $P700^+$. This nanosecond spectral diffusion is likely associated with large-scale changes in the protein arrangement surrounding P700, triggered by the electric fields that attend charge separation.

INVESTIGATIONS OF ANTI-STOKES EMISSION IN COLLOIDIAL SEMICONDUCTOR QUANTUM DOTS

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We had previously reported the first observation of photoluminescence (PL) up-conversion (anti-Stokes PL) in quantum-confined semiconductor colloids. Here we present the results of further investigations that were conducted with the intent to characterize the mechanism of this process, and to elucidate the chemical nature of the states involved.

Colloidal quantum dots (QDs) were synthesized by colloidal chemistry methods. The up-converted PL (UCPL) exhibits a unique spectral shape, a tailing spectrum to the blue of the excitation wavelength; the maximum blue shift is about 300 meV. The relative intensity of the UCPL generally follows the intensity distribution of the normal global PL emission across the whole PL spectrum (both band-edge and deep trap emission). The UCPL exhibits a saturable, linear dependence on excitation intensity. Temperature dependent experiments on the dots showed that the intensity of the normal PL increased with decreasing temperature, while the intensity of the UCPL decreased with temperature; a characteristic of a process associated with activation energy.

We suggest that the observed photon up-conversion involves initial photoexcitation of electrons from a sub-gap state (eg. HOMO levels- possibly associated with a P orbital) into the QD conduction band. In particles that are small enough, the photexcited electron may relax to a sub-gap surface trap site. The photogenerated hole may subsequently be promoted to the valance band by an energy transfer mechanism (we believe phonon absorption is the likely mechanism; the low level excitation density excludes the possibility of non-linear effects, and the linear dependence negates a two-photon absorption event). Once in the final electronic states, the electrons can then undergo radiative recombination with holes in the valence band states.

In order to more fully understand the mechanism of the observed UCPL, we performed a series of characterization experiments. It was first demonstrated that by etching with HF, the UCPL efficiency was increased. Thus, in the case of InP we were able to conduct IR absorbance experiments before (low UCPL efficiency) and after (much higher UCPL efficiency) etching with HF. Results of Temperature Programmed Thermal Desorption experiments are also presented. In the case of CdSe, we compared an as-prepared sample that did not exhibit any appreciable UCPL with a different sample that did show a fair amount of UCPL in a series of different characterization experiments.

In summary, we report highly efficient PL up-conversion in colloidal InP and CdSe QDs at low light intensity. We believe the mechanism for UCPL is a two-step process first involving excitation from defect state near valence band, followed by hole up-conversion to the valance band.

RED-ABSORBING CHLOROPHYLL *a* ANTENNA STATES OF PHOTOSYSTEM I OF CYANOBACTERIA

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Photosystem I (PSI) of green plants and cyanobacteria possess Chl *a* Q_y-antenna states that lie lower in energy than P700*, the primary electron donor state of the reaction center (RC). P700 is known to be a strongly coupled Chl *a* dimer ("special pair"). The red antenna states serve as traps for excitation energy from bulk Chl *a* antenna states, efficiently transfer energy to the RC at biological temperatures and extend absorption further to the red. Thus, they play a very important role in the functioning of PSI. We performed a detailed study of the red antenna states of the cyanobacterium *Synechocystis* PCC 6803 (wild type trimer and monomer forms) and mutants deficient in the PsaF, K, L and M protein subunits. The main objectives were (i) to determine whether they are due to strongly coupled Chl *a* dimers or Chl *a* monomers with unusual protein interactions, and (ii) to obtain information on the location of the red antenna Chls within the PSI structure that consists of 11 protein subunits and ~ 90 Chl *a* molecules. The hole spectra and Stark and high pressure hole burning data identified two red antenna states at 706 and 714 nm both of which could be assigned to strongly coupled Chl *a* dimers with the coupling for the 714 nm state being the stronger of the two.[1] (It had been previously believed that *Synechocystis* possesses only one red antenna state at ~ 708 nm.[2]) For example, the values of the pressure shift rate R_p, $f \cdot \Delta\mu$ (f the local field correction factor) and S factor due to low frequency phonons for the 714 nm state are $-0.5\ \mathrm{cm}^{-1}$/MPa, 2.4 D and ~ 2, values far too large for assignment to a Q_y-state localized on a *monomer* Chl *a*. These values strongly point to a dimer state with significant CT character, i.e. a "special pair" antenna state. Reference 3 reports on theoretical simulations of the dependencies of the hole spectra on burn wavelength and fluence that led to a more complete characterization of the 706 and 714 nm states including their electron-phonon coupling strengths and site distribution functions. It was concluded that the "red" Chl *a* molecules are located close to the interfacial regions at the trimer forming side between PsaL/PsaM and the PsaA/B heterodimeric core and that they are bound to PsaA and/or PsaB.

This is in agreement with the very recently reported 2.5 Å resolution structure of *Synechococcus elongatus*[4] that allowed for identification of three Chl *a* dimers and one trimer as candidates for the red Chl *a*'s. Recently obtained results for PSI of *Synechococcus* from experiments of the type performed on *Synechocystis* will be reported and compared with those for *Synechocystis*. As of this writing it is clear that *Synechococcus* possesses three red antenna states at ~ 708, 715 and 719 nm and, furthermore, that the properties of the 719 nm state are very similar to those of *Synechocystis*' lowest energy 714 nm state.

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3. L.-O. Pålsson, C. Flemming, B. Gobets, R. van Grondelle, and E. Schlodder, *Biophys. J.* **1998**, 74, 2661.
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THEORETICAL STUDIES OF QUANTUM DOT ARRAY SYSTEMS

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Collections of essentially isolated quantum dots (QDs) have been extensively studied theoretically and experimentally. Prodigious effort has also been devoted to electronically interacting QDs in arrays because of important applications, especially those which involve QD array superlattices. But understanding of QD arrays lags behind isolated systems. The former systems are important in our NREL experimental program, and are the focus of this theoretical poster.

We employ a number of theoretical methodologies. For calculations on smaller systems the basic core of our programs is state of the art density functional theory (DFT), using both plane wave and real space frameworks. For large scale calculations we are currently primarily employing simplified pseudopotential methods fit to ab initio DFT results, but we are making a transition to use of O(N) SCF methods coupled with our new state selective algorithms. The majority of the calculations are performed on static systems, but atomic dynamics calculations are utilized when appropriate. We also propagate electron wave packets through these systems for transport studies.

Our results highlight the importance of state localization in these systems, and its sensitivity to system characteristics (perfectly ordered arrays of identical QDs are an idealization, and may remain so far into the future). We find the electronic properties of QD array systems can be significantly affected by QD surface structure (oxidation, reconstruction, adsorbates etc.), crystal face orientation, spacing, dot size, and many kinds of interactions with an organic matrix. All this can greatly affect where (in energy and space) states will be localized in QD arrays, and the character of miniband formation. In general our calculations predict mixed extended and localized state conduction through disordered real world QD array systems, in accord with existing experiments. Many experimental observables depend on how disordered the system is, and consequently how localized the states are. Many of our theoretical predictions are directly comparable to experiment.

In short, theoretical studies like ours can serve to elucidate real world systems, and help lead the way to practical QD array solar devices.

ULTRAFAST ELECTRON TRANSFER IN COFACIALLY ALIGNED, π-STACKED AROMATIC SYSTEMS

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The synthesis, spectroscopy, and solution structure, as well as the conformational and ET dynamical properties, of a series of unusually rigid π-stacked porphyrin-spacer-quinone systems have been elucidated. One exceptional aspect of these donor-spacer-acceptor (D-Sp-A) species is the fact that the interplanar distances that separate adjacent, cofacially aligned aromatic moieties is fixed by the 1,8-substitution pattern of naphthalene (2.95 Å); these synthetic constructs thus define D-Sp-A systems in which the stacked aromatic units are fixed at a distance significantly less than the sum of their van der Waals radii (3.45 Å).

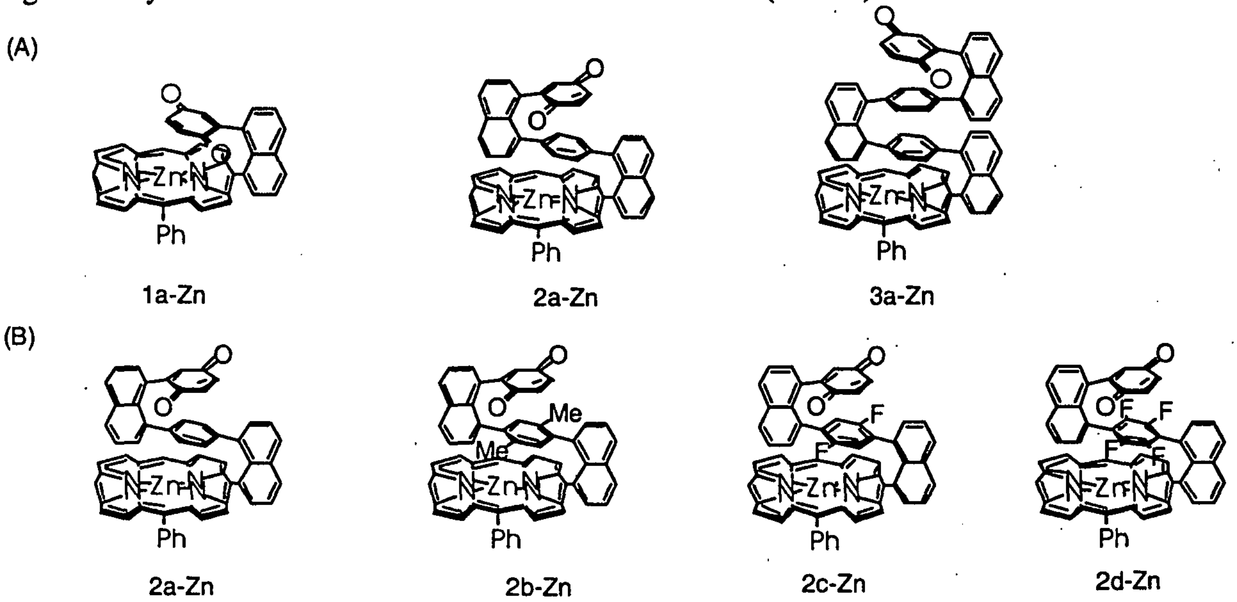

Figure 1. Exemplary rigid D-Sp-A systems based on naphthyl pillars to probe the magnitude of electronic coupling in stacked aromatic systems at sub van der Waals contact. (The 20-phenyl ring has been omitted for clarity.)

Analyses of both photoinduced electron transfer and thermal charge recombination rate data show that the distance dependence of ET rate constants for both the CS and CR reactions in these systems is remarkably weak, differing markedly from that elucidated for DNA-mediated charge transfer reactions. These results indicate that ET reactions in these π-stacked aromatic structures manifest relatively small values of the damping factor β, despite the fact that the tunneling energy lies several eV from the medium frontier orbitals, and that the sub van der Waals interplanar separations enforced by the 1,8-naphthyl pillaring motif can facilitate fast ET reactions even at low thermodynamic driving force.

A Cu^{2+} SITE IN PHOTOSYNTHETIC BACTERIAL REACTION CENTERS THAT MODULATES ELECTRON TRANSFER

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Electron transfer reactions that occur within proteins are often intimately coupled with 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. A useful system to study is that found in photosynthetic bacteria, wherein an integral membrane reaction center (RC) protein couples light-induced sequential electron transfer with proton transfer reactions. Proton uptake occurs following the photoexcitation of a special pair of bacteriochlorophylls (P) which decays through a one-electron transfer reaction via a monomeric bacteriochlorophyll and bacteriopheophytin to the primary (Q_A) and secondary (Q_B) quinone acceptors. 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. In RCs from *Rb. sphaeroides*, the electron transfer between Q_A and Q_B ($Q_A^-Q_B \rightarrow Q_AQ_B^-$) is temperature activated, believed to be rate limited by protein motion, and modulated by metal ions. $Q_A^-Q_B \rightarrow Q_AQ_B^-$ electron transfer and Q_B proton uptake reactions in RCs from different species of purple bacteria have not been as well characterized. We have extended our work to investigate the metal binding properties of RCs from *Rb. capsulatus* and *Rps. viridis*, specifically searching for a surface metal site involved in electron transfer.

The interaction of metal ions with photosynthetic RCs from the purple bacteria *Rb. sphaeroides*, *Rb. capsulatus* and *Rps. viridis* has been investigated with transient optical and magnetic resonance techniques. In RCs from all 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+}, similar to the metal ion effect observed for RCs from *Rb. sphaeroides* where Zn^{2+} was bound to a specific site on the surface of the RC (Utschig, L. M., et. al. (1998) *Biochemistry 37*, 8278). The coordination environments of the Cu^{2+} sites were probed with electron paramagnetic resonance (EPR) spectroscopy, providing the first direct spectroscopic evidence for the existence of a second metal site in RCs from *Rb. capsulatus and Rps. viridis*. In the dark, RCs with Cu^{2+} bound to the surface exhibit axially symmetric EPR spectra. Electron spin echo envelope modulation (ESEEM) spectral results indicate multiple weakly hyperfine coupled ^{14}N nuclei in close proximity to Cu^{2+}. These ESEEM spectra resemble those observed for Cu^{2+} RCs from *Rb. sphaeroides* (Utschig, L. M. et. al. (2000) *Biochemistry 39*, 2961) and indicate that two or more histidines ligate the Cu^{2+} at the surface site in each RC. Thus, RCs from all three species each have a structurally analogous Cu^{2+} binding site that is involved in modulating the electron transfer process. Inspection of the *Rps. viridis* crystal structure reveals four potential histidine ligands from three different subunits (M16, H178, H72, L211) located beneath the Q_B binding pocket. The location of these histidines is surprisingly similar to the grouping of four histidine residues (H68, H126, H128, L211) observed in the *Rb. sphaeroides* RC crystal structure. Further elucidation of these Cu^{2+} sites will provide a means to investigate localized proton entry into the RCs of *Rb. capsulatus* and *Rps. viridis* as well as locate a site of protein motions coupled with electron transfer.

STRUCTURE AND STRUCTURAL DYNAMICS OF NATURAL AND ARTIFICIAL PHOTOSYNTHETIC ASSEMBLIES MEASURED IN SOLUTION USING HIGH ANGLE X-RAY SCATTERING

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This project is resolving structure and reaction-linked structural change of natural and artificial photosynthetic assemblies in "real-world", noncrystalline media by exploiting new capabilities for making wide-angle ($0.002\ \text{Å}^{-1} < q < 1.5\ \text{Å}^{-1}$, where $q=(4\pi/\lambda)\sin 2\theta$, and λ is the X-ray wavelength, and 2θ is the scattering angle) X-ray and anomalous X-ray scattering measurements at the Advanced Photon Source[1]. The ability to measure higher angle scattering for macromolecular assemblies in solution is significant because of the ability to probe structure on a dimension scale, $d \geq 4$ Å, that is small compared to macromolecular structure. Our previous work has shown that higher angle scattering patterns are sensitive to macromolecular fine-structure and structural dynamics[2,3], for example, permitting resolution of oxidation-linked structural change in cytochrome c with as little as a 0.3 Å rms difference in protein backbone configuration. This sensitivity and ability to resolve structure in disordered media makes the scattering technique well-suited for investigating atomic reorganization associated with photochemical reactions. We are investigating correlations between macromolecular structure and reaction-linked structural change in natural and artificial photochemical assemblies.

1. The Photosynthetic Reaction Center. Scattering patterns for detergent solubilized reaction centers show pronounced, characteristic detergent and temperature dependencies. Temperature dependent changes in the range 1° C to 25° C can be modeled to arise from reaction center dimerization. Binding of divalent metals ions to the surface site[4] prevents this association. These results suggest a possible correlation between the surface metal ion binding site and the puf X/antenna linking site. Higher angle scattering measurements have been carried out with sufficient precision to resolve light-induced structural change associated with quinone reduction in crystals, and current work is developing techniques to follow reaction-linked reorganization in non-crystalline states.

2. Artificial Photochemical Assemblies. Preliminary high angle scattering measurements have been made on water-soluble and organic soluble porphyrins and porphyrin assemblies[5]. These experiments have demonstrated the ability to resolve scattering for porphyrin monomers, dimers, and higher order assemblies, and has demonstrated the sensitivity of the scattering measurements to molecular assembly, porphyrin substituants, and structural dynamics. This work establishes a foundation for investigating solvent association and light-driven dynamics.

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[3]Zhang, R., Marone, Thiyagarajan, P., Tiede, D.M. (1999) Langmuir 22: 565-568.
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EPR STUDY OF THE PHOTOEXCITED TRIPLETS OF C_{60} ADDUCTS

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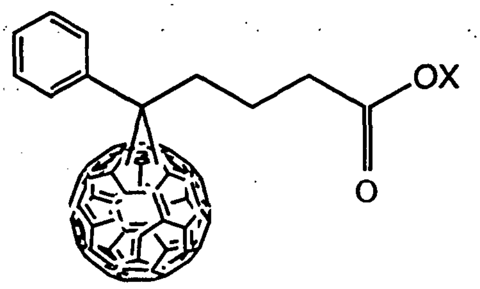
The photophysics and photochemistry of 1-(3-(methoxycarbonyl)propyl)-1-phenyl[6,6]C61 (M1-OMe) and 1-(3-(carboxypropyl)-1-phenyl[6,6]C61 (M1-OH) was studied with time-resolved EPR . Frozen solution cw TR-EPR spectra of the photoexcited triplets of these C_{60} adducts are compared with those of ${}^3C_{60}$. The introduction of the substituents has a striking effect on the EPR spectra of the triplets. This is attributed to the lifting of the orbital degeneracy of the triplet state.



M1-OX, X = H or CH_3

Fourier Transform (FT) EPR was applied in an investigation of electron transfer reactions in liquid solution mediated by the photoexcited triplets of the C_{60} adducts. Of particular interest was the system M1-OMe (or M1-OH)/perylene/chloranil where excitation of the C_{60} derivatives leads to formation of the perylene cation radical (Pe^{+}) and chloranil anion radical (CA^{-}). From Chemically Induced Dynamic Electron Polarization (CIDEP) patterns observed in the FT-EPR spectra and the dependence of reaction kinetics on reactant concentrations it can be deduced that electron transfer involves the following competing reaction paths:

$$C_{60} \xrightarrow{h\nu} {}^1C_{60} \xrightarrow{isc} {}^3C_{60}$$

I. ${}^3C_{60} + CA \rightarrow C_{60}^{+} + CA^{-}$

$C_{60}^{+} + Pe \rightarrow C_{60} + Pe^{+}$,

or

II. ${}^3C_{60} + Pe \rightarrow C_{60} + {}^3Pe$

${}^3Pe + CA \rightarrow Pe^{+} + CA^{-}$.

CW TREPR was used to monitor the adsorption of the compounds dissolved in toluene onto a TiO_2 film deposited on the window of an EPR cell. The TREPR spectrum of the photoexcited triplets was recorded while pumping solutions of the C_{60} adducts over the semiconductor layer. It is found that M1-OH is rapidly adsorbed from solution as evident from the change of the spectrum from that characteristic of a triplet in solution to that of an immobilized triplet. By contrast, the spectrum of M1-OCH_3 does not display this transformation. M1-OH adsorption is attributed to chemical bond formation between the –COOH group and TiO_2. It is noteworthy that the chemisorbed C_{60} derivative gives rise to a reasonably strong triplet EPR spectrum. There is no evidence of electron transfer quenching of the exited state.

PHOTOINDUCED CHARGE TRANSFER STUDIES IN NANODOMAINS OF CONFINED LIQUID CRYSTALS

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Photosynthetic proteins have complex relaxational processes that span the range of picoseconds to seconds. This unusually wide temporal range of dielectric relaxation of proteins is recognized as an important contributor to efficient charge separation in natural photosynthesis. It enables the protein environment in reaction centers to act as a "solvent" that can reorganize to produce an optimized free energy for each charge separation step. An interesting class of solvents that mimic the broad temporal responses of protein relaxation are liquid crystals. Nematic and smectic liquid crystals possess an unusually wide range of dielectric reorganizational responses that range from picoseconds to microseconds and are thus separated from the more homogeneous responses of conventional isotropic liquids. It is also known that confinement of liquid crystals on 100 nm length scales or less can extend the range of dielectric responses by orders of magnitude. Thus, confined nanodomains of liquid crystals represent unique biomimetic environments for the study of photoinduced electron transfer reactions.

We report time-resolved absorption/emission studies of chromophores with emissive charge separated states in nanodomains of liquid crystals. The energy of the emissive charge separated states are useful for ascertaining the energy levels of photoinduced ion pairs in these unique environments to a reasonable degree of precision, and the transient studies permit analysis of the solvation response. The nanodomains themselves are created by using anodic aluminum oxide (AAO), shown in Figure 1. It is an unusually homogeneous and nanoporous matrix with a tunable pore size from 4 to 300 nm. This work uses pore sizes of 50 nm and a film thickness of 20 μm. It is transparent, permitting a wide range of spectroscopies. Furthermore, the ordering of liquid crystals on nanometric to bulk length scales permits additional spectroscopies that are sensitive to structural reorganization, such as X-ray scattering and EXAFS. Temperature dependent studies are also reported, since the phase transition between the liquid crystal and isotropic phases is unique in that nanometric swarms of order exist well into the isotropic phase of liquid crystals. The data show large changes in the ion pair stabilization as a function of domain or swarm size.

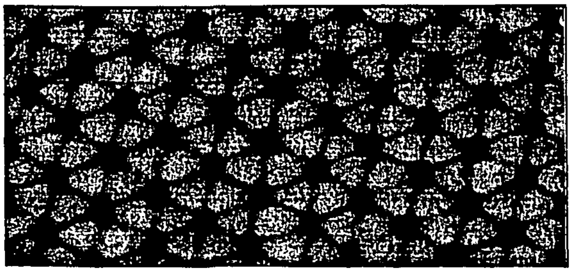

Figure 1. An AFM image of anodic aluminum oxide with 50 nm pores (in black) is shown. The thickness of the film is 20 μm.

NEAR-FIELD HIGH RESOLUTION IMAGING OF PHOTOSYNTHETIC MEMBRANES

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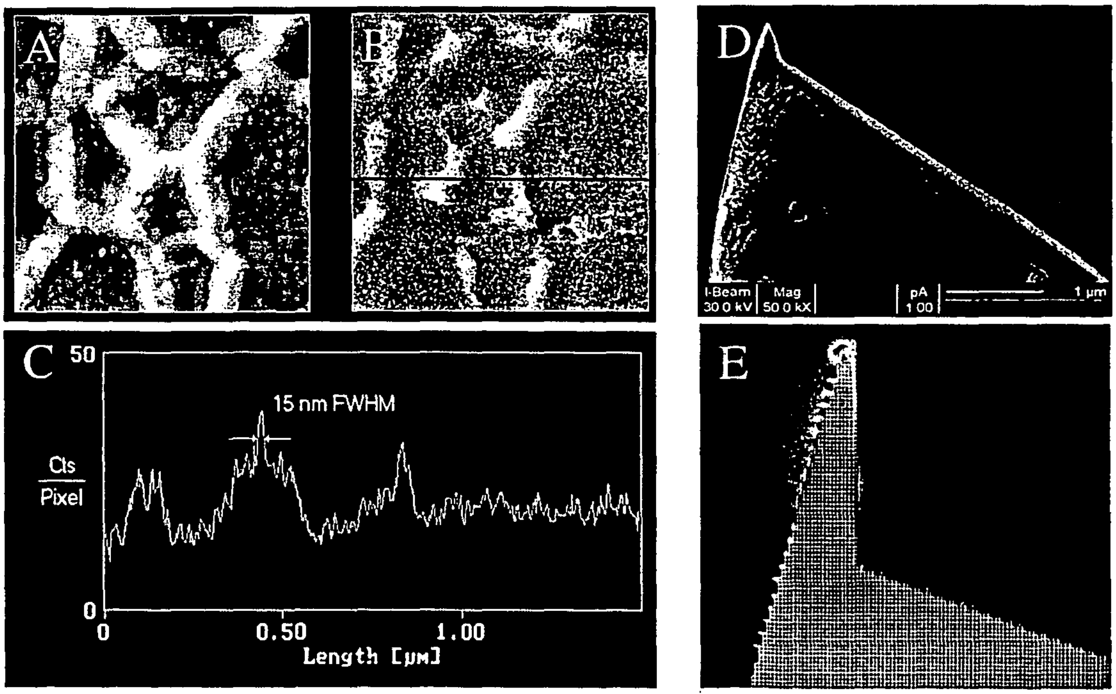
Recent advances in aperture-less near-field microscopy [1,2] make it possible to obtain spectroscopic mapping of photosynthetic membranes with better than 20 nm resolution. The key behind this technique is a sharp metal tip, illuminated with light of a proper polarization. The highly enhanced and localized field around the tip results in two-photon excitation (TPE) of the sample fluorescence. We use 3D electromagnetism simulation based on the finite difference time domain method (FDTD) to design new tip shapes and use a dual beam focused ion beam (FIB) instrument to fabricate the tips. These new tips have high field enhancement and provide unprecedented spatial resolution, comparable to the size of individual protein molecules. With this resolution we image and spectroscopically identify different regions in the thylakoid membrane fragments extracted intact from Spinach chloroplasts (*Spinacia oleracea*).



(**A**) Simultaneous topographic and (**B**) near-field TPE fluorescence images of thylakoid membranes, (**C**) and the cross-section of the black line in (B) with a feature with FWHM of 15 nm. (**D**) Electron micrograph of the FIB milled Au tip, and (E) Electric field distribution based on a FDTD simulation for the Au tip used for obtaining the images. The field is strongest at the apex of the tip, with a field enhancement of 80.

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MECHANISTIC STUDY OF $CH_3OH + O_2$ PHOTOREDOX REACTION IN $FeAlPO_4$ SIEVE BY TIME-RESOLVED FT-IR SPECTROSCOPY

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Substantial progress in the understanding of the multi-step processes following interaction of donor and acceptor molecules with excited framework metals of molecular sieves is expected to emerge from time-resolved monitoring of the chemistry. In order to obtain insight into the detailed mechanism of a prototypical redox reaction in a microporous material, we have employed rapid-scan and step-scan FT-IR spectroscopy to follow CH_3OH oxidation and O_2 reduction in ligand-to-metal charge-transfer (LMCT) excited Fe aluminophosphate sieve. In this poster, we present the results of time-resolved FT-IR measurements on the microsecond to second time scale in order to elucidate the mechanism of the $CH_3OH + O_2$ photoredox chemistry in LMCT-excited $FeAlPO_4$ sieve.

An unexpected observation of our previous study of the single photon-induced $CH_3OH + O_2$ reaction in this microporous solid by static infrared spectroscopy was that the only detectable species were the 4-electron transfer products HCO_2^- and H_2O. Specifically, no $CH_2{=}O$ was observed, a likely 2-electron oxidation product of methanol. The lack of observation of formaldehyde could, in principle, be due to efficient reaction with reactants, other intermediates, or products present in the sieve. Therefore, we loaded formaldehyde gas into the sieve at 250 K and found that it reacts with adsorbed H_2O, CH_3OH, H_2O_2, or with lattice OH groups to yield the corresponding addition product, namely $CH_2(OH)_2$, CH_3OCH_2OH, HO_2CH_2OH, or $POCH_2OH$, respectively. By far most efficient was the reaction with H_2O_2. Moreover, among these adducts of formaldehyde, only HO_2CH_2OH was found to be sufficiently labile in the dark and under irradiation for playing a role as a 2-electron transfer intermediate of the $CH_3OH + O_2$ system.

Rapid-scan FT-IR spectroscopy of the $CH_3OH + O_2$ photoreaction revealed that the final products, $HCO_2^- \cdots$ Fe and H_2O, emerge with a rise time of 4 seconds (250 K) by rearrangement of HO_2CH_2OH. Intermediacy of this hydroperoxide was established by direct detection by step-scan FT-IR spectroscopy on the 500 microsecond time scale, and by monitoring of its photodissociation products $HCO_2H + H_2O$ on the millisecond second time scale. Experiments were conducted with $^{13}CH_3OH$, CD_3OH, and $^{18}O_2$. The photo-fragmentation products were dominant in time-resolved spectra taken at photolysis repetition rates faster than the spontaneous decay time of HO_2CH_2OH (4 seconds), and reflect the high efficiency of the hydroperoxide photodissociation.

The fast rise of HO_2CH_2OH strongly suggests that this 2-electron transfer intermediate is formed by direct coupling of HOO and CH_2OH radicals, the presumed one-electron redox products. Progress towards the detection of these primary radical intermediates on the nanosecond time scale will be presented. This work constitutes the most direct insight thus far into a redox reaction of gas phase molecules at an excited framework metal center.

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