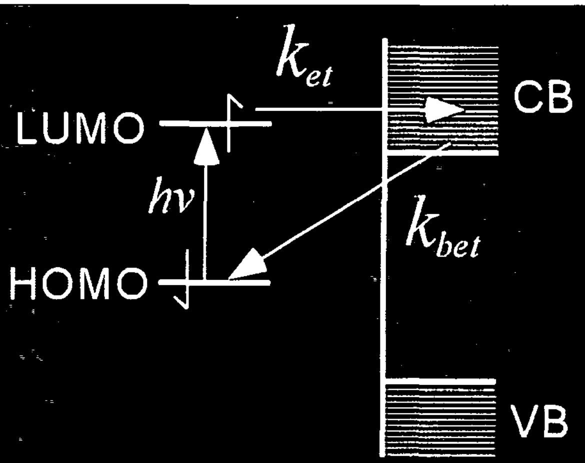
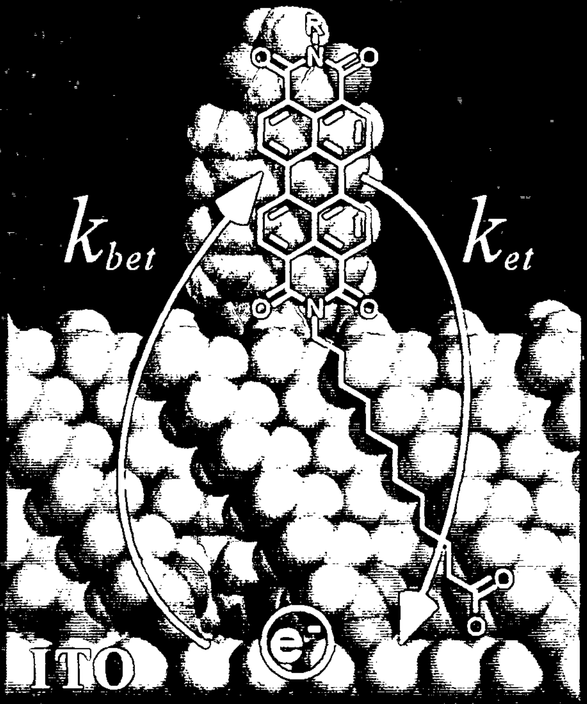
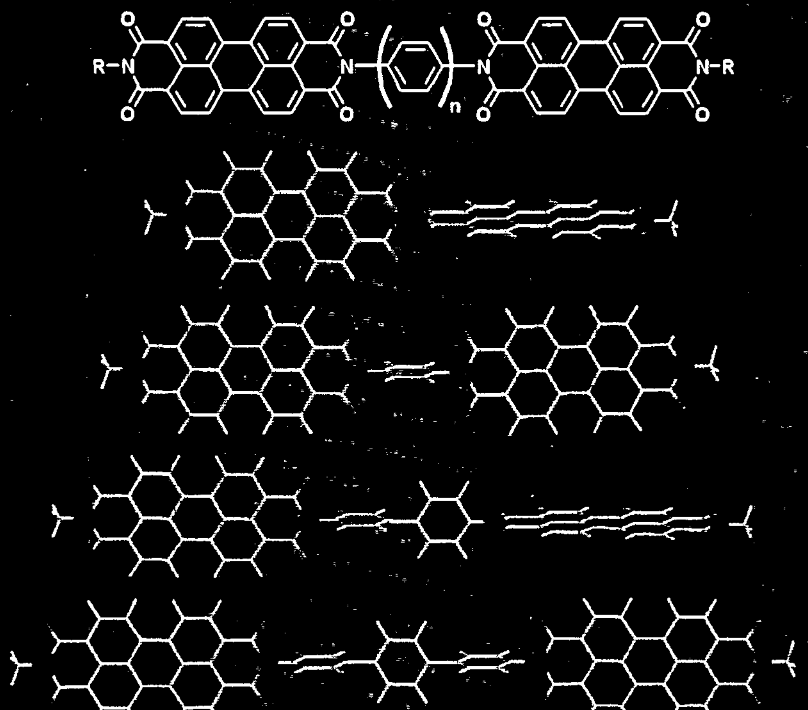
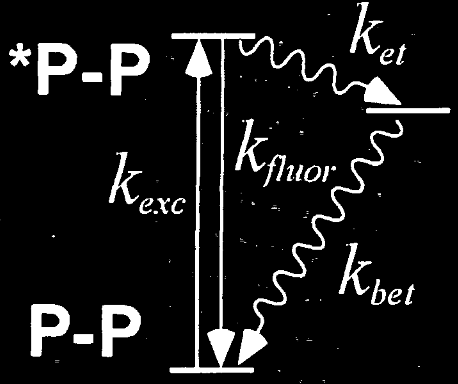
### Proceedings of the

# Twenty-Sixth DOE Solar Photochemistry Research Conference









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

*Held at:*
**Granlibakken Conference Center**
**Tahoe City, California**
**June 8-12, 2003**

# Cover Graphics

The figures at the upper right depict perylene bisimide dyes in self-assembled monolayers on a tin-doped indium oxide, p-type semiconductor, which undergo photoinduced electron transfer to the semiconductor electrode. Fluorescence trajectories from single molecules show each discrete electron transfer event, enabling the measurement of both forward and backward electron transfer rates at the single molecule level. In the figures at the lower left, symmetric perylene bisimide dimers connected by oligophenylene bridges of varying length show fluorescence quenching due to photoinduced intramolecular electron transfer. Solution and single-molecule fluorescence experiments, along with theoretical modeling, have been used to study this electron transfer, which is found to depend on both the distance and relative orientation between the two chromophores. (Michael W. Holman and David M. Adams, Columbia University)

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# FOREWORD

The 26th Department of Energy (DOE) Solar Photochemistry Research Conference is being held June 8-12, 2003, at the Granlibakken Conference Center in Tahoe City, California. The meeting is sponsored by the Chemical Sciences, Geosciences and Biosciences Division of the Office of Basic Energy Sciences. These proceedings include the agenda for the meeting, a list of the 87 participants, and abstracts of 29 formal presentations and 49 posters presented at the conference.

The annual Solar Photochemistry Research 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 meeting provides an opportunity for scientists in the program to present and exchange information about subjects of common interest, to establish collaborations among research groups, to identify research needs, and to discern areas for future research directions.

The special guest plenary lecturer is Professor Mark Ratner of Northwestern University, who will discuss theoretical aspects of transport at molecular junctions. The topical sessions that follow will address charge transport at nanoparticle interfaces; photoelectrochemistry; transition metal excited states; light-driven intramolecular electron and energy transfer; photoinduced water splitting; and photosynthetic light-harvesting. In the Monday session on charge transfer at nanoparticle interfaces, much of the research is relatively new to the program as a result of research awards in Nanoscale Science, Engineering and Technology. You may find that the distinction is imperceptible at times between the themes of that session and those of the Tuesday session on photoelectrochemistry.

Earlier this year, in his State of the Union Address, President Bush announced the FreedomCAR and Fuel Initiative for development of technologies for hydrogen production and distribution infrastructure needed to power fuel cell vehicles and stationary fuel cell sources. The DOE solar photochemistry program is well positioned to contribute to basic research in support of this initiative, in the area of photoinduced water splitting for hydrogen production. On Wednesday evening, Professor Thomas Mallouk will report on the DOE Basic Energy Sciences-sponsored workshop "Basic Research for Hydrogen Production, Storage, and Use," held May 13-15, 2003, in which he served as chair of the Hydrogen Production panel.

I would like to express my sincere appreciation to Bill Parson and his staff at Granlibakken for their gracious hospitality, and to Andreene Witt of the Oak Ridge Institute of Science and Education for preparation of this volume. The scientific success of the meeting is due to the participants for their generous sharing of knowledge and for instilling an atmosphere of inquiry and excitement. The willing participation of all the speakers, session chairs, and poster presenters is gratefully acknowledged in making the conference a stimulating and rewarding experience.

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

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# *Program*

# 26th DOE SOLAR PHOTOCHEMISTRY RESEARCH CONFERENCE

**June 8-12, 2003**

**Granlibakken Conference Center**
**Lake Tahoe, California**

## PROGRAM

### Sunday, June 8

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

### Monday Morning, June 9

7:30 - 8:30 a.m. Breakfast, Granhall

## SESSION I

## Plenary Session

Mary E. Gress, Chairman

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

8:45 a.m. **Plenary Lecture.** Molecular Junction Transport and Electron Transfer – The Same and Not the Same
**Mark A. Ratner**, Northwestern University

9:45 a.m. Coffee Break, Garden Deck

## SESSION II

## Charge Transfer at Nanoparticle Interfaces

Gregory A. Voth, Chairman

10:15 a.m. Single Molecule Spectroscopy of Electron Transfer
**David M. Adams**, Columbia University

10:45 a.m. Single Molecule Raman Spectroscopy at the Junctions of Large Ag Nanocrystals
**Louis Brus**, Columbia University

11:15 a.m. Charge Injection through Rigid Bridges at Molecule-Semiconductor Nanoparticle Interfaces
**Elena Galoppini**, Rutgers University

Lunch, Garden Deck

## Monday Afternoon, June 9

1:15 p.m. Ground- and Excited-State Charge Transfer in Molecular- and Nanoscale Systems
**Carol Creutz**, Brookhaven National Laboratory

1:45 p.m. Charge Distribution and Fermi-Level Equilibration in Semiconductor-Metal Nanocomposites
**Prashant V. Kamat**, Radiation Laboratory, University of Notre Dame

2:15 p.m. Break, Garden Deck

2:45 p.m. Quantum Dot Molecules Assembled with Genetically Engineered Proteins
**Garry Rumbles**, National Renewable Energy Laboratory

3:15 p.m. Healing of Nanoparticle Surfaces: Opportunity for the Design of Functional Materials on Nanoscale
**Tijana Rajh**, Argonne National Laboratory

## Monday Evening, June 9

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

## SESSION III

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

## Tuesday Morning, June 10

## SESSION IV
### Photoelectrochemistry
Bruce A. Parkinson, Chairman

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

9:00 a.m. Ultrafast Electron Injection from Adsorbates to Nanocrystalline Semiconductor Thin Films: Bridge Length and Semiconductor Dependence
**Tim Lian**, Emory University

9:30 a.m. Preparation of Small Band Gap Colloidal Quantum Dot Systems for Impact Ionization and Dye Sensitization
**Suzanne Ferrere**, National Renewable Energy Laboratory

10:00 a.m. Coffee Break

10:30 a.m. Ultrafast Charge Carrier Relaxation and Separation Dynamics in Colloidal Nanostructured Absorbers
**Randall J. Ellingson**, National Renewable Energy Laboratory

11:00 a.m. Chemical Control over the Electrical Properties of III-V Semiconductor Surfaces and over Charge Transport in Mesoporous Photoelectrodes
**Nathan S. Lewis**, California Institute of Technology

11:30 a.m. Femtosecond Spectroscopy of Transition Metal-Based Charge-Transfer Chromophores
**James K. McCusker**, Michigan State University

**Tuesday Evening, June 10**

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

## SESSION V

### Charge Transfer Excited States of Transition Metal Complexes

Etsuko Fujita, Chairman

7:30 p.m. Photophysical Behavior of Transition Metal Complexes Having Multiple Photoactive Excited States
**Russell Schmehl**, Tulane University

8:00 p.m. Platinum Diimine Bis(acetylide) Complexes for Photoinduced Charge Separation
**Richard Eisenberg**, University of Rochester

8:30 p.m. Break

8:45 p.m. Excited State Molecular Structures Captured by Pulsed X-Rays
**Lin X. Chen**, Argonne National Laboratory

9:15 p.m. Theory of Electron Transfer in Complex Systems
**David Chandler**, University of California, Berkeley

9:45 p.m. Social Hour, Cedar House

**Wednesday Morning, June 11**

## SESSION VI
## Light-Driven Intramolecular Electron and Energy Transfer
Dirk M. Guldi, Chairman

8:30 a.m. Direct Measurement of Electronic Coupling for Charge Recombination within Rod-Like Photogenerated Radical Ion Pairs
**Michael R. Wasielewski**, Northwestern University

9:00 a.m. Photoinduced Electron Transfer in New Donor-Spacer-Acceptor Structural Motifs
**Michael J. Therien**, University of Pennsylvania

9:30 a.m. Light-Driven Charge Transfer in Face-to-Face Donor-Spacer-Acceptor Supramolecular Systems
**Frederick D. Lewis**, Northwestern University

10:00 a.m. Coffee Break

10:20 a.m. Theoretical Aspects of Electron Transfer: Some Issues Involving Electronic Structure and the Role of Nuclear Modes
**Marshall D. Newton**, Brookhaven National Laboratory

10:50 a.m. Molecular Wires for Solar Energy Conversion?
**John R. Miller**, Brookhaven National Laboratory

11:20 a.m. Excited State Coupling and Energy Transfer in Phenylethynylene Dendrimers
**Christopher J. Bardeen, Todd J. Martinez**, University of Illinois Urbana-Champaign

12:10 p.m. Lunch

**Wednesday Evening, June 11**

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

## SESSION VII
## Photoinduced Water Splitting
Arthur J. Frank, Chairman

| | |
|---|---|
| 7:30 p.m. | Water Oxidation Catalyzed by Ruthenium μ-Oxo Dimers<br>**James K. Hurst**, Washington State University |
| 8:00 p.m. | Report on the DOE Workshop "Basic Research for Hydrogen Production, Storage, and Use"<br>**Thomas E. Mallouk**, The Pennsylvania State University |
| 8:15 p.m. | Posters (Even numbers), Pavilion |

**Thursday Morning, June 12**

## SESSION VIII
## Photosynthetic Light-Harvesting
Thomas A. Moore, Chairman

| | |
|---|---|
| 8:30 a.m. | Photosynthetic Molecular Wires<br>**James R. Norris, Jr.**, University of Chicago |
| 9:00 a.m. | Photosynthetic Light Harvesting and Its Regulation<br>**Graham R. Fleming**, Lawrence Berkeley National Laboratory |
| 9:30 a.m. | Coffee Break |
| 9:45 a.m. | Hunt for the Red Absorbing Antenna Chlorophylls of Photosystem I<br>**Gerald J. Small**, Ames Laboratory |
| 10:15 a.m. | Electron Transport Involving Carotenoid and Chlorophyll Molecules in Photosystem II<br>**Gary W. Brudvig**, Yale University |
| 10:45 a.m. | Closing Remarks<br>**Mary E. Gress**, U.S. Department of Energy |

# *Session I*

# *Plenary Session*

# MOLECULAR JUNCTION TRANSPORT AND ELECTRON TRANSFER - THE SAME AND NOT THE SAME

Mark A. Ratner and Abraham Nitzan[§]

Department of Chemistry, Northwestern University, Evanston, IL 60208
[§]Department of Chemistry, Tel Aviv University, Tel Aviv, Israel

Electron transfer is one of the fundamental processes of nature; molecular transport junctions are one of the prototype systems for molecular electronics. There are striking mechanistic similarities and differences between these two manifestations of charge transfer. Both of them depend fundamentally on electron tunneling, but the differing boundary conditions can lead to entirely different rules for optimizing and controlling these charge transfer processes. Finally, the differing boundary conditions make interaction of these transfer processes with photonic excitations extremely different from one another.

We will discuss transport similarities and differences, mechanistic implications and some unusual aspects including gating, switching and bridge dynamics. Some issues of quenching and injection, that are complementary to the molecular situation but are of striking importance in junctions, will be stressed.

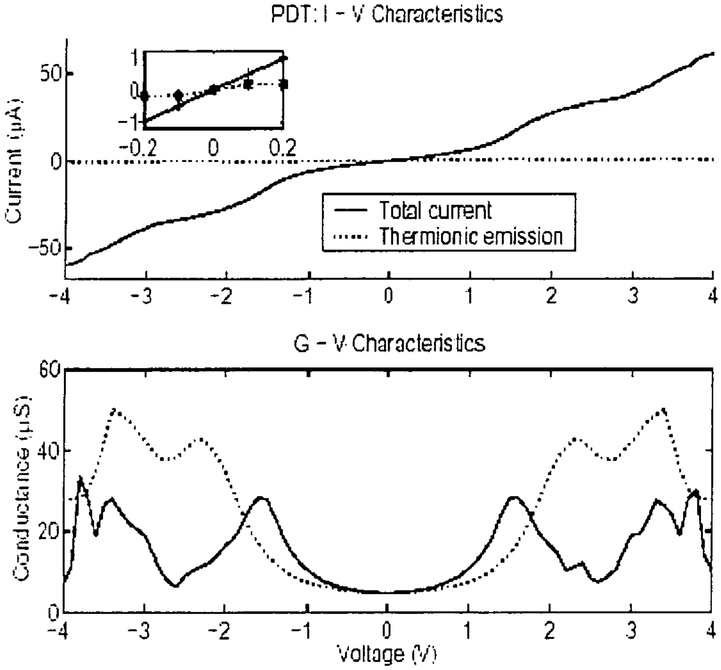


Figure 1. Computed transport in the Au/benzenedithiol junction.

One simple example of the similarity is the transition between simple coherent tunneling and vibronically or thermally assisted motions. We will mention criteria for this transition in both junctions and intermolecular transfer. Figure 1 shows the relative contributions to the current in a simple molecular junction (Au/benzenedithiol/Au); note the relative amplitudes for motion due to coherent tunneling and to thermionic emission. These mechanistic behaviors suggest that switching and transport both can be done both coherently and vibronically. Discussions of possible effects of both mechanisms in wires and in molecules will be significant.

Switching examples are also intriguing. Figure 2 shows a calculated switching behavior in a molecule that can undergo conformational switching in a two-gate, source/drain circuit. The large rectification ratio arises from the change in stereochemistry.

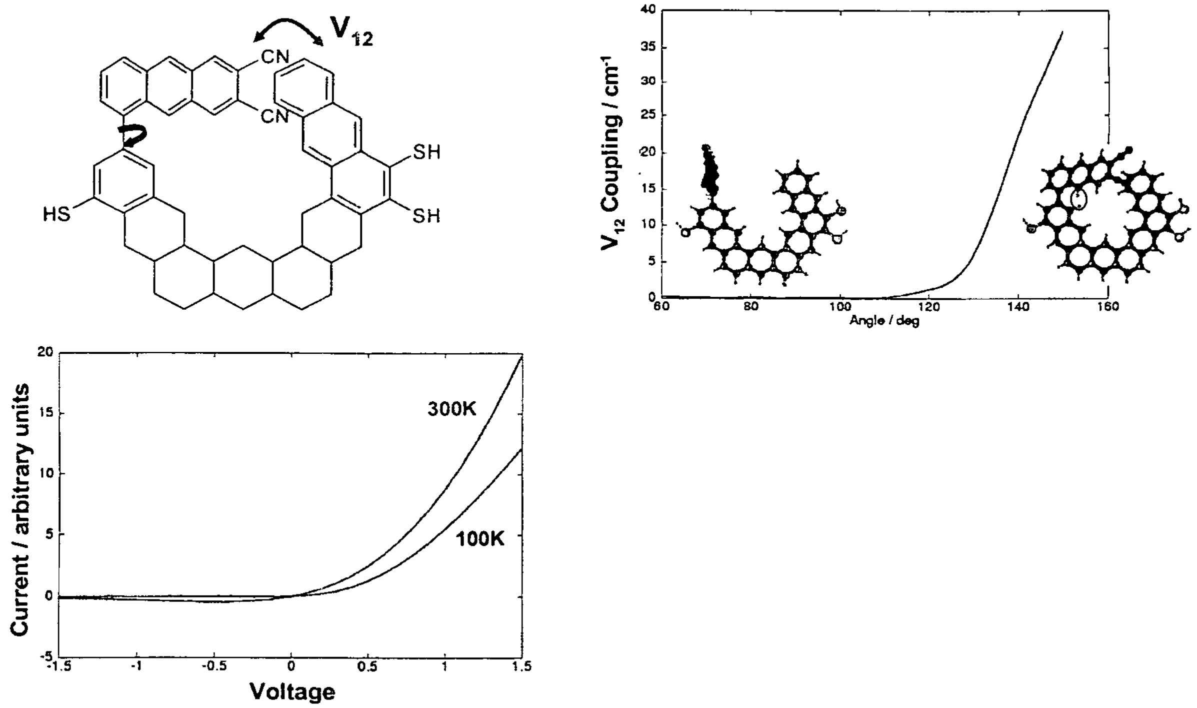


Figure 2. A system with only one through-space coupling
and high on/off conductance ratio.

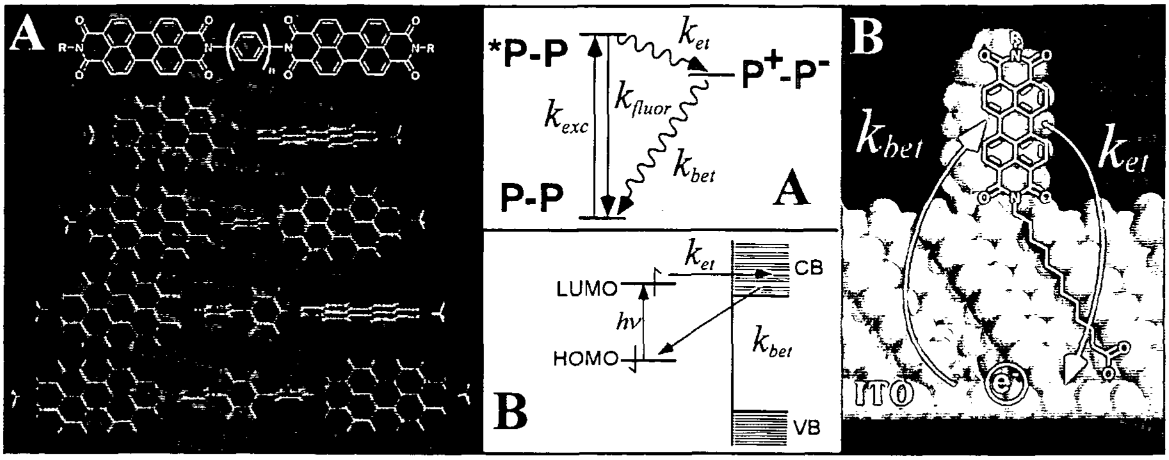
# *Session II*

# *Charge Transfer at Nanoparticle Interfaces*

# SINGLE MOLECULE SPECTROSCOPY OF ELECTRON TRANSFER

Michael Holman, Ling Zang, Ruchuan Liu, David M. Adams
Department of Chemistry, Columbia University
New York, New York 10027

The objectives of this research are threefold: (1) to develop methods for the study electron transfer processes at the single molecule level, (2) to develop a series of modifiable and structurally well defined molecular and nanoparticle systems suitable for detailed single molecule/particle and bulk spectroscopic investigation, (3) to relate experiment to theory in order to elucidate the dependence of electron transfer processes on molecular and electronic structure, coupling and reorganization energies. We have begun the systematic development of single molecule spectroscopy (SMS) of electron transfer and summaries of recent studies are shown below.



There is a tremendous need for experiments designed to probe the discrete electronic and molecular dynamic fluctuations of *single molecules* near electrodes and at nanoparticle surfaces. Single molecule spectroscopy (SMS) has emerged as a powerful method to measure properties of individual molecules which would normally be obscured in an ensemble-averaged measurement. Fluctuations in the fluorescence time trajectories contain detailed molecular level statistical and dynamical information of the system. The full distribution of a molecular property is revealed in the stochastic fluctuations, giving information about the range of possible behaviors that lead to the ensemble average. In the case of electron transfer, this level of understanding is particularly important to the field of molecular and nanoscale electronics: from a device-design standpoint, understanding and controlling this picture of the overall range of possible behaviors will likely prove to be as important as designing in the ideal behavior of any given molecule.

**Donor-Bridge-Acceptor Systems.** We have used SMS to investigate intramolecular electron transfer (IET) processes in a series of model dimer systems composed of two perylene chromophores connected via an adjustable bridge (Fig A).

The fluorescence behaviors of a large number of molecules were cataloged and the results statistically analyzed to gauge information about the range of behaviors of the ensemble. Single-molecule fluorescence time trajectories reveal "blinks", momentary losses in fluorescence (> 20 ms to seconds in duration), which are attributed to discrete IET excursions to the charge separated (CS) state. The observed statistical trends corroborate the assignment of the blinking behavior to IET. We find that fluorescence blinking behavior is dependent on bridge length and chromophore geometry, which affect the electronic coupling and therefore the IET.

**Donor-Bridge-Electrode Systems.** We have used SMS to measure the rates of photoinduced interfacial electron transfer in chromophore-bridge-electrode systems composed of perylene molecules in mixed self-assembled monolayers on ITO semiconductor electrodes (Fig. B). We have observed that the fluorescence of single perylene molecules in these structures display blinking behavior with characteristic millisecond off periods. These off periods are ascribed to discrete ET events - the molecule is not fluorescent in the charge transfer state. The fluorescence blinking is not seen for molecules on polymer coated glass surfaces since there are not states available for ET (i.e. electrode states). Electron transfer rates were obtained directly from the analysis of the fluorescence time trajectories. For many molecules studied, single exponential behavior is observed for both forward and back ET processes. Variability in the observed rates is attributed to local variations in the monolayer structure.

We are presently studying at the single molecule and bulk levels, the electric field and dielectric dependence of electron transfer rates in these systems. We are also incorporating Marcus theory for electron transfer into our analysis of the experimental data and are using quantum mechanical methods to calculate the electronic structure and electron transfer coupling matrix elements. Ongoing and future work includes the extension of this methodology to study electron transfer in other molecular structures and devices and in heterodimer systems composed of single perylene molecules[1] and high quality nanoparticles of $TiO_2$.

1) We previously developed perylene chromophores that bind to oxide surfaces. See Ling Zang, Ruchuan Liu, Michael W. Holman, Kim T. Nguyen, and David M. Adams, "A Single Molecule Probe Based on Intramolecular Electron Transfer", J. Am. Chem. Soc. 2002, 124, 10640.

Publications under DOE Basic Energy Sciences Funding (2002-2003)

1) Michael W. Holman, Ruchuan Liu, and David M. Adams, "Single Molecule Spectroscopy of Interfacial Electron Transfer", submitted to J. Am. Chem. Soc.

2) Ruchuan Liu, Michael W. Holman, Ling Zang, and David M. Adams, "Single Molecule Spectroscopy of Intramolecular Electron Transfer in Donor-Bridge-Acceptor Systems", submitted to J. Phys. Chem.

# SINGLE MOLECULE RAMAN SPECTROSCOPY AT THE JUNCTIONS OF LARGE Ag NANOCRYSTALS

Jiang Jiang, Peter Redmond, Ken Bosnick, and Louis Brus
Chemistry Department, Columbia University, New York, NY 10027

This talk will emphasize our DOE effort in understanding single molecule Raman Scattering. We also have a DOE funded effort in single wall carbon nanotubes, including the infrared band gap luminescence of semiconductor tubes, and use of Raman Scattering to identify structure. We have started a DOE collaboration with R. Friesner on very large scale, ab initio, all electron, geometrically optimized DFT calculations on 1-2 nm nanocrystals. This effort has recently yielded insight on how an oxide capped Si nanocrystal is fundamentally different than a H atom capped nanocrystal.

SERS is old subject where fundamental understanding has been hampered by the extreme heterogeneity and complexity of the rough Ag and Au surfaces which give rise to this effect. In this talk I describe how confocal microscopic optical techniques, applied to single molecules on single aggregate scattering centers, have shown how a single molecule at 23 C, under optimal circumstances, can show a spectrally integrated Stokes Raman signal that is $10^2$-$10^3$ stronger than a fully allowed, free space single molecule luminescence signal. It seems likely that in many past ensemble experiments when a relatively low average enhancement was reported, only a few molecules in junction-like or crack-like sites actually dominated the signal. The use of Ag colloids with annealed, faceted large Ag particles, rather than the cold deposited rough Ag surfaces of early studies, has lead to clear geometrical models for high enhancement sites. Such junction models now allow us to begin rational EM design of Ag particle substrates for practical use of high sensitivity SERS. The role of electron exchange between molecule and metal points to the importance of Ag and Au as noble metals without surface oxide, in addition to their role as EM field enhancers. In a sense Au is a good SERS substrate for the same reason it is preferred for electrical contacts.

In the past year we have focused on Raman depolarization studies which reveal spatial symmetry, and possible molecular rotational averaging, in the scattering process. Single Rhodamine 6G molecule SERS is complicated by strong intensity fluctuations (including blinking) for fixed incident and scattering angles We simultaneously record S and P polarized scattering spectra from a single aggregate composed of several touching 50 nm Ag particles. While the unpolarized Stokes intensity fluctuates quite dramatically on a time scale of seconds, the depolarization ratio $\rho = (I_{ss}-I_{sp})/(I_{ss}+I_{sp})$ is time-independent. This depolarization ratio in most cases follows a $\cos(2\theta)$ curve as a function of the incident angle of irradiation in the plane of the scattering center. This uniaxial symmetry result suggests that the R6G molecule is permanently located in one junction, and both excitation and Stokes radiating dipoles are along the local enhanced field – the line of centers of the two touching particles. More generally, a $\cos(2\theta)$ depolarization ratio is expected for a single (i.e., not spatially degenerate and not rotationally averaged) dipole attached to the substrate, and rotating about Z with the substrate The uniaxial symmetry of the junction site creates a substantially depolarized

Raman signal when averaged over all incident angles, even for totally symmetric molecular modes. This result helps us to understand the Raman depolarization commonly observed in early ensemble studies.

Both sharp R6G Raman lines and underlying continuum originate in one anisotropic junction with dipoles pointing in the same direction, and also fluctuate together. We suggest both Stokes components are triggered by one R6G that experiences the local field at a fixed place in the aggregate. For R6G to undergo a strong molecular resonance Raman enhancement, the EM field must be parallel to the long xanthene aromatic axis, as this is the direction of the $\pi$- $\pi^*$ transition dipole. The observed fluctuations represent changes in absolute cross section, not tensor properties. We assign the fluctuations, as do Weiss and Haran, to changes in the strength of adsorption.

Ag electronic Raman is inelastic photon scattering that creates an electron-hole pair in the nanocrystal, that is, excites an electron from below to above the Fermi surface. It is normally very weak in faceted, annealed nanocrystals because Q, the photon momentum transferred to the electron-hole pair, is only large enough to create an electron-hole pair of a few $cm^{-1}$ energy above the Fermi surface. However, when R6G is present in the junction site, we see both continuum and R6G vibrational lines. Plasmon scattering off a surface defect or ad atom can provide the momentum necessary for electronic Raman. We suggest that the SERS continuum is electronic Raman caused by an adsorbed R6G exchanging electrons with the metal, and acting as a defect. Scattering of the coherently driven plasmon surface electrons off this adsorbed molecule creates both the R6G first layer SERS and Ag electronic Raman. The density of plasmon excited state metallic electrons on the Ag surface in the junction is linked to the enhanced field intensity by Gauss's Law. We report calculations on the excited state electron density inside the Ag nanocrystals as a function of position. The fundamental nature of the metallic excited state changes from a volume excitation to a surface excitation as two 50nm particles approach each other within 1nm.

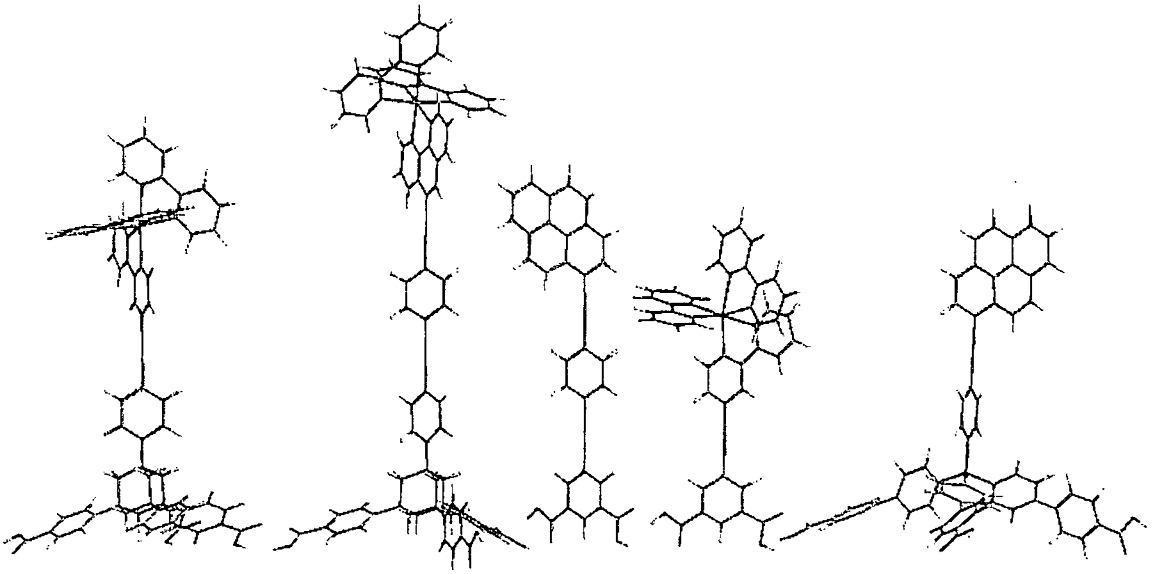
Publications 2001-2003:

1) Jiang Jiang, Mathieu Maillard, Ken Bosnick, Louis Brus "Single Molecule Raman Spectroscopy at the Junctions of Large Ag Nanocrystals" Invited Feature Article, Journal of Physical Chemistry, submitted March 2003.
2) Zhiyong Zhou, Louis Brus, Richard Friesner, "Electronic Structure and Luminescence of 1.1 and 1.4 nm Silicon Nanocrystals: Oxide Shell versus Hydrogen Passivation", Nano Letters *3*, 167 (2003).
3) Ken Bosnick, Jiang Jiang, Louis Brus "Fluctuations and Local Symmetry in Single-Molecule Rhodamine 6G Raman Scattering in Silver Nanocrystal Aggregates", J. Phys. Chem. *B106*, 8096 (2002).
4) Zhonghua Yu and Louis Brus, "(n,m) Structural Assignments and Chirality Dependence in Single-Wall Carbon Nanotube Raman Scattering", J. Phys. Chem. *B105*, 6831 (2001)
5) Zhonghua Yu and Louis Brus, "Rayleigh and Raman Scattering from Individual Carbon Nanotube Bundles" J. Phys. Chem. *B105*, 1123 (2001).

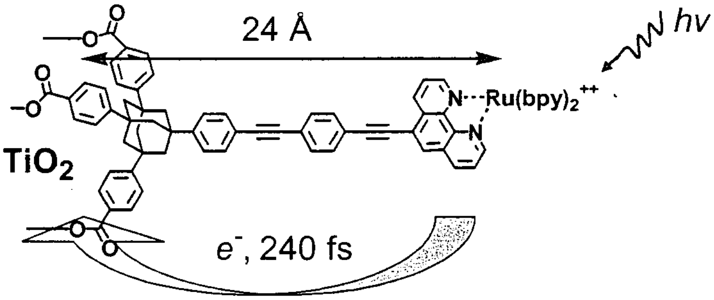
# CHARGE INJECTION THROUGH RIGID BRIDGES AT MOLECULE-SEMICONDUCTOR NANOPARTICLE INTERFACES

Qian Wei, Dong Wang, Wei Zhang, Giovanni Zordan and Elena Galoppini
Chemistry Department, Rutgers University, Newark, NJ 07102

Sensitization processes resulting from the photoexcitation of chromophores (sensitizers) bound to semiconductor nanoparticles are of great importance for solar energy conversion. To study key aspects of electron transfer processes in these systems, including charge injection, charge recombination and distance dependence, we have prepared a series of rigid sensitizers made of tripodal and rigid-rod bridges of various length substituted with Ru(II)-polypyridyl complexes and other chromophores. These molecules bind covalently to $TiO_2$ nanoparticle thin films through COOR groups, and, since are rigid, fix the position of chromophoric groups on nanoparticle surfaces. Key differences between the tripods and the rods will be discussed.



The binding of a variety of carboxylic acid derivatives of the sensitizers were studied by IR and Raman. IR data are consistent with the formation of three surface ester linkages in the tripods and two ester linkages in the rods. The excited state and redox properties of the tripodal and rigid-rod sensitizers were studied in solutions, as well as on nanocrystalline $TiO_2$ or $ZrO_2$ mesoporous thin films to which were bound. Pulsed 532 nm light excitation of the rigid sensitizers substituted with Ru(II)-complexes and bound to $TiO_2$ films, resulted in the immediate appearance of the absorption difference spectra of the interfacial charge separated state comprised of an electron in $TiO_2$ and the oxidized sensitizer, Ru(III). Recently, we have reported the observation of ultrafast charge injection from the longest tripods prepared in our laboratories, in which the Ru-to-footprint distance is 24 Å



Finally, we will present preliminary results for the preparation of solar cells and our progress towards the preparation of new systems analogous to the one studied, but with saturated spacers, and of Si-based tripodal sensitizers with very large footprints.

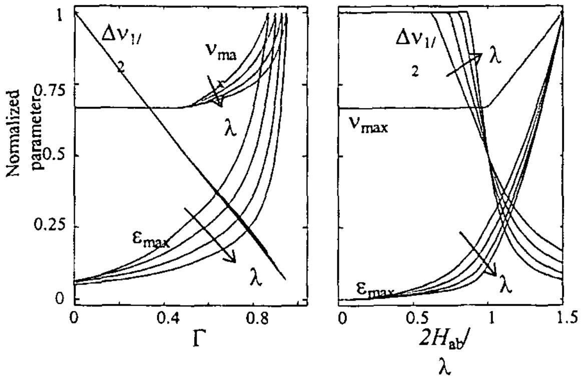
## DOE-SPONSORED PUBLICATIONS (November 2001-June 2003)

1. *Subpicosecond Photoinduced Charge Injection from "Molecular Tripods" into Mesoporous TiO$_2$ over the Distance of 24 Å.* Piotr Piotrowiak, Elena Galoppini, Qian Wei, Gerald J. Meyer, Piotr Wiewiór *J. Am. Chem. Soc.* **2003**, in press.
2. *Organic Rigid-Rod Linkers for Coupling Chromophores to Metal Oxide Nanoparticles.* P.G. Hoertz; R. Carlisle; G.J. Meyer; D. Wang, P. Piotrowiak, E. Galoppini, *Nanoletters* **2003**, *3*, 325-330.
3. *Synthesis of Rigid-Rod Linkers to Anchor Organic and Inorganic Chromophores to Semiconductor Nanoparticles.* Wang, D.; Schlegel, J. M.; Galoppini, E. *Tetrahedron* **2002**, *58*, 6027-6032.
4. *Long-Range Electron Transfer across Molecule-Nanocrystalline Semiconductor Interfaces Using Tripodal Sensitizers.* Galoppini, E.; Guo, W.; Zhang, W.; Hoertz, P.G.; Qu, P.; Meyer, G. J. *J. Am. Chem. Soc.* **2002**, 124, 7801-7811.
5. *Electroabsorption (Stark effect) Spectroscopy of Tripodal and Rigid-Rod Ruthenium Complexes.* Wei Zhang, Dong Wang, Bruce S. Brunschwig, Elena Galoppini to be submitted to J. Phys Chem B in May 2003.
6. *Perylene-Substituted TiO$_2$ Sensitizers with a Large Footprint,* in preparation with F. Willig.

# GROUND- AND EXCITED-STATE CHARGE TRANSFER IN MOLECULAR- AND NANOSCALE SYSTEMS

Carol Creutz
Chemistry Department, Brookhaven National Laboratory, Upton NY

**The class II-III mixed-valence transition.**[iii] Mixed-valence systems at the Class II/III borderline are "almost delocalized" and difficult to characterize.[1] To provide better experimental probes and greater theoretical understanding of the borderline behavior, a semiclassical model has been developed.[2] In this model, free-energy surfaces are constructed for harmonic diabatic (zero-order) states that satisfy the Generalized Mulliken Hush condition[3] and characterized as a function of increasing electronic coupling to simulate the Class II to III transition. Spectral band shapes and intensities have been calculated utilizing increasingly complex models including two to four states. The properties of the charge-transfer absorption bands predicted for borderline mixed-valence systems are compared with experimental data. A particularly useful parameter is $\Gamma = 1 - (\Delta\nu_{1/2})/(2310\nu_{max})^{1/2}$ at 298 K, which is readily evaluated from $\Delta\nu_{1/2}$, the experimental full width at half band intensity, and $\nu_{max}$, the experimental absorption band maximum.

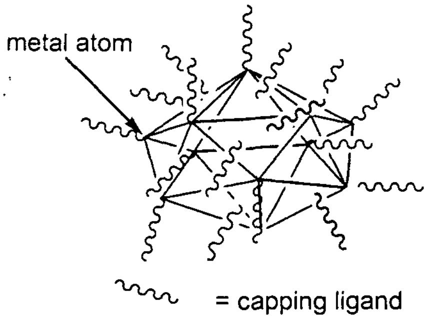


The predictions of the two-state model were compared with experimental data for two families of diruthenium complexes, those bridged by a dicyanamide ($dicyd^{2-}$) and those bridged by a pyrazine (pz) ligand. The metal-metal separation is essentially constant within each family (pz 6.9 Å; $dicyd^{2-}$ 13.2 Å). The two-state analysis of the shapes of the MMCT bands of the two series of bridged, binuclear ruthenium mixed-valence complexes was found to be a useful and apparently valid one. This is the first such systematic comparison and is the first time intensity comparisons have been made.

### Transition metal complexes to probe nanoscale charge transfer

As the size of a metal is reduced from the bulk to the nanoscale (1 to 100 nm), its electronic properties evolve from the bulk band structure toward the molecular.[4] We are interested in determining how the size of a cluster affects its reactivity and its interaction with molecular excited states.

For solution studies nanoparticles must be stabilized by a shell of adsorbate or ligands that prevents aggregation of the nanoparticles. Characterization of the particle-ligand binding and understanding how it influences the properties of the particle are important to designing and interpreting experiments that probe the particles' reactivity. For example, far infrared studies of alkane thiolate covered particles[5] are revealing how the Au-S bonding varies with alkane chain



length and how it differs from the two-dimensional self-assembled monolayer. The kinetics and thermodynamics of the binding of the ligand shell are also important when the nanoparticle is studied in solution. Exchange or loss of thiol from gold nanoparticles is very slow. By contrast, exchange of triphenyl phosphine is very rapid. Such fundamental reactivity differences have implications for synthesis, purification, and utilization of the nanoparticles.

We have begun to examine the interaction of metal-to-ligand charge transfer (MLCT) excited states of transition-metal complexes with gold nanoparticles. In principle, bulk metals can quench molecular excited states with high efficiency, but there is now evidence that the excited states of fullerene[6] and fluorene[7] (among others) attached to gold persist sufficiently long that their electron and/or energy transfer to the particle can be characterized. We have found that diffusional quenching of $(bpy)_2Ru^{II}L_2$ (bpy = 2,2'-bipyridine; L2 = $-(SCN^-)_2$ or bpy) by 20-nm and 3-4 nm gold particles is inefficient, in sharp contrast to the behavior of 1-nm particles for which $k_q$ exceeds $10^{10}\ M^{-1}s^{-1}$. To explore the size dependence we have prepared reporter molecules such as $Ru(bpy)_2(bpy')$ (bpy' = e.g. 4'-methyl-2,2'-bipyridine-4-carboxylic acid[8]). These are being covalently attached to nanoparticle-ligands terminated by amine groups through the formation of amide bonds.

An important aspect of interpreting the charge-transfer behavior of nanoscale systems is access to appropriate models for the thermodynamics and electron-transfer barriers. We are developing dielectric continuum models to describe semiconductor and metal nanoparticles in dielectric media.[v] Size-dependent properties emerge from these models. For example, for metal nanoparticles, the energy gap between one-electron addition and one-electron loss processes is size dependent. Since the ionization energy (*IP*) and electron affinity (*EA*) of a bulk metal are both equal to the work function of the metal, $IP_\infty = EA_\infty$ $(r = \infty)$. When $IP_\infty = EA_\infty$, the difference between $IP(r)$ and $EA(r)$, the energy gap for a metal cluster of radius $a$ in a medium of dielectric constant $D_s$, is simply equal to

$$IP_r - EA_r = \frac{e^2}{D_s a} = \frac{1.44}{D_s a}\ \text{eV}\ (a\ \text{in nm})$$

The predicted gaps, for example 0.04 eV for an $a$ = 11-nm particle and 0.8 eV for a 0.63-nm particle for $D_s = 3$, are in good agreement with experimental spectroscopic, electrochemical, or STM (scanning tunneling microscope) data, where available. For the charging of metal nanoparticles surrounded by a shell of ligands of dielectric constant $D_{\text{shell}}$ and thickness $L$ in a solvent of dielectric constant $D_s$, the $E^0$ gap between one-electron oxidation and one-electron reduction processes is

$$\Delta E^0_{\text{r,shell}} = 0.72\left(\left(\frac{1}{a} - \frac{1}{a+L}\right)\frac{1}{D_{\text{shell}}} + \frac{1}{(a+L)D_s}\right)\ \text{eV}\ (a\ \text{in nm})$$

## Publications 2001-2003

(i) "Catalysis Research of Relevance to Carbon Management: Progress, Challenges, and Opportunities," Arakawa, H.; Aresta, M.; Armor, J. N.; Barteau, M. A.; Beckman, E. J.;

Bell, A. T.; Bercaw, J. E.; Creutz, C.; Dinjus, E.; Dixon, D. A.; Domen, K.; Dubois, D. L.; Eckert, J.; Fujita, E.; Gibson, D. H.; Goddard, W. A.; Goodman, D. W.; Keller, J.; Kubas, G. J.; Kung, H. H.; Lyons, J. E.; Manzer, L. E.; Marks, T. J.; Morokuma, K.; Nicholas, K. M.; Periana, R.; Que, L.; Rostrup-Nielson, J.; Sachtler, W. M. H.; Schmidt, L. D.; Sen, A.; Somorjai, G. A.; Stair, P. C.; Stults, B. R.; Tumas, W. *Chem. Rev.* **2001**, *101*, 953-996.

(ii) "Pulse Radiolysis Studies of Water-Soluble Tungsten Hydride Complexes: One-Electron Reduction of Metal Hydrides and Hydrogen Atom Transfer Reactions," Cabelli, D. E.; Shafiq, F.; Creutz, C.; Bullock, R. M. *Organometallics* **2001**, *20*, 3729-3737.

(iii) "Optical Transitions of Symmetrical Mixed-valence Systems in the Class II/III Transition Regime," Brunschwig, B. S.; Creutz, C.; Sutin, N. *Chem. Soc. Rev.* **2002**, *31*, 168-184.

(iv) "Charge Transfer on the Nanoscale," Adams, D.; Brus, L.; Chidsey, C. E. D.; Creager, S.; Creutz, C.; Kagan, C. R.; Kamat, P. V.; Lieberman, M.; Lindsay, S.; Marcus, R. A.; Metzger, R. M.; Michel-Beyerle, M. E.; Miller, J. R.; Newton, M. D.; Rolison, D. R.; Sankey, O.; Schanze, K. S.; Yardley, J.; Zhu, X. *J. Phys. Chem. B* **in press**.

(v) "Electron Transfer from the Molecular to the Nanoscale" Creutz, C.; Brunschwig, B. S.; Sutin, N. In *Comprehensive Coordination Chemistry II*; McLeverty, J., Meyer, T. J., Eds.; Elsevier: Amsterdam, in press.

## References

(1) "The Localized-to-Delocalized Transition in Mixed-Valence Chemistry," Demadis, K. D.; Hartshorn, C. M.; Meyer, T. J. *Chem. Rev.* **2001**, *101*, 2655 - 2686.

(2) "Reflections on a two-state model" Brunschwig, B. S.; Sutin, N. In *Electron Transfer in Chemistry*; Balzani, V., Ed.; Wiley-VCH, 2001; Vol. 2, pp 583-617.

(3) "Calculation of Electronic Coupling Matrix Elements for Ground and Excited State Electron Transfer Reactions: Comparison of the Generalized Mulliken Hush (GMH) and Block Diagonalization (BD) Methods," Cave, R. J.; Newton, M. D. *J. Chem. Phys.* **1997**, *106*, 9213-9213.

(4) "Molecular Electronics; Some Directions" Ratner, M. A.; Jortner, J. In *Molecular Electronics*; Ratner, M. A., Jortner, J., Eds.; Blackwell, Oxford, UK, 1997, pp 5-72 and references therein.

(5) "Monolayer-Protected Cluster Molecules," Templeton, A. C.; Wuelfing, W. P.; Murray, R. W. *Acc. Chem. Res.* **2000**, *33*, 27-36.

(6) "Fullerene-Functionalized Gold Nanoparticles. A Self-Assembled Photoactive Antenna-Metal Nanocore Assembly," Sudeep, P. K.; Ipe, B. I.; George Thomas, K.; George, M. V.; Barazzouk, S.; Hotchandani, S.; Kamat, P. V. *Nano Lett.* **2002**, *2*, 29-35.

(7) "Energy Transfer from a Surface-Bound Arene to the Gold Core in -Fluorenyl-Alkane-1-Thiolate Monolayer-Protected Gold Clusters," Gu, T.; Whitesell, J. K.; Fox, M. A. *Chem. Mater.* **2003**, *15*, 1358-1366.

(8) "Synthesis of redox derivatives of lysine and related peptides containing phothiazine or tris(2,2'-bipyridine)ruthenium(II)," Peek, B. M.; Ross, G. T.; Edwards, S. W.; Meyer, G. J.; Meyer, T. J.; Erickson, B. W. *Int. J. Protein Res.* **1991**, *38*, 114-123.

# CHARGE DISTRIBUTION AND FERMI-LEVEL EQUILIBRATION IN SEMICONDUCTOR-METAL NANOCOMPOSITES

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Metal nanoparticles or islands deposited on a semiconductor surface play an important role in catalyzing interfacial charge transfer processes.[1] For example, in our earlier work[2,3] a 3-to-5 fold improvement in the photoelectrochemical performance of nanostructured $TiO_2$ films was achieved by coupling them with noble metal nanoparticles. Unlike bulk films, metal nanoparticles exhibit an unusual property of quantized double layer charging effects.[4] Gold nanoparticles capped with organic molecules exhibit unusual redox activity by readily accepting electrons from a suitable donor (e.g., a charged semiconductor particle).

The major goal of this project is to improve charge rectification and charge separation efficiency of light-harvesting nanoassemblies and to probe the charge equilibration and charge transfer dynamics in semiconductor-metal nanocomposite systems. Semiconductor nanoparticles such as $TiO_2$ and ZnO store electrons following bandgap excitation. Since the Fermi level of gold ($E_F$=0.4 V vs. NHE) is more positive than the conduction band energy of $TiO_2$ and ZnO ($E_{CB}$= -0.5 V vs. NHE at pH 7), we expect a quick distribution of electrons between excited semiconductor and metal nanoparticles. As illustrated in Figure 1, the electrons transferred to a gold nanoparticle increase the electron density within the nanoparticle, thus shifting the Fermi level towards more negative potentials. The transfer of electrons to metal continues until the Fermi level equilibrates with the conduction band edge of the semiconductor.

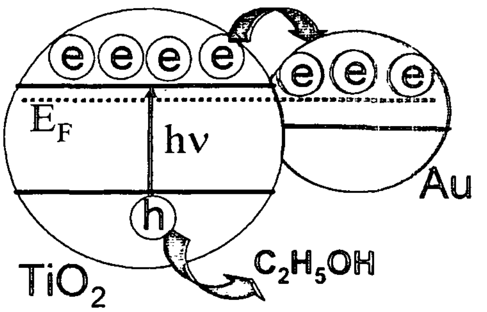

Figure 1. Charge distribution is semiconductor-metal composite system leads to Fermi-level equilibration.

By employing $C_{60}$/ $C_{60}^-$ as a probe-redox couple we were able to estimate the apparent Fermi levels of $TiO_2$ and $TiO_2$/Au nanoparticles. Furthermore, we also succeeded in demonstrating the particle size effect on the Fermi level of the composite. For example, the Fermi level shift observed with 5 nm Au nanoparticle was -40 mV as compared to –22 mV for 8 nm Au nanoparticles in the Au-$TiO_2$ nanocomposite system. The shift of Fermi level to more negative potentials is indicative of increased charge storage and improved charge separation in semiconductor-metal composite systems. These results, in turn, elucidate the indirect role of noble metals towards improving the charge separation as well as promoting interfacial charge transfer kinetics in semiconductor assisted photocatalysis.

In order to investigate charging effects on the excited state of a surface-bound sensitizer we have functionalized gold nanoparticles with two different thiols, one containing a fluorophore (pyrene) and the other containing a carboxylic acid. Mercaptopropionic acid having two bifunctional surface-linking groups (-SH and -COOH groups) serves to link the gold nanoparticle to the $TiO_2$ surface. The electrode exhibits weak emission with a maximum around 395 nm as most of the emission of surface-bound pyrene is quenched by the gold nanocore. Decreased singlet lifetime as well as formation of the oxidation product, pyrene cation radical, indicated the ability of gold nanoparticles to accept electrons from excited pyrene. Spectroelectrochemical experiments were conducted using a thin layer electrochemical cell in a spectrofluorimeter with front-face geometry.

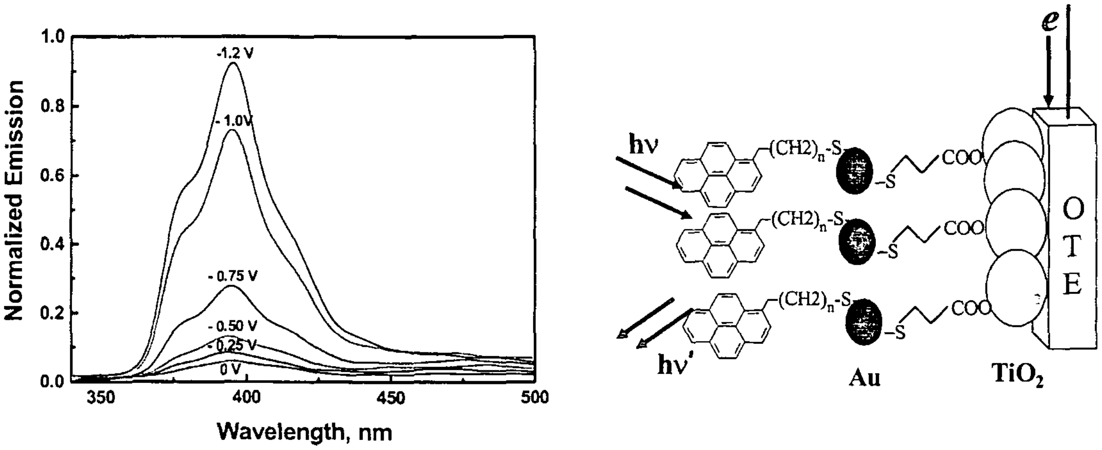

Figure 2 Emission spectra (left) of OTE/$TiO_2$/OOCR-S-(Au)-S-Pyrene electrode (right) at different applied potentials.

Figure 2 shows the emission spectra of OTE/$TiO_2$/OOCR-S-(Au)-S-Pyrene electrode at different applied potentials. As we bias the electrode to more negative potentials, the electron density within the gold core increases and the charge transfer interaction of the surface bound pyrene moiety decreases. At potentials more negative than -1.0 V we completely suppress the interaction between the fluorophore and the gold nanocore and we achieve saturation in the emission increase. We were able to restore more than 90% of the quenched emission by simply charging the gold nanoparticle with an externally applied electrochemical bias. The possibility of electrochemically modulating the fluorescence of a fluorophore at a nanostructured gold electrode opens up new avenues to probe interfacial charge transfer processes in nanoassemblies.

**Future Work:** Functionalized gold nanoparticles and semiconductor quantum dots will be assembled as three-dimensional arrays for maximizing light energy harvesting efficiency of photoresponsive electrodes. Spectroelectrochemical investigation will focus on the modulation of the charge separation and charge recombination in semiconductor-metal composites using externally applied electrochemical bias and probing the charge transport within these nanostructures. In particular, emphasis will be placed on elucidating the role of metal nanoclusters in shuttling charges across hybrid nanostructures.

**References:**

(1) Kamat, P. V. *J. Phys. Chem. B* **2002**, *106*, 7729.
(2) Subramanian, V.; Wolf, E.; Kamat, P. V. *J. Phys. Chem. B* **2001**, *105*, 11439.
(3) Chandrasekharan, N.; Kamat, P. V. *J. Phys. Chem. B* **2000**, *104*, 10851.
(4) Templeton, A. C.; Wuelfing, W. P.; Murray, R. W. *Acc. Chem. Res.* **2000**, *33*, 27.

**List of Publications (2001-2003)**

1. Peller, J.; Wiest, O. ; Kamat, P,V, Sonolysis of 2,4-Dichlorophenoxyacetic Acid in Aqueous Solutions. Evidence for ·OH-Radical-Mediated Degradation. **J. Phys. Chem. A** 2001, *105,* 3176-3181.
2. Chandrasekharan, N.; Kamat, P.V., Assembling Gold Nanoparticles as Nanostructured Films using an Electrophoretic Approach. **Nano Lett.** 2001, *1,* 67-70.
3. Das, A.; Joshi, V.; Kotkar, D.; Pathak, V.S.; Swayambunathan, V.; Kamat, P.V.; Ghosh, P.K., Understanding the Facile Photooxidation of Ru(bpy)32+ in Strongly Acidic Aqueous Solution Containing Dissolved Oxygen. **J. Phys. Chem. A** 2001, *105,* 6945-6954.
4. Zacheis, G.A.; Gray, K.A.; Kamat, P.V., Radiation Induced Catalytic Dechlorination of Hexachlorobenzene on Various Oxide Surfaces. **J. Phys. Chem. B** 2001, *105,* 4715-4720.
5. Dawson, A.; Kamat, P.V., Semiconductor-metal Nanocomposites. Photoinduced Fusion and Photocatalysis of Gold-capped $TiO_2$ ($TiO_2$/Au) Nanoparticles. **J. Phys. Chem. B** 2001, *105,* 960-966.
6. Biju, V.; Barazzouk, S.; George Thomas, K.; George, M.V.; Kamat, P.V., Photoinduced Electron Transfer Between 1,2,5-Triphenylpyrrolidinofullerene Cluster Aggregates and Electron Donors. **Langmuir** 2001, *17,* 2930-2936.
7. Kamat, P.V., Electrochromic and Photoelectrochromic Aspects of Semiconductor Nanostructure- Molecular Assembly, in The Electrochemistry of Nanostructures, G. Hodes, Editor. 2001, Wiley-VCH: New York. p. 229-246.
8. Subramanian, V.; Wolf, E.; Kamat, P.V., Semiconductor-Metal Composite Nanostructures. To What Extent Metal Nanoparticles (Au, Pt, Ir) Improve the Photocatalytic Activity of $TiO_2$ Films? **J. Phys. Chem. B** 2001, *105,* 11439-11446.
9. Imahori, H.; Hasobe, T.; Yamada, H.; Kamat, P.V.; Barazzouk, S.; Fujitsuka, M.; Ito, O.; Fukuzumi, S., Spectroscopy and Photocurrent Generation in Nanostructured Thin Films of Porphyrin-Fullerene Dyad Clusters. **Chem. Lett.** 2001, 784-785.
10. Kamat, P.V.; Barazzouk, S.; Hotchandani, S., Electrochemical Aspects of $C_{60}$-Ferrocene Cluster Films, in *Fullerenes-2001*, P.V. Kamat, D.M. Guldi, and K. Kadish, Editors. 2001, The Electrochemical Society: Pennigton, NJ.
11. Kamat, P.V.; Barazzouk, S.; Hotchandani, S., Nanostructured Fullerene Films. **Adv. Mater.** 2001, *13,* 1614-1617.
12. Biju, V.; Barazzouk, S.; Thomas, K.G.; George, M.V.; Kamat, P.V., Photoinduced Electron Transfer between 1,2,5-Triphenylpyrrolidinofullerene Cluster Aggregates and Electron Donors. **Langmuir** 2001, *17,* 2930-2936.
13. Kamat, P.V.; Flumiani, M.; Dawson, A., Metal-Metal and Metal-Semiconductor Composite Nanoclusters. **Colloids and Surfaces A. Physicochemical and Engineering Aspects** 2002, *202,* 269-279.
14. Kamat, P.V.; Huehn, R.; Nicolaescu, R., A Sense and Shoot Approach for Photocatalytic Degradation of Organic Contaminants in Water. **J. Phys. Chem. B** 2002, *106,* 788-794.

15. Ipe, B.I.; George Thomas, K.; Barazzouk, S.; Hotchandani, S.; Kamat, P.V., Photoinduced Charge Separation in a Fluorophore-Gold Nanoassembly. **J. Phys. Chem. B** 2002, *106,* 18-21.
16. Sudeep, P.K.; Ipe, B.I.; George Thomas, K.; George, M.V.; Barazzouk, S.; Hotchandani, S.; Kamat, P.V., Fullerene Functionalized Gold Nanoparticles. A self assembled Photoactive Antenna-Metal Nanocore Assembly. **Nano Lett.** 2002, *2,* 29-35.
17. Biju, V.; Sudeep, P.K.; George Thomas, K.; George, M.V.; Barazzouk, S.; Kamat, P.V., Clusters of Bis- and Tris-Fullerenes. **Langmuir** 2002, *18,* 1831-1839.
18. Sant, P.A.; Kamat, P.V., Inter-Particle Electron Transfer between Size-Quantized CdS and TiO2 Semiconductor Nanoclusters. **Phys. Chem. Chem. Phys.** 2002, *4,* 198-203.
19. George Thomas, K.; Zajicek, J.; Kamat, P.V., Surface Binding Properties of Tetraoctylammomium Bromide Capped Gold nanoparticles. **Langmuir** 2002, *18,* 3722-3727.
20. Barazzouk, S.; Hotchandani, S.; Kamat, P.V., Unusual Electrocatalytic Behavior of Ferrocene Bound Fullerene Cluster Films. **J. Mater. Chem.** 2002, *12,* 2021-2025.
21. Kamat, P.V.; Barazzouk, S.; Hotchandani, S., Electrochemical Modulation of Fluorophore Emission at a Nanostructured Gold Film. **Angew. Chem. (Int. Ed.)** 2002, *41,* 2764-2767.
22. Chandrasekharan, N.; Kamat, P.V., Tuning the Properties of CdSe Nanoparticles in Reverse Micelles,. **Res. Chem. Intermed.** 2002, *28,* 847-856.
23. Kamat, P.V., Photophysical, Photochemical and Photocatalytic Aspects of Metal Nanoparticles. **J. Phys. Chem. B** 2002, *106,* 7729-7744 (Feature Article).
24. Kamat, P.V.; Barazzouk, S.; George Thomas, K.; George, M.V., Molecular Assembly of Fullerenes as Nanoclusters and Films, in Fullerenes-2002, P.V. Kamat, D.M. Guldi, and F. D'Souza, Editors. 2002, The Electrochemical Society: Pennigton, NJ.
25. Kamat, P.V.; Meisel, D., Nanoparticles in Advanced Oxidation Processes. **Current Opinion in Colloid & Interface Science** 2002, *7,* 282-287.
26. Kamat, P.V., Photoinduced Transformations in Semiconductor-Metal Nanocomposite Assemblies. **Pure and Applied Chemistry** 2002, *74,* 1693-1706.
27. George Thomas, K.; Biju, V.; Guldi, D.M.; Kamat, P.V.; George, M.V., Photoinduced Electron Transfer Processes in Fullerene Based Dyads with Heteroaromatic Donors. **Chem. Phys. Chem.** 2003, in press.
28. Peller, J.; Wiest, O.; Kamat, P.V., Mechanism of Hydroxyl Radical-Induced Breakdown of the Herbicide 2,4-Dichlorophenoxyacetic Acid. **Chemistry, European J.** 2003, submitted.
29. Subramanian, V.; Wolf, E.E.; Kamat, P.V., Influence of Metal/Metal --Ion Concentration on the Photocatalytic Activity of TiO$_2$-Au Composite Nanoparticles. **Langmuir** 2003, *19,* 469-474.
30. Adams, D., et al., Charge Transfer on the Nanoscale. **J. Phys. Chem. B** 2003, *106,* in press. (Feature Article)

31. Vinodgopal, K.; Subramanian, V.; Carrasquillo, S.; Kamat, P.V., Electrophoretic Deposition of Naturally Occurring Humic Substances as Thin Films. **Environ. Sci. Technol.** 2003, *37,* 761-765.
32. Lahiri, D.; Subramanian, V.; T.Shibata; Wolf, E.E.; Bunker, B.A.; Kamat, P.V., Photoinduced Transformations at Semiconductor/Metal Interfaces: XAFS Investigation of UV-irradiated $TiO_2$ /Au Films. **J. Appl. Phys.** 2003, *93,* 2575-2582.
33. Kamat, P.V.; George Thomas, K., Molecular Assembly of Fullerenes as Nanoclusters and Nanostructured Films, in Nanoscale Materials, L. Liz-Marzan and P.V. Kamat, Editors. 2003, Kluwer Academic/Plenum Publishers: Boston. p. 475-494.
34. Peller, J.; Wiest, O.; Kamat, P.V., Synergy of Combining Sonolysis and Photocatalysis in the Degradation and Mineralization of Chlorinated Aromatic Compounds Peller, Wiest & Kamat. **Environ. Sci. Technol.** 2003, *37,* in press.
35. Nicolaescu, R.; Wiest, O.; Kamat, P.V., Radical Induced Oxidative Transformations of Quinoline. **J. Phys. Chem. A** 2003, *107,* 427-433.
36. Subramanian, V.; Wolf, E.E.; Kamat, P.V., Green Emission to Probe Photoinduced Charging Events in ZnO-Au Nanoparticles. Charge Distribution and Fermi-Level Equilibration. **J. Phys. Chem. B** 2003, *107,* in press.
37. Sharma, S.; Pillai, Z.S.; Kamat, P.V., Photoinduced Charge Transfer between Cdse Nanocrystals and p-Phenelenediamine. **J. Phys. Chem. B** 2003, *107,* submitted for publication.
38. Jakob, M.; Levanon, H.; Kamat, P.V., Charge Distribution between UV-Irradiated $TiO_2$ and Gold Nanoparticles. Determination of Shift in Fermi Level,. **Nano Lett.** 2003, *3,* 353-358.
39. George Thomas, K.; Kamat, P.V., Photoresponsive Organic-Inorganic Nanohybrids. **Acc. Chem. Res.** 2003, *36,* submitted.
40. Kamat, P.V.; Meisel, D., Nanoscience Opportunities in Environmental Remediation. **Comptes Rendus Chimie** 2003, submitted.
41. Liz-Marzan, L.; Kamat, P.V., Nanoscale Materials. 2003, Boston: Kluwer Academic/Plenum Publishers. 499 (Edited Book).

# QUANTUM DOT MOLECULES ASSEMBLED WITH GENETICALLY ENGINEERED PROTEINS

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Colloidal quantum dots (QDs) exhibit unique optical and electronic properties due to their physical size being smaller than the Bohr radius of an exciton associated with the semiconductor material from which they are made. While the isolated properties of these nanoparticles has a number of uses, such as bioimaging, their use in novel electronic devices often requires large arrays of known order. Assembling these arrays is non-trivial and requires a monodisperse sample of quantum dots in order to facilitate the self-assembling process.

In this presentation, we report the assembly of quantum dots using a directed approach that capitalizes on the self-assembling properties of naturally occurring proteins. A cellulosomal protein, cohesin, genetically modified by removing the native enzyme domain and adding 6 histidine peptide clusters was incubated with quantum dots made of cadmium selenide core and a zinc sulfide shell, CdSe(ZnS), that had been rendered soluble in a pH 6.5 buffer solution. High-pressure size exclusion chromatography (HPSEC) was used to separate the resulting mixture and the fractions collected were studied using photoluminescence spectroscopy and scanning transmission electron microscopy (STEM).

Some initial data from this study are given below and reveal two important observations (i) QD-protein bioconjugates that are soluble and stable in an aqueous environment, (ii) The formation of large 'trefoil' structures that contain a number of closely spaced QDs. We also note that the spectroscopy of the two eluted fractions differ suggesting a different composition of QDs as well as a different physical size of the structures.

Our current efforts are aimed at understanding what drives the construction of trefoil structures and how unique they actually are. It is unclear what role the protein plays in the assembly process, whether it directs the assembly, as hoped, or whether the QDs self-assembly and are then coated by the protein. The absence of the QDs that emit to very low energy (1.81eV) from these trefoil structures is also of interest. Are they absent? Or is energy transfer to the largest, lowest energy quantum dot very facile? This latter explanation would suggest that these structures exhibit very efficient light harvesting properties. To help answer these questions we are creating new QD-protein structures that contain two distinct sizes of quantum dot distributions, which will help resolve the energy transfer issue. We are using a number of other microscopy techniques, such as AFM that require different sample preparation procedures to help understand the uniqueness of the trefoil structures. Dynamic light scattering is also being used to detect these species in fluid solution. The electronic communication between the quantum dots in the trefoils will be investigated using time-resolved photoluminescence and transient absorption spectroscopy.

These studies are being carried out in parallel with attempts to bind the QDs to genetically-modified dockerins, which will then couple to the cohesins to create structures similar to the cellulosomes that are found in nature.

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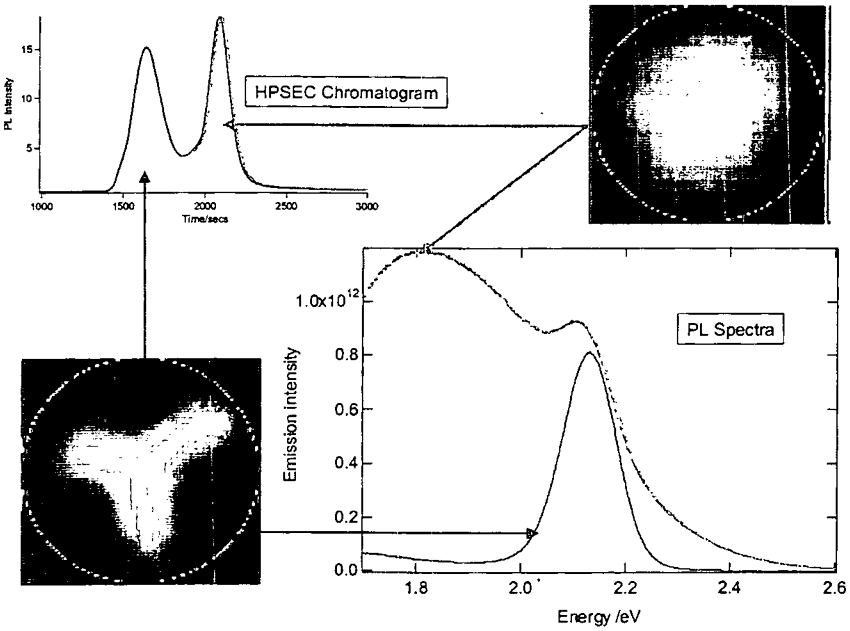

Figure legend - The HPSEC data (top left) exhibit two distinction peaks that were detected using PL. The first eluted peak corresponds to large structures dominated by species that are shaped like trefoils (STEM image, bottom left). This image shows a structure that contains a number of well-defined quantum dots in the trefoil structure, with a surrounding nimbus of protein and an image size that fits inside a 250Å diameter circle. The emission spectrum (excitation wavelength = 400nm) of this species exhibits a sharp, exciton emission peak at 2.13 eV (582nm), with a width of 130meV, which is slightly less than the original quantum dot sample. The second eluted peak, corresponding to smaller species, contains structures that resemble single quantum dots (STEM image, top right). This image contains a single, ~15Å quantum dot surrounded by a nimbus of protein that fits inside a 70Å circle. PL from this fraction is broad and intense with a dominant peak centered at 1.81eV (685nm) that is almost 700meV wide.

DOE Publications 2001-2003

1. Rumbles, G., D.C. Selmarten, R.J. Ellingson, J.L. Blackburn, P.R. Yu, B.B. Smith, O.I. Micic, and A.J. Nozik, *Anomalies in the linear absorption, transient absorption, photoluminescence and photoluminescence excitation spectroscopies of colloidal InP quantum dots.* Journal of Photochemistry and Photobiology a-Chemistry, 2001. **142**(2-3): p. 187-195.
2. G.Rumbles, D.Selmarten, R.E.Ellingson, J.Blackburn, P.Yu, B.B.Smith, O.I.Micic and A.J.Nozik, *Excited State Relaxation Mechanisms in InP colloidal Quantum Dots.* Materials Research Society Symposium Proceedings, **667**, G6.3.1-G6.3.7 (2001).
3. Ellingson, R.J., J.L. Blackburn, P.R. Yu, G. Rumbles, O.I. Micic, and A.J. Nozik, *Excitation energy dependent efficiency of charge carrier relaxation and photoluminescence in colloidal InP quantum dots.* Journal of Physical Chemistry B, 2002. **106**(32): p. 7758-7765.
4. Ellingson, R.J., J.L. Blackburn, J. Nedeljkovic, G. Rumbles, M. Jones, H.X. Fu, and A.J. Nozik, *Theoretical and experimental investigation of electronic structure and relaxation of colloidal nanocrystalline indium phosphide quantum dots.* Physical Review B, 2003. **67**(7): p. art. no.-075308.

# HEALING OF NANOPARTICLE SURFACES: OPPORTUNITY FOR THE DESIGN OF FUNCTIONAL MATERIALS ON NANOSCALE

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A new class of semiconductor based artificial photosynthetic systems that duplicate the primary photoinduced charge separation mechanism in natural photosynthesis was created by ligand induced restructuring of the surface of metal oxide nanoparticles. The forces that are involved in binding the ligands are large enough to induce structural deformation and heal surface defect sites to bulk-like octahedral geometry. As a result of this strong interaction between nanoparticle surface atoms and organic ligands, the surface trapping sites are removed and highly delocalized bands of metal oxide nanoparticles are electronically coupled to organic materials that have localized molecular wave functions and interact by dipolar and exchange processes. In this system, as in natural photosynthesis, photoinduced charge pairs (holes on the ligands and electrons on nanoparticles) experience only weak coupling allowing for subsequent chemistry. The surface bound ligands can act as conduits that bridge the electronic properties of semiconductor particles to attached electroactive biological moieties such as DNA. The sequence specificity of DNA introduces templating capabilities allowing for precise placement of inorganic nanoparticles into arrays of two or three dimensional structures.

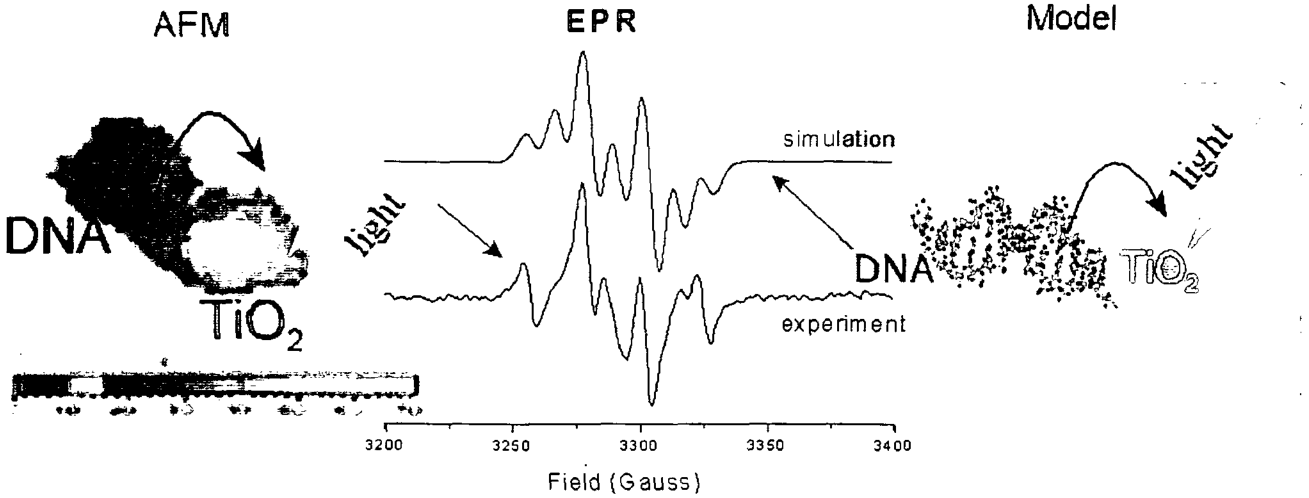

Figure 1. AFM image of $TiO_2$ nanoparticles linked to 20-base pair long DNA oligonucleotides in conjunction to photoinduced EPR spectrum obtained at 4.2 K.

DNA oligonucleotides were linked to metal oxide nanoparticles by using dopamine as conduits. Dopamine binds to the $TiO_2$ nanoparticle surface by chelating surface titanium atoms with both ortho hydroxyl groups, establishing optimal octahedral geometry of surface Ti atoms. Resulting hybrid properties of this nanocomposite material are manifested in the shift in the onset of the optical absorption to the red part of the spectrum that can be used for tuning their spectral properties as well as determining the composite stoichiometry. Composition and stabilities of surface bound complexes were examined using a variety of magnetic resonance, electrochemical, and spectroscopic techniques. The important aspect of bidentate binding is that the rate of adsorption is significantly larger than the rate of desorption. As a consequence, linking of biomolecules is a favorable process, while their desorption is less favorable.

Existence of the shell of appendant amino groups of dopamine around the $TiO_2$ core also allows for chemical linking of biomolecules containing terminus carboxyl groups. DNA oligonucleotides having carboxyl groups at 5' ends were linked to appendant amino groups of dopamine via the N-hydroxyl-succinimide ester intermediate. Dopamine end-substituted DNA oligonucleotides were bound to $TiO_2$ nanoparticles. The functionality of DNA oligonucleotides upon binding was preserved and oligonucleotides were successfully hybridized to their complementary strands in the desired stoichiometric ratio (Figure 1). The stoichiometry of binding was determined spectroscopically and height histograms were obtained using AFM imaging. EPR spectroscopy was employed to study the role of sequential electron transfer and electrochemical parameters, and how they affect the charge separation distances in this system. EPR was also used to probe the molecular environment of paramagnetic intermediates by attaching oligonucleotides with different sequences to the appendant amino groups of dopamine. The sequence was adjusted to have doublet guanine trapping sites at different distances from the $TiO_2$ surface or to have nonconductive poly-thymine bridges that suppress charge separation. Following photoexcitation at 4.2 K, a distinct multi-line EPR spectrum with a total width of 100 Gauss was observed in composites having double-stranded DNA. The main features of the signal were reasonably well simulated with parameters used for the carboxyl deoxythymidine (CdT) cation radical having one proton from the CH group in the 7th position and two nitrogen atoms in the pyrimidine ring. This result suggests that the initial charge separation occurs between the $TiO_2$ nanoparticles and CdT, which is the nucleoside closest to the nanoparticle surface. In the single-stranded $TiO_2$/DNA nanocomposite charge separation terminates at dopamine and never reaches the adjacent CdT nucleotide. This suggests formation of a new class of functional hybrid materials that weld the robustness and photoresponsiveness of inorganic nanoparticles with the recognition properties of biological molecules.

Once the photogenerated holes are injected into DNA oligonucleosides, the charge transfer was found to proceed in the same manner as in sole double-stranded DNA. Warming of the sample induces a change in the EPR spectrum indicating further charge hopping. Upon annealing at 80K, the EPR signal collapses into a signal with a very weakly resolved hyperfine structure and weak satellite lines. The EPR spectrum of the guanosine radical cation obtained by reaction with radiolytically generated OH radicals matches the 80K spectrum. This result indicates that sequential hole transfer to guanine in DNA follows the initial charge separation between the end-group CdT radical and $TiO_2$ nanoparticle. In this way, the absorption of light in the $TiO_2$/DNA system is followed by sequential electron transfer of photogenerated electrons through a series of electron trapping sites. Therefore, illumination of the $TiO_2$/DNA composites results in an efficient light conversion event in which light energy is transduced into separated electrons and positive holes which are stabilized by physical separation and control the ensuing chemistries. Full realization of these potential implementations requires detailed understanding of charge separation in these composite materials. Future studies will address the effects of length, sequence, and the DNA structure (mismatches) on charge accumulation and consequently signal transduction.

**Publications 2001-2003**

SPIN POLARIZATION MECHANISMS IN EARLY STAGES OF PHOTOINDUCED CHARGE SEPARATION IN SURFACE MODIFIED $TiO_2$ NANOPARTICLES
T. Rajh, O. Poluektov, A. A. Dubinski, G. Wiederrecht, M. C. Thurnauer, and A. D. Trifunac
Chem. Phys. Lett., 344, 31-39 (2001)

RADIOLYTICALLY INDUCED FORMATION AND OPTICAL ABSORPTION SPECTRA OF COLLOIDAL SILVER NANOPARTICLES IN SUPERCRITICAL ETHANE
N. M. Dimitrijevic, D. M. Bartels, C. D. Jonah, K. Takahashi, and T. Rajh
J. Phys. Chem., 105, 954 (2001)

ANALYTICAL TREATMENT OF EPR SPECTRA OF WEAKLY COUPLED SPIN CORRELATED RADICAL PAIRS IN DISORDERED SOLIDS: APPLICATION TO THE CHARGE SEPARATED STATE IN $TiO_2$ NANOPARTICLES
A. A. Dubinski, G. D. Perekhotsev, O. G. Poluektov, T. Rajh, and M. C. Thurnauer
J. Phys. Chem. B 106, 938-944 (2002)

ELECTRON AND HOLE ADDUCTS FORMED IN ILLUMINATED InP COLLOIDAL QUANTUM DOTS STUDIED BY ELECTRON PARAMAGNETIC RESONANCE
O. I. Micic, A. J. Nozik, E. Lifshitz, T. Rajh, O. G. Poluektov, and M. C. Thurnauer
J. Phys. Chem. B 106 (17), 4390-4395 (2002)

$Fe_2O_3$ NANOPARTICLE STRUCTURES INVESTIGATED BY X-RAY ABSORPTION NEAR EDGE STRUCTURE, SURFACE MODIFICATIONS, AND MODEL CALCULATIONS
L. X. Chen, T. Liu, M. C. Thurnauer, R. Csencsits, and T. Rajh
J. Phys. Chem. B 106 (34), 8539-8546 (2002)

SURFACE RESTRUCTURING OF NANOPARTICLES: AN EFFICIENT ROUTE FOR LIGAND - METAL OXIDE CROSSTALK
T. Rajh. L. X. Chen, K. Lukas, T. Liu, M. C. Thurnauer, and D. M. Tiede
J. Phys. Chem. B 106 (41), 10543-10552 (2002)

CHARGE SEPARATION IN TITANIUM OXIDE NANOCRYSTALLINE SEMICONDUCTORS REVEALED BY MAGNETIC RESONANCE
T. Rajh, O. G. Poluektov and M. C. Thurnauer
Chapter 4 in *Chemical Physics of Nanostructured Semiconductors*, NOVA Science Publ., Inc., New York, 2002, Ed., A. I. Kokorin

SURFACE MODIFICATION OF $TiO_2$: A ROUTE FOR EFFICIENT SEMICONDUCTOR ASSISTED PHOTOCATALYSIS
T. Rajh, O. V. Makarova, D. Cropek, and M. C. Thurnauer
In *Synthesis, Functionalization and Surface Treatment of Nanoparticles*, American Scientific Publishers, California, 2002, Ed., M.-I. Baraton, pp. 147-171

BIOLOGY OF $TiO_2$ - OLIGONUCLEOTIDE NANOCOMPOSITES
T. Paunesku, T. Rajh, G. Wiederrecht, J. Maser, S. Vogt, N. Stojicevic, M. Protic, B. Lai, J. Oryhon, M. C. Thurnauer, and G. E. Woloschak
Nature Materials, in press, 2003

EXPLAINING THE ENHANCED PHOTOCATALYTIC ACTIVITY OF MIXED PHASE $TiO_2$ USING EPR
D. C. Hurum, A. G. Agrios, K. A. Gray, T. Rajh, and M. C. Thurnauer
J. Phys. Chem. B, in press, 2003

REVEALING THE NATURE OF TRAPPING SITES IN NANOCRYSTALLINE TITANIUM DIOXIDE BY SELECTIVE SURFACE MODIFICATION
N. M. Dimitrijevic, Z. V. Saponjic, D. M. Bartels, M. C. Thurnauer, D. M. Tiede, and T. Rajh
J. Phys. Chem. B, in press, 2003

# *Session IV*

# *Photoelectrochemistry*

# ELECTRON TRANSFER DYNAMICS IN EFFICIENT MOLECULAR SOLAR CELLS

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Our DOE-supported research has focused on the mechanisms for interfacial electron transfer at nanocrystalline $TiO_2$ interfaces. Our approach has been to characterize novel molecular and supramolecular sensitizers, based on $(d\pi)^6$ coordination compounds of our own design, with steady state and time resolved spectroscopic and electrochemical techniques. A summary of our recent research accomplishments and manuscripts are given below.

*1. **Tuning Interfacial Energetics.*** Tuning molecular reduction potentials relative to the energy levels of semiconductor solids is important for the development of molecular devices, such as the dye-sensitized solar cell. There is presently no unambiguous method for quantifying the energetic position of the $TiO_2$ conduction band (or 'empty states') on an absolute scale. We have undertaken electrochemical, optical, and chemical trapping studies designed to provide reliable methods for determining $TiO_2$ energetics under conditions that may be relevant to the dye sensitized solar cell. We have recently synthesized thin film actinometers for nanosecond transient absorption measurements that allow us to quantify the electron injection yields spectroscopically. These injection yields can then be compared to the photocurrent efficiency of the same material in an operational solar cell. Interesting cases have been identified where the electron injection yield is near unity yet the photocurrent efficiency is $< 0.1$. These and related findings have prompted us to measure cage escape yields at sensitized semiconductor interfaces in the presence of electron donors. A long-term goal of these studies is to optimize the Gibbs free energy stored in interfacial charge separated states by independently tuning semiconductor and sensitizer energetics.

*2. **Control of Interfacial Charge Transfer Dynamics.*** Molecular control of interfacial electron transfer kinetics and yields is an important goal. We have developed models that can differentiate between injection from vibrationally 'hot' excited states or the thermally equilibrated excited state. Our data suggests that hot vibrational electron transfer does not change the excited state lifetime of the surface bound sensitizer. This observation has led to applications of sensitized $TiO_2$ thin film materials as ratio-metric photoluminescent sensors for alkali and alkaline earth cations. Kinetic models for the recombination of the injected electron with the oxidized dye have also recently been developed and tested in our laboratories. We have quantified interfacial electron transfer rate constants as a function of ionic strength and the distance between the chomophoric ligand and the surface with well-defined sensitized $TiO_2$ interfaces. A specific goal is to identify conditions where electron injection into the semiconductor is quantitative and recombination is inhibited.

*3. **Charge Transfer Reorganization Energies.*** Molecules attached to semiconductor surfaces are exposed to the external environment and the semiconductor surface.

Therefore, the reorganization energy for charge transfer is expected to include components from both. At present, there exists little experimental data on charge transfer reorganization energies at molecular-semiconductor interfaces. We have prepared novel sensitizers that serve as solvatochromic probes of the interface and can provide this important experimental data. For example, the electrochemical and spectroscopic properties of $Ru(dcb)(CN)_4^{2-}/TiO_2$, where dcb is 4,4'-$(CO_2H)_2$-2,2'-bipyridine, in different organic electrolytes have allowed us to quantify charge transfer reorganization energies for the first time. Comparative studies with $Ru(dcb)(CN)_4^{2-}$ in fluid solution demonstrate that the interface plays a significant role in charge transfer reorganization. In ongoing work, these studies will be extended to related sensitizers set at variable distances from the semiconductor surface.

*4. **Antenna Interfaces.*** Intermolecular energy transfer across nanocrystalline semiconductor surfaces occurs efficiently under conditions where interfacial electron injection is energetically unfavored. Intermolecular energy transfer across the semiconductor surface has been exploited to sensitize a specific compound on the semiconductor surface. For example, the Ru* → Os energy transfer yield is within experimental error of unity for anatase $TiO_2$ nanoparticles sensitized with both $Ru(dcb)(bpy)_2^{2+}$ and $Os(dcb)(bpy)_2^{2+}$ in acetonitrile. Isoenergetic Ru* → Ru energy transfer dynamics have been modeled by Monte-Carlo simulations and compared to experimental data measured in controlled environments with ruthenium complexes having different excited state lifetimes. Our preliminary analysis indicates that intermolecular energy transfer occurs on an approximately 1 ns time scale. The rate constants can be tuned by controlling the distance between sensitizers bound to the semiconductor surface.

*5. **Intramolecular Hole Hopping.*** Diffusion of the mobile electron donor to the oxidized sensitizer can limit the power output of the dye-sensitized cell under conditions of high irradiance, viscous electrolytes, and/or in solid-state embodiments of the cell. We have studied novel dyads that regenerate undergo intramolecular hole hopping after electron injection into the semiconductor surface. In ongoing research we have compared these rate constants to intermolecular cases where the donor is co-anchored to the semiconductor surface. In related studies, the bimetallic sensitizer $[Ru(dcb)_2(Cl)\text{-bpa-}Os(bpy)_2(Cl)](PF_6)_2$, abbreviated Ru-bpa-Os, where bpa is 1,2-bis(4-pyridyl)ethane, was anchored to $TiO_2$ for interfacial electron transfer studies. Pulsed 417 nm or 532.5 nm light excitation of a $TiO_2$|Ru-bpa-Os results in rapid interfacial electron transfer and intramolecular electron transfer (Os(II) → Ru(III)) to ultimately form an interfacial charge separated state with an electron in $TiO_2$ and an oxidized Os(III) center, $TiO_2(e^-)$|Ru-bpa-Os(III). This same state can 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 rate constants for charge recombination was not significantly different than that for an $Os(dcb)_2(bpa)Cl^+$ model compound, presumably because the Os center is proximate to the surface in $TiO_2$|Ru-bpa-Os. We have designed new bimetallic compounds that will produce a better-defined surface-sensitizer orientation. A long-term goal of these studies is to correlate the kinetic rate constants for charge recombination with open circuit photo voltages of operational solar cells.

DOE Supported Publications (2001-2003)

**Excited State Processes at Sensitized Semiconductor-Interfaces Characterized by Nanosecond Absorption Spectroscopy.** Kelly, C.A.; Meyer, G.J. *Coord. Chem. Rev.* **2001**, *211*, 295-315.

**Phosphonate-Based Bipyridine Dyes for Stable Photovoltaic Devices.** Bignozzi, C.A.; Costa, E.; Alebbi, M.; Gillaizeau-Gauthier, I.; Odobel, F.; Qu, P.; Meyer, G.J. *Inorg. Chem.* **2001**, *40*, 6073-6079.

**Long Distance Electron Transfer Across Molecular-Nanocrystalline Semiconductor Interfaces.** Galoppini, E.; Guo, W.; Qu, P.; Meyer, G.J. *J. Am. Chem. Soc.* **2001**, *123*, 4342-4343.

**Proton Controlled Electron Injection from Molecular Excited States to the Empty States in Nanocrystalline $TiO_2$.** Qu, P.; Meyer, G.J. *Langmuir* **2001**, *17*, 6720-6728.

**Dye Sensitized Electrodes.** Qu, P.; Meyer, G.J. in *Electron Transfer in Chemistry*. V. Balzani, Ed.; John Wiley & Sons; NY **2001**, Chapter 2, Part 2, Vol. IV, pp 355-411.

**New Approaches for Energy Conversion at Dye Sensitized Electrodes.** Bergeron, B.V.; Meyer, G.J. in *Photovoltaics for the 21st Century*. R. McConnell Ed.; Electrochemistry Society, Washington DC. **2001**, pp 173-183.

**Sensing Alkali and Alkaline Earth Cations by Conduction Band Quenching of Dye Photoluminescence.** Stux, A.M.; Meyer, G.J. *J. Fluorescence* **2002**, *12*, 419-423.

**Solvatochromic Dye Sensitized Nanocrystalline Solar Cells.** Argazzi, R.; Bignozzi, C.A.; Yang, M.; Hasselmann, G.M.; Meyer, G.J. *NanoLett.* **2002**, *2*, 625-628.

**Long-Range Electron Transfer Across Molecule-Nanocrystalline Semiconductor Interfaces Using Tripodal Sensitizers.** Galoppini, E.; Guo, W.; Hoertz. P.; Qu, P.; Meyer, G.J. *J. Am. Chem. Soc.* **2002**, *124*, 7801-7811.

**Ligand Localized Electron Trapping at Sensitized Semiconductor Interfaces.** Hoertz, P.G.; Thompson, D.W.; Friedman, L.A.; Meyer, G.J. *J. Am. Chem. Soc.* **2002**, *124*, 9690-9691.

**Rapid Excited State Structural Reorganization Captured by Pulsed X-Rays.** Chen, L.X.; Jennings, G.; Liu, T.; Gosztola, D.J.; Hessler, J.P.; Scaltrito, D.V.; Meyer, G.J. *J. Am. Chem. Soc.* **2002**, *124*, 10861-10867.

**Molecular Control of Photo-Induced Electron and Energy Transfer at Nanocrystalline Semiconductor Interfaces.** Meyer, G.J. *J. Photochem. Photobiol. A: Chem.* **2003**, *6247*, 1-6.

**The MLCT State Structure and Dynamics of a Cu(I) Diimine Complex Characterized by Pump-probe X-ray and Laser Spectroscopies and DFT Calculations.** Chen, L.X.; Shaw, G.B.; Liu, T.; Jennings, G.; Attenkofer, K.; Meyer, G.J.; Coppens, P. *J. Am. Chem. Soc.* **2003**, *in press.*

**Organic Rigid-Rod Linkers for Coupling Chromophores to Metal Oxide Nanoparticles.** Hoertz, P.G.; Carlisle, R.A.; Meyer, G.J.; Wang, D.; Piotrowiak, P.; Galloppini, E. *Nanolett.* **2003**, *3*, 325-330.

**Picosecond Photoinduced Charge Injection from "Molecular Tripods" into Mesoporous $TiO_2$ Over the Distance of 24 Å.** Piotrowiak, P.; Galoppini, E.; Wei, Q.; Meyer, G.J.; Wiewiór, P. *J. Am. Chem. Soc.* **2003**, *in press.*

**Photo- and Redox-Active Coordination Compounds as Molecular Components in Devices.** Bignozzi, C.A.; Meyer, G.J. in *Molecules as Components of Electronic Devices*; Lieberman, M., Ed.; ACS Symposium Series 844; American Chemical Society: Washington, DC, **2003**.

**Sensitization and Stabilization of $TiO_2$ Photoanodes with Electropolymerized Films of Ruthenium and Zinc Polypyridyl Complexes**. Moss, J.A.; Yang, J.C.; Stipkala, J.M.; Wen, X.; Bignozzi, C.A.; Meyer, T.J.; Meyer, G.J. *submitted.*

**Thin Film Actinometers for Nanosecond Transient Absorption: Applications to Dye-Sensitized Solar Cells.** Bergeron, B.V.; Kelly, C.A.; Meyer, G.J. *submitted.*

# ULTRAFAST ELECTRON INJECTION FROM ADSORBATES TO NANOCRYSTALLINE SEMICONDUCTOR THIN FILMS: BRIDGE LENGTH AND SEMICONDUCTOR DEPENDENCE

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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.

Using femtosecond infrared spectroscopy, we have carried out a systematic study of the dependence of electron injection rate on the property of adsorbate, spacer, anchoring group, semiconductor and the interfacial environment. In this talk, we will summarize the following recent results:

**Parameters affecting electron injection from Ru dyes to TiO2 nanocrystalline thin films:** Electron injection rates from $Ru(dcbpy)_2(X)_2$ [X=2NCS, 2CN, and dcbpy; dcbpy=2,2'-bipyridine-4,4'-carboxylate] (called Ru535 or RuN3, Ru505, and Ru470) to $TiO_2$ nanocrystalline thin films are examined as a function of adsorbate redox potential, pH of the solution, excitation wavelength and solvent. For all three dyes, the injection kinetics are bi-phasic, consisting of a distinct ultrafast (< 100fs) and slower components. Under different experimental conditions, the partitioning between these two components and rate of slow components change, but the rate of fast component show no noticeable variations within the ~200fs time resolution of the measurement. Comparing Ru535, Ru505 and Ru470 at the same pH, increasing amplitude and decreasing rate of slow component were observed, correlating with less negative excited state redox potentials in these dyes. An analogous trend was seen for Ru N3/$TiO_2$ by increasing the pH of the solution from pH=2 to 8 and changing from pH=2 aqueous solution to a (1:1) ethylene/propylene carbonate mixture. The injection dynamics are also dependent on excitation wavelength. The relative amplitude of slow component increases when excitation wavelength is changed from 400 nm to 630 nm. All data can be described by a two-state injection model, which attributes the fast (<100fs) component to injection from a non-thermalized excited state and the slow component to injection from the thermalized excited state. The partitioning between these two components and rate of the slow components depend on the relative energetics between dye excited states and the conduction band edge.

**Dependence of injection rate on semiconductor.** We previously showed that electron injection from Ru dye depends critically on the nature of semiconductor. Injection rate from Ru N3 to ZnO is characterized by a ~100 ps stretched exponential rise. It is much slower than the ~4ps, and ~100 fs injection time observed for $SnO_2$. A recent paper by Sweden group reports ~100 fs injection time from a similar Ru dye to ZnO. To resolve this potential discrepancy and more importantly to understand the dependence on the nature of semiconductor, we have carried out a systematic study on semiconductor dependence. So far, we have examined the injection dynamics of a series of Ru dyes on $SnO_2$ and ZnO. For all Ru dyes, slow injection, on the 100ps time scale, on ZnO was observed under various experimental condition (excitation wavelength, film preparation method), consistent with our previous resport. More interestingly, injection in all films can be characterized by a two-state injection model with ZnO and $SnO_2$ films showing much smaller (although non-negligible) fast injection components. Using two-state injection model, we compare the amplitude of the fast components and the rate of the slow components in three semiconductors. The comparison suggest an interesting dependence on density of states and electronic coupling.

**Dependence of injection rate on electronic coupling** The electron transfer rate from methylene-bridged molecular adsorbate to $SnO_2$ semiconductor nanocrystalline film was systematically investigated for short bridge lengths. The specific molecules used were $Re(CO)_3Cl(dcbpy)$ [dcbpy=2,2'-bipyridine-4,4'-biscarboxylate] (ReC0A) and bridged derivatives prepared by inserting $(CH_2)_n$ (n=1-5) between the bipyridine ring and the carboxylate anchoring groups (ReCnA). Use of femtosecond infrared spectroscopy provided the time resolution necessary to study the ultrafast transfer that occurs with very short bridges. Electron injection is unambiguously observed by signals arising from both the injected electron and the CO stretching mode of the oxidized molecule. Nonexponential electron injection was observed for all dyes, likely due to a distribution of electronic coupling between adsorbate and semiconductor. Kinetic traces for different spacers can be superimposed on each other by scaling their time axes, which allows a quantitative comparison of these nonexponential injection rates. This comparison revealed an exponential decrease of injection rate with bridge length for $3 \leq n \leq 5$ with a decay constant (β value) of 1.0 per $CH_2$ unit. Deviation from the exponential dependence was observed for n=1 and n=2. The applicability of the time-scaling technique also implies a nominally bridge length-independent rate distribution for all bridged samples.

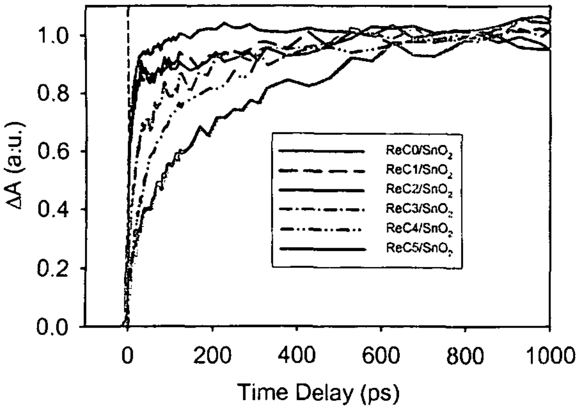

Fig. 1. Comparison of electron injection dynamics in ReCn (n=0-5) to $SnO_2$ thin film

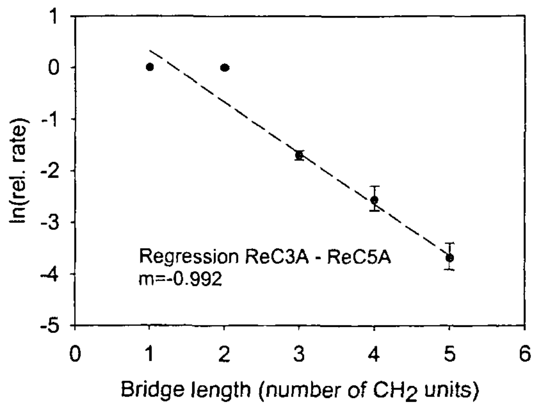

Fig. 2. Dependenc of Electron injection rate on the number of $CH_2$ units inn ReC0n sensitized $SnO_2$ thin films

## DOE-Supported Publications (2001-2003)

1) J. B. Asbury, Y.-Q. Wang, E. Hao, H. N. Ghosh, and T. Lian, *Evidences of Hot Excited State Electron Injection from Sensitizer Molecules to $TiO_2$ nanocrystalline Thin Films,* **Research on Chemical Intermediates, 2001**, 27, 393-406.
2) J. B. Asbury, Encai Hao, Yongqiang Wang, H. N. Ghosh, and T. Lian, *Ultrafast electron transfer dynamics from adsorbate molecules to nanocrystalline semiconductor thin films,* **J. Phys. Chem. B (feature article), 2001**, 105, 4545-4557.
3) Asbury, John B.; Hao, Encai; Wang, Yongqiang; Lian, Tianquan. *Femtosecond IR study of ultrafast electron injection in nanocrystalline thin film electrodes.* Springer Ser. Chem. Phys. 2001, 66 **(Ultrafast Phenomena XII)**, 450-452.
4) Neil A. Anderson, John B. Asbury, Encai Hao. Xin Ai, Tianquan Lian, *Dynamics Of Interfacial Charge Separation In Sensitized Nanocrystalline Semiconductor Thin Films,* in **Photovoltaics for the 21st Century II** (Proceedings of the electrochemical society), 2001, Vol. 2001-10, 97-105.
5) John B. Asbury, Neil A. Anderson, Encai Hao, Xin Ai, and Tianquan Lian "Parameters affecting electron injection dynamics from Ru dyes to $TiO_2$ nanocrystalline thin film", **J. Phys. Chem. B**, accepted (special issue for Henglein, 2003).
6) Neil A. Anderson, Xin Ai, Daitao Chen, Debra L. Mohler, Tianquan Lian, "Bridget assisted ultrafast interfacial electron transfer to nanocrystalline $SnO_2$ thin films", **submitted to J. Am. Chem. Soc**, (March 2002)
7) N. Anderson, Xin Ai, Chungxin She and T. Lian, Electron injection dynamics in Ru dye-sensitized ZnO nanocrystalline thin films **(to be submitted to J. Phys. Chem. B.)**
8) N. Anderson, Xin Ai, Chungxin She and T. Lian, Electron injection dynamics in Ru dye-sensitized $SnO_2$ nanocrystalline thin films **(to be submitted to J. Phys. Chem. B.)**

# PREPARATION OF SMALL BAND GAP COLLOIDAL QUANTUM DOT SYSTEMS FOR IMPACT IONIZATION AND DYE SENSITIZATION

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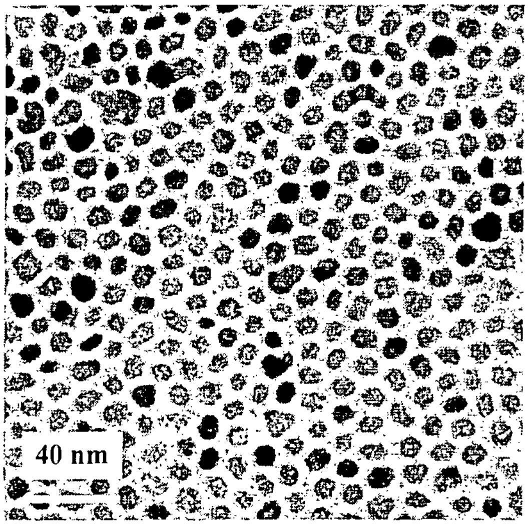
A central theme of my work is the utilization of non-relaxed excited states, with the objective of harnessing increased energy and/or photons from photoconversion processes. Typically it is assumed that excitation energy in excess of $E_{0,0}$ (in the case of molecular species) or $E_g$ (in the case of semiconductors) is lost to the solvent or lattice. However, capturing and converting this additional energy can increase solar conversion efficiencies, either through photovoltage increases or quantum yield increases. Electron transfer from upper excited states of molecules and impact ionization in quantum dots (QD's) are possible ways of realizing this goal. In some instances, converting a "hot" excited state may be the only way to capture photoexcitation, as is the case for iron bipyridyl complexes sensitizing nanocrystalline $TiO_2$. For quantum dots, it may be possible to demonstrate impact ionization spectroscopically and in the dye sensitized solar cell (DSSC).

My dye sensitization work focuses on the structural characterization of dye systems to understand the dye-semiconductor interaction that facilitates electron transfer from upper excited states. Earlier work involved developing iron bipyridyl sensitizers for the dye sensitized solar cell, and investigating the structural properties affecting their quantum efficiencies. The iron bipyridyl systems were distinct from the widely used ruthenium bipyridyl sensitizers in that photosensitization was likely only occurring from an upper excited state of the molecule. Thus, these systems provide a way to isolate and study upper excited state electron transfer. Indeed, it was found that there was a more severe dependence of photosensitization on changes in the linkage between the sensitizer and the $TiO_2$ than there was for systems in which electron transfer could occur from lowest excited states.

Increasingly, colloidal quantum dots are supplanting traditional molecular dyes in applications requiring excellent absorption or emission properties. Optically tuning a molecular dye usually requires chemical derivatization – thus for every absorber, one must synthesize and purify a new compound. For quantum dots, a single reaction of one material can yield a variety of "dyes", which can be separated by size selective techniques. The preparation and purification of QD's typically utilizes less solvent and needs no chromatographic material; thus, it is also less resource intensive and generates less waste than preparing individual dyes.

More recent work has focused on the preparation of small band gap semiconductor QD's for impact ionization experiments. Small band gap QD materials are also potentially useful for thermophotovoltaics, infrared detection and optical communication. In particular, lead salts are interesting systems and are receiving much attention recently. They have large excitonic radii and simple electronic structures, so the strong confinement limit is accessible, and they are well suited for fundamental studies and nonlinear applications. Indeed, the infrared region may be the optical niche for quantum dots. Recently, Guyot-Sionnest demonstrated that for PbSe, the infrared fluorescence was significantly greater than the highest efficiency commercial dye for the same wavelength region.

Quantum dots of InAs, PbSe and PbTe have been prepared and characterized. PbTe is a novel system and can be synthesized in narrow size distributions. Like PbSe, PbTe also shows spontaneous ordering into arrays (figure below). The size, shape, and aggregation properties of the particles are highly dependent upon reaction conditions.



The quantum dots can also be employed as photosensitizers in the dye sensitized solar cell. InAs and PbSe adsorb to films of $TiO_2$ without a specialized linker. The QD's are able to photosensitize $TiO_2$ at higher energies, but not from their lower energy excitonic transitions. In addition, efficiency for electron injection is high at low light intensity but at higher light intensity appears limited by transport through the film. Furthermore, the use of the $LiI/I_2$ couple is problematic for these systems and other redox couples must be developed.

Future work will establish the linking chemistry necessary to strongly couple the excited state of the QD to the conduction band of the $TiO_2$, as is the case for the carboxylated dye systems. Although a variety of QD's have been established as sensitizers in the DSSC, adsorption to the oxide surface is usually non-specific. Future research will focus on designing more elegant linkages to bridge quantum dots to the $TiO_2$ surface.

## DOE Supported Publications 2001-2003

"Colloidal Quantum Dots of PbTe", Ferrere, S., Norman, A.G., Nozik, A.J., in preparation.

"Enhanced Dye-Sensitized Photoconversion Efficiency via Reversible Production of UV-Induced Surface States in Nanoporous $TiO_2$", Gregg, B. A., Chen, S.-G., Ferrere, S., *J. Phys. Chem. B*, **2003**, 107, 3019-3029.

"New Perylenes for Dye Sensitization of $TiO_2$", Ferrere, S. and Gregg, B.A. *New Journal of Chemistry*, **2002**, 26, 1155-1160.

"Interfacial Processes in Organic-Based Solar Cells", B.A. Gregg, S. Ferrere and F. Pichot, Organic Photovoltaics II, Z.H. Kafafi, Ed, Proceedings of SPIE Vol. 465 (2002) 31-41.

"New Photosensitizers Based Upon $[Fe(L)_2(CN)_2]$ and $[Fe(L)_3]$, Where L is Substituted 2,2'-Bipyridine", Ferrere, S. *Inorg. Chim. Acta* **2002**, 329, 79-92.

"Large Increases in Photocurrents and Solar Conversion Efficiencies By UV Illumination of Dye Sensitized Solar Cells." Ferrere, S. and Gregg, B.A. *J. Phys. Chem. B* **2001**, 105, 7602-7605.

"Interfacial Recombination Processes in Dye-Sensitized Solar Cells and Methods to Passivate the Interfaces." Gregg, B.A.; Pichot, F.; Ferrere, S.; Fields, C.L., *J. Phys. Chem. B* **2001**, 105, 1422-1429.

# ULTRAFAST CHARGE CARRIER RELAXATION AND SEPARATION DYNAMICS IN COLLOIDAL NANOSTRUCTURED ABSORBERS

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The search for new approaches to efficient and economical solar energy conversion technologies has led in part to the intensified study of systems for which combinations of molecules and nanostructures enable light absorption rapidly followed by charge separation. High surface area interface designs suit the desired simultaneous properties of both (a) strong device photoabsorption and (b) proximity of the photoexcited species to the charge separating interface. Systems such as those based on $C_{60}$-doped polymers or dye-sensitized nanocrystalline $TiO_2$ electrodes, enable ultrafast (sub-100 fs) charge separation across the absorber/electron transporter interface. Such fast charge separation has the potential to compete with hot carrier relaxation, which typically occurs within a few hundred femtoseconds of photoexcitation. We have been studying colloidal nanostructured absorbers such as semiconductor quantum dots (QDs) and single wall carbon nanotubes (SWNTs) to measure charge carrier relaxation dynamics, and ultrafast charge separation, which have implications for both solar energy conversion and the prospect of hot carrier conversion.

Utilizing theoretical techniques and ultrafast laser spectroscopy, we have studied the electronic structure and charge carrier relaxation dynamics for colloidal semiconductor quantum dots and rods, and SWNTs. Colloidal semiconductor QDs exhibit qualities attractive for energy conversion. Their size-dependent, discrete, and potentially sparse electronic structure offers substantial flexibility in optical properties as well as the potential to slow the cooling of hot carriers; furthermore, their exceptional surface-to-volume ratio coordinates with the possibility of fast charge separation. Similarly, semiconductor quantum rods (QRs) exhibit strong quantum confinement effects with reduced or no confinement along the axial direction. Alivisatos has shown that CdSe QR-based solar cells may provide a viable approach to efficient solar energy conversion, due apparently to the benefit of charge transport along the axes of the QRs [Science **295**, 2425 (2002)].

We have recently completed a detailed study of 42 Å InP QDs. Using femtosecond transient absorption (TA) spectroscopy, we find that the rate of relaxation of hot photogenerated excitons to the lowest-energy exciton level varies depending upon excitation energy and surface chemistry. As expected, we find that as we excite carriers further above the first exciton absorption, they take longer to relax to this first exciton state. Etching the QDs passivates surface electron traps and yields enhanced carrier cooling, which we ascribe to improved confinement of charge carriers to the QD core. When exciting near or slightly above the first exciton state, we observe a sub-picosecond decay of the first exciton TA bleach signal which we attribute to a thermalization process. We also present size-selective transient absorption measurements providing experimental evidence which confirms the existence of two s-like exciton states spaced by ~100 meV. The relatively close proximity of the exciton levels concurs with the understanding that the phonon bottleneck effect, attributable to large gaps within the electronic spectrum which inhibit phonon-scattering-based relaxation, slows cooling less for excitons than for single electrons. In collaboration with H. Fu (U. Arkansas), we have calculated the electronic structure for 41.8 Å InP QDs using an atomistic pseudopotiential approach; we find that these calculations yield very good agreement with our experimentally measured TA spectra (see Figure 1).

In a similar manner, and as part of the new BES Nanoscale Science Engineering and Technology (NSET) program, we have measured the transient absorption of colloidally suspended SWNTs to elucidate their electronic structure and relaxation dynamics. SWNTs exhibit diverse properties exemplary of good energy conversion components, including high surface area, linear conductivity coupled with extremely large aspect ratios, low defect density, and absorption across the ultraviolet, visible, and near-IR regions. Laser vaporization synthesis of SWNTs yield nanotubes with diameters in the range of ~ 1.0 – 1.4 nm, and samples consist of a broad variety of distinct tube types based on their diameter and on whether they are semiconducting or metallic. By measuring transient absorption spectra and dynamics for samples of dispersed SWNTs, we observe electronic structure and charge carrier

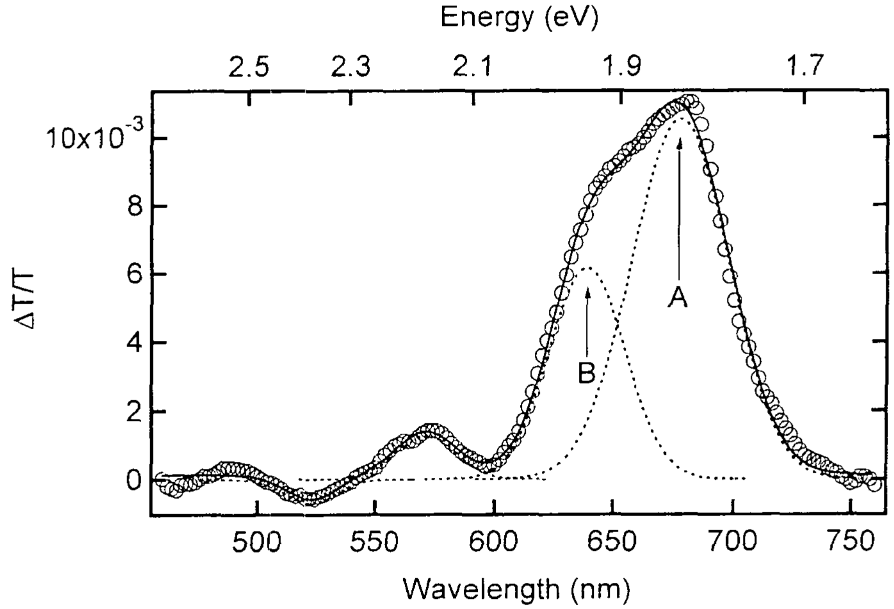

**Figure 1**: Transient absorption spectrum for 42 Å diameter InP QDs at 300 fs delay following size-selective 690 nm excitation. Asymmetry in the S exciton peak indicates the presence of two transitions. Dotted lines show Gaussian fit components which when summed produce the solid line; peaks A and B are spaced by ~ 105 meV.

relaxation dynamics analogous to those found for colloidal semiconductor QDs and QRs. We are attempting to assign the observed transition energies to specific tube types, which will further allow us to make targeted measurements on relaxation dynamics. These measurements are designed in part to provide a foundation on which we can continue studies of charge separation/transfer for coupled QD-SWNT and perhaps QR-SWNT nanostructure combinations.

Future research will investigate the charge separation dynamics for photoexcited colloidal QDs in solutions and adsorbed on surfaces of molecular and nanoscale acceptors of electrons and/or holes. Recent measurements suggest that ultrafast charge transfer from colloidal QDs to $C_{60}$ may be readily verifiable though the near-IR electron signature of the electron acceptor. Additional future research, alluded to above, will study the dynamics of charge transfer between coupled QDs, or QRs, and SWNTs as part of the new NSET program. We will also continue efforts to understand charge carrier relaxation in nanostructures to address opportunities for slowed relaxation.

## DOE Supported Publications 2001-2003

1. R. J. Ellingson, J. L. Blackburn, J. Nedeljkovic, G. Rumbles, M. Jones, H. Fu, and A. J. Nozik, "Theoretical and Experimental Investigation of Electronic Structure and Relaxation of Colloidal Nanocrystalline Indium Phosphide Quantum Dots," *Phys. Rev. B* **67**, 075308 (2003).

2. J. L. Blackburn, R. J. Ellingson, O. I. Micic, A. J. Nozik, "Electron Relaxation in Colloidal InP Quantum Dots with Photogenerated Excitons or Chemically Injected Electrons," *J. Phys. Chem. B* **107**, 102 (2003).

3. R. J. Ellingson, J. L. Blackburn, P. Yu, G. Rumbles, O. I. Micic, and A. J. Nozik, "Excitation Energy Dependent Efficiency of Charge Carrier Relaxation and Photoluminescence in Colloidal InP Quantum Dots," *J. Phys. Chem. B* **106**, 7758 (2002).

4. G. Rumbles, D. Selmarten, R. J. Ellingson, J. L. Blackburn, P. Yu, B. B. Smith, O. I. Micic, A. J. Nozik, "Anomalies in the Linear Absorption, Transient Absorption, Photoluminescence and Photoluminescence Excitation Spectroscopies of Colloidal InP Quantum Dots," *J. Photochem. and Photobiol., A*: Chemistry **142**, 187 (2001).

# CHEMICAL CONTROL OVER THE ELECTRICAL PROPERTIES OF III-V SEMICONDUCTOR SURFACES AND OVER CHARGE TRANSPORT IN MESOPOROUS PHOTOELECTRODES

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Two aspects of the chemistry of semiconductor/liquid interfaces will be discussed. The first aspect focuses on measurement of interfacial charge transfer rate constants using ZnO/liquid contacts, while the second aspect describes work directed towards developing new passivation chemistry for III-V semiconductor surfaces.

The first portion of the work involves measurement of robust rate constants at semiconductor/liquid contacts with the goal of elucidating rate constants as a function of driving force and reorganization energy especially in the Marcus inverted region. Accordingly, we have synthesized a series of non-adsorbing, one-electron outer-sphere redox couples, $[OsB_3]^{3+/2+}$ and $[OsB_2L_2]^{3+/2+}$ where B = bipyridyl or 4,4;-dimethyl bipyridyl and L = imidazole or 4-methyl imidazole, with reduction potentials spanning over 400 mV and similar, well-defined reorganization energies. The value of the reorganization energies of $[OsB_3]^{3+/2+}$ were determined from the self exchange rate constants resulting from NMR line broadening experiments. A value for the reorganization energy of 0.68 eV has been found under our experimental conditions.

Differential capacitance and current density measurements have been used to investigate the interfacial energetic and kinetic behavior of n-ZnO in contact with these osmium redox couples. n-ZnO in contact with $[OsB_3]^{3+/2+}$ and $[OsB_2L_2]^{3+/2+}$ displays ideal energetic and kinetic features; the rates of electron transfer were found to be first order in both surface-electron and acceptor concentration. Additionally, differential capacitance measurements indicate that, for a given ZnO electrode, the band edges remain fixed as the electrochemical potential of the solution is changed. This behavior enables full characterization of the driving force dependence of interfacial electron transfer reactions in terms of the Marcus formalism. Recent results have shown a clear driving force dependence with an indication that rate constants are in fact in the inverted region, in that the rate constant for $[Os(bpy)_3]^{3+/2+}$ is an order of magnitude lower than that of $[Os(bpy)_2(him)_2]^{3+/2+}$, despite the latter having a 350 mV greater driving force.

Maximum rate constants were found to be consistently lower than those obtained for Si/viologen contacts. Preliminary x-ray photoelectron spectroscopy studies show no indication for the existence of an insulating layer at the surface, which might result in a smaller electronic coupling of the acceptor species with the semiconductor. Concerns remain that the imidazole ligand in $[Os(bpy)_2(him)_2]^{3+/2+}$ deprotonates and results in a more effective coupling. We have synthesized $[Os(bpy)_2(4\text{-}mehim)_2]^{3+/2+}$, where the hydrogen of the imidazole is replaced by a methyl group. To further map out the driving force dependence, we will measure rate constants for ZnO in contact with $[Os(dmbpy)_2(Him)_2]^{3+/2+}$, $[Os(dmbpy)_2(4\text{-}meHim)_2]^{3+/2+}$, and $[Os(phen)_3]^{3+/2+}$.

In the second portion of the work, we describe chemistry that has been developed to control the electrical and chemical properties of III-V semiconductor surfaces, specifically GaAs. When compared to the rich surface chemistry available for Si, there are a very limited number of ways to chemically passivate GaAs. Thermal oxides analogous to the $SiO_2$ layers used on industrial Si processing cannot be grown on GaAs, as the oxide/semiconductor interface is not stable and degrades to $Ga_2O_3$ and As metal. As(0) acts as trap state for carrier recombination, adversely affecting device performance. Thus, it is important to find alternate ways of chemically protecting the surface. Grignard reactions on Cl-terminated (111)A surfaces do not appear to form stable Ga-C bonds and show no additional resistance to oxidation in air, suggesting that an alkylation strategy analogous to that explored for Si will not be effective for GaAs. However, XPS studies of GaAs(111)A and (111)B surfaces show that simple treatments with $PCl_3$ form a phosphorous oxide layer over the surface. The layer effectively inhibits the formation of $As_2O_3$ on air exposed surfaces for periods of a week or longer. This route therefore provides a promising approach to the wet chemical modification of the electrical and chemical properties of GaAs surfaces.

## DOE Supported Publications 2001-2003

Darius Kuciauskas, Michael S. Freund, Harry B. Gray, Jay R. Winkler, and Nathan S. Lewis, "Electron Transfer Dynamics in Nanocrystalline Titanium Dioxide Solar Cells Sensitized with Ruthenium or Osmium Polypyridyl Complexes," *J. Phys. Chem., B,* **2001**, 105, 392-403.

Nathan S. Lewis, "Frontiers of Research in Photoelectrochemical Solar Energy Conversion" *J. Electroanal. Chem.*, **2001**, *508*,1-10.

Darius Kuciauskas, Michael S. Freund, Jay R. Winkler, Harry B. Gray, and Nathan S. Lewis, "Electron Transfer Dynamics in Nanocrystalline Titanium Dioxide Solar Cells Sensitized With Ruthenium and Osmium Polypyridyl Complexes, *Proc. 2001 ECS and ISE Joint International Mtg*, San Francisco, CA, USA, Vol. 2001-2, **2001.**

Darius Kuciauskas, Jeremy Monat, Randy Villahermosa, Harry B. Gray, Nathan S. Lewis, and James K. McCusker, "Transient Absorption Spectroscopy of Ruthenium and Osmium Polypyridyl Complexes Adsorbed onto Nanocrystalline $TiO_2$ Photoelectrodes,"*J. Phys. Chem., B,* **2002**, *106*, 9347-9358.

Kristine Kilsa, Elizabeth I. Mayo, Darius Kuciauskas, Randy Villahermosa, Nathan S. Lewis, Jay R. Winkler, Harry B. Gray, "Effects of Bridging Ligands on the Current-Potential Behavior and Interfacial Kinetics of Ruthenium-Sensitized Nanocrystalline $TiO_2$ Photoelectrodes" *J. Phys. Chem., B,* **2002**. Submitted for publication.

Nick Prokopuk and Nathan S. Lewis, "Eneretics and Kinetics of Interfacial Electron-Transfer Processes at Chemically Modified InP/Liquid Junctions," *J. Phys. Chem., B,* **2002**. Submitted for publication.

Nathan S. Lewis, "Artificial Photosynthesis and Photoconversion", *Encyclopedia of Energy,* **2002**. Submitted for publication.

Jae-Joon Lee, George M. Coia, and Nathan S. Lewis, "Current-Voltage Characteristics of Dye-Sensitized Nanostructured Semiconductor Photoelectrodes. I. Analytical Expressions." **2002**. Submitted for publication.

Jae-Joon Lee, George M. Coia, and Nathan S. Lewis, "Current-Voltage Characteristics of Dye-Sensitized Nanostructured Semiconductor Photoelectrodes. II. Simulations." **2002**. Submitted for publication.

# FEMTOSECOND SPECTROSCOPY OF TRANSITION METAL-BASED CHARGE-TRANSFER CHROMOPHORES

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The process of charge separation is the physical phenomenon that forms the underpinning for virtually all schemes geared toward the conversion of light into chemical, electrical, and/or mechanical energy. Inorganic compounds have long been a centerpiece for the study of photo-induced charge-transfer processes as well as the quest for achieving efficient solar energy conversion. Efforts over the past several decades by a large number of groups have helped to forge our understanding of the dynamics of the lowest-energy excited states of inorganic systems at an impressive level of sophistication; however, details concerning the processes by which these states are formed in the first place remain largely obscure. It is these latter processes that are the focus of our work. We have structured our research program to address the following four questions: 1) what is the time scale of the formation of low-energy excited states following photoexcitation? 2) what are the nature and dynamics of the processes involved in this excited-state evolution? 3) what correlations can we establish between excited-state evolution and the geometric and electronic properties of the molecules, as well as other variables such as temperature, pressure, the solvent, etc.? and finally, 4) given this knowledge, to what extent can we manipulate these various processes through synthetic or other means in order to effect some measure of control over charge-transfer formation and/or reactivity?

Our most recent efforts have concentrated in three areas: (1) the influence of solvent; (2) vibrational relaxation dynamics; and (3) injection dynamics in $TiO_2$-based photovoltaics. Two different effects on charge-transfer state evolution due to non-diffusive solvent dynamics have been observed. Absorption anisotropy studies of $[Ru(bpy)_3]^{2+}$ in a series of linear chain nitriles revealed variations in the excited state dynamics across the series.[1] Specifically, a correlation between the time scale for charge localization and the inertial mass of the solvent was observed. This result suggests an important role for solvent inertial motion in the dynamics of charge-transfer state formation and thermalization. The response of solvent to large-amplitude motion of the chromophore has also been investigated. We have previously shown that the peripheral aryl rings of $[Ru(dpb)_3]^{2+}$ (where dpb is 4,4'-diphenyl-2,2'-bipyridine) undergoes rotation in the course of excited-state formation and/or thermalization.[2] Two types of interactions by which solvent may couple to this process are mechanical friction and dielectric friction. The former is expected to correlate with the bulk viscosity of the solvent ($\eta$), whereas the latter should reflect the solvent's longitudinal relaxation time ($\tau_L$). Data were acquired in a series of linear chain alcohols (i.e., $CH_3(CH_2)_nOH$, n = 0-7), which afforded systematic variation of both of these quantities. The results are summarized in Figure 1.[3] Whereas the kinetics observed in MeOH and EtOH are distinct, data collected in all other solvents were superimposable with the EtOH data within experimental error. This observation was

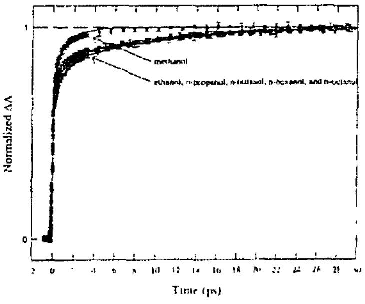

*Figure 1. Transient absorption data for $[Ru(dpb)_3]^{2+}$ at 530nm following ~100fs excitation at 400nm in the solvents indicated (from ref 3).*

interpreted in terms of a failure of bulk descriptions of the solvent to adequately treat the solvent's influence on the ring rotation process. Instead, we suggest a model in which local solvent-solute interactions (primarily involving rotation about the C-O bond) is/are responsible for the saturation effect evident from the data in Figure 1.

Data we have acquired thus far relating to vibrational relaxation dynamics come from femtosecond differential electronic absorption spectroscopy. Initial results on compounds such as $[Ru(dmb)_3]^{2+}$ (where dmb is 4,4'-dimethyl-2,2'-bipyridine) suggested that vibrational cooling in charge-transfer excited states was highly localized, implying a local mode (as opposed to normal mode) character to the evolving excited state.[2d] We have now examined this issue more thoroughly by way of variable-pump/variable-probe wavelength studies of $[Ru(dmb)_x(dea)_{3-x}]^{2+}$ (where dea is 4,4'-diethylamino-2,2'-bipyridine and x = 0-3). Variable-probe wavelength measurements at longer probe wavelengths (i.e., $\lambda > 650$nm) in particular revealed the presence of a small-amplitude increase in the excited-state LMCT absorbance. The lack of such a rise at shorter probe wavelengths is likely the result of offsetting negative and positive transient features in regions of spectral overlap between radical anion and LMCT contributions to excited-state absorption (as evidenced by spectroelectrochemical data). It therefore appears that energy is dissipated over a larger portion of the chromophore concomitant with excited-state thermalization than previously thought. Current work on vibrational relaxation dynamics is shifting toward their direct measurement using femtosecond infrared spectroscopy; initial efforts along these lines involving CN-substituted bipyridyl probe ligands will be briefly discussed.

Finally, in collaboration with Nate Lewis' group at Cal Tech, we have examined the dynamics electron injection from transition metal charge-transfer chromophores in $TiO_2$-based photovoltaic cells.[4] One of the more striking observations is illustrated in Figure 2, in which the dynamics of injection are shown to be dependent upon the excitation wavelength employed. In the present example, tuning the excitation source from 500nm to 560nm increases the relative fraction of $^3$MLCT state produced upon excitation. The absence of the sub-100fs kinetic component in the latter strongly suggests that the ultrafast injection dynamics seen in these systems arises from the non-thermalized $^1$MLCT state, whereas the ps-time scale process is due to injection from the $^3$MLCT. Recent results of injection dynamics on related systems will also be presented.

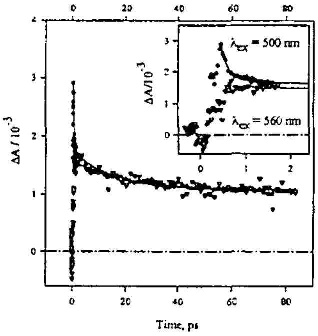

*Figure 2. Femtosecond time-resolved absorption data for a Ru(dcbpy)$_2$(NCS)$_s$-sensitized TiO$_2$ solar cell. The inset shows the effect of changing the excitation wavelength on the short-time scale kinetics (from ref. 4).*

**References**

[1] Yeh, A.T.; Shank, C.V.; McCusker, J.K. *Science* **2000**, *289*, 935-938.

[2] a) Damrauer, N.H.; Boussie, T.R.; Devenney, M.; McCusker, J.K. *J. Am. Chem. Soc.* **1997**, *119*, 8253-8268. b) Damrauer, N.H.; Weldon, B.T.; McCusker, J.K. *J. Phys. Chem. A* **1998**, *102*, 3382-3397. c) Damrauer, N.H.; McCusker, J.K. *Inorg. Chem.* **1999**, *38*, 4268-4277. d) Damrauer, N.H.; McCusker, J.K. *J. Phys. Chem. A* **1999**, *103*, 8440-8446.

[3] Damrauer, N.H.; Curtright, A.E.; McCusker, J.K. *J. Phys. Chem. A*, submitted for publication.

[4] Kuciauskas, D.; Monat, J.E.; Villahermosa, R.; Gray, H.B.; Lewis, N.S.; McCusker, J.K. *J. Phys. Chem. B* **2002**, *106*, 9347-9358.

## Publications, 2001 – 2003

1. "An Attenuated Total Reflection Design for *in Situ* FTIR Spectroelectrochemical Studies", Hendrik Visser, Aimee E. Curtright, James K. McCusker, and Kenneth Sauer, *Anal. Chem.* **2001**, *73*, 4374-4378.

2. "Fuel from Photons", James K. McCusker, *Science* **2001**, *293*, 1599-1601.

3. "Ultrafast Solvent-Induced Charge Localization in Tris(2,2'-bipyridine)ruthenium(II)", Alvin T. Yeh, Charles V. Shank, and James K. McCusker, in *Ultrafast Phenomena XII*, Springer Series in Chemical Physics 66, T. Elsässer, S. Mukamel, M.M. Murnane, and N.F. Scherer eds., Springer-Verlag, Heidelberg, 2001, pp. 494-496.

4. "Synthesis of Mono-Substituted 2,2'-bipyridines", Joseph G. Cordaro, James K. McCusker, and Robert G. Bergman, *Chem. Comm.* **2002**, 1496-1497.

5. "Ground- and Excited-State Electronic Structure of the Solar Cell Sensitizer bis(4,4'-dicarboxylato-2,2'-bipyridine)bis(isothiocyanato)ruthenium(II)", Jeremy E. Monat, Jorge H. Rodriguez, and James K. McCusker, *J. Phys. Chem. A* **2002**, *106*, 7399-7406.

6. "Electron Injection Dynamics of Ruthenium and Osmium Polypyridyl Complexes Adsorbed Onto Nanocrystalline $TiO_2$ Photoelectrodes", Darius Kuciauskas, Jeremy E. Monat, Randy Villahermosa, Harry B. Gray, Nathan S. Lewis, and James K. McCusker, *J. Phys. Chem. B* **2002**, *106*, 9347-9358.

7. "Femtosecond Absorption Spectroscopy of Transition Metal Charge-Transfer Complexes", James K. McCusker, *Acc. Chem. Res.*, submitted for publication.

8. "Solvent and Structual Dependence of Primary Relaxation Processes in Arylated Bipyridyl Complexes of Ruthenium(II)", Niels H. Damrauer, Aimee E. Curtright, and James K. McCusker, *J. Phys. Chem. A*, submitted for publication.

9. "(Possibly) The Last Word on the First Events Following Photoexcitation of $[M(bpy)_3]^{2+}$ (M = Ru, Os)", James K. McCusker and John M. Papanikolas, *J. Phys. Chem. A*, manuscript in preparation.

10. "Electronic Structure and Solvation Dynamics in the Excited-State Formation of $[Ru(bpy)_3]^{2+}$: An Ab Initio and Molecular Dynamics Simulation Study", Preston T. Snee and James K. McCusker, *Chem. Phys. Lett.*, manuscript in preparation.

11. "Ultrafast Photophysics and Photochemistry of Transition Metal Compounds in Condensed Phase", James K. McCusker, *Chem. Rev.*, manuscript in preparation.

# *Session V*

# *Charge Transfer Excited States of Transition Metal Complexes*

# PHOTOPHYSICAL BEHAVIOR OF TRANSITION METAL COMPLEXES HAVING MULTIPLE PHOTOACTIVE EXCITED STATES

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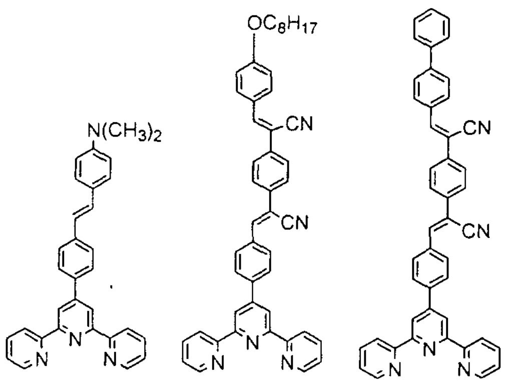
Research on this project over the past year has focused on the synthesis and photophysical examination of transition metal complexes having mixed charge transfer excited states. The introduction of intraligand charge transfer (ILCT) excited states into metal complexes having metal-to-ligand charge transfer (MLCT) states of comparable energy provides another potential route to the development of photoactive chromophores with broad absorption throughout the visible and reasonably long lived excited states. Recent work has focused on three areas: (a) the synthesis of phenylene vinylene ligands likely to have photoactive ILCT states upon metal ion coordination (b) the characterization of ILCT states in Zn(II) complexes lacking MLCT states and (c) the examination of MLCT and ILCT excited state involvement in Ru(II), Os(II) and Pt(II) complexes.

A. Synthesis of terpyridyl phenylene vinylene ligands. Previously we had prepared a variety of ligands having a stilbene or distyrylbenzene core capped at one or both ends (in the para position of the terminal phenyl) with a terpyridyl linked through the central pyridine. The ligands are all strongly fluorescent ($\phi_{em} \sim 0.5 - 1.0$ ; $\tau \sim 1$ ns) and the distyrylbenzene derivatives have Ru(II) analogs that have long excited state lifetimes (10 –15 μs) and emission in the red. Such behavior is unprecedented for bis-terpyridyl Ru(II) derivatives having MLCT absorption and strongly suggests involvement of either a ligand localized or ILCT state. The stilbene derivatives coordinated to Ru(II) exhibit photophysical behavior more typical of unperturbed Ru(II) terpyridyl complexes ( $\tau_{MLCT}$ < 2 ns).

In an effort to broaden this investigation we have prepared related ligands that should have ILCT absorption and emission that differs significantly from the stilbene and distyrylbenzene derivatives investigated. To achieve this derivatives having both electron donating and electron withdrawing substituents were prepared, as shown below. The cyano substituted derivatives are strongly emissive in the solid state as well as solution, whereas the ligands lacking cyano substituents are weakly emissive as solids.



B. ILCT absorption and emission of terpyridyl phenylenevinylene ligands All of the ligands prepared exhibit strong fluorescence when coordinated to Zn(II) and Al(III) in chloroform. The emission is strongly solvatochromic for complexes of all the ligands, while the absorption is altered only very slightly. Such behavior is characteristic of systems having a very small ground state dipole and a large excited state dipole and strongly suggests the emitting excited state is of charge transfer nature. The ILCT absorption of the complexes is observed between 380 and 440 nm while the fluorescence maxima appear between 500 and 620 nm, depending on the extent of unsaturation and substitution of the ligands. In work carried out by Claire Johnson, an undergraduate, the solvent dependence of the fluorescence of a variety of Zn(II) and Al(III) derivatives was treated using a simple dipole in a sphere model that yields a linear relationship between the fluorescence energy and a parameter derived from the static and optical dielectric constants. With this model, and the assumption that the ground state dipole is essentially zero, excited state dipoles of between 20 and 30 D were obtained for all the metal complexes.

C. MLCT and ILCT states of Ru(II), Os(II) and Pt(II) complexes The terpyridyl ligands form bis complexes with Ru(II) and Os(II). The principal feature of the behavior of the Ru(II) complexes is the observation of a long lived (~ 10 μs), weakly emissive excited state with ligands having a distyrylbenzene substituent. The excited state appears to contain components of both MLCT and ILCT excited states.

Our recent work has focused on investigation of Os(II) complexes of with distyrylbenzene derivative ligands. Since the energy of Os to tpy MLCT states is substantially lower in energy than the comparable Ru(II) complexes, it is possible that the MLCT state of the Os(II) terpyridyl phenylenevinylene derivatives would be lower in energy than the ligand localized states as well. By examining the luminescence, excited state lifetime and transient absorption, an assessment of the lowest energy excited state of the Os(II) complexes can be made.

Pt(II) diimine complexes are interesting because of their potential to function as two electron donors in light induced electron transfer processes. We began to investigate systems having Pt(II) coordinated to terpyridyl phenylenevinylene ligands, in part to explore the possibility of using square planar complexes of the type [ClPt(tpy-pvp-tpy)PtCl] as starting materials for preparing coordination polymers by linking the bimetallic complexes together with 4,4'-bipyridine and other related bridging ligands. To begin, we have prepared $[ClPt(L)]^+$ derivatives (L= phenylene vinylene ligand) and examined the solution photophysical behavior. Both complexes are luminescent and emit at lower energies than the parent complex, $[ClPt(mpt)]^+$ ; room temperature emission lifetimes are comparable to that of the parent complex. In addition, both complexes have transient absorption that extends into the red. The transient spectra bear features similar to the Ru(II) and Os(II) complexes and the result may be due to the fact that all the complexes share a common ILCT state. Our plans are to examine the temperature dependence of the luminescence lifetime, luminescence spectra and transient absorption. In addition, the Pt(II) complexes are ideal candidates for luminescence polarization examination to address issues relating to the relative orientation of the excitation and emission dipoles.

## Publications 2001 –2003

*Published, in press or submitted:*

Sujoy Baitalik and Russell H. Schmehl "Photochemistry of Polyoxometalates" submitted to Coordination Chemistry Reviews, April, 2003.

Gerald A. Simon and Russell H. Schmehl "Emission of Coordination Compounds" in "Comprehensive Coordination Chemistry II", volume I, B. Lever, ed., Elsevier : New York, to be published 2003.

Xian-yong Wang, Andre DelGuerzo and Russell H. Schmehl "Preferential Solvation of an ILCT Excited State in Bis-(terpyridine-phenylenevinylene)Zn(II) Complexes", J. Chem. Soc., Chem.Comm., **2002**, 2344-5.

André Del Guerzo, Stéphanie Leroy, Fréderic Fages, Russell H. Schmehl "Photophysics of Re(I) and Ru(II) Diimine Complexes Covalently Linked to Pyrene :Luminescence from Intraligand Charge Transfer Excited States", Inorg. Chem., **2002**,*41*(2), 359-366.

Wen-Sheng Xia, Russell H. Schmehl, Chao-Jun Li, Joel T. Mague, Chu-Ping Luo, and Dirk M. Guldi ; "Chemosensors for Lead(II) and Alkali Metal Ions Based on Self-Assembling Fluorescence Enhancement (SAFE)" The Journal of Physical Chemistry B; **2002**; *106*(4); 833-843.

Ann-Margret Andersson and Russell H. Schmehl "Sensors Based on Electrogenerated Chemiluminescence", in "Optical Sensors and Switches", Ramamurthy, V. and Schanze, K. S. (Eds.); Molecular and Supramolecular Photochemistry, vol. 7; Marcel Dekker: New York, 2001, pp. 153-189.

*Manuscripts in Preparation*:

With Xian-Yong Wang "Synthesis and photophysical characterization of bis-terpyridyl-phenylene vinylene derivatives and their Zn(II) Complexes" to be submitted to the Journal of Organic Chemistry.

With Claire Johnson and Xian-Yong Wang "Solvatochromism of Zn(II) and Al(III) terpyridyl phenylenevinylene complexes", in preparation.

With Andre DelGuerzo and Xian-yong Wang "Synthesis, redox and photophysical behavior of Ru(II) terpyridyl phenylenevinylene complexes", to be submitted to Inorganic Chemistry.

With Seema Wadhwa and Marco Montalti "Intermolecular Exchange Energy Transfer Through an Ionic Bridge in Ru/Os(II) bipyridyl-phosphonate complexes bridged by Zn(II)"

# PLATINUM DIIMINE BIS(ACETYLIDE) COMPLEXES FOR PHOTO-INDUCED CHARGE SEPARATION

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Research has focused on four-coordinate $d^8$ complexes possessing long-lived excited states and their incorporation into multi-component systems that may be utilized in light-to-chemical energy conversion. The specific complexes are of square planar Pt(II) containing an unsaturated diimine ligand and anionic ligands in the form of either a dithiolate chelate or monodentate acetylides to complete the coordination sphere. Connections for these chromphores to donors and acceptors in order to make dyads and triads for photo-induced charge separation has been undertaken with the ultimate goal of linking these dyads and triads to other components for light-driven energy-storing reactions.

An extensive investigation of the photophysical properties of the Pt diimine bis(acetylide) complexes has been conducted in which both diimine and acetylide ligands were varied systematically to assess their influence on excited state energies, lifetimes, emission quantum yields and redox potentials. In solution, the lowest energy absorption band is solvatochromic (*ca.* 400-450 nm with $\lambda_{abs}^{max}$ increasing as solvent polarity decreases) and it exhibits a variation consistent with a Pt-$\pi^*_{diimine}$ metal-to-ligand charge transfer (MLCT). The emission maxima for these bis(acetylide) complexes reveal a parallel variation, indicating that the orbital parentage of the emissive state is the same as the low energy MLCT seen in absorption spectra. Lifetime measurements in solution show a spin forbidden character to the emissive excited state, consistent with a $^3$MLCT assignment. Except for compounds containing nitro substituents, the nonradiative decay rate constants were found to increase exponentially with decreasing excited state energy consistent with the energy gap law.

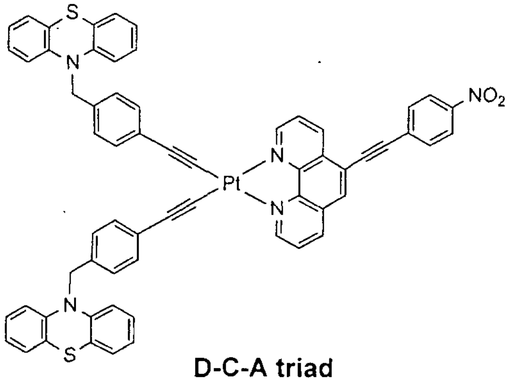
The Pt diimine bis(acetylide) complexes undergo electron transfer quenching of both oxidative and reductive types. As with the corresponding dithiolate systems, the acetylide complexes are photostable in the presence of electron donors but undergo photodecomposition with electron acceptors present. Both results are consistent with the observed electrochemistry of these complexes and the electronic structural model that has developed. For $Pt(dbbpy)(C{\equiv}CPh)_2$, reductive quenching using 10-methylphenothiazine and *N,N,N',N'*-tetramethylbenzidine show Stern-Volmer behavior with essentially diffusion controlled $k_q$'s. From estimates of $E_{00}$ and reversible reduction potentials of the complexes, approximate excited state reduction potentials were calculated to be in the range of 1.0 - 1.3 V vs SCE. The complexes thus appear to be reasonable photo-oxidants.

The incorporation of Pt diimine chromophores into larger structures and assemblies for carrying out light-driven energy-storing reactions relies heavily on the synthesis of functionalized ligands and their attachments to donors and acceptors for photo-induced charge separation, with donors attached to the anionic ligands of the chromophore and acceptors linked to the diimine on which the LUMO resides.

Several donor-chromophore dyads in which a phenothiazine is linked to tolyl acetylide ligands have been synthesized and studied. Solvent effects on charge separation are significant with complete quenching of the chromophore in acetonitrile, but no quenching in toluene. The observations indicate the *relative* stabiliies of the charge separated state and the $^3$MLCT excited state in the two solvents. The energetics of charge recombination for the dyads suggest that it lies firmly in the Marcus inverted region.

The anionic ligand *p*-(formyl)phenylacetylide offers a versatile functionality for coupling to donors and other components. Accordingly, several brightly emissive complexes have been synthesized including the structurally characterized derivatives Pt(4,7-$R_2$phen)(C≡C-*p*-$C_6H_4CHO)_2$ (R = H, Ph). Excited state lifetimes range from 100 to 800 ns depending on the diimine. The dpphen derivative has been elaborated into a number of dyads using Schiff base condensations and reductive aminations. In all cases, quenching is essentially quantitative but the imine linkage is found to be photochemically unstable. Other coupling reactions are currently being examined.

For connection of acceptors to the diimine side of the Pt chromophores, 5-Brphen was found to work in Sonogashira-Hagihara coupling reactions with different alkynes. In this way, phen-5-C≡C-*p*-$C_6H_4NO_2$ has been synthesized in several steps from *p*-iodonitrobenzene. With these elements of ligand synthesis and functionalization in place, the first donor-chromophore-acceptor (D-C-A) triad based on Pt diimine complexes has been synthesized and its spectroscopic properties studied along with those of the chromophore alone and model D-C and C-A dyads. For both the triad and the D-C dyad, emission is completely quenched in fluid solution, while only very weak emission is seen for the C-A dyad under similar conditions. The transient absorption spectrum of the triad reveals a charge separated species having a 70 ns lifetime, a $PTZ^+$ signal at *ca.* 525 nm and a bleach at around 360 nm corresponding to the neutral nitrophenyl moiety. From electrochemical results, one can estimate that the triad transiently stores about 1.7 volts. It appears necessary to further separate charge and increase the lifetime of the charge-separated state in order to carry out the goal of energy-storing chemistry with such a system.



**D-C-A triad**

On a different front, interest in electron transfer in DNA has stimulated extensive research in many laboratories around the world, with experimental studies leading to values of the distance dependence parameter β ranging from 0.2 $Å^{-1}$ for almost wire-like behavior to 1.4 $Å^{-1}$ for electron transfer equivalent to that through proteins. Theoretical models have described competing superexchange and hopping mechanisms to explain the large range of β's determined experimentally. In all of these studies, the electron transfer is initiated by oxidation of a DNA base (guanine), and the problem is one of hole transport or conduction by radical cation bases.

In view of the fact that square planar Pt(II) complexes are known to bind DNA intercalatively, we considered examining these systems for initiating electron transfer by electron, as opposed to hole, injection into the DNA base stack. In order to assess the feasibility of using Pt diimine complexes for this unique role, a series of quenching experiments was performed using Pt(phen)(C≡C-*p*-$C_6H_4CHO)_2$, that serves as a precursor to a cationic, aqueous soluble Pt diimine bis(acetylide) complex, and the 4-TBDMS protected DNA nucleosides (A, T, C, G) as quenchers. It was found that all bases except T serve to quench the Pt(diimine) excited state, exhibiting good Stern-Volmer behavior with the fastest $k_q$'s corresponding to the most easily oxidized bases G and A ($k_q = \sim 10^8$). The rate of quenching with C is approximately an order of magnitude slower than with G or A ($k_q = \sim 10^7$) and two orders of magnitude slower than with good reductive quenchers like phenothiazine ($k_q = \sim 10^{10}$). Quenching by T is not observed even at high quencher concentrations. Since C and T are the *most easily reduced bases* and they are the least effective quenchers, our results strongly suggest that Pt(diimine)(arylacetylide)$_2$ complexes will *not* be able to serve as photo-reductants for the study of charge transfer through DNA via base radical anions.

## DOE-SUPPORTED PUBLICATIONS (2000-2003)

Platinum Diimine Complexes: Towards a Molecular Photochemical Device, Hissler, M.; McGarrah, J. E.; Connick, W. B.; Geiger, D. K.; Cummings, S. D.; Eisenberg, R. *Coord. Chem. Rev.* **2000**, 115-137.

Platinum Diimine Bis(acetylide) Complexes: Synthesis, Characterization and Luminescence Properties, Hissler, M.; Connick, W. B.; Geiger, D. K.; McGarrah, J. E.; Lipa, D.; Lachicotte, R. J.; Eisenberg, R. *Inorg. Chem.* **2000**, *39*, 447-457.

The Synthesis and Structural Characterization of Luminescent Platinum(II) Complexes Containing Di-t-butylbipyridine and New 1,1-Dithiolate Ligands, Huertas, S.; Hissler, M.; McGarrah, J. E.; Lachicotte, R. J.; Eisenberg, R. *Inorg. Chem.* **2001**, *40*, 1183-1188.

Toward a Molecular Photochemical Device: A Triad for Photoinduced Charge Separation Based on a Platinum Diimine Bis(acetylide) Chromophore, McGarrah, J. E.; Kim, Y.-J.; Hissler, M.; Eisenberg, R. *Inorg. Chem.* **2001**, *40*, 4510-4511.

Luminescence and Photochemistry of Metal Dithiolene Complexes, Cummings S. D.; Eisenberg, R. *Prog. Inorg. Chem.* **2003**, accepted for publication.

Photo-induced Charge Separation in Dyads Based on a Platinum Diimine Bis(acetylide) Complexes. Solvent Dependent Properties, McGarrah, J. E.; Hissler, M.; Eisenberg, R. *Inorg. Chem.* **2003**, accepted for publication.

New Platinum Diimine Bis(arylacetylide) Complexes Containing Easily Derivatizable Ligands, Wadas, T. J.; Eisenberg, R. *Inorg. Chem.* **2003**, accepted for publication.

Synthesis, Characterization and Photophysical Properties of Platinum Diimine Bis(arylacetylide) Donor-Chromophore Dyads, Wadas, T. J.; Chakraborty, S.; Kloek, S. M.; Eisenberg, R. Manuscript in preparation.

Dyads and Triads for Photo-Induced Charge Separation Based on the Platinum Terpyridyl Arylacetylide Chromophore, Wadas, T. J.; Eisenberg, R. Manuscript in preparation.

# EXCITED STATE MOLECULAR STRUCTURES CAPTURED BY PULSED X-RAYS

Lin X. Chen[a], George B. Shaw[a], Tao Liu[a], Guy Jennings[b], Klaus Attenkofer[b], Donald V. Scaltrito, Gerald J. Meyer[c], Irina Novozhilova[d], Philip Coppens[d]

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The development of ultrafast laser spectroscopy has revealed the fundamental aspects of excited state dynamics, coherence, and energetics, but the excited structures have been elusive until recently, largely due to the lack of pulsed X-rays for capturing the transient molecular structures. Such a deficiency hinders complete understanding of ultrafast processes in photochemistry. Recent development of ultrafast X-ray technology allows transient excited state structures to be captured for the first time in disordered media, which brings new insight into photochemistry, especially the structural origins of the excited state properties.

The excited states of metalloporphyrins and metal polypyridine complexes are important ingredients in artificial photosynthesis, solar cells, and molecular devices. We have been conducting a series of studies on the excited state structures of these molecules in solution with newly developed laser pulse pump, X-ray pulse probe X-ray absorption spectroscopy using X-ray pulses of 100-ps fwhm from one of the third generation synchrotron sources, the Advanced Photon Source at Argonne. Using unprecedented X-ray photon flux within each X-ray pulse, the excited state with a lifetime as short as 450 ps has been captured. In this presentation, we will focus on our recent work of probing the MLCT excited state structures of copper(I) diimine complexes in different solutions (Fig. 1). The photoexcitation of a cuprous diimine compound, such as $Cu^I(dmp)_2^+$, where dmp is 2,9-dimethyl-1,10-phenanthroline can be described as, $Cu^I(dmp)_2^+ + h\nu \rightarrow Cu^{II}(dmp^-)(dmp)^{+*}$. The $Cu^I$ ground state has a $d^{10}$ electronic configuration with pseudo-tetrahedral geometry. Absorption of a visible photon promotes an electron from copper to a dmp ligand, formally generating a MLCT excited state with a $Cu^{II*}$ center coordinated to one reduced and one neutral dmp ligand. The $Cu^{II*}$ center in the excited state has $d^9$

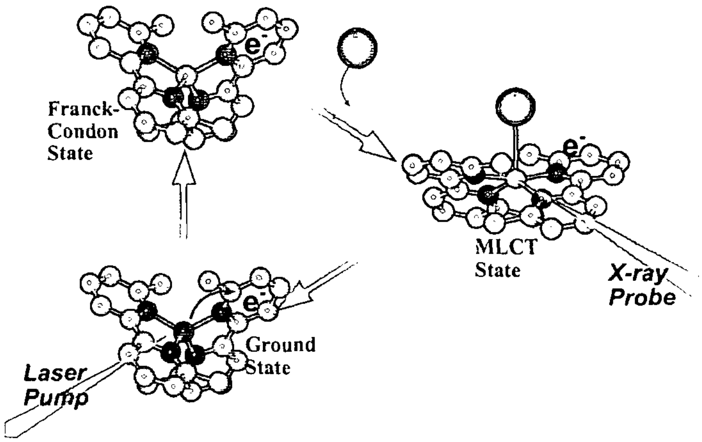

Fig. 1 The outline of the photoexcitation process for $Cu^I(dmp)_2^+$ in solution. X-ray pulses were used to probe the thermally equilibrated MLCT state structure.

electron configuration and is subject to a Jahn-Teller distortion. The observations of large "Stokes-like" shifts between the absorption and photoluminescence and 'exciplex' quenching represent strong evidence that the excited state adopts a more $Cu^{II}$ like geometry.

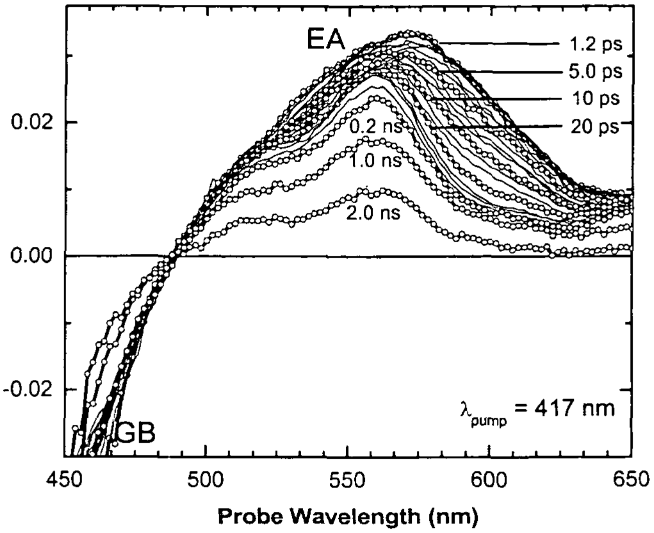

Fig. 2 Transient optical absorption spectra of $Cu^I(dmp)_2^+$ in acetonitrile

The molecular structure and dynamics of the photoexcited MLCT state of $[Cu^I(dmp)_2]^+$ in toluene and in acetonitrile have been investigated by time-domain pump-probe X-ray absorption spectroscopy, femtosecond optical transient spectroscopy, and by density functional theory (DFT). The copper ion in the thermally equilibrated MLCT state has the same oxidation state as the corresponding copper(II) complex in the ground state and was found to be penta-coordinated with an average nearest neighbor Cu-N distance 0.04 Å shorter in acetonitrile, but 0.04 Å longer in toluene than that of the ground state $Cu^I(dmp)_2^+$. The evolution from the photoexcited Franck-Condon MLCT state to the thermally equilibrated MLCT state was followed by fs transient spectroscopy, revealing two time constants of 500-700 fs and 10-20 ps that are similar in both solvents and related respectively to the formation of the triplet MLCT state and the structural relaxation in the thermally equilibrated MLCT state. The third time constant corresponding to the MLCT state decay back to the ground state is 1.6-1.7 ns in acetonitrile and 100 ns in toluene.

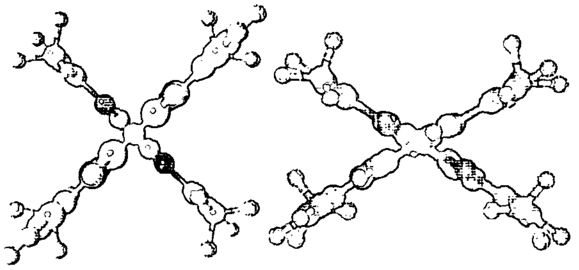

Fig. 3. The calculated ground and triplet excited state structure of $Cu^I(dmp)_2^+$.

The variation of the MLCT state structures in different solvents confirmed that the origin of distinctly different excited state behavior is due to formation of MLCT state-solvent complexes with different electronic interactions. When the interaction is strong, the MLCT state lifetime is shortened significantly and the luminescence is quenched, which has been characterized by the "exciplex" formation in previous literature. Therefore, the pump-probe XAFS measurements in the time domain provide new insights into the fundamental aspects in the structural factors that may influence photoinduced electron and energy transfer processes. Further studies on the ultrafast dynamics of the $[Cu^I(dmp)_2]^+$ MLCT state in different media are in progress.

Future direction includes investigating different excited state structures using the same technique, expanding the pump-probe approach into other structural techniques, and exploring ultrafast X-rays studies using other facilities.

**PUBLICATIONS** (2001- present):

Effects of Chemical Modifications on Photophysics and Exciton Dynamics of $\pi$-Conjugation Attenuated and Metal-Chelated Photoconducting Polymers
Lin X. Chen, Wighard J. H. Jäger, David J. Gosztola, Mark P. Niemczyk, Michael R. Wasielewski, *Synthetic Metals*, **116**, 229-234 (2001).

Capturing a Photoexcited Molecular Structure Through Time-Domain X-ray Absorption Fine Structure
Lin X. Chen, Wighard J. H. Jäger, Guy Jennings, David J. Gosztola, Anneli Munkholm, Jan P. Hessler, *Science*, **292**, 262-264 (2001).

Probing Transient Molecular Structures with Time-resolved Pump/probe XAFS Using Synchrotron X-ray Sources
Lin X. Chen, *J. Electronic Spectroscopy*, **119**, 161-174 (2001).

Taking Snapshots of Molecular Structures in Fast Photo-driven Processes Using Pump-probe XAFS
Lin X. Chen, Wighard J. H. Jäger, Guy Jennings, David J. Gosztola, Tao Liu, Anneli Munkholm, Jan P. Hessler, APS Forefront 1 (ANL/APS/TB-42), pp. 67-70, Argonne National Laboratory (2001).

Application of Multielement Ge Detector in Laser Pump/X-ray Probe XAFS
Guy Jennings, Wighard J. H. Jäger, Lin X. Chen, *Rev. Sci. Instrum.* **73**, 362-368 (2002).

Rapid Excited-State Structural Reorganization Captured by Pulsed X-rays
Lin X. Chen, Guy Jennings, Tao Liu, David J. Gozstola, Jan P. Hessler, Donald V. Scaltrito, Gerald. J. Meyer, *J. Am. Chem. Soc.* **124**, 10861-10867 (2002).

$Fe_2O_3$ Nanoparticle Structures Investigated by X-ray Absorption Near Edge Structure, Surface Modifications, and Model Calculations
Lin X. Chen, Tao Liu, Marion C. Thurnauer, Roseann Csencsits, Tijana Rajh, *J. Phys. Chem. B.* **106**, 8539-8546 (2002).

Identification of Highly Active Iron Sites in $N_2O$-Activated Fe/MFI
Jifei Jia, Qi Sun, Bin Wen, Lin X. Chen, and Wolfgang M.H. Sachtler, *Catalysis Letters* (2002) **82**,7-11.

Surface Restructuring of Nanoparticles: an Effective Route for Ligand -Metal Oxide Crosstalk
Tijana Rajh, Lin X. Chen, Katie Lukas, Tao Liu, Marion C. Thurnauer, David M. Tiede *J. Phys. Chem. B* **106** 10543-10552 (2002).

Excited State Molecular Structure Determination in Disordered Media Using Laser Pump/X-ray Probe Time-domain X-ray Absorption Spectroscopy
Lin X. Chen, *Faraday Discussion,* **122**, 315-329 (2002).

Synergism of Cobalt and Palladium in MFI Zeolite of Relevance to NO Reduction with Methane
Bin Wen, Wolfgang M. H. Sachtler, Jifei Jia, Shuyou Li, Tao Liu, Lin X. Chen, *Phys. Chem. Chem. Phys.* **4**, 1983-1989 (2002).

The MLCT State Structure and Dynamics of a Cu(I) Diimine Complex Characterized by Pump-probe X-ray and Laser Spectroscopies and DFT Calculations
Lin X. Chen, George B. Shaw, Irina Novozhilova, Tao Liu, Guy Jennings, Klaus Attenkofer, Gerald J. Meyer, Philip Coppens. *J. Am. Chem. Soc.,* in press.

Taking Snapshots of Photoexcited Molecular Structures in Disordered Media Using Pulsed X-rays
Lin X. Chen
*Angew. Chemie Intl. Ed.*, (Review) in press.

Structural Changes in Light-induced Electron Transfer from $Q_A$ to $Q_B$ in Photosynthetic Reaction Center Proteins Probed by X-ray Absorption Fine Structure
Lin X. Chen, Lisa M. Utschig, Sandra L. Schesselman, David M. Tiede, *submitted.*

# THEORY OF ELECTRON TRANSFER IN COMPLEX SYSTEMS

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The effects of a molecular environment on electron transfer are determined by the nature of polarization fluctuations in that environment – the distributions of sizes and relaxation times for these fluctuations. When the environment is part of a well-equilibrated homogeneous liquid, these distributions are well described by dielectric continuum theory and related models. There are still interesting questions to answer about such materials, e.g., [1], but by and large, the level of understanding is advanced. On the other hand, the understanding is far less developed when considering highly heterogeneous systems, disordered or slowly relaxing, systems like glasses, proteins, nano particles or assemblies of nano particles. Approaching these less well understood systems, my prior presentation to this group focused on the issue of statistically characterized frozen disorder. I described our then soon to be completed theory of dielectric response within this picture [2,3]. In the intervening three years, my group's attention has turned towards the cause or origin of "frozen" disorder or heterogeneity, and the mechanism by which such structure ultimately changes or ages. This presentation outlines what we have recently learned about these issues, what techniques were applied in making these advances, and where these techniques may be of use in future scientific work.

In systems exhibiting long-lived disorder or heterogeneity, excitations that can lead to aging or reorganization are spatially localized and sparse. Were they not sparse, the system would have access to rapid pathways for relaxation, leading quickly to a homogeneous state. The actual slow relaxation is the result of correlated motion of excitations. In space-time, this motion can be viewed in terms of the geometry of directed polymers. These polymers are excitation lines. Their statistics are governed, as I will describe, by interactions that lead to something akin to an order-disorder transition in space-time. In the context of glass forming super cooled liquids, fluctuations in excitation lines coincide with the phenomenon known as "dynamical heterogeneity," and the order-disorder transition coincides with the onset of glassy behavior. But the nature of dynamics with local sparse excitations is much more general than this one example. As I will discuss, it also pertains to signal transduction in materials that carry out multiple tasks. These include biological cells, and may in the future include synthetic nano clusters.

Excitation lines depict trajectories. To learn about their behavior, we have found it necessary to develop a perspective of molecular systems in which one considers trajectory space rather than state space. That is to say, we have created a statistical mechanics and thermodynamics of trajectories. Here, a time correlation function is a ratio of partition functions of ensembles of trajectories, and the logarithm of a correlation function is the reversible work to change an ensemble of trajectories. With this perspective, one may exploit all the efficient sampling schemes already developed for analyzing the statistics of state space, but now applied to trajectory space. This observation leads to our transition path sampling method [4]. It is a method that we have used in many studies, including investigations of the dynamics of driven systems [5], the isomerization of clusters [6], and the auto ionization of water [7]. It has led us to new paradigms for interpreting dynamics [8]. Soon, we expect to have extensions of this methodology that can treat phase transitions of nano clusters under strain.

Publications

1.Merrolle, M. and D. Chandler, "Statistics of dipole density fluctuations in water," manuscript in preparation (2003).

2. Song, X. and D. Chandler, "Dielectric response of a polarizable system with quenched disorder," Phys. Rev. E **62**, 7949 (2000).

3. Yu, Z.G., X. Song and D, Chandler, "Polarizability in dielectric Materials with quenched disorder," Phys. Rev. E **62**, 4698 (2000).

4. Bolhuis, P. G., D. Chandler, C. Dellago, and P. Geissler, "Transition Path Sampling: Throwing ropes over mountain passes, in the dark," Ann. Rev. of Phys. Chem. **59**, 291 (2002).

5. Crooks, G.E. and D. Chandler, "Efficient transition path sampling for nonequilibrium stochastic dynamics," Phys. Rev. E **64**, 026109 (2001).

6. Laria, D., J. Rodriguez, C. Dellago and D. Chandler, "Dynamical aspects of isomerization and melting transition in $[H_2O]_8$," J. Phys. Chem.**105**, 2646 (2001).

7. Geissler, P.L., C. Dellago, D. Chandler, J. Hutter and M. Parrinello, "Auto ionization in liquid water," Science **291**, 2121 (2001).

8. McCormick, T. and D. Chandler, "Grid-Flux Method for Learning the Solvent Contribution to the Mechanisms of Reactions", J. Phys. Chem. B **107**, 2796 (2003).

# *Session VI*

# *Light-Driven Intramolecular Electron and Energy Transfer*

# DIRECT MEASUREMENT OF ELECTRONIC COUPLING FOR CHARGE RECOMBINATION WITHIN ROD-LIKE PHOTOGENERATED RADICAL ION PAIRS

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Determining the electronic coupling matrix element, $V_{DA}$, for an electron transfer reaction is challenging both experimentally and theoretically. The spin-spin exchange interaction in a radical ion pair, *2J*, is directly proportional to $V_{DA}^2$ so that a direct measurement of *2J* can be used to obtain the coupling. We will present magnetic field effect and time-resolved EPR results on a series of intramolecular triads with linear, rod-like structures that undergo quantitative two-step electron transfer following direct excitation of a 4-(*N*-piperidinyl)naphthalene-1,8-dicarboximide (6ANI) chromophore. Four examples from this series are shown in Chart 1 below. Attachment of a *p*-methoxyaniline (MeOAn) donor by means of the piperazine bridge and naphthalene-1,8:4,5-bis(dicarboximide) (NI) or pyromellitimide (PI) acceptors directly to 6ANI results in the triads MeOAn-6ANI-NI and MeOAn-6ANI-PI, while insertion of a dimethylphenyl bridge results in MeOAn-6ANI-$Me_2$Ph-NI and MeOAn-6ANI-$Me_2$Ph-PI. Two-step charge separation from the lowest excited singlet state of 6ANI yields singlet radical ion pairs in which the charges are separated by 14 to 19 Å, and whose lifetimes range from about 15 to 200 ns. These lifetimes are long enough so that radical pair intersystem crossing occurs to form the triplet radical ion pair, which then recombines to form a neutral excited triplet state, which is localized either on 6ANI or NI. The yield of this locally excited triplet state, monitored by nanosecond transient absorption as a function of applied magnetic field strength, exhibits distinct resonances that directly yield *2J*, Figure 1. These measurements provide a highly sensitive method for determining the dependence of the electronic coupling for charge recombination on the structure of the radical ion pair, which is essential for optimizing systems for photochemical conversion and storage of solar energy.

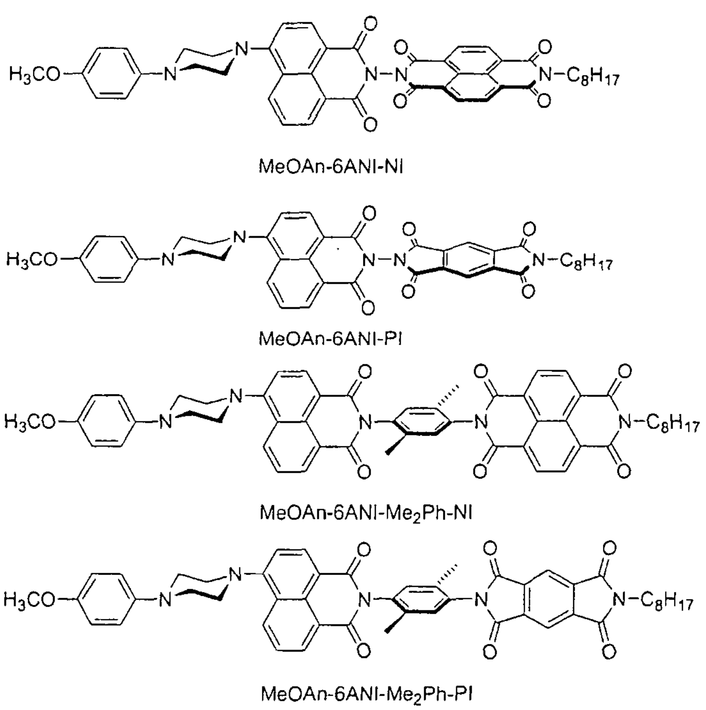

**Chart 1.** Structures of donor-acceptor molecules.

Over the past several years we have prepared and characterized a wide variety of aryleneimide and arylenediimide electron donors and acceptors that are robust and have excellent photophysical and electrochemical properties tuned for specific use in structures designed for the photoconversion and storage of solar energy. In our future research we will

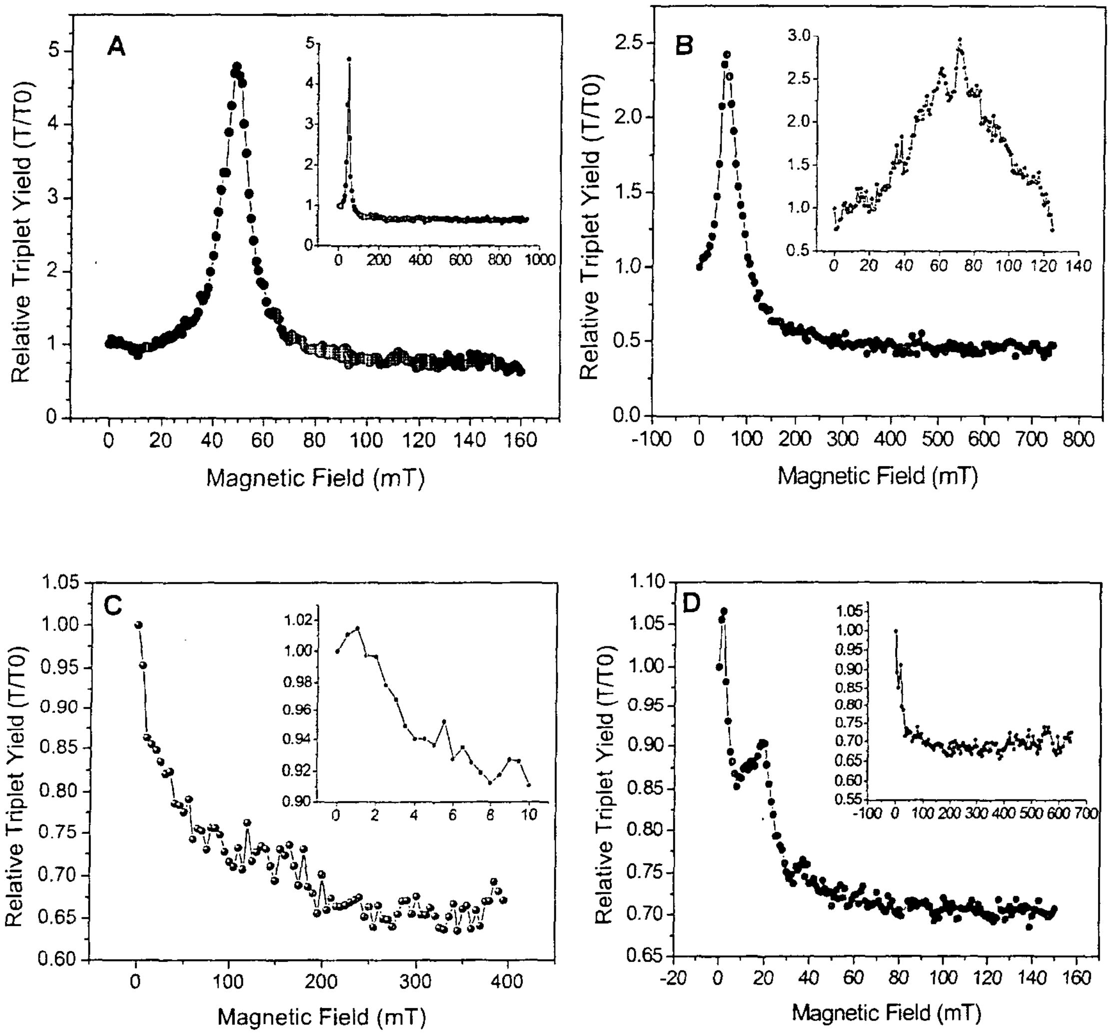

**Figure 1.** Triplet yields as a function of magnetic field for A) MeOAn-6ANI-NI; B) MeOAn-6ANI-PI; C) MeOAn-6ANI-$Me_2$Ph-NI; D) MeOAn-6ANI-$Me_2$Ph-PI. The insets provide expanded or contracted views of the data.

exploit this library to prepare new molecular assemblies that will be used to develop the fundamental understanding of photochemical charge separation and transport essential for constructing molecule-based solar cells. We will synthesize and study new wire-like molecular structures designed to transport charge over long distances. We will use spin dynamics in photogenerated radical ion pairs to map how the molecular structure of a donor-acceptor molecule determines the electronic coupling matrix element for charge recombination, and as a consequence, the lifetime of charge separation. We will explore how media-assisted charge separation in liquid crystals and symmetry breaking in novel chromophoric dimers and oligomers can be used to understand the influence of the surrounding environment on charge separation. We will also develop self-assembly strategies for preparing solid-state systems based on new donor-acceptor molecules. Time-resolved optical and magnetic resonance techniques will be used to characterize charge transport in these systems.

**DOE Chemical Sciences Publications 2001-2003**

Electrochemical and Photophysical Properties of Phenothiazine/Pyrene-Based Dyads, J. Daub, R. Engl, J. Kurzawa, S. E. Miller, S. Schneider, A. Stockmann, and M. R. Wasielewski, *J. Phys. Chem. A*, **105**, 5655-5665 (2001).

Conformational Gating of Long Distance Electron Transfer through Wire-like Bridges in Donor-Bridge-Acceptor Molecules, W. B. Davis, M. A. Ratner, M. R. Wasielewski, *J. Am. Chem. Soc.*, **123**, 7877-7886 (2001).

Photophysics of π-Conjugated Metal-Organic Oligomers. Phenylene-ethylenes that Contain the (bpy)Re(CO)$_3$Cl Chromophore, K. A. Walters, K. D. Ley, C. S. P. Cavalaheiro, S. E. Miller, D. Gosztola, M. R. Wasielewski, A. P. Bussandri, H. van Willigan, and K. S. Schanze, *J. Am. Chem Soc.* **123**, 8329-8342 (2001).

Ultrafast Electron Transfer Reactions Initiated by Excited CT States of Push-Pull Perylenes, S. E. Miller, R. Schaller, V. Mulloni, Y. Zhao, E. M. Just, R. C. Johnson, and M. R. Wasielewski, *Chem. Phys.*, **275**, 167-183 (2002).

High Time Resolution Q-Band EPR Study of a Sequential Electron Transfer in a Triad Oriented in a Liquid Crystal. U. Heinen, T. Berthold, G. Kothe, E. Stavitski, T. Galili, H. Levanon, G. Wiederrecht, and M. R. Wasielewski, *J. Phys. Chem. A*, **106**, 1933-1937 (2002).

Electron Transfer Involving Non-Bonded Superexchange Interactions in Rigid Donor-Acceptor Arrays, A. S. Lukas, P. J. Bushard, and M. R. Wasielewski, *J. Phys. Chem. A*, **106**, 2074-2082 (2002).

Biomimetic Electron Transfer using Low Energy Excited States: A Green Perylene-Based Analog of Chlorophyll *a* A. S. Lukas, Y. Zhao, S. E. Miller, and M. R. Wasielewski *J. Phys. Chem.B*, **106**, 1299-1306 (2002).

Functional Asymmetry of Photosystem II D1 and D2 Peripheral Chlorophyll Mutants of *Chlamydomonas reinhardtii,* J. Wang, D. Gosztola, S. V. Ruffle, C. Hemann, M. Seibert, M. R. Wasielewski, R. Hille, T. L. Gustafson, R. T. Sayre, *Proc. Natl. Acad. Sci. USA* **99**, 4091-4096 (2002).

Charge Transport in Photofunctional Nanoparticles Self-Assembled from Zinc 5,10,15,20-Tetrakis(perylenediimide)porphyrin Building Blocks, T. van der Boom, R. T. Hayes, Y. Zhao, P. J. Bushard, E. A. Weiss, and M. R. Wasielewski, *J. Am. Chem. Soc.* **124**, 9582-9590 (2002).

Dynamics and Energetics of Hole Trapping in DNA by 7-Deazaguanine, F. D. Lewis, J. Liu, X. Zuo, R. T. Hayes, and M. R. Wasielewski, *Angew Chemie Int. Ed. Engl.* **41**, 1026-1028 (2002).

Dynamics and Inter- and Intra-Strand Hole Transport in DNA Hairpins, F. D. Lewis, J. Liu, X. Zuo, R. T. Hayes, and M. R. Wasielewski, *J. Am. Chem. Soc.* **124**, 4568-4569 (2002).

Excited State Symmetry Breaking in Cofacial and Linear Dimers of a Green Perylenediimide Chlorophyll Analog Leading to Ultrafast Charge Separation, J. M. Giaimo, A. V. Gusev, and M. R. Wasielewski, *J. Am. Chem. Soc.* **124**, 8530-8531 (2002).

A Perspective on Four New Porphyrin-Based Functional Materials and Devices, C. M. Drain, J. T. Hupp, K. S. Suslick, M. R. Wasielewski, and X. Chen, *J. Porphyrins and Phthalocyanines*, **6**, 243-258 (2002).

Dependence of Electron Transfer Dynamics in Wire-like Bridge Molecules on Donor-Bridge Energetics and Electronic Interactions, W. B. Davis, M. A. Ratner, and M. R. Wasielewski, *Chem. Phys.*, **281**, 333-346 (2002).

Dynamics of Electron Injection in DNA Hairpins, F. D. Lewis, X. Liu, S. E. Miller, R. T. Hayes, and M. R. Wasielewski, *J. Am. Chem. Soc.* **124**, 11280-11281 (2002).

DNA-mediated Electron Transfer Across Synthetic T:A*T Triplex Structures, F. D. Lewis, Y. Wu, R. T. Hayes, and M. R. Wasielewski, *Angew. Chem.Int. Ed. Engl.* **41**, 3485-3487 (2002).

Formation and Decay of Localized Contact Radical Ion Pairs in DNA Hairpins, F. D. Lewis, X. Liu, S. E. Miller, R. T. Hayes, and M. R. Wasielewski, *J. Am. Chem. Soc.* **124**, 14020-14026 (2002).

Effects of Solvent and Structural Dynamics on Electron Transfer Reactions of 4-Aminonaphthalene-1,8-dicarboximide Donor-Acceptor Molecules in Nematic Liquid Crystals and Isotropic Solvents, L. E. Sinks and M. R. Wasielewski, *J. Phys. Chem A.* **107**, 611-620 (2003).

Mapping the Influence of Molecular Structure on Rates of Electron Transfer Using Direct Measurements of the Electron Spin-Spin-Exchange Interaction, A. S. Lukas, P. J. Bushard, and M. R. Wasielewski, *J. Am. Chem. Soc.* **125**, 3921-3930 (2003).

Dynamics and Energetics of Single Step Hole Transport in DNA, F. D. Lewis, J. Liu, X, Zuo, R. T. Hayes, and M. R. Wasielewski, *J. Am. Chem. Soc.* **125**, 4850-4861 (2003).

Direct Measurement of Electronic Coupling for Charge Recombination within Rod-like Photogenerated Radical Ion Pairs Using Magnetic Field Effects, E. A. Weiss, M. A. Ratner, and M. R. Wasielewski, *J. Phys. Chem. A.* (2003) in press.

The Isolated Photosystem II Reaction Center: First Attempts to Directly Measure the Kinetics of Primary Charge Separation, M. Seibert and M. R. Wasielewski, *Photosynthesis Research*, (2003) in press.

Dynamics and Equilibrium for Single Step Hole Transport Processes in Duplex DNA, F. D. Lewis and M. R. Wasielewski, *Topics in Current Chemistry* (2003) in press.

Using Spin Dynamics of Covalently Linked Radical Ion Pairs to Probe the Impact of Structural and Energetic Changes on Charge Recombination, S. Shaakov, T. Galili, E. Stavitski, H. Levanon, A. S. Lukas, and M. R. Wasielewski, *J. Am. Chem. Soc.* (2003) in press.

# PHOTOINDUCED ELECTRON TRANSFER IN NEW DONOR-SPACER-ACCEPTOR STRUCTURAL MOTIFS

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This program seeks to understand how medium electronic and topological features can be used to control photoinduced electron transfer (ET) reactions and how such processes can ultimately be utilized to define new photoconversion schemes. Recent work has focused on the development of new donor-spacer-acceptor (D-Sp-A) complexes designed to probe specific issues relevant to bridge-mediated electronic coupling, and the elaboration of new porphyrin-based synthons for the fabrication of supramolecular ET assemblies. Examples of projects carried out over the past two years include:

*Synthesis, Electronic Structure, and Electron Transfer Dynamics of (Aryl)ethynyl-Bridged Donor-Acceptor Systems.* The ET dynamics of a series of donor-spacer-acceptor (D-Sp-A) systems featuring (porphinato)zinc(II), (aryl)ethynyl bridge, and arene diimide units were investigated by pump-probe transient-absorption spectroscopy. Analysis of these data within the context of the Marcus-Levich-Jortner equation suggests that the π-conjugated (aryl)ethynyl bridge plays an active role in the charge recombination (CR) reactions of these species by augmenting the extent of (porphinato)zinc(II) cation radical electronic delocalization; this increase in cation radical size decreases the reorganization energy associated with the CR reaction, and thereby attenuates the extent to which the magnitudes of the CR rate constants are solvent dependent. The symmetries of porphyrin-localized HOMO and HOMO-1, the energy gap between these two orbitals, and D-A distance appear to play key roles in determining whether the (aryl)ethynyl bridge simply mediates electronic superexchange, or functions as an integral component of the D and A units.

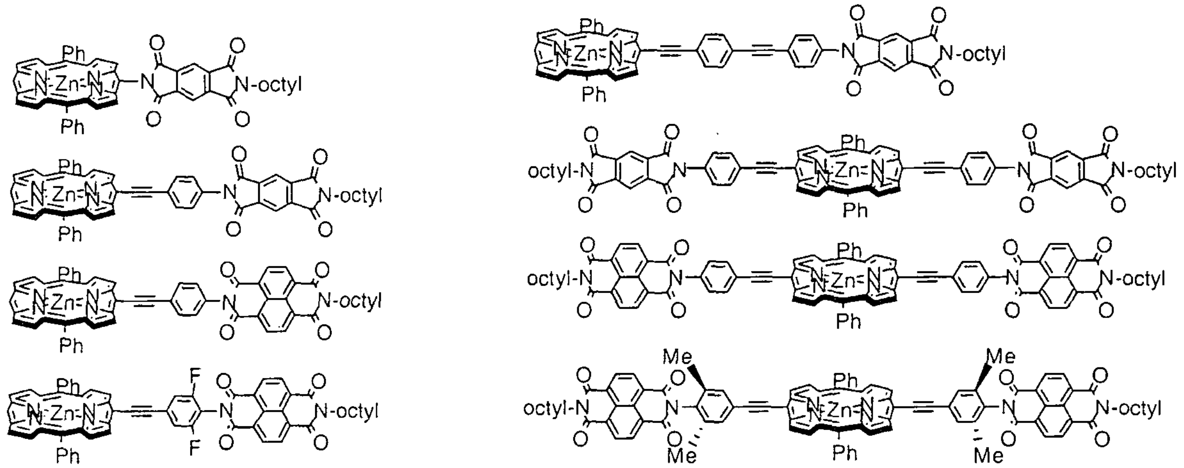
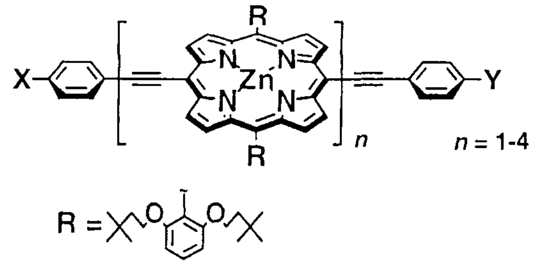


Figure 1. A family of rigid D-Sp-A structures designed to probe the extent to which the cyllindrically π-symmetric ethyne impacts electronic delocalization and D-A coupling within the electronically excited and charge-separated states.

*Distance Dependence of Electron Transfer in Rigid, Cofacially Compressed, π-Stacked Porphyrin-Bridge-Quinone Compounds.* The electron transfer (ET) dynamics of a series unusually rigid π-stacked porphyrin-quinone (P-Q) systems, in which sub van der Waals interplanar distances separate juxtaposed porphyryl, aromatic bridge, and quinonyl components of these assemblies, have been examined. These studies constitute the first ET experiments in π-stacked D-Sp-A systems in which sub van der Waals interplanar distances (closest atom-atom contacts = 2.97 Å) separate juxtaposed D, Sp, and A moieties. Pump-probe experiments carried out in methylene chloride solvent show that the phenomenological distance dependence of the photoinduced charge separation and thermal charge recombination reactions in the species over D-A distances ranging between 3.3 and 10.5 Å (porphyrin plane-to-quinonyl centroid) is soft ($\beta_{CS}$ = 0.43 Å$^{-1}$; $\beta_{CR}$ = 0.35 ± 0.16 Å$^{-1}$), and demonstrates that simple aromatic building blocks like benzene, which are characterized by highly stabilized filled molecular orbitals and large HOMO-LUMO gaps, can provide substantial D-A electronic coupling when organized within a π-stacked structural motif that features a modest degree of arene-arene interplanar compression. Solvent-dependent ET data coupled with variable temperature experiments suggest that photoinduced CS and thermal CR in these species are mechanistically distinct.

*Impact of Electronic Asymmetry on Triplet State Photoexcitations in Conjugated Porphyrin Oligomers.* Utilizing multi-pigment species that feature unusual degrees of chromophore-chromophore conjugation in photoinduced energy conversion schemes require intimate knowledge of the nature of their respective low-lying electronically excited singlet and triplet states. Towards this end, we have characterized the photophysics of triplet excitons in a series of electronically asymmetric "push-pull" π-conjugated *meso*-ethyne-linked porphyrinic oligomers along with their corresponding electronically symmetric analogs, using X-band EPR spectroscopy under continuous-wave (CW) optical pumping conditions in the 4-100 K temperature range. The spatial extent of the triplet wavefunction, as inferred from the |D| zero-field splitting parameter (ZFS), is clearly demonstrated to be confined to not more than one monomeric unit; |D| values for the series for n = 1-4 (n = number of porphyrinic units) are 0.0301, 0.0303, 0.0300, and 0.0301 cm$^{-1}$, respectively, indicating a triplet excitation with an associated spatial extent of approximately 0.35 nm. These dat are in stark contrast to the evolution of the $S_1 \leftarrow S_0$ energy gap where for this series, which signals a scaling of singlet exciton delocalization with conjugation length. Experimentally determined electron spin-lattice relaxation times corroborate this picture, evincing that these conjugated oligomers manifest an S = 1 spin system that is spatially confined to a single porphyrin monomeric unit.



| Compound | n | X | Y |
|---|---|---|---|
| 1 | 1 | $NMe_2$ | $NO_2$ |
| 2 | 2 | $NMe_2$ | $NO_2$ |
| 3 | 3 | $NMe_2$ | $NO_2$ |
| 4 | 4 | $NMe_2$ | $NO_2$ |
| 5 | 1 | $NMe_2$ | $NMe_2$ |
| 6 | 1 | $NO_2$ | $NO_2$ |
| 7 | 3 | $NMe_2$ | $NMe_2$ |

Figure 2. Conjugated, D--A derivatized porphyrin oligomers studied via pump-probe and photoexcited - triplet EPR spectroscopic methods.

## DOE-Supported Publications (2001-2003)

(1) Trends in Triplet Excitation Delocalization in Highly Conjugated (Porphinato)zinc(II) Arrays Probed by EPR Spectroscopy, P. J. Angiolillo, K. Susumu, H. T. Uyeda, V.S.-Y. Lin, R. Shediac, and M. J. Therien, *Synthetic Metals* **2001**, *116*, 247-253.

(2) High Resolution Structure and Conformational Dynamics of Rigid, Cofacially Aligned Porphyrin-Bridge-Quinone Systems As Determined By Two-Dimensional NMR Spectroscopy, Hybrid Molecular Dynamics/ Simulated Annealing, and Variable Temperature NMR Spectroscopic Methods, P. M. Iovine, G. Veglia, G. Furst, and M. J. Therien, *J. Am. Chem. Soc.* **2001**, *123*, 5668-5679.

(3) Synthesis, Excited-State Dynamics, and Reactivity of a Directly-Linked Pyromellitimide-(Porphinato)zinc(II) Complex, N. P. Redmore, I. V. Rubtsov, and M. J. Therien, *Inorg. Chem.* **2002**, *41*, 566-570.

(4) Distance Dependence of Electron Transfer in Rigid, Cofacially Compressed, π-Stacked Porphyrin-Bridge-Quinone Systems, Y. K. Kang, I. V. Rubtsov, P. M. Iovine, J. Chen, and M. J. Therien, *J. Am. Chem. Soc.* **2002**, *124*, 8275-8279.

(5) Dipyrryl and Porphyrinic Precursors to Supramolecular Conjugated (Porphinato)metal Arrays. Syntheses of Dipyrrylmethane and (5,15-Diphenylporphinato)zinc(II), V. S.-Y. Lin, P. M. Iovine, S. G. DiMagno, and M. J. Therien, *Inorg. Syntheses*, **2002**, *33*, 55-61.

(6) Synthesis, Electronic Structure, and Electron Transfer Dynamics of Aryl(ethynyl)-Bridged Donor-Acceptor Systems, N. P. Redmore, I. V. Rubtsov, and M. J. Therien, *J. Am. Chem. Soc.* Accepted for publication.

(7) Impact of Electronic Asymmetry on Triplet State Photoexcitations in Conjugated Porphyrin Oligomers: EPR and Transient Photoinduced Absorption Spectroscopy, P. J. Angiolillo, H. T Uyeda, and M. J. Therien, *Phys. Rev. B.* Submitted.

# 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 $\pi$-stacked geometric relationship. The $\pi$-stacked base pairs in duplex DNA possess such a geometry and have been proposed to function as a "molecular wire." Our approach to the study of electronic interactions in DNA is based on the use of hairpin-forming bis(oligonucleotide) conjugates in which a chromophore serves as a linker connecting two complementary oligonucleotide arms.[7] Second generation systems contain an additional chromophore at the opposite end of the duplex from the hairpin linker. Results of four experiments will be described: hole injection, electron injection, hole migration, and exciton coupling.

The dynamics of photoinduced electron transfer processes in which the linker chromophore serves as an electron acceptor and one or more nucleobase as an electron donor is investigated by means of femtosecond time resolved transient absorption spectroscopy and nanosecond time resolved fluorescence spectroscopy (in collaboration with Wasielewski). Our previous studies established that charge separation occurs via a superexchange or tunneling mechanism, for which the distance dependence is described by: $k_{cs} = k_0 e^{-\beta R}$, where R is the distance between the excited state acceptor (A) and nucleobase donor (D) and $\beta$ 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 other laboratories (Reviews 2 and 3). Recent studies have shown that the value of $\beta$ can vary from 0.4 to 1.1 Å$^{-1}$ and are dependent upon donor-bridge-acceptor energetics. The values of $\beta$ can be correlated with either the injection energy or the tunneling energy.[3]

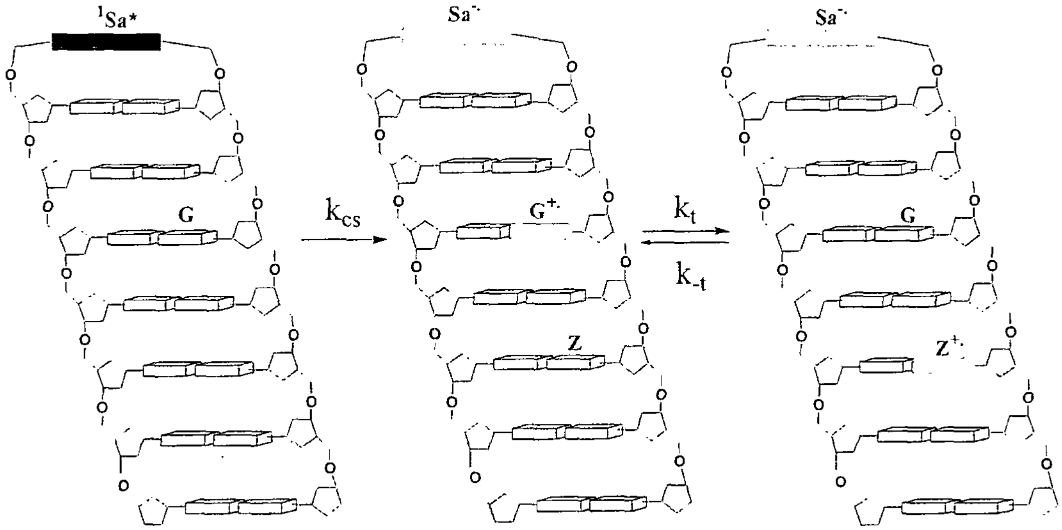
Most studies of photoinduced charge separation in DNA have employed an excited acceptor and guanine as the electron donor. We have investigated the dynamics of electron injection in stilbene-linked hairpins using a stilbenediether linker as excited donor and nucleobases as electron acceptors.[5] Rate constants for electron injection by neighboring base pairs increase with increasing base reduction potential (T:A > I:C > G:C). Slower rates are observed for hairpins containing one or more G:G base pairs between the stilbene and first T:A base pair, in accord with the high reduction potential of guanine. The use of G:G base pairs to mediate long-distance electron injection in DNA is under further investigation.

Much of our effort during the past two years has been focused on investigating the dynamics of hole migration in DNA. We have attempted to promote hole migration in contact radical ion pairs by constructing charge gradients in hairpins possessing diphenylacetylene-4,4'-dicarboxamide linkers and A or G donors.[4] These attempts were unsuccessful: contact radical ion pairs decay exclusively by charge recombination. The absence of hole migration is attributed to Coulombic attraction in the contact radical ion pair and the low effective dielectric constant of the base-pair core of DNA.

Hole migration (Scheme 1) has been investigated in hairpins possessing a stilbenediamide linker, guanine primary donor, and a secondary donor consisting of a GG or GGG sequence or Z (deazaguanine).[2,6,8] The primary donor must be separated from the stilbene by more than two base pairs, in order for charge separation to compete with charge recombination. The equilibrium constant for hole transport in a $G^{+\cdot}AZ \leftrightarrow GAZ^{+\cdot}$ is much larger than that for the hole transport sequence $G^{+}AG \leftrightarrow GAGG^{+\cdot}$ (1,800 vs. 8!). Thus Z serves as a hole trap, preventing migration across Z, whereas GG and GGG form relatively shallow hole traps, permitting hole migration to compete with strand cleavage. We have recently completed a extensive study of the factors which determine the dynamics of hole transport.[8] Hole transport across A is much fast than across T. Addition of a second A to the hole transport sequence slows the rate constant by a factor or 20, similar to the rate factor for charge separation and charge recombination. Hole transport across strands is retarded by a smaller factor.

Electron transfer processes in synthetic duplex and triplex DNA molecules which possess both an electron donor and electron acceptor linker placed at opposite ends of a short stack of based paired nucleotides are currently being investigated. 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.[6] Weak exciton coupling between stilbene chromophores separated by as many as 11 A:T base pairs (40 Å) can be detected by exciton-coupled circular dichroism. DNA serves as a helical ruler by determining both the distance and the dihedral angle between chromophores.

Scheme 1. Charge separation and reversible hole transport in DNA hairpins.



## DOE-Supported Publications 2001-2003

### A. Research Articles

1. Dynamics and energetics of hole trapping in DNA by 7-deazaguanine, F. D. Lewis, J. Liu, X. Liu, X. Zuo, R. T. Hayes, and M. R. Wasielewski, *Angew. Chem. Internat. Ed.* **2002,** *41,* 1026-1028.

2. Dynamics of inter- and intra-strand hole transport in DNA hairpins. F. D. Lewis, X. Zuo, J. Liu, R. T. Hayes, and M. R. Wasielewski, *J. Am. Chem. Soc.* **2002**, *124*, 4568-4589.

3. Donor-bridge-acceptor energetics determine the distance dependence of electron tunneling in DNA, F. D. Lewis, J. Liu, W. Weigel, W. Retting, I. V. Kurnikov, and D. N. Beratan, *Proc. Nat. Acad. Sci.*, **2002**, *99*, 12536-12541.

4. Formation and decay of localized contact radical ion pairs in DNA hairpins, F. D. Lewis, X. Liu, S. E. Miller, R. T. Hayes, and M. R. Wasielewski, *J. Am. Chem. Soc.* **2002,** *124,* 14020-14026.

5. Dynamics of electron injection in DNA hairpins, F. D. Lewis, X. Liu, S. E. Miller, R. T. Hayes, and M. R. Wasielewski, *J. Am. Chem. Soc.*, **2002**, *124,* 11280-11281.

6. DNA-mediated electron transfer across synthetic T:A*T triplex structures, F. D. Lewis, Y. Wu, R. T. Hayes, and M. R. Wasielewski, *Angew. Chem.*, **2002**, *41*, 3485-3487.

7. Synthesis, structure, and photochemistry of exceptionally stable synthetic DNA hairpins with stilbene diether linkers, F. D. Lewis, Y. Wu, and X. Liu, *J. Am. Chem. Soc.*, **2002**, *124*, 12165-12173.

8. Dynamics and energetics of single step hole transport in DNA, F. D. Lewis, J. Liu, X. Zuo, R. T. Hayes, and M. R. Wasielewski, *J. Am. Chem. Soc.* ASAP.

### B. Review Articles

1. Electron transfer and charge transport processes in DNA, F. D. Lewis, in *Electron Transfer in Chemistry*, V. Balzani, ed. Wiley-VCH, Weinheim, 2001, Volume 3, 105-175.

2. Dynamics of photoinduced charge transfer and hole transport in synthetic DNA hairpins, F. D. Lewis, R. L. Letsinger, and M. R. Wasielewski, *Acc. Chem. Res.* **2001,** *34,* 159-170.

3. Dynamics of superexchange photoinduced electron transfer in duplex DNA, F. D. Lewis and Y. Wu, *J. Photochem. Photobiol. C, Reviews* **2001,** *2,* 1-16.

4. Dynamics and equilibrium for single step hole transport in Duplex DNA, F. D. Lewis and M. R. Wasielewski, *Topics in Current Chemistry,* submitted.

# THEORETICAL ASPECTS OF ELECTRON TRANSFER: SOME ISSUES INVOLVING ELECTRONIC STRUCTURE AND THE ROLE OF NUCLEAR MODES

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The overall goal of this program is to achieve a quantitative account of mechanistic factors controlling thermal and photoinduced long-range charge transfer in large scale molecular assemblies (organic, inorganic, and organometallic) by development and implementation of refined theoretical and computational techniques. These techniques must accommodate a number of interrelated aspects of electronic structure, energetics and dynamics of charge transfer systems ("solutes") and their surrounding media ("solvent"), including both homogeneous and interfacial situations. Experience to date in efforts to carry out realistic modeling and simulation of charge transfer kinetics, indicate the need to move beyond a number of limitations in models currently in common use, including the so-called two-state linear-response transition state models (typically in the non-adiabatic (weak-coupling) limit), with donor/acceptor coupling generally taken as independent of system coordinates (Condon approximation), and with either homogeneous dielectric continuum or non-polarizable molecular-level representation of medium response.

The modeling and analysis of charge transfer processes involves a number of electronic structural issues. The necessary electronic structural information continues to be based on Self Consistent Field (SCF) or Configuration Interaction (CI) calculations (using *ab initio* or semiempirical Hamiltonians), and the evaluation of donor/acceptor (D/A) electronic coupling (for arbitrary nuclear coordinates, thus obviating the constraints of approaches requiring the use of artificial external "forces" to achieve "resonance") is carried out in the framework provided by the Generalized Mulliken Hush (GMH) formulation of diabatic states. In support of the use of semi-empirical, all-valence-electron semiempirical methods, shown to be of increasing value in the treatment of ground and excited states of extended organic and inorganic D/A systems, validation studies are carried out using ab initio wavefunction-based methods. SCF results remain a useful point of reference, allowing orbital approximations for full (many-electron) D/A coupling elements ($H_{DA}$); however, for the general case of excited states pertinent to photoinduced electron transfer processes of interest, the SCF level is not practically available, thus requiring the use of CI or other many-electron wavefunction models, with explicit attention given to charge and state-specific many-electron effects (e.g., state-specific polarizability, which can appreciably influence charge transfer energetics).

In addressing typical examples of photoinitiated electron transfer involving perhaps several electronic states, special focus is placed on determining the minimal number of states requiring explicit inclusion in modeling the component steps in the overall process. This question involves both the size of the state-space and the particular representation within it (e.g., diabatic or adiabatic). While sequential use of suitable two-state approximations may suffice in some cases, larger spaces may be required (e.g., in the case of low-lying states due to splitting of spatial degeneracy or multiple spin states, or in cases where intensity borrowing in optical absorption and emission complicates attempts to relate the optical data to the corresponding thermal electron transfer process in a given molecular system). In this effort, the many-state flexibility of the GMH model is being fully exploited.

Combined analysis of electronic nodal structure and near-degeneracy of alternative initial states in long-range electron transfer has revealed a very strong variation in electron tunneling behavior of thermally accessible states in related molecular systems. In both ferroene (Fc ) and the isoelectronic variant in which a cyclopentadienyl-iron moiety is replaced by cyclobutadienyl cobalt (Cc), covalent linkage to organic spacers leads to facile coupling (and hence tunneling) for one state and very weak coupling (due to nodal structure) for the other thermally accessible state. In the case of Fc, the ground state is the "tunneling-active" one, whereas for Cc, the situation is reversed. This phenomenon suggests possible mechanisms for control of electronic transport, using either thermal excitation or chemical substitution.

Application of linear response theory to cases of long-range electron transfer in materials with low tunneling gaps (≤1 eV) has yielded detailed but transparent expressions for the pronounced modulation of tunneling probability due to thermal fluctuations in polar media. In particular, the tunneling probability for a thermally activated electron transfer system may differ markedly from that for the equilibrium system. A quantitative account of this effect requires knowledge of the energetics of the various relevant charge transfer events – specifically, the charge injection into the intervening spacer as well as the overall donor to acceptor charge transfer. This information, together with equilibrium thermodynamic data (e.g., reduction potentials) will permit refined estimates of superexchange tunneling.

Unified theories of long-range electron tunneling mediated by insulating materials provide the basis for quantitative comparisons of different electronic transport processes involving a common spacer. By employing models for interfacial electron transfer kinetics (rate constant, $k_{et}$) and conductance (g) between metal electrodes, we have demonstrated that experimental ratios of $k_{et}$ and g for several alkane spacers are in agreement with theoretical predictions to within one or two orders of magnitude. Similar results were obtained for some cases involving unsaturated organic spacers. These findings, which depend crucially on taking proper account of the distinct self energies and densities of states pertaining to the respective kinetic and conductive events, support the notion of a common tunneling mechanism underlying different electronic transport processes.

## Publications (2001-2003)

Electron Transfer: Theoretical Models and Computational Implementation; M. D. Newton, in *Electron Transfer in Chemistry*, Vol I, Ed., P. Piotrowiak; Wiley-VCH Verlag GmbH: Weinhein, Germany, 2001, p3

Adiabatic Interfacial Electron Transfer over 26 Å through Oligophenylenevinylenes; H. D. Sikes, J.F. Smalley, S. P. Dudek, A. R. Cook, M. D. Newton, C. E. D. Chidsey, and S. W. Feldberg; *Science* **291**, 1519-23 (2001)

Understanding the Optical Band-Shape: Coumarin-153 Steady-State Spectroscopy; D.V. Matyushov and M. D. Newton; *J. Phys. Chem.* **A105** , 8516-32 (2001)

Emission State of Tris(8-Quinolinolato)Aluminum and its Related Compounds: a Theoretical Study; M. Sugimoto, S. Sakaki, K. Sakanoue, and M. D.Newton; *J. Appl. Phys.* **B90**, 6092-97 (2001)

Distance-Dependent Activation Energies for Hole Injection from Protonated 9-Amino-6-Chloro-2-Methoxyacridine into Duplex DNA; W. B. Davis, S. Hess, I. Naydenova, R. Haselsberger, A. Ogridnik, M. D. Newton, and M-E. Michel-Beyerle; *J. Am. Chem. Soc.* **124,** 2422 (2002)

Application of the Linearized MD Approach for Computing Equilibrium Solvation Free Energies of Charged and Diplar Solutes in Polar Solvents; M. V. Vener, I. V. Leontyev, Y. A. Dyakov, M. V. Basilevsky and M. D. Newton; *J. Phys. Chem.* **A106**, 13078 (2002)

Heterogeneous Electron Transfer Kinetics for Ruthenium and Ferrocene Redox Moieties Through Alkanethiol Monolayers on Gold; J. F. Smalley, H. O. Finklea, C. E. D. Chidsey, M. R. Linford, S. E. Creager, J. P. Ferraris, K. Chalfant, T. Zawodzinski, S. W. Feldberg and M. D. Newton; *J. Am. Chem. Soc.* **125**, 2004 (2003)

Electronic Coupling of Donor/Acceptor Sites Mediated by Homologous Unsaturated Organic Bridges; M. D. Newton; *ACS Symposium Series* **844**, 196 (2003)

Thermal and Optical Electron Transfer Involving Transition Metal Complexes: Insights from Theory and Computation; M. D. Newton; Coord. Chem. Reviews (in press)

The Indirect Laser Induced Temperature Jump Method for Characterizing Fast Interfacial Electron Transfer: Concept, Application and Results; S. W. Feldberg, M. D. Newton and J. F. Smalley, in *Electroanalytical Chemistry Series*, Eds., A. J. Bard and I. Rubinstein, Marcel Dekker, New York, NY (in press)

Thermal and Optical Electron Transfer Involving Transition Metal Complexes: Theoretical Perspectives;M. D. Newton, in *Comprehensive Coordination Chemistry II, From Biology to Nanotechnology*, Ed., A. B. P. Lever, Elsevier (in press)

Charge Transfer on the Nanoscale; D. Adams, L. Brus, C. E. D. Chidsey, S. Creager, C. Creutz, C. R. Kagan, P. V. Kamat, M. Lieberman, S. Lindsay, R. A. Marcus, R. M. Metzger, M. E. Michel-Beyerle, J. R. Miller, M. D. Newton, D. R. Rolison, O. Sankey, K. S. Schanze, J. Yardley and X. Zhu; *J. Phys. Chem. B* (in press)

Estimate of the Reorganization Energy for Charge Transfer in DNA; K. Siriwong, A. A. Voityuk, M. D. Newton and N. Rosch; *J. Phys. Chem. B* 107, 2595-2601 ( 2003 )

Distance Dependence of Electron Transfer Across Peptides with Different Secondary Structures: the Role of Peptide Energetics and Electronic Coupling; Y-.g. K. Shin, M. D. Newton and S. S. Isied; *J. Amer. Chem. Soc.* (in press)

Theory and Computation of Electron Transfer Reorganization Energies with Continuum and Molecular Solvent Models; I.V. Leontyev, M. V. Basilevsky and M. D. Newton; *Theoretical Chemistry Accounts* (in press)

# MOLECULAR WIRES FOR SOLAR ENERGY CONVERSION?

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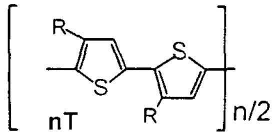
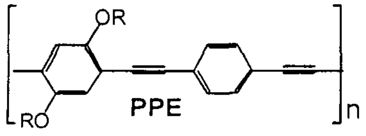
Nanoscale molecular wires having diameters of 0.5-1.0 nm and lengths of 2-20 nm have potential for aiding charge separation to promote efficient solar energy conversion and storage. Good nanoscale molecular wires must be excellent charge carriers, even at very long lengths, while satisfying the somewhat contradictory requirement that their energetics not change drastically with length. They should be reasonably immune to the effects of stray charges or other impurities, a requirement that will place more stringent demands on molecular design, as the wires become longer. They must have states appropriate to exchange electrons or holes with energy levels in electrodes, nanostructures or molecules with which they function, so the energy levels (redox potentials) must be known.

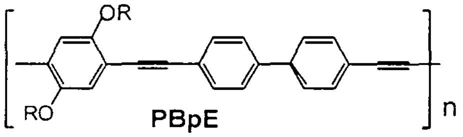
This work investigates spectroscopy and transport in "wire" segments composed of repeating molecular units with the intent to learn what are the energy levels for electron or hole transport and how fast and effective is the transport. In the experiments electrons or holes are added into wires in solution using ionizing pulses from the LEAF accelerator, which produces 6-30 ps pulses of 10 MeV electrons. Addition of a single electron to polyalkylthiopehene (nT) or an electron or hole to polyalkylphenylethnylene (PPE) produces intense visible and NIR spectra that indicate delocalized charges in the wires. For $nT^{\bullet -}$ the NIR band is not seriously perturbed by the presence of $Na^+$ ions indicating that they do not lead to localization of the charge. In polyalkylbiphenylethnylene (PBpE) the spectra suggest that the moderate change in structure represented by two adjacent phenyls leads to weaker delocalization.



nT



PPE

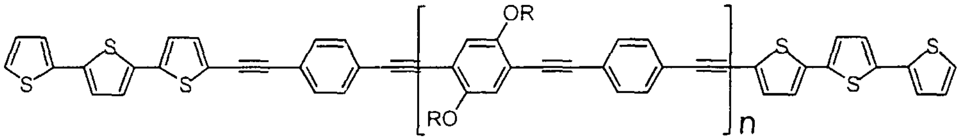


PBpE

The rate constants for electron or hole capture by these long molecules in solution increases slowly with the length of the molecule. An increase in length by a factor of 8 results in rate constants increased by a factor of only ~ 3. This is expected by theories in diffusion-controlled reactions by long arrays of capture sites and other experiments.

The anion formed by attachment of one electron to poly-3-decylthiophene (nT) can transfer charge to electron accepting molecules such as acridine, quinones or TCNE in bimolecular reactions. The rate constants for these reactions in solution will be regulated by reaction energetics as expected by electron transfer theories like the Marcus theory. It can be argued that influence of energetics on rates will be enhanced by the delocalized nature of the charges in these conjugated polymers. Measured rates for these bimoleuclar reactions of $nT^{\bullet -}$ do show enhanced control of rates by energy. On the other hand reactions of the anion of a shorter oligomer, tetrathiophene ($4T^{\bullet -}$) showed much less control by energetics, in the well-known manner of bimolecular reactions in the diffusion-controlled limit. These experiments also obtain an estimate of the reduction potential of nT.

Because electrochemistry is not facile on these large molecules the redox levels for placing charges in PPE or PBpE are not easily measured. But redox equilibria can be obtained in the accelerator experiments to show that the oxidation potential of PPE is slightly more positive than that of terthiophene ($T_3$). It is therefore expected that attachment of $T_3$ end cap groups to the ends of PPE would result in capture of injected holes by the $T_3$ groups. For this long molecule, $T_3PPET_3$ with n=13, hole transfer to the $T_3$ groups does occur as indicated by alteration of the spectrum formed, but the alteration is not as large as that typically seen upon charge capture by a group in a non-conjugated molecule. Hole transfer to the $T_3$ end groups occurs in <10 ns even though most positive charge must be captured in the 18 nm long PPE portion of the $T_3PBpET_3$ molecule. In the same molecule the $T_3$ groups cause almost no change in spectra of formed by addition of an electron. For a related molecule $T_3PBpET_3$ the $T_3$ groups alter neither the spectrum of the negative or positive ion; the charges remains in the polymer.



One aim of future work will gain understanding of charge transport in long molecules by direct observation of the rates. In the example above, the 10 ns time resolution was determined by the rate at which charge could be injected into the polymer. Two approaches will be followed to observe transport: 1) Molecules will be constructed and studied in which conjugation is weaker and transport is therefore expected to be slower. For such molecules NIR spectra are likely to give indication of more localized charges. A goal is to learn whether there is a measurable relationship between spectroscopy and transport. 2) In the other approach new experimental techniques under development at the LEAF accelerator will use combinations of electron and laser pulses to perform experiments having much shorter time resolution. Another aim will be to develop a library of conjugated molecules having different, known energies and a range of chemical properties.

### Publications

Benzene radical ion in equilibrium with solvated electrons, Marasas, R. A.; Iyoda, T.; Miller, J. R. *J. Phys. Chem. A* **2003**, *107*, 2033-2038.

# EXCITED STATE COUPLING AND ENERGY TRANSFER IN PHENYL-ETHYNYLENE DENDRIMERS

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Todd J. Martinez, and Christopher J. Bardeen
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We report on combined synthetic, experimental, and theoretical work designed to understand the origins of excited state energy transfer in phenyl-ethynylene (PE) dendrimers. In these PE dendrimers, there are not well-defined, separated light absorbing and connecting units, since each segment overlaps the next. These molecules are unique in that they are multichromophoric systems where the chromophore serves as both a structural and optical element.

Early work on these systems showed that the absorption spectra were relatively insensitive to the number of chromophores in the dendrimer, despite the fact that their small separations should lead to strong electronic coupling. This lack of coupling indicated that the excited state wavefunctions are localized on individual segments. We have synthesized the series of molecules shown in Figure 1, with the goal of understanding their photophysics as a prelude to a detailed treatment of highly efficient energy transfer that occurs in these molecules. While the absorption spectrum is consistent with localization of the absorbing state along individual dendrimer arms, dramatic changes in the emission spectrum and radiative lifetime indicate that the emitting state is different from the absorbing state. The data in Figure 2 are typical: the absorption barely shifts or changes shape, while the emission undergoes large changes. This behavior is general for all the molecules in Figure 1.

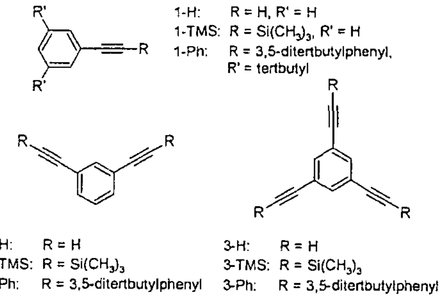

Figure 1. Building blocks of PE dendrimers studied in this work.

To investigate the origin of this effect, we used *ab initio* quantum chemistry to investigate the nature of the excited states of these molecules. In order to accurately model these states, even for the simplest molecules in Figure 1, electronic correlations at a fairly high level (CASPT2) must be taken into account. The results of these calculations for di- and tri-ethynyl benzene, **2-H** and **3-H**, are shown in Figure 3, for both the optimized ground and excited state nuclear geometries. The excited state level structure is completely different in the two geometries: in the absorbing geometry, there are three excited states that are nearly degenerate, corresponding to excited state wavefunctions localized on each of the three arms of

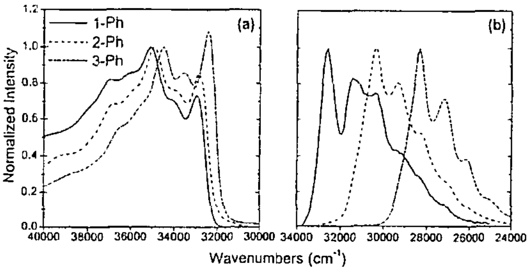

Figure 2. Absorption (a) and emission (b) spectra in cyclohexane.

the molecule. In the emitting geometry, the degeneracy is lifted and the lowest energy state, from which emission occurs, is only weakly allowed relative to the absorbing states. This rearrangement of level structure is due to a geometry-dependent electronic coupling. As the molecule relaxes on the excited state, its changing nuclear structure causes changes in the electron density and thus the electronic coupling between the three ethynyl segments. This change in coupling then leads to new, low-lying states with weaker oscillator strengths and more delocalized wavefunctions.

This observation is significant because it shows that these entirely conjugated systems can demonstrate novel photophysical phenomena, e.g. new states not visible in the absorption spectrum, which may be harnessed to improve light harvesting in engineered molecules.

In addition to our work on the fundamental photophysics of phenylethynylene dendrimers, we will also report preliminary work investigating energy transfer in these PE networks. An important comparison is between structures with various types of branching geometries, in order to determine the optimum geometry for energy transfer in highly conjugated macromolecules.

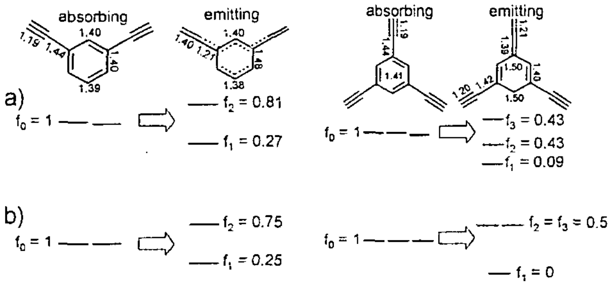

Figure 3. *a*) Calculated electronic level structure for the **2-H** and **3-H** dendrimers for both absorbing and emitting geometries. Also shown are the transition energies and transition dipole moments. *b*) The results of a simple exciton model with intramolecular coupling *V* growing more negative after absorption and relaxation on the excited state.

## Publications Resulting from This Work

"Meta-conjugation and excited state coupling in phenylacetylene dendrimers," Kevin M. Gaab, Alexis L. Thompson, Jianjun Xu, Todd J. Martínez, and Christopher J. Bardeen, J. Amer. Chem. Soc., submitted.

# *Session VII*

# *Photoinduced Water Splitting*

# WATER OXIDATION CATALYZED BY RUTHENIUM $\mu$-OXO DIMERS

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The central focus of this program is to explore ways in which aqueous-organic interfaces and microphase compartmentation can be used to promote or regulate photoinitiated charge separation and other chemical processes germane to solar photoconversion. Specific projects within this broad objective include:

(*1*) identifying molecules that are capable of functioning as cyclic electroneutral transmembrane electron carriers and combining this function with photosensitization to develop efficient assemblies for long-lived charge separation;

(*2*) developing closed membrane assemblies that contain two active elements whose functions are indirectly coupled via membrane polarization, analogous to energy transduction processes in living cells;

(*3*) investigating mechanisms of water oxidation catalyzed by dimeric ruthenium $\mu$-oxo complex ions and related dimeric complexes that are suitable for incorporation into integrated systems for water photolysis.

***This presentation is limited to a discussion of our ongoing research in specific area (3).***

*Progress summary*--Recent advances from my lab in specific area (*1*) include development of transmembrane electron carriers based upon classes of N-alkylpyridinium and pyrylium ions, which derive their abilities to function cyclically by co-transporting protons and counter-transporting hydroxyl ions, respectively. Both classes of compounds efficiently oxidatively quench photoexcited sensitizer molecules and promote long-lived charge separation by partitioning into the membrane hydrocarbon phase. Visible-near uv absorption by the pyrylium ions also generates strongly oxidizing excited states; thus, is possible to contemplate using these compounds to perform the dual functions of photosensitizer and electron carrier, considerably simplifying component requirements for transmembrane charge separation. Recent activities in specific area (*2*) have focused on the photoswitching capabilities of amphiphilic spiropyrans and spirooxazines in bilayer membranes. We have now shown that not only can electrolyte leak rates across bilayers be controlled by photoisomerization between spiro and merocyanine forms of the dyes, but also the relative order of leakage (spiro > mero vs. mero> spiro) can be reversed by appropriate derivatization, i.e., by appending crown ether substituents to the indolene N-atom. The rationale for these designs followed from transient spectrophotometric investigations that characterized the spatial relocation of the dye within the membrane microphase following spiro $\rightleftharpoons$ mero interconversions. Ongoing efforts include synthesizing a $Ru(bpy)_2$-acceptor dyad that is bridged by a phenanthroline-based spirooxazine that could function as a photoregulated transmembrane electron transport system.

*Catalyzed water oxidation (specific area (3))*--Investigations of the mechanism of $O_2$ formation from water by Meyer's catalyst (cis,cis-$[(bpy)_2Ru(OH_2)]_2)O^{4+}$) and analogs have been severely hampered by the inability to prepare in pure form the highest oxidation states of the complexes. We have surmounted this technical problem by utilizing a high surface area columnar-flow carbon fiber electrode for constant potential electrolysis. This instrumentation has enabled us to access all of the formal oxidation states between $Ru_2(III,III)$ and $Ru_2(V,V)$ (hereafter, {3,3} ⇔ {5,5}). The cumulative results of resonance Raman (RR) and optical spectrophotoelectrochemical measurements and redox titrations of effluent solutions have led to the following major conclusions:

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

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

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

Isotope-labeling studies have been used to probe the reaction mechanism(s). Earlier research from both Meyer's and my labs had established that two major isotopic products were formed, one in which both O atoms of $O_2$ derived from solvent $H_2O$ and the other in which one atom derived from the coordinated aqua ligand. To aid in mechanistic interpretations of this unusual result, we have determined labilities of the cis-coordinated oxo ligands in various oxidation states by an indirect RR technique that made use of the large O-isotopic shifts observed for $\nu$(Ru=O). The only species undergoing detectable substitution was the {3,3} ion, whose water exchange rate constant ($7\times10^{-3}$ $s^{-1}$) was $10^3$-$10^5$ fold greater than that normally observed for simple monomeric ruthenium(III) complexes. This labilization can be attributed to strong $\sigma$-donation from the $-ORu(OH_2)(bpy)_2^+$ unit. Isotopic substitution at the bridging O, detectable by shifts in the Ru-O-Ru symmetric stretching ($\nu_s$) modes, did not occur even after several cycles of catalytic turnover. Thus, the bridging O plays no direct role in $O_2$ formation. Small downfield shifts in $\nu_s$(Ru-O-Ru) were observed in $D_2O$, suggesting that the bridging O may function in catalysis by H-bonding to solvent water, thereby promoting nucleophilic attack of the coordinated ruthenyl oxo groups. Decomposition of the {5,5} ion in $D_2O$ indicated a modest normal kinetic isotope effect of $k_H/k_D \approx 2$. Since the $^{18}O$ isotope-labeling studies suggest the existence of two independent pathways for water oxidation, interpretation of the kinetic isotope results will require determining $^{18}O$-isotopic distributions for reactions in both $H_2O$ and $D_2O$ (in progress).

Cryogenic EPR spectra of frozen {5,5} solutions revealed a relatively narrow axial $g = 2$ signal that was quite unlike those normally observed for Ru $\mu$-oxo dimers. This signal, whose relative intensity depended linearly upon the catalyst concentration, exhibited a 6-line hyperfine component comprising ~20% of the total intensity. These properties suggest that it may be a $\pi$-radical cation, formed by one-electron oxidation of the bpy ligand. Studies directed at identifying this signal via characterization of its magnetic properties are in progress. Results of additional studies designed to explore the influence of "push-pull" asymmetry within the dimeric unit upon catalytic activity, also in progress, will be described. These studies utilize a "combinatorial" approach that seeks to identify unusually reactive species within synthesized dimer mixtures by comparing RR analysis of component distributions with measured $O_2$ evolution rates.

## DOE-Sponsored Publications 2001-2003

(1) R. F. Khairutdinov & JKH: "Photocontrol of Ion Permeation through Bilayer Membranes using an Amphiphilic Spiropyran", *Langmuir* **2001**, *17*, 6881-6886.

(2) H. Yamada, T. Koike & JKH: "Water Exchange Rates in the Diruthenium μ-Oxo Ion *cis,cis*-$[(bpy)_2Ru(OH_2)]_2O^{4+}$" *J. Am. Chem. Soc.* **2001,** *123*, 12775-12780.

(3) R. F. Khairutdinov & JKH: "Cyclic Transmembrane Charge Transport Mediated by Pyrylium and Thiopyrylium Ions" *J. Am. Chem. Soc.* **2001,** *123*, 7352-7359.

(4) R. F. Khairutdinov & JKH: "Light Driven Transmembrane Ion Transport by Crown Ether—Spiropyran Supramolecular Assemblies", manuscript submitted

In preparation:

H. Yamada & JKH: "Isotopic Analysis of Mechanisms of Water Oxidation Catalyzed by the cis,cis-$[(bpy)_2Ru(OH_2)]_2)O^{4+}$ Ion"

# *Session VIII*

# *Photosynthetic Light-Harvesting*

# PHOTOSYNTHETIC MOLECULAR WIRES

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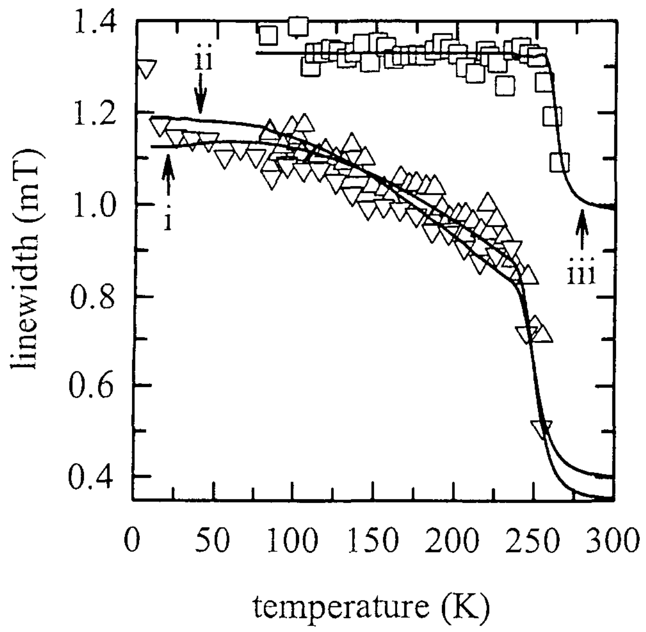
Various molecular arrays mimic the light harvesting complexes of bacterial photosynthesis where circular or semicircular arrays of bacteriochlorophyll molecules capture solar photons for conversion into chemical energy. The captured photons migrate through the arrays to distant chemical complexes where the excited state energy is trapped in the form of reducing and oxidizing power. The photon energy must travel extremely rapidly to the chemical trap to prevent energy loss as heat. Consequently, the light harvesting molecules are required to be very close to each other. This mandatory proximity of the adjacent molecules of the array has the intriguing side effect that upon chemical oxidation, some natural and artificial light harvesting complexes (LH1) become thermally assisted molecular wires in the Ratner sense.

In liquid solutions or suspensions, these natural and artificial complexes allow rapid charge migration among the members of the array. Upon freezing, the typical artificial light harvesting complex no longer acts as a molecular wire while the natural light harvesting complex does. To reveal the molecular-wire properties of both natural and artificial light harvesting arrays in the liquid and solid state, we have relied mostly on electron paramagnetic resonance (EPR) spectroscopy. Various treatments of Marcus electron–transfer theory have been applied to our EPR results using Kubo theory. The figure compares calculated EPR line widths (inversely corresponding to electron transfer rates) versus temperature (lines) to experimental data of LH1$^+$ (△, ▽) and a dimeric form of LH1$^+$, B820$^{\cdot+}$ (□). The assumed Kubo monomer EPR line width was 1.25 mT for line (i), 1.4 mT for line (ii) and 1.33 mT for line (iii). In the case of LH1$^{\cdot+}$, the assumption for electron transfer and the EPR model was that charge migration occurs via nearest neighbors along a loop containing 32 bacteriochlorophyll molecules. The electron transfer rates used to simulate the EPR line widths of the figure were calculated with Hoffman and Ratner's "glassing" electron–transfer model. Significantly, other electron transfer methods failed to simulate the EPR line width changes over the temperature range of the figure.



Crucial to the understanding of these thermally assisted molecular wires is the role of heterogeneity on the EPR time scale. When going from the liquid state to the solid state, the system goes from homogeneous to inhomogeneous. Consequently, for both the liquid and the solid state, we have also developed an electron–transfer model based on a redox heterogeneity associated with the molecular wire properties of the LH1 complexes.

Investigation of these molecular arrays suggests important factors for the engineering of artificial molecular wires for applications in the solid state as well as implications for the mechanism of photo–induced charge separation in both natural and artificial photosynthesis. Future work will attempt to implement these findings more fully in model systems.

Publications (2001–2003)

1. Srivatsan, N. and J.R. Norris, *Electron paramagnetic resonance study of oxidized B820 complexes*. Journal of Physical Chemistry B, 2001. 105(49): p. 12391 -12398.
2. Jager, M. and J.R. Norris, *A time-resolved EPR study of the electron-spin-polarization pathways of p-benzosemiquinone*. Journal of Magnetic Resonance, 2001. 150(1): p. 26-34.
3. Jager, M. and J.R. Norris, *Computation of time-resolved EPR spectra of systems exhibiting electron spin polarization complicated by magnetization transfer*. Journal of Physical Chemistry A, 2002. 106(15): p. 3659-3664.
4. Jager, M., B.C. Yu, and J.R. Norris, *Exploring complex CIDEP of p-benzosemiquinones with time resolved CW-EPR*. Molecular Physics, 2002. 100(9): p. 1323-1331.
5. Kolbasov, D. and J.R. Norris, *Contribution of Colliding Parallel Electron Spins to EPR Spectral Narrowing*. In press, Journal of Chemical Physics, 2003.
6. Kolbasov, D., N. Srivatsan, N. Ponomarenko, M. Jäger, and J.R. Norris, *Modeling Charge Transfer in Oxidized Bacterial Antenna Complexes*. Journal of Physical Chemistry B, 2003. 107(10): p. 2386-2393.
7. Ostafin, A.E., N.S. Ponomarenko, J.A. Popova, M. Jäger, E.J. Bylina, and J.R. Norris, *Characterization of Expressed Pigmented Core Light Harvesting Complex (LH1) in a Reaction Center Deficient Mutant of Blastochloris viridis*. In press, Photosynthesis Research, 2003.
8. Srivatsan, N., S. Weber, D. Kolbasov, and J.R. Norris, *Exploring Charge-Migration in Light-Harvesting Complexes Using Electron Paramagnetic Resonance Line Narrowing*. Journal of Physical Chemistry B, 2003. 107(9): p. 2127-2138.
9. Srivatsan, N., D. Kolbasov, and J.R. Norris, *Cryogenic Charge Transport in Oxidized Purple Bacterial Light Harvesting 1 Complexes*. In press, Journal of Physical Chemistry B, 2003.
10. Kolbasov, D., N. Srivatsan, and J.R. Norris, *Glass Transition and Redox Heterogeneity in Bacterial Light Harvesting-1 Complexes of Rhodobacter Sphaeroides Studied by Means of EPR Spectroscopy*. Submitted, Chemical Physics, 2003.

# PHOTOSYNTHETIC LIGHT HARVESTING AND ITS REGULATION

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Our efforts to understand the primary steps of photosynthesis have focused on three main areas over the past two years: (1) extending our understanding of energy transfer and electronic interactions in confined molecular geometries from the highly symmetric LH1 and LH2 structures of purple bacteria to the spatially and energetically disordered Photosystem I structure of cyanobacteria, (2) beginning to study the regulation of light harvesting efficiency in the Photosystem II supercomplex via the nonphotochemical quenching mechanism and (3) developing new experimental and theoretical techniques for the study of complex molecular aggregates.

Photosystem I (PSI) has 96 non-equivalent chlorophyll molecules. We used quantum chemical methods to calculate the electronic excitation energies of all 96 molecules and their Coulombic coupling. We then diagonalized to 96 x 96 Hamiltonian to find the exciton states and calculate the spectrum at low temperature. We used lineshape functions from hole burning spectroscopy to calculate the room temperature spectrum. PSI has highly heterogeneous electronic coupling, and it is not immediately obvious how to calculate the energy transfer dynamics. We developed a new theory of energy transfer that allows consistent treatment of systems with the full range from weak to strong coupling, based on a modified form of Redfield theory. The resulting rate matrix produces clusters of eigenvalues (timescales) that are in remarkable agreement with our fluorescence upconversion data. We analyzed bottlenecks and investigated the optimization of the energy transfer process by "shuffling" the energy assignments of the 96 chl molecules. The results show that PSI is highly robust with respect to the energy landscape of the antenna. However, the energy profile of the "reaction center" (electron transfer pigments + the two linker chls) is highly optimized. A method of analyzing pathways and revealing bottlenecks in arbitrary energy transfer networks has been developed and will prove useful in putting intuitive "compartment" models for complex systems (e.g., PS II) on a firm basis.

Nonphotochemical quenching (NPQ) refers to a process that regulates light harvesting efficiency in plants as a response to changes in light intensity. NPQ protects the system against photooxidative damage. To understand the physical mechanism of NPQ we carried out femtosecond transient absorption measurements on intact thylacoid membranes from spinach and transgenic plants of *Arabidopsis thaliana*. Our results show that a specific carotenoid, zeaxanthin is directly related to the NPQ process. Models for the molecular role of zeaxanthin will be described.

We have developed two-color photon echo peak shift spectroscopy. This new spectroscopic technique is sensitive to correlations between initial and final states and to electronic mixing between strongly coupled molecular pairs. We are currently applying the technique to a number of systems with the goal of characterizing energy transfer pathways in highly heterogenous light harvesting systems.

We have continued our studies of the 1- and 2-photon spectroscopy and electronic structure of carotenoids.

## Publications

1. Excitation Energy Transfer in Dimeric Light-Harvesting Complex I: A Combined Streak-Camera/Fluorescence Upconversion Study, B. Gobets, J. T. M. Kennis, J. A. Ihalainen, M. Brazzoli, R.Croce, I H.M. van Stokkum, R. Bassi, J. P. Dekker, H. van Amerongen, G. R. Fleming, and R. van Grondelle. *J Phys Chem B.*, **105**, 10132-10139 (2001).

2. The Mechanism of Energy Transfer in the Antenna of Photosynthetic Purple Bacteria, M. Yang, R. Agarwal, and G. R. Fleming. Porter Issue of *Journal of Photochemistry and Photobiology*, Part A., **142**, 107-119 (2001).

3. Excited-State Kinetics of the Carotenoid $S_1$ State in LHC II and Two-Photon Excitation Spectra of Lutein and ß-Carotene in Solution:Efficient Car $S_1 \longrightarrow$ Chl Electronic Energy Transfer via Hot $S_1$ States?, P. J. Walla, P. A. Linden, K. Ohta, and G. R. Fleming. *J. Phys. Chem.* A, **106**(10), 1909-1916 (2002) *Mataga Festschrift Issue.*

4. The Role of the $S_1$ State of Carotenoids in Photosynthetic Energy Transfer: The Light Harvesting Complex II of Purple Bacteria, C-P. Hsu, P. J. Walla, M. Head-Gordon, and G. R. Fleming. *J. Phys. Chem. B*, **105**, 11016-11024 (2001).

5. The Nature of Disorder and Inter-complex Energy Transfer in LH2 at Room Temperature: A Three Pulse Photon Echo Peak Shift Study, R. Agarwal, A. H. Rizvi, B.S. Prall, J. D.Olsen, C. Neil Hunter, and G. R. Fleming. *J. Phys. Chem. A.*, **106**, 7573-7578 (2002).

6. Chlorophyll Excitations in Photosystem I of *Synechococcus elongatus*, A. Damjanovic, H. M. Vaswani, P. Fromme, and G. R. Fleming. *J. Phys. Chem. B.* **106**, 10251-10261 (2002).

7. Two Photon Excitation Study of Peridinin in Benzene and in the Peridinin Chlorophyll a-Protein (PCP), J. Zimmermann, P.A. Linden, H.M. Vaswani, R.G. Hiller, and G.R. Fleming. *J. Phys. Chem. B.* **106**(36), 9418-9423 (2002).

8. Energy transfer in photosystem I of cyanobacteria *Synechococcus elongatus*: Model study with structure-based semi-empirical Hamiltonian and experimental spectral density, M. Yang, A. Damjanovic, H. Vaswani, and G.R. Fleming. *Biophysical Journal.* In press.

9. Evidence for Direct Carotenoid Involvement in the Regulation of Photosynthetic Light Harvesting, Y.-Z. Ma, N. Holt, X.-P. Li, K.K. Niyogi, and G. R. Fleming. *Proc National Acad Sci USA.* In press.

10. Quantum Chemical Evidence of an Intramolecular Charge Transfer State in the Carotenoid Peridinin of Peridinin-Chlorophyll-Protein, H. M. Vaswani, C.-P. Hsu, M. Head-Gordon and G. R. Fleming. *J. Phys Chem B.* Submitted.

11. Charge-Transfer State as a Possible Signature of a Zeanthin-Chlorophyll Dimer in the Non-Photochemical Quenching Process in Green Plants, A. Dreuw, G. R. Fleming, and M. Head-Gordon. *J. Phys. Chem B.* Submitted.

12. Construction of Kinetic Domains in Energy Trapping Processes and Application to a Photosynthetic Light Harvesting Complex, M. Yang and G. R. Fleming. *J. Chem. Phys.* Submitted.

13. Energy Transfer and Photosynthetic Light-Harvesting, G. D. Scholes and G. R. Fleming. *Adv. Chem. Phys.* Submitted.

# HUNT FOR THE RED ABSORBING ANTENNA CHLOROPHYLLS OF PHOTOSYSTEM I

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An important goal of this program continues to be the use of high resolution spectral hole burning spectroscopies at low temperatures to provide detailed information on the excited state ($S_1(Q_y)$) excitonic structure, excitation energy transfer and primary charge separation dynamics of photosynthetic protein-chlorophyll (Chl) complexes. The experimental facility at Ames Laboratory is unique in that it combines hole burning with high pressure and external electric (Stark) fields. Hole burning spectroscopies (non-photochemical, triplet population bottleneck) have, by themselves, provided results of much importance for understanding the early time events of photosynthesis. Included here is characterization and determination of electron-phonon and electron-intramolecular vibration couplings that figure importantly in the spectral density of rate expressions for transport; quantitative determination of the contribution of static inhomogeneous broadening of the optical transitions of Chl states; proof that the site excitation distribution functions of different Chl $Q_y$ states are generally uncorrelated (electronic energy gaps are distributed due to the glass-like structural heterogeneity of proteins); and resolution of closely spaced exciton levels[1]. It is worth noting that with spectral hole burning one measures excitation energy transfer and primary charge separation rates from the total zero-point vibrational level of the donor $Q_y$ state. Stark and high pressure hole burning spectroscopies provide even higher resolution but more important is that they can be used to distinguish between $Q_y$ states involving weakly coupled Chls and strongly coupled Chls. Of particular interest is the case when electron exchange coupling, which introduces charge transfer character to the $Q_y$ states, is as or more important than electrostatic coupling[2]. It is to be appreciated that accurate calculation of electron exchange coupling matrix elements still remains as a formidable theoretic problem. The Stark and high pressure experiments yield the permanent dipole moment change ($\Delta\mu$) of a $S_0 \rightarrow S_1$ ($Q_y$) transition and the linear pressure shift rate $R_p$ (to the red) of that transition. Both observables are very sensitive to the amount of charge transfer character in the $Q_y$ state. Our studies of several photosynthetic complexes have established that there is *positive correlation between electron-phonon coupling strength,* $\Delta\mu$ *and* $R_p$.

In the *first part* of the presentation the attributes of nonphotochemical hole burning will be illustrated using results obtained for red-absorbing antenna Chl *a* molecules of photosystem I of cyanobacteria (good models for PS I of green plants). The presentation will end with a status report on the design and construction of an apparatus for the spectroscopic study of *single* photosynthetic complexes. The design is novel in that it allows for the use of pressure and external electric field.

Photosystem I (PS I) is but one example of a photosystem featuring antenna Chl states that lie lower in energy than the primary electron donor ('special Chl pair') state of the RC. The primary donor state of PS I, P700*, is associated with a strongly coupled Chl *a* / Chl *a*' dimer (absorption at ~700 nm). The red absorption of the antenna Chl *a* molecules for *Synechocystis* 6803 and *Synechococcus elongatus* are encircled in Fig. 1. Three questions immediately arise: are the red antenna states due to strongly coupled Chl a molecules or Chl *a* 'monomers' in

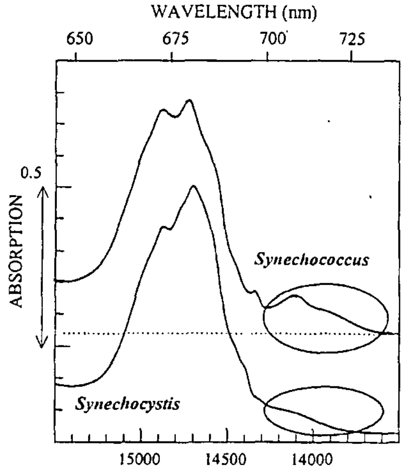

Figure 1.

unusual protein environments; if the former is true, can red antenna Chls *a* be identified with certain dimers and a trimer identified in the 2.5Å X-ray structure of *Synechococcus elongatus*[3]; and, third, what are the functions of the red Chls? These questions will be addressed. However, the hunt for the red Chls *a* is by no means over. PS I of *Synechococcus elongatus* contains 96 Chl *a* molecules, including 6 of the RC. Most of the Chls (~70) are bound to the core proteins, PsaA and PsaB (Fig.2). In addition, there are 7 integral membrane proteins (PsaF...PsaX) and 3 peripheral proteins (not shown).

Persistent nonphotochemical hole burned spectra obtained with different burn wavelengths ($\lambda_B$) throughout the red antenna absorption region allow for determination of the number and nature of the red states. Examples for *Synechococcus* are shown (Fig. 3) where the sharpest feature in each spectrum is the zero-phonon hole (ZPH), coincident with $\lambda_B$. The relatively broad hole features to the immediate left and right of the ZPH are due to protein phonons. Theoretical simulations of the spectra allowed for determination of electron-phonon coupling parameters. The response of the ZPH to Stark fields and pressure gives $\Delta\mu$ and $R_p$. Three red states were identified for *Synechococcus* at 708, 715 and 719 nm and two for *Synechocystis* at 708 and 714 nm. It had been previously thought that they possessed 2 and 1, respectively, at 708/719 nm and 708 nm. The properties of the 719 nm state of *Synechococcus* and the 714 nm state of *Synechocystis* are very similar with a total Huang-Rhys factor S (for phonons) of ~2.1, $f\Delta\mu$=2.2 D and $R_p$~−0.45 $cm^{-1}$/MPa. It can be concluded that these states are due to a strongly coupled dimer and that they probably correspond to the same two Chl *a* molecules. They are characterized by significant charge transfer character. The other red antenna states appear to be due to a dimer or trimer in which the Chl *a* molecules are less strongly coupled. Our assignments to specific dimers and a trimer identified in the X-ray structure will be compared with those of the groups of Graham Fleming, Klaus Schulten and Eberhard Schlodder. The role of the red antenna states in energy transfer from the higher energy antenna states to the RC will be discussed.

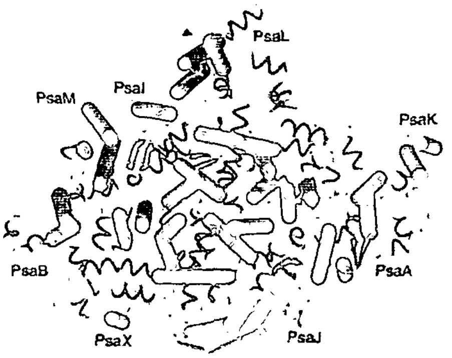

Figure 2.

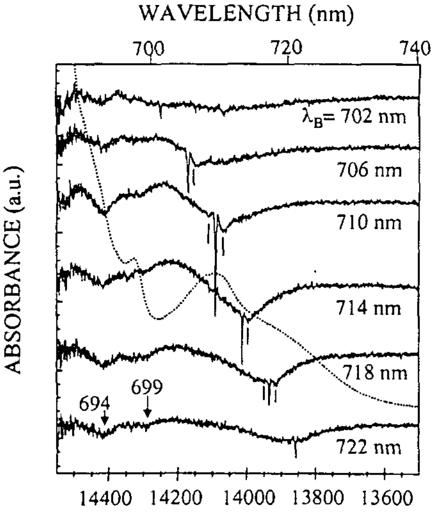

Figure 3.

1. For a review see G. J. Small, *Chem. Phys.* **197**, 239 (1995).
2. T. Reinot, V. Zazubovich, J. M. Hayes and G. J. Small, *J. Phys. Chem.* B (feature article) **105,** 5083 (2001).
3. P. Jordan et al. *Nature* **411**, 909 (2001).

## PUBLICATIONS (2001– 2003)

1. S. Matsuzaki, V. Zazubovich, N. J. Fraser, R. J. Cogdell, and G. J. Small, "Energy Transfer Dynamics in LH2 Complexes of *Rps. acidophila* Containing Only One B800 Molecule," *J. Phys. Chem. B*, **105**, 7049 (2001).

2. T. Reinot, V. Zazubovich, J. M. Hayes and G. J. Small, "New Insights on Persistent Nonphotochemical Hole Burning and its Application to Photosynthetic Complexes," *J. Phys. Chem. B* (invited feature article) **105**, 5083 (2001).

3. V. Zazubovich, I. Tibe, R. J. Cogdell, and G. J. Small, "Bacteriochlorophyll *a* Franck-Condon Factors for the $S_0 \rightarrow S_1(Q)_y$ Transition," *J. Phys. Chem. B*, **105**, 12410 (2001).

4. V. Zazubovich, S. Matsuzaki, T. W. Johnson, J. M. Hayes, P. R. Chitnis, and G. J. Small, "Red Antenna States of Photosystem I from Cyanobacterium *Synechococcus elongatus*: A Spectral Hole Burning Study," *Chem. Phys.* **275**, 47 (2002).

5. V. Zazubovich, R. Jankowiak, and G. J. Small, "On B800→B800 Energy Transfer in the LH2 Complex of Purple Bacteria," *J. Luminescence*, **98**, 123 (2002).

6. J. M. Hayes, M. Ruehlaender, C. Soukalis, and G. J. Small, "Monte Carlo Simulation of Energy Transfer Rates: Application to Downward Energy Transfer within the 825 nm Absorption Band of the FMO Complex of *P. aestuarii*," *J. Luminescence*, **98**, 249 (2002).

7. R. Jankowiak, J. M. Hayes, and G. J. Small, "An Excitonic Pentamer Model for the Core $Q_y$-States of the Isolated Photosystem II Reaction Center," *J. Phys. Chem. B*, **106**, 8803 (2002).

8. V. Zazubovich, R. Jankowiak and G. J. Small, "A High-Pressure Spectral Hole Burning Study of Correlation between Energy Disorder and Excitonic Coupling in the LH2 Complex from *Rhodopseudomonas acidophila*," *J. Phys. Chem. B*, **106**, 6802 (2002).

9. R. Jankowiak, M. Rätsep, J. Hayes, V. Zazubovich, R. Picorel, M. Seibert and G. J. Small, "The Primary Charge Separation Rate at 5 K in Isolated Photosystem II Reaction Centers Containing 5 and 6 Chlorophyll *a* Molecules," *J. Phys. Chem. B*, **107**, 2068 (2003).

10. V. Zazubovich, R. Jankowiak, K. Riley, M. Seibert, R. Picorel and G. J. Small, "How Fast is Excitation Energy Transfer in the Photosystem II Reaction Center in the Low Temperature Limit: Hole Burning vs. Photon Echo," *J. Phys. Chem. B*, **107**, 2862 (2003).

# ELECTRON TRANSPORT INVOLVING CAROTENOID AND CHLOROPHYLL MOLECULES IN PHOTOSYSTEM II

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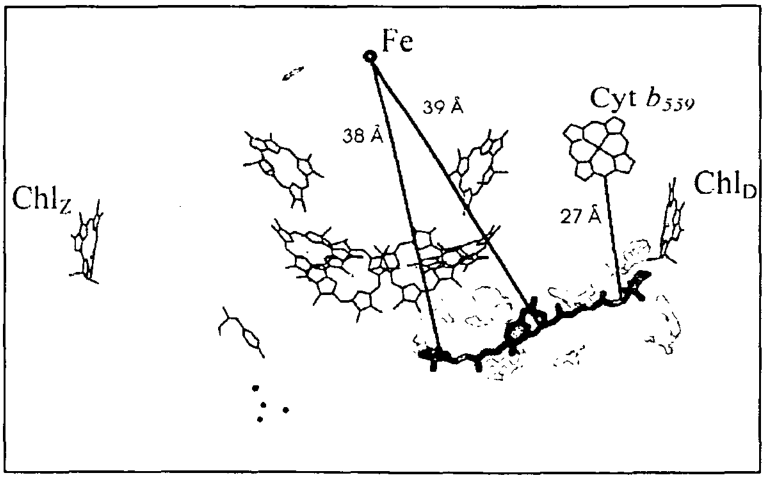
Carotenoids have long been known to function in photosynthetic systems as light-harvesting pigments, as photoprotective molecules in triplet energy-transfer processes, as singlet $O_2$ scavengers and as components that stabilize pigment-protein structures. Recently, photosystem II (PS II) has been found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

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

Previously, we demonstrated that high-frequency EPR spectroscopy (at 130 GHz), together with deuteration of PSII, yields resolved Car$^+$ and Chl$^+$ EPR signals.[3] Pulsed high-frequency EPR spectroscopy has been used to measure the location of Car$^+$ and Chl$^+$ relative to the non-heme Fe(II) in *Synechococcus lividus* PSII. Using the known tyrosine D (Tyr$_D$)-Fe(II) distance for calibration, the Car$^+$-Fe(II) and Chl$^+$-Fe(II) distances are estimated to be 38 ± 1 Å and ≥40 Å, respectively. The shorter distance of Car$^+$ to the non-heme Fe(II) than Chl$^+$ is consistent with the Car being an earlier electron donor to P680$^+$. Based on the observation that aromatic residues pack around carotenoid molecules in structurally characterized carotenoid-binding proteins, we identify two possible Car-binding sites in the PS II reaction center where there are clusters of aromatic residues ~38 Å from the non-heme iron. One of the potential Car-binding sites is located near Tyr$_D$ (see figure).



Cofactors in the PS II reaction center (pdb 1IZL), the cluster of aromatic amino acids (yellow) near Tyr$_D$ (blue), and a potential location of the redox-active β-carotene (pink).

Factor analysis of near-IR

absorption spectra indicates that two kinetically and spectroscopically distinct $Car^+$ are formed by illumination at temperatures from 20-160 K. $Car_A^+$ has an absorbance maximum of 982 nm and $Car_B^+$ has an absorbance maximum of 1027 nm. The near-IR spectrum of $Car^+$ shifts to shorter wavelength when $Tyr_D$ is oxidized which is explained by an electrostatic interaction between $Tyr_D^•$ and a nearby β-carotene that disfavors oxidation of $Car_B$. This result is in good agreement with the Car-binding site near $Tyr_D$ identified in our EPR distance measurements. The secondary electron donation pathways have been considered in light of these results and the recent X-ray crystallographic structures of PS II. This analysis suggests a novel electron-transfer pathway for the photooxidation of cytochrome $b_{559}$ (Cyt $b_{559}$) and chlorophyll Z ($Chl_Z$).

Future work is aimed at determining the rates and yields of the secondary electron transfer reactions in PS II. These data can then be correlated with the emerging structural information in order to understand the factors that tune the redox role of β-carotene in PS II. In addition, experiments are in progress to study the redox reactions of carotenoids in two new systems. In collaboration with Jim Allen at Arizona State University, we are reconstituting a series of photooxidizable carotenoids into bacterial reaction center proteins that have been engineered to have a very high potential primary electron donor. This will enable a systematic study of the factors important for the electron- vs. energy-transfer roles of carotenoids. In collaboration with Bruce Diner at DuPont, we are investigating carotenoid photooxidation in cyanobacterial mutants with altered carotenoid composition. Studies of these samples, in which the secondary electron transfer pathways in PS II have been modified, will provide new information of the sequence of secondary electron transfers and on their function.

## References

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

[2]Tracewell, C. A.; Brudvig, G. W. (2001) *Arch. Biochem. Biophys.* **385**, 61-69.

[3]Lakshmi, K. V.; Reifler, M. J.; Brudvig, G. W.; Poluektov, O. G.; Wagner, A. M.; Thurnauer, M. C. (2000) *J. Phys. Chem. B* **104**, 10445-10448.

## DOE-Supported Publications 2001-2003

1. "Electronic Structure of the $P_{700}$ Special Pair from High-Frequency EPR Spectroscopy", Oleg G. Poluektov, Lisa M. Utschig, Sandra L. Schlesselman, K. V. Lakshmi, Gary W. Brudvig, Gerd Kothe and Marion C. Thurnauer (2002) *J. Phys. Chem. B* **106**, 8911-8916.
2. "Pulsed High-Frequency EPR Study on the Location of Carotenoid and Chlorophyll Cation Radicals in Photosystem II", K. V. Lakshmi, Oleg G. Poluektov, Michael J. Reifler, Arlene M. Wagner, Marion C. Thurnauer and Gary W. Brudvig (2003) *J. Am. Chem. Soc.* **125**, 5005-5014.
3. "The X-ray Structure of Photosystem II Reveals a Novel Electron Transport Pathway Between P680, Cytochrome $b_{559}$ and the Energy-quenching Cation, $Chl_Z^{+}$", Sergej Vasil'ev, Gary W. Brudvig and Doug Bruce (2003) *FEBS Lett.*, submitted.
4. "Two Redox-Active β-Carotene Molecules in Photosystem II", Cara A. Tracewell and Gary W. Brudvig (2003) *Biochemistry*, submitted.

# *Posters*

**Poster # 1**

# SOLVENT SEPARATED RADICAL ION PAIRS AND FREE ION YIELDS: A TEMPERATURE DEPENDENCE STUDY

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Free ion yields of geminate ion pairs formed after photoinduced electron transfer quenching are measured by transient photocurrent in several polar solvents. 9,10-Dicyanoanthracene is used as the acceptor and alkyl-substituted benzenes as donors. It was found that, generally, there is no significant increase in free ion yield as the temperature increases. Based on a theoretical model developed by Hong and Noolandi (K. M. Hong and J. Noolandi, *J. Chem. Phys.* 68(1978), 5163-71) under Collins-Kimball boundary conditions (F. C. Collins and G. E. Kimball, *J. Colloid Sci.* 4(1949), 425-437), several key factors influencing free ion yields are analyzed. These include dielectric constants, viscosities of solvents, initial separation distances of geminate ion pairs and changes in recombination rates. We compared escape probabilities of geminate ion pairs calculated at different initial formation and recombination separation distances with measured free ion yields. It is clear that free ions are mainly produced from the solvent separated ion pairs (SSRIPs) that are initially formed after electron transfer quenching. The calculation also implies that recombination through tunneling at separation distances larger than 7 Å can be understood as the main decay process for SSRIPs (Figure 1). There is a direct competition between the above tunneling recombination and separation processes on ion pairs at that distance. Both calculated and measured photocurrent risetime indicate that the change in temperature has very limited influence on the recombination rate. On the other hand, the increase in temperature will decrease the viscosity of the solvent and increase the mobility of cations and anions significantly, which should, in turn, make a favorable contribution to the escape rates and free ion yields. Quantitative analysis indicates that the observed weak dependence of free ion yields on temperature can well be attributed to an unfavorable contribution from decreased dielectric constant at higher temperature.

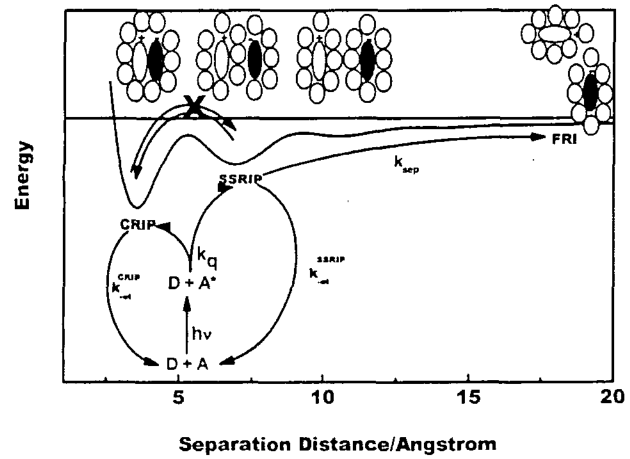

**Figure**. Schematic of free ion formation in medium-polarity solvent.

# TIME-RESOLVED X-RAY STUDIES AND DFT CALCULATIONS OF PHOTOINDUCED TRANSIENT EXCITED STATES

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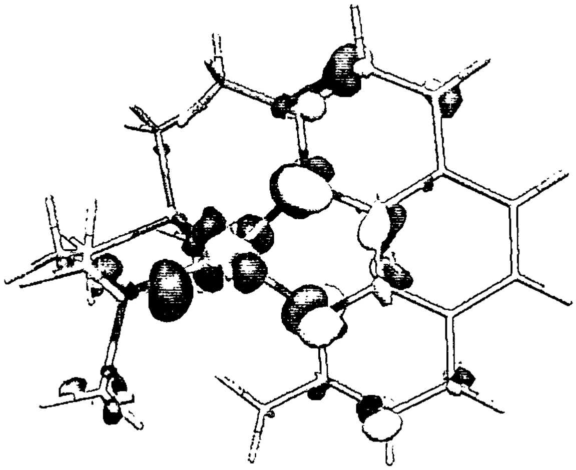
Time-resolved diffraction experiments have been combined with extensive DFT calculations of ground and excited states of molecular complexes. The X-ray experiments were initiated at the SUNY-X3 beamline at the National Synchrotron Light Source at Brookhaven National Laboratory[1] and continued at the CARS ID-15 beamline at the Advanced Photon Source at Argonne National Laboratory. The experiments are performed with monochromatic radiation and conducted at He temperature to provide maximal heat dissipation. Pulsed laser light is focused on a microcrystal of typically 50-80 μm diameter. Results include the shortening of the Pt-Pt distance upon excitation in the $[Pt_2(pop)_4]^{4-}$ ion (pop = pyrophosphate, $(H_2P_2O_5)^{2-}$),[2] and the distortion on metal-to-ligand charge transfer (MLCT) of Cu(I) complexes.[3] Parallel density functional calculations are performed with the ADF program package. For the $[Pt_2(pop)_4]^{4-}$ ion different functionals have been tested in order to select the optimal treatment for the calculation of excited state properties.[4] Calculations on the Cu(I) complexes shed light on the geometric relaxation after excitation and on the nature of the electron transfer.[5] Theoretical *electron-transfer* density maps indicate that in the Cu(I)bis-dimethylphenanthroline ion $(Cu(dmp)_2)^+$ the transferred charge density is essentially localized on the ligand nitrogen atoms, while in heteroleptic Cu(I)dmp diphos (diphos=1,2-bis(diphenylphosphino)ethane) complex the transferred charge is less localized and partially emanates from the phosphorous atoms, as illustrated in the figure (white surfaces positive, blue surfaces negative, surfaces at 0.005 au).

1) W. K. Fullagar, G. Wu, C. Kim, L. Ribaud, G. Sagerman and P. Coppens, *J. Synchr. Rad.* 7, 229-235 (2000).
2) C. D. Kim, S. Pillet, G. Wu, W. K. Fullagar and P. Coppens, *Acta Crystallogr. A* **58**, 133-137 (2002).
3) T. Graber, I Vorontsov, G. Wu, A. Kovalesky, M. Gembicky, Y.-S Chen and P.Coppens to be published.
4) I. Novozhilova, A. V. Volkov and P. Coppens, *J. Am. Chem. Soc.* **125**, 1079-1087 (2003).
5) I. Novozhilova and P. Coppens, to be published.



# LIGHT-INDUCED CHARGE SEPARATION AT THE SURFACE OF $TiO_2$/HOST-GUEST HYBRID NANOPARTICLES

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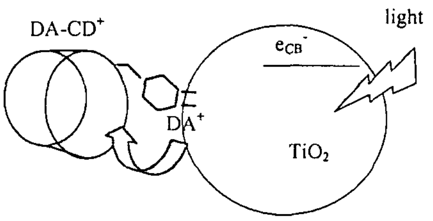
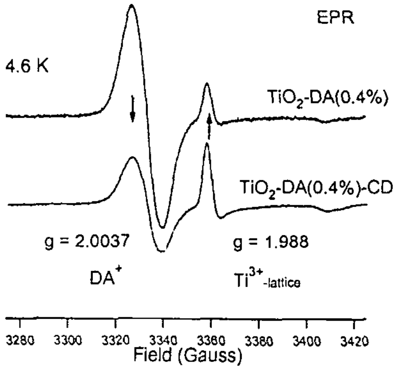
Successful photochemical energy conversion requires extended separation of photogenerated charges. In semiconductor nanoparticles the separation between photogenerated electrons and holes is limited by the particle size and results in fast recombination of charge carriers. Our approach to achieving enlarged separation distances is to remove one of the photogenerated charges such as valence band holes by strong coupling of electron-donating agents to the surface of $TiO_2$ nanoparticles (d = 45 Å). For this purpose, we linked β-cyclodextrin, β-CD, to $TiO_2$ particles. β-CD comprises seven glucopyranose units organized in a torus-like macro-ring structure. β-CD was chosen as a multiple charge relay for possible tailored semiconductor-receptor design. Due to the relative hydrophobicity of their inner cage, cyclodextrins are generally used as host molecules in host-guest inclusion complexes of water insoluble compounds. Bare $TiO_2$ particles were modified with β-CD linked to the surface Ti atoms through carboxyl groups attached to the cyclodextrin ring. EPR was used to examine light-induced charge separation in these surface-modified $TiO_2$ particles. It was found that upon photoexcitation of $TiO_2$, valence band holes localize at carboxyl groups of surface-conjugated cyclodextrin at 4 K. The photoinduced charge-transfer complex between $TiO_2$ and β-CD was not affected by the presence of adamantane in the cyclodextrin cavity, due to the unfavorable oxidation potential of adamantane ($E_{ox}$ = 2.96 V vs NHE). However, when ferrocene ($E_{ox}$ = 0.24 V vs NHE) was used as guest molecules the formation of ferricene was observed, revealing electron-transfer from guest molecules to $TiO_2$ nanoparticles. We also used dopamine as conduit from β–CD to $TiO_2$ nanoparticles. The linking of cyclodextrin to dopamine-modified $TiO_2$ was obtained by condensation of a carboxyl group of cyclodextrin with an amino group of dopamine. The EPR spectra revealed enhanced charge separation for dopamine-linked cyclodextrin, improving the efficiency of photoinduced charge-transfer reactions. The ability of electrons to reduce silver nitrate on the surface of particles was used to probe the efficiency of extended charge separation of photogenerated carriers at ambient temperature. Our results suggest potential use of hybrid $TiO_2$/cyclodextrin particles as selective molecular recognition charge-transfer relays for various host-guest inclusion complexes.





# SPECTROSCOPY AND DYNAMICS AT LIQUID INTERFACES

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The ubiquity of interfaces and their unique chemical and physical properties make them a field of intense scientific and technological activity. The special character of interfaces derives from their asymmetrical environment that results from the different bulk media making up the interface and from its molecularly thin dimensions. Our aim is to provide a molecular level description of dynamics at liquid interfaces by probing the motion of interfacial solvent molecules and organic adsorbates.

The spectroscopy and solvation dynamics of coumarin molecules at air/water and at charged amphiphile/water interfaces are obtained using the interface selective method of second harmonic spectroscopy. The solvation dynamics and spectrum of an infrared organic dye at a liquid/solid interface, namely the silica/acetonitrile interface will be discussed. It was found that the absorbance peak for the molecule IR144 shifts from 738nm in bulk acetonitrile to 803 +/- 1 nm at the silica/acetonitrile interface as obtained from second harmonic measurements. Figure 1. This red shift, found for IR144, which has a negative solvatochromism due to the fact that the dipole moment in the excited state is smaller than the ground state, indicates that the silica/acetonitrile interface is considerably less polar than bulk actetonitrile. The interface polarity of the silica/acetonitrile interface corresponds to a bulk polarity between hexane and toluene. It was found that the solvation dynamics was slower at the water interfaces than in bulk water whereas for acetonitrile at a solid silica interface the solvation dynamics was faster than in bulk acetonitrile.

The molecular orientational motions of adsorbed solute molecules were studied at air/water and at charged amphiphile/water interfaces. For the first time we succeeded in obtaining both the out of plane and in-plane motions of the adsorbed molecules. The orientational dynamics of coumarin was found to be slower than in bulk water suggesting that molecular friction experienced by the adsorbed coumarin was larger at the interface than in bulk water. Figure 2.

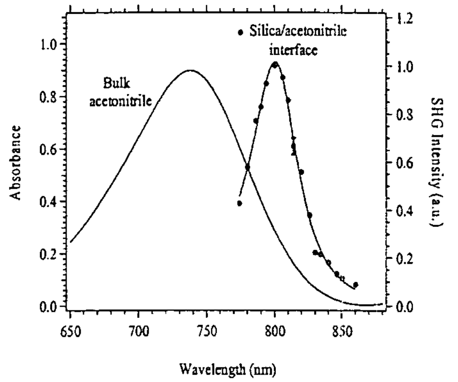

Figure 1

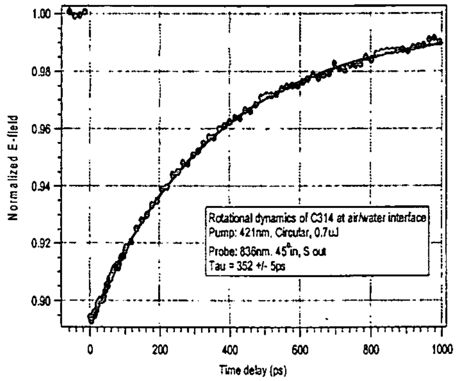

Figure 2

# TRANSITION METAL MLCT EXCITED STATE LIFETIMES: THE ROLE OF HIGH-FREQUENCY VIBRATIONAL MODES

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The lifetimes of potential donor excited states are among the many factors taken into consideration in the design of photosynthetic arrays. An important property of transition metal complexes is the appreciable number of configurationally different electronic excited states with somewhat similar energies. This property is probably important in the catalytic roles of transition metal complexes, but it can greatly complicate the determination of the factors that determine their charge-transfer excited state lifetimes. Thus, the short MLCT excited state lifetimes of some polypyridyl-ruthenium(II) complexes have often been attributed to similar in energy, metal centered *dd* excited states that relax to the ground state very efficiently. For example, the failure to detect MLCT luminescence in some am(m)ine-polypyridyl-ruthenium(II) complexes has commonly been attributed to the facile crossing to a near-in-energy *dd* excited state, since the energy of the *dd* excited states decreases markedly when a polypyridine is replaced by an am(m)ine. However, the MLCT absorption maxima also decrease in this same order, the emission maxima should decrease much more markedly due to the increasing reorganizational energies (Seneviratne, *et al., Inorg. Chem.* **2002**, *41*, 1502) and increases in the number of am(m)ines is expected to result in shortened MLCT excited state lifetimes owing to the increase in the number of high frequency H-H vibrational modes.

By using a calibrated InGaAs array detector-based luminescence system, we have found that the complexes $[Ru(bpy)_n(NH_3)_{6-2n}]^{2+}$ and $[Ru(bpy)_n(en)_{3-n}]^{2+}$ with n = 1 or 2 all exhibit MLCT emissions in 77 K glasses. The emission maxima of the tetraam(m)ines are weak and at about 800 nm, about 200 nm longer wavelength than the $[Ru(bpy)_3]^{2+}$ emission. The MLCT excited state lifetimes of these complexes decrease systematically with the number of N-H moieties. The emission bandwidths and bandshapes also change systematically, the bands are narrower and the vibronic contributions are smaller, as the number of N-H moieties is increased. This is consistent with increasing electronic delocalization and less excited state distortion through the series of complexes. While the values of the non-radiative relaxation rate constant increase in direct proportion to the number of N-H moieties, the isotope effects, $k_{NH}/k_{ND}$, are all about 2, an order of magnitude smaller than observed for the DACT emissions of the $[(Am)Cr^{III}(CN)Ru(NH_3)_5]^{m+}$ complexes (Endicott, *et al., Coord. Chem. Rev.* **2000**, *208*, 61). In the latter, $k_H/k_D$ is roughly proportional to the number of N-H moieties coordinated to the donor and acceptor centers. It is postulated that this contrast in isotope effects arises from some relaxation channel (possibly involving the C≡N stretch) that makes a Franck-Condon contribution comparable to that of N-D in the cyanide-bridged complexes, while no such high frequency relaxation channel is important for the polypyridyl complexes. Thus, the number of degenerate modes cancels in the latter, but not the former complexes.

**Poster # 6**

# TOWARD QUANTUM DOT / SINGLE-WALL NANOTUBE ARCHITECTURES

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J. Nedeljkovic, M. Jones, O.I. Micic, G. Rumbles, A.J. Nozik, and M.J. Heben

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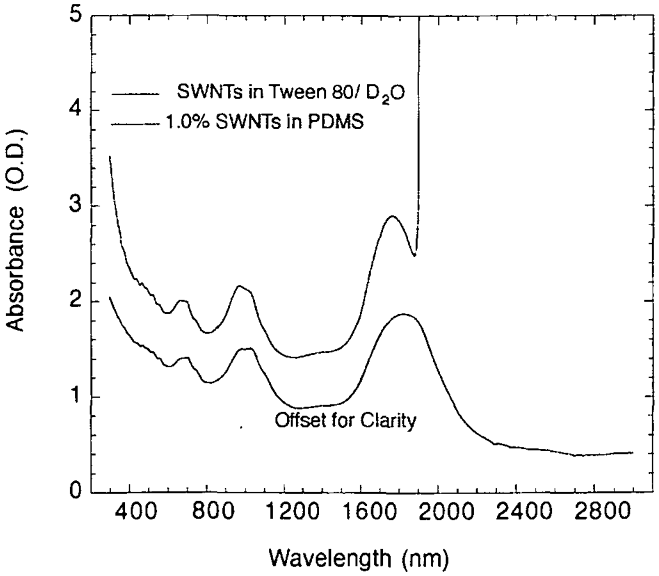
We are interested in using colloidal semiconductor quantum dots (QDs) and carbon single-wall nanotubes (SWNTs) as nanoscale building blocks for managing charge and energy transfer during solar energy conversion. QDs can be fabricated from a variety of materials, in controlled sizes, with discreet 3-D quantized energy levels and well-defined surface terminations, and therefore offer a diverse range of electronic and optical properties. SWNTs are available in both semiconducting and metallic conformations, in diameters ranging from 0.7 to 2 nm with a size-dependent 2-D quantized density of states, and may therefore be useful for "wiring-up" quantum dots.

The optical characterization of QD/SWNT composite films prepared previously by co-precipitating the nanoscale building blocks from pyridine was hampered by a luminescence signal associated with entrapped pyridine oligomers. Currently, a new procedure yields cleaner composites, but the optical characterization is still limited by the high optical density and by tube-tube interactions even for very thin films of SWNTs. SWNTs typically exist in dense bundles with the number of tubes per bundle increasing with the purity of the laser-grown materials. Optical absorption or fluorescence measurements in transmission require bundles to be broken-up to produce isolated, stable suspensions of SWNTs that are homogeneous on a nanoscale. Two general approaches involve; (i) cutting SWNTs into short segments and applying ultracentrifugation and surfactants, and (ii) dispersions in polymers. In the surfactant approach we followed the work of Smalley et al. (Science **2002,** *297*, 593) and dispersed purified, laser grown SWNTs in $D_2O$-surfactant solutions. Alternatively, uncut purified samples were dispersed in Nafion or polydimethylsiloxane (PDMS). The solution- and polymer/SWNT dispersions yielded similar, well-resolved optical absorption spectra, with the PDMS sample permitting investigation deeper into the infrared (figure). The surfactant stabilized samples yielded reproducible transient absorption (TA) spectroscopy signals which were in good agreement with the linear absorption data and the TA results from the previously measured Nafion-suspended samples.

The development of these dispersion methods provide two different routes toward assembling QDs and SWNTs. The surfactant solubilized samples can be directly combined with ZnS capped CdSe dots in aqueous solutions, while the polymer solubilized SWNTs can be combined with InP dots in non-aqueous solutions. Raman, photoluminescence excitation spectroscopy, TEM, and TA spectroscopy can be used to probe the QD/SWNT contact and the charge carrier dynamics.



# PHOTOCHEMISTRY OF NICKEL PORPHYRINS: DYNAMICS OF LIGATION AND DELIGATION

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Distortions from planarity are increasingly implicated as contributing to the electronic properties of porphyrins in vivo and in vitro. Nickel porphyrins offer some of the most striking examples of the (photo) physical and chemical consequences of such distortions. Photosynthetic reaction center and light-harvesting complexes, and heme proteins have recently been reconstituted with Ni (bacterio) chlorophylls and porphyrins which serve both to modulate electron or energy transfer and to act as spectroscopic probes. The Ni chromophores are typically ligated by nearby residues (histidines, e.g.) in the protein.

To probe the interplay between nonplanarity, axial ligation and excited states, the ground and excited state metal-axial ligand dynamics of nonplanar Ni (II) 2, 3, 5, 7, 8, 10, 12, 13, 15, 17, 18, 20-dodecaphenylporphyrin (NiDPP) and two fluorinated analogs ($NiF_{20}DPP$ and $NiF_{28}DPP$) have been investigated by time-resolved absorption spectroscopy in ligating media.

Because of the electronic consequences of nonplanarity, NiDPP does not bind axial ligands in the ground state but metal coordination does occur after photoexcitation to the Ni (d, d) state with dynamics that depend on the basicity, aromaticity and steric encumbrance of the ligand: 25, 55 and 85 ps in pyridine, piperidine and 3, 5 lutidine, respectively. Subsequently, ligand release occurs to reform the unligated NiDPP in competition with conformational / electronic relaxation to the ground state of the still coordinated photoproduct which then releases the ligands.

In sharp contrast to the behavior of NiDPP, $NiF_{20}DPP$ and $NiF_{28}DPP$ do coordinate axial ligands in the ground state (because of the multiple electron-withdrawing fluorines) and *eject* them after photoexcitation, followed by slow rebinding (>5ns) to yield the ligated ground state.

Ground state crystal structures of NiDPP, $NiF_{20}DPP$, $NiF_{20}DPP(pyridine)_2$, $NiF_{28}DPP$, and $NiF_{28}DPP(pyridine)_2$ illustrate the different conformations that the chromophores can adopt in the ligated and unligated states and thus offer previews into the likely structural landscapes of the excited states.

Collectively, these results demonstrate the sensitivity with which the electronic and structural characteristics of the macrocycle can govern and fine-tune the photophysical and chemical properties of porphyrins.

**Poster # 8**

# FORWARD AND BACK ELECTRON TRANSFER IN LIQUIDS: ULTRAFAST MEASUREMENTS OF PHOTOINDUCED ION GENERATION AND DECAY

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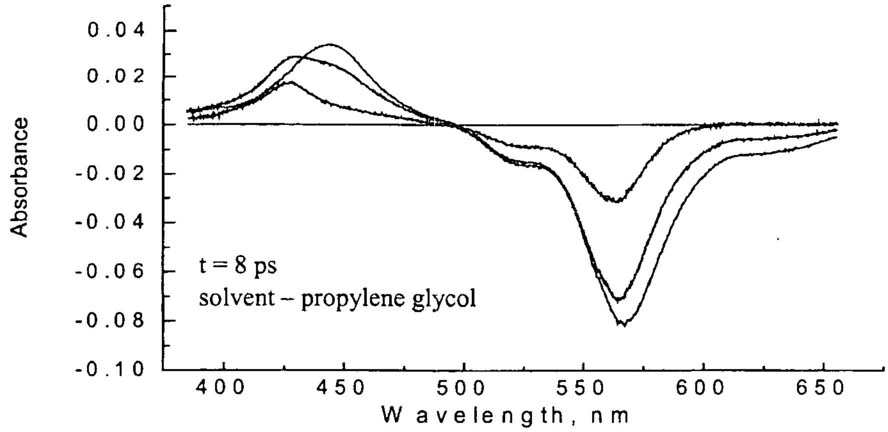
Ultrafast transient absorption and stimulated emission experiments are employed to examine photoinduced electron transfer and geminate recombination between donor and acceptor molecules in several liquid solutions. Rhodamine 3B ($R3B^+$) is optically excited and an electron is transferred from dimethylanaline (DMA).

$$R3B^+ + DMA + h\nu \rightarrow R3B + DMA^+$$

Following electron transfer, geminate recombination depletes the $DMA^+$ concentration.

$$R3B + DMA^+ \rightarrow R3B^+ + DMA.$$

The process is followed using a Ti:Sapphire/OPA/white light/monochromator-CCD system that covers the entire visible spectrum. The forward process is observed by monitoring the simulated emission from $R3B^+$, which tracks the decay of the initially prepared excited state.



In the figure, the red curve is the $R3B^+$ difference spectrum with no acceptors showing the ground state bleach (570 nm) and an excited state absorption (450 nm). The blue curve is with 0.3 M DMA. A new absorption, $DMA^+$, appears at ~425 nm. The black curve is the difference of the red curve and the blue curve after proper normalization. The black curve shows the $DMA^+$ radical ion spectrum and the ground state bleach of $R3B^+$ caused by electron transfer.

A detailed theoretical treatment of photoinduced electron transfer and geminate recombination, which has been developed over the last number of years, is used to analyze the time dependence of the forward electron transfer and the back electron transfer for solvents of low to high viscosity. The theory includes the distance dependence of electron transfer, diffusion of the species, the radial distribution function, and the hydrodynamic effect. Past experiments examined only forward transfer on time scales >60 ps. In those experiments, excellent agreement was obtained between theory and experiment. The new results show excellent agreement with theory for low viscosity samples to subps time scales, but there are significant deviations for times <50 ps for high viscosity samples. At the time of this writing, preliminary experiments indicate that there may be an angular dependence to the electron transfer that is important in the high viscosity samples in which orientational relaxation is slow. The time dependence of the appearance and the decay of the $DMA^+$ radical cation population is being compared to the theoretical description of geminate recombination.

**Poster # 9**

# PHOTOCATALYZED REDUCTION OF $CO_2$ WITH A PHTHALOCYANINE HOMOLOGUE

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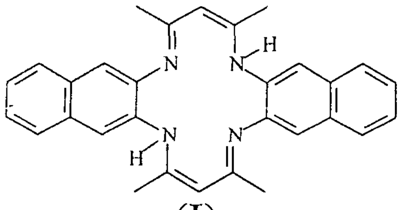
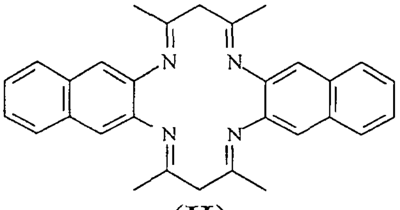
Deaerated solutions of Ni(II) and Cu(II) complexes of the Napho$_2$[14]-2,4,6,9,11,13-hexaeneN$_4$, (I), macrocycle exhibited medium-dependent luminescence when they were irradiated at 337 or 351 nm in $CH_3CN$. The addition of $Cu(CH_3CN)_6^{2+}$ in increasing concentrations resulted in the formation of a ground state adduct and led to a blue shift in the emission spectrum. It also caused a progressive quenching of the luminescence. Steady state irradiations of the Ni(II) and Cu(II) Napho$_2$[14]-2,4,6,9,11,13-hexaeneN$_4$ complexes at 370 nm induced a minor conversion among tautomeric forms, (II) - (IV). Transient photochemical products with lifetimes of several hundred ns were observed via flash photolysis and assigned as metal-ligand radical species. The photoreduction of $CO_2$ to CO in methanol was catalyzed by Ni(II) complexes of (I) and 2,4,9,11-tetra(1,1'-dimethylethyl)-Napho$_2$[14]-2,4,6,9,11,13-hexaeneN$_4$. In these experiments, the charge transfer excited state of $Ru(bipy)_3^{2+}$ was used as the reductant of the Ni(II) complexes and 2,2',2"-nitrilotriethanol was used as a sacrificial donor. Intermediates in these reactions were investigated by pulse radiolytic and flash photochemical procedures. Flash irradiations at 351 nm of the Ni(II) and Co(III) complexes in methanol resulted in the oxidation of the solvent. Similar Ni(II) ligand-radical species were produced in the photolysis of the complexes or when the radiolytically generated $CH_2OH^{\cdot}$ radicals reacted with them. The pulse radiolysis and flash photolysis-generated Ni(II) ligand-radical transients incorporated $CO_2$ and the resulting species could mediate in the formation of CO.



(I)



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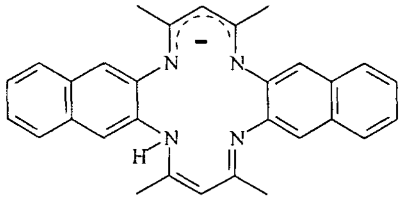
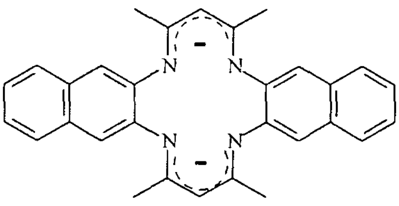


(III)



(IV)

Poster # 10

# INFLUENCE OF NETWORK GEOMETRY ON ELECTRON-TRANSPORT DYNAMICS IN MESOPOROUS NANOPARTICLE SOLAR CELLS

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The effect of nanoparticle network topology in models describing electron transport has been generally ignored. Electrons are presumed to diffuse in three dimensions, restricted by the macroscopic dimensions of the film and electrostatic interaction with the electrolyte (ambipolar diffusion). The principal factor limiting electron transport is assumed to be trapping in localized states. In this paper, we describe the first clear evidence that network geometry strongly influences the electron-transport dynamics in dye-sensitized nanoparticle $TiO_2$ solar cells and show that percolation theory describes quantitatively this influence. The dependence of the electron-transport dynamics on film porosity was modeled using simulated mesoporous $TiO_2$ films and the random-walk approach, and the predicted results were in quantitative agreement with transient photocurrent measurements. Both the experimental measurements and simulations of electron transport are explained in terms of percolation theory, which predicts a power-law dependence of the electron diffusion coefficient on the film *porosity* with respect to some critical value of the porosity (i.e., a percolation threshold). It is shown that as the porosity increases, electron transport becomes slower owing to a longer path length for transport through the nanoparticle network. This study establishes that even within a multiple-trapping framework, the network geometry has a significant effect on the electron-transport dynamics.

**Poster # 11**

# VISIBLE LIGHT-ABSORBING Ti(IV)-O-Ni(II) MMCT CHROMOPHORE COVALENTLY ANCHORED ON MCM-41 SIEVE

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Excited states redox properties of transition metals that are either part of the framework or covalently anchored on the inner surface of micro or mesoporous materials offer new opportunities for demanding photosynthetic transformations. The M41S family of mesoporous silicates has opened up the preparation of transition metal sieves by covalent anchoring (grafting) of isolated metal centers on the pore surface via oxo bridges. This method of introducing robust transition metal chromophores and redox centers into the sieve is very general, but the majority of materials have been prepared so far by using organometallic precursors. Grafting of the latter requires calcination, a procedure that often precludes the selection of well-defined oxidation states, an important aspect in the case of photochemical applications. This holds especially for metals like Ru or Ni that feature a whole series of accessible oxidation states.

In attempts to covalently attach Ni(II) and Ru(III) centers on the pore surface of MCM-41 silicate sieve, we found ion-exchange of the corresponding aqueous ammine complexes under basic conditions to afford up to tripodal anchoring of the metal center via oxo bridges to Si. In the case of Ru(III), the hexammine or the $Ru(NH_3)_5Cl$ complex was used, while $Ni(NH_3)_6$ was the starting material for Ni(II) grafting. The anchoring consists of replacement of $NH_3$ (or Cl) by surface siloxy groups as inner sphere ligands. No formation of polymeric Ni silicate structures was observed, a problem encountered previously in the case of amorphous silica. This work demonstrates that simple coordination complexes free of organics can be used for accomplishing covalent attachment of single metal centers on a mesoporous silicate sieve in high yield.

The structure and the step-by-step process leading to surface-anchored metal centers was established by in-situ FT-IR, UV-Vis, and XANES spectroscopy. In the case of Ni(II) grafting, the observed red shifts of the d-d peaks, which are very sensitive to the ligand field or distortion from octahedral symmetry, allowed us to determine the step-wise covalent anchoring of the complex to the pore surface. In addition, the intensities of the $NH_3$ infrared ligand absorptions gave a direct count of the ligands replaced by the surface siloxy groups. The combined optical and infrared information showed that the Ni centers are dipodally anchored in the presence of $H_2O$ solvent, but reversibly form tripodal attachment upon removal of the solvent from the pores. When conducting the grafting of Ni(II) centers onto MCM-41 silicate sieve containing tripodally anchored Ti-OH groups, a new optical absorption was observed. It starts around 320 nm and shows a long tail extending beyond 600 nm in the red. The absorption, which is absent in the corresponding monometallic materials, is attributed to the Ti(IV)-O-Ni(II)→ Ti(III)-O-Ni(III) MMCT chromophore. This result demonstrates that MMCT moieties with the metal in a selected oxidation state can be assembled and anchored in mesoporous silicates by a simple step-wise grafting procedure.

# THEORETICAL STUDIES OF ELECTRON TRANSFER AND OPTICAL SPECTROSCOPY IN COMPLEX MOLECULES

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Our most recent work has been focused on the application of density functional (DFT) cluster methods to nanoparticles and solids. We have made a lot of progress with regard to methods development in that our codes now run reliably for materials type systems in the 100-200 atom range, and that we can treat ionic systems (e.g. metal oxides) effectively via a quantum cluster embedded in a matrix of classical ions. We are furthermore in the process of exploring calculations in the 200-300 atom regime which appears to be accessible via the use of increased memory in our PC cluster, which we use for the great majority of calculations. Following is a description of the two major applications that we have been pursuing. The work discussed below has been performed in collaboration with Prof. Louis Brus.

**Semiconductor Clusters:** We have carried out extensive modeling of silicon nanoclusters using DFT methods. Our first publication in this area has appeared recently, and several more are in preparation. Initially we studied the effects of passivation of the Si surface with hydrogen, fluorine, and hydroxyl groups, and were able to explain for the first time the dramatic difference in bandgap for oxygen that has been observed experimentally. More recently we have been investigating defects and doping in nanoclusters, examining a variety of issues including defect structures, energetics of various spin states at the defect site, and the new electronic states arise when a single atom of phosphorus or aluminum is introduced into a nanoparticle. Various charge states of the particle have been examined as well as effects of locations of the defect or dopant (interior vs. surface). Ultimately the goal is to understand the electronic states of these nanoparticles as a function of size, structure, and chemical composition, make comparisons with experimental data to validate the methodology, and gain insights that will facilitate device design.

**Work Function of the $TiO_2$ Anatase Surface:** We have carried out self-consistent embedding calculations of the anatase surface of $TiO_2$. The surface structure was generated using the VASP program, a plane wave DFT code that complements our embedding methods (which are much more suitable for studying models with net charge). The work function was computed as a function of cluster size, and convergence was demonstrated with regard to both the cluster surface area and depth. The results are in good agreement with indirect experimental estimates (no direct experiments have been carried out for this particular surface).

Poster # 13

# REACTIVITY OF LIGAND RADICALS PRODUCED BY PHOTOINDUCED Re-Re BOND HOMOLYSIS: EXPERIMENTAL AND THEORETICAL INVESTIGATION

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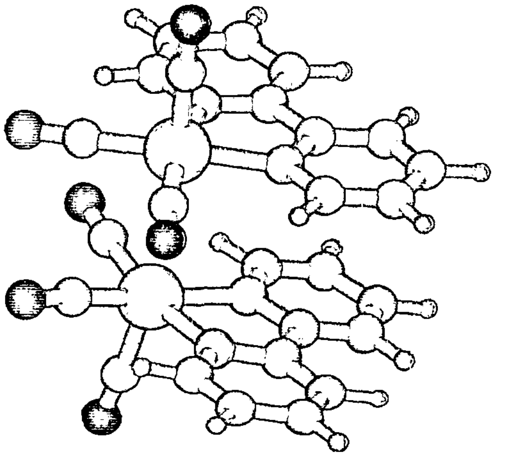
Rhenium(I) diimine complexes have been shown to act as photocatalysts and/or electrocatalysts for $CO_2$ reduction to CO. We have found that the one-electron-reduced species, $Re(dmb)(CO)_3S$ (dmb = 4,4′-dimethyl-2,2′-bipyridine and S = solvent), where the odd electron resides on the ligand, reacts with $CO_2$ to form the dinuclear species, $(CO)_3(dmb)Re\text{-}CO(O)\text{-}Re(dmb)(CO)_3$, as an intermediate in the $CO_2$ reduction system. When $CO_2$ is not present, $Re(dmb)(CO)_3(THF)$ and $Re(bpy)(CO)_3(THF)$ (where bpy = 2,2′-bipyridine) dimerize with rate constants $k_d = 40 \pm 5$ and $21 \pm 7$ $M^{-1}$ $s^{-1}$, respectively, in THF. The dimerization processes are strikingly slow compared to those of typical metal radicals ($k_d \cong 10^9$ $M^{-1}$ $s^{-1}$). Activation parameters for the dimerization reaction are $\Delta H^{\ddagger} = 11$ kcal·$mol^{-1}$, $\Delta S^{\ddagger} = -14$ eu for $Re(dmb)(CO)_3(THF)$ and $\Delta H^{\ddagger} = 14$ kcal $mol^{-1}$, $\Delta S^{\ddagger} = -5$ eu for $Re(bpy)(CO)_3(THF)$. If the dimerization process proceeds *via* a preequilibrium with the Re centered radical, the equilibrium constant (*i.e.*, between $Re(diimine^{\bullet})(CO)_3(THF)$ and $Re^{\bullet}(diimine)(CO)_3$) is $10^{-4} - 10^{-5}$ favoring the ligand-centered radical. In flash photolysis experiments on $[Re(dmb)(CO)_3]_2$, we did not see the formation of long-lived $Re(dmb^{\bullet})(CO)_3S$, consistent with the low quantum yield of the homolysis determined by the CW photolysis.



We have performed B3LYP hybrid DFT and fully *ab initio* RHF/MP2 calculations on several conformations of the $[Re(bpy)(CO)_3]_2$ dimer (*cis*, *trans*, skewed *cis*, skewed *trans*), and for the constituent monomer radical and anion. Although the skewed *trans* conformer (*i.e.*, *trans* conformer rotated about the Re-Re bond by 41 degrees) is calculated to be the lowest-energy structure (by less than 3 kcal/mol at the B3LYP level of theory with solvation by THF), the experimental infrared spectrum and photochemical properties of the $[Re(CO)_3(dmb)]_2$ dimer are best described by the calculated properties of the skewed *cis* conformer (*i.e.*, *cis* conformer rotated about the Re-Re bond by 56 degrees, see figure) in which the first antibonding Re-Re unoccupied orbital is LUMO+29. Although the HOMO in all the dimer conformations is a Re-Re σ bonding orbital, the HOMO of the monomer radical is largely delocalized onto the bipyridine ligand while retaining some Re *d* orbital character. The HOMO in the monomer anion has even more delocalization of its pair of electrons. The monomer radical binds THF in the sixth coordination site, but the monomer anion does not. This fact suggests that the extremely slow dimerization rate of the monomer radical may arise from the solvent blocking the binding site (*i.e.*, the equilibrium concentration of 5-coordinated monomer being very small).

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**Poster # 14**

# N-TYPE DOPING OF A LIQUID CRYSTAL PERYLENE DIIMIDE

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We show that the conductivity of liquid crystal perylene diimide (PPEEB) films can be increased by ~10 orders of magnitude by doping with 1 mol% of a zwitterionic perylene diimide. The charge of the "free" electron on the dopant is neutralized by a covalently bound positive charge, the immobility of which is a requirement for stable doping. EPR studies show that the dopant exists in monomeric form in solution by itself, but forms aggregates with the PPEEB. Thus, there is a strong driving force to delocalize the electron over multiple chromophores. The spin density of the doped films increases approximately linearly with increasing dopant concentration but the conductivity increases much more rapidly. We explain this with a model that treats the electrostatic changes in the film caused by the increasing dopant concentration, resulting in:

$$\sigma = q\, \mu_e\, n_d \exp(-E_{a,max}/kT) \exp(q^2 n_d^{1/3}/2\pi kT\varepsilon\varepsilon_o)$$

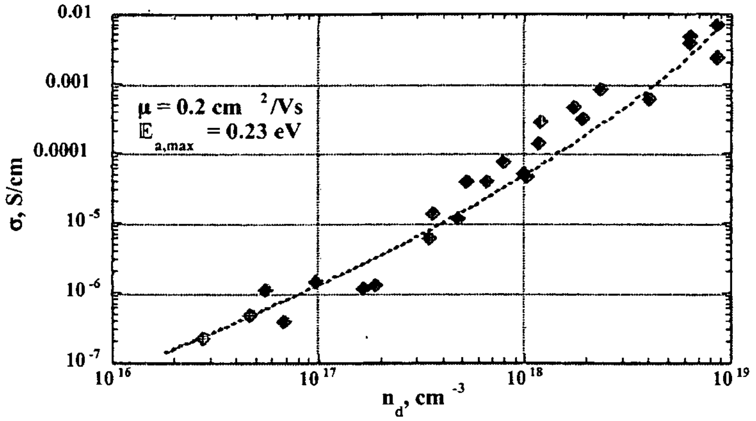

**Figure.** Experimental conductivity of PPEEB films (at 0.9 V/μm) versus dopant concentration, data are fit to the equation above.

The superlinear increase in conductivity with doping concentration is expected to be a universal attribute of excitonic semiconductors. This follows directly from the characteristics that define excitonic semiconductors: the strong electrostatic attraction between opposite charges and the relatively localized wavefunctions of the charge carriers. Together, these factors result in the creation of strongly bound electron-hole pairs (excitons) upon light absorption, and in the creation of charge carriers that are strongly bound to their conjugate dopant molecules upon doping. These same factors are also expected be important in the interpretation of a number of other experiments.

**Poster # 15**

# CONTROL OVER ENERGY AND ELECTRON TRANSDUCTION IN DENDRITIC DONOR-ACCEPTOR ENSEMBLES

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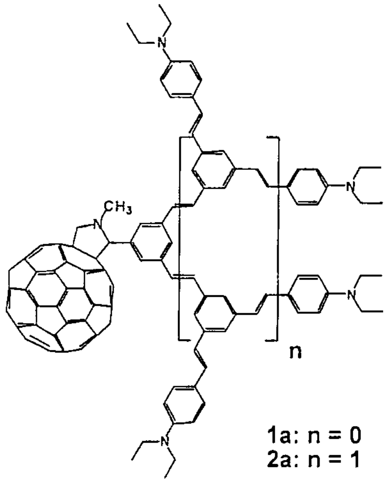
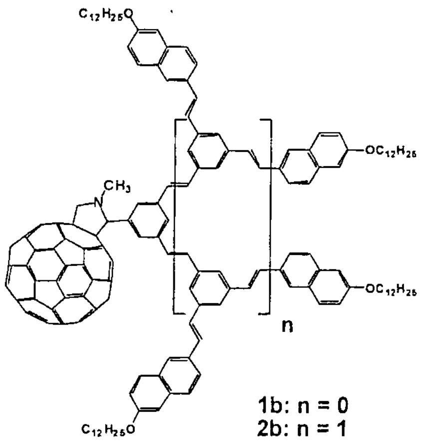
Several generations of phenylenevinylene dendrons, covalently attached to a $C_{60}$ core, have been developed as synthetic model systems with hierarchical, fine-tuned architectures. End-capping of these dendritic spacers with dibutylaniline or dodecyloxynaphthalene – as antennas / electron donors – yielded new donor-bridge-acceptor ensembles in which, one, two, or four donors are allocated at the peripheral positions of the well-defined dendrons, while the electron accepting fullerene is placed at the focal point of the dendron.

Photophysical investigations show that in all dyads, an efficient and rapid transfer of singlet excited state energy ($6 \times 10^{10} - 2.5 \times 10^{12}$ $s^{-1}$), as confirmed in a series of steady-state and time-resolved photolytic experiments, dominates the deactivation of the initially excited dendron antennas, generating the fullerene singlet excited state in nearly quantitative yields. A detailed spectroscopic and kinetic analysis prompts, nonetheless, to an alternative intramolecular electron transfer, from which an energetic $C_{60}^{\bullet -}$-dendron$^{\bullet +}$ radical pair evolves. Most importantly, variation of the energy gap modulates the character of this electron transfer reaction: Depending on the energetic position of the $C_{60}^{\bullet -}$-dendron$^{\bullet +}$ radical pair either a competitive (*i.e.*, **1b, 2b**) or a sequential pathway (*i.e.*, **1a, 2a**) is activated.

Our strategy to devise 1st and 2nd generations of $C_{60}$-(dendron) ensembles demonstrates that significantly higher absorption cross-sections (**2a,2b**) and stabilization of an efficiently formed $C_{60}^{\bullet -}$-dendron$^{\bullet +}$ radical pair (**2a**) are achieved. Considering the overall efficiency of 76 % for *(i)* funneling light from the antenna chromophores to the fullerene core and *(ii)* charge-separation evolving from the fullerene singlet excited state this model systems reproduces natural photosynthesis very well.



1a: n = 0
2a: n = 1



1b: n = 0
2b: n = 1

# NEXT GENERATION STRATEGIES FOR ORGANIZING QUANTUM DOTS WITH ENGINEERED PROTEINS

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The future use of quantum dots in novel electronic devices will require large arrays of known order and dimension. Assembling these arrays is non-trivial and requires knowledge of the forces governing interaction of inorganic and organic molecules at the nanometer scale. In this presentation, we report the successful attachment of protein-stabilized quantum dots to tobacco mosaic virus (TMV) particles confirmed by scanning transmission electron microscopy (STEM) and propose that viral "raceways" may be used to order scaffolding proteins conjugated to quantum dots.

In fy2002, we pioneered a method for treating CdSe(ZnS) quantum dots with genetically modified cohesin protein polymers which resulted in hard/soft conjugates capable of remaining stable and dispersed at pH 6.5 in aqueous buffer. These conjugates also withstood chromatographic column fractionation, which permitted samples of quantum dot clusters and single quantum dots to be separated and analyzed spectrophotometrically. As a consequence of conducting the examination of grids from electron microscopy, we realized that at low dilution the protein polymer wrapped quantum dots were binding tightly to the TMV particles added as size standards. All viruses contain nucleic acid, either DNA or RNA (but not both), and a protein coat or capsid, which encases the nucleic acid. It is to this protein coat that the cohesin polymer cloud surrounding the quantum dots interacts. Although not confirmed at this time, we propose that the poly histidine tags used to conjugate cohesin proteins to the CdSe(ZnS) quantum dots also facilitated strong binding to the slightly negatively charged surface of the TMV particles.

There are predominantly two kinds of shapes found among viruses: rods, or filaments, and spheres. The rod shape is due to the linear array of the nucleic acid and the protein subunits making up the capsid and TMV rods can be from 150 to 5000 Å in length. The viral spherical shape is actually a 20-sided polygon (icosahedron) and may also pose some interesting dimensional options for our project. Because the protein polymer (single) quantum dots are about 120 to 160 Å in diameter and the TMV measures 170 Å in width, localizing quantum dots on short TMV fragments should place them in close proximity, although the protein wraps will prevent actual contact between quantum dots surfaces. Once the TMV-protein quantum dot fractions have been prepared, photoluminescence analysis will be carried out to determine the nature of energy dispersion from this system.

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Poster # 17

# POROUS DYE FRAMEWORKS FOR PHOTOELECTROCHEMICAL ENERGY CONVERSION

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Photoelectrochemical solar cells based on sensitization of high area titanium dioxide electrodes with surface-bound molecular dyes often display very good injection yields and high incident-photon-to-current conversion efficiencies. At the same time, they generally display low photovoltages and, therefore, lower than hoped for overall energy conversion efficiencies. One of the factors responsible for low photovoltages is the overpotential required to drive the oxidized dye/iodide regeneration reaction. Another is the preponderance of electron traps having energies well below the photoelectrode's conduction band edge energy. Notably, the electrode's very high area and porous nanocrystalline morphology – properties that make possible efficient light collection and high photocurrents – are also the properties primarily responsible for the deleteriously high trap populations.

To overcome the trap and photovoltage problem without sacrificing light collection and photocurrent production we have been developing and exploring an alternative strategy – one based on low area (and low trap density) photoelectrodes and intrinsically porous, high area dye frameworks. Building blocks for the frameworks are porphyrins organized as molecular squares using high-yield supramolecular coordination chemistry. The squares feature greater than 20 angstrom diameter cavities that, within an assembled dye framework, motivate efficient ion transport. This poster will focus on the fundamental photochemical and photophysical behavior of these frameworks, especially their energy transfer, electron injection, and dye regeneration behavior. An unexpected but instructive outcome of preliminary photoelectrochemical studies is the discovery of special experimental conditions where the photoelectrodes run backwards, i.e. very substantial photocurrents of opposite sign to the intended currents are generated. The findings and the accompanying mechanistic information have been of real value to us in terms of understanding how to optimize current yields from the high-area dye frameworks and low-area electrodes under conventional experimental conditions.

# MULTICHROMOPHORIC AND NONEQUILIBRIUM GENERALIZATION OF THE FÖRSTER-DEXTER THEORY FOR EXCITATION ENERGY TRANSFER REACTION

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Recent interest in nanoscale luminescent materials has brought renewed interest in the excitation energy transfer (EET) reaction between multichromophoric macromolecules. The fundamentals of the EET kinetics were established by Förster and Dexter, which have enabled main conceptual understandings of the EET kinetics in general. However, the Förster-Dexter (FD) theory in its present form lacks two crucial aspects that are of prime importance in many of modern experimental systems: (i) the multichromophoric nature of the energy donor and/or acceptor, and (ii) the nonequilibrium effects induced by an ultrafast laser excitation of the donor. While increasing number of spectroscopic results provide examples of EET in light harvesting complexes, conjugated polymers, and dendrimers, which are in qualitative agreement with the FD theory, quantitative deviations from the theory are also significant. The present work provides a generalization of the FD theory that can account for the multichromophoric and nonequilibrium nature of the EET kinetics so as to explain the experimental results more quantitatively on a rigorous theoretical ground.

The main result of the theory is that the reaction rate can be expressed as a sum of overlap integrals between functions characterizing the emission of the donor and the absorption of the acceptor, as in the case of Förster's spectral overlap expression. However, the expression involves matrix elements of Green functions, rather than single line shape profiles. Therefore, simple experimental line shapes for unpolarized radiation are insufficient for the determination of the reaction rate. At least, line shape profiles for different polarizations are necessary for unambiguous characterization of the reaction rate. For photo-induced situations, the theory also shows that the Green functions corresponding to the stimulated emission rather than those for the stationary emission should be used. Other important and new features are the interplay between intramolecular quantum coherence and the intermolecular kinetics manifest in the nonequilibrium contribution, and nontrivial distance and temperature dependence of the reaction rate that vary with the specifics of a system. Calculations for simple model systems are presented to illustrate these new aspects, which can also provide guidance in designing an optimal structure so as to maximize the EET rate.

**Poster # 19**

# PHOTOENHANCEMENT OF LUMINESCENCE IN COLLOIDAL CdSe QUANTUM DOT SOLUTIONS

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Enhancement of the photoluminescence (PL) of colloidal CdSe and core(shell) CdSe(ZnS) quantum dots has been observed when the dots are illuminated above the band gap energy. The effect occurs in dots suspended in a variety of organic or aqueous environments and is illustrated in Figure 1. Repeated measurements of the steady state PL, during constant illumination at 488nm from an $Ar^+$ laser, revealed that the PL quantum yield peaked at up to 60 × that of the original solution and, if illumination continued, subsequently declined slowly due to photo-oxidation. When returned to the dark, the PL reverted back to near its original value. The rate and magnitude of photoenhancement is found to depend on the illumination wavelength, the presence of a ZnS shell, the solvent environment and on the concentration of surfactant molecule; e.g., addition of methanol to a hexane solution of TOPO capped CdSe(ZnS) quantum dots causes the rate photoenhancement to increase markedly.

Time-resolved measurements of the fluorescence decay reveal nonexponential kinetics and an average lifetime that lengthens during the illumination period and shortens when returned to darkness. Stabilization of surface trap states, lengthening their average lifetime, could occur by light activated rearrangement of surfactant molecules, thus increasing the probability of thermalization back to the emitting exciton ground state and enhancing the quantum dot PL.

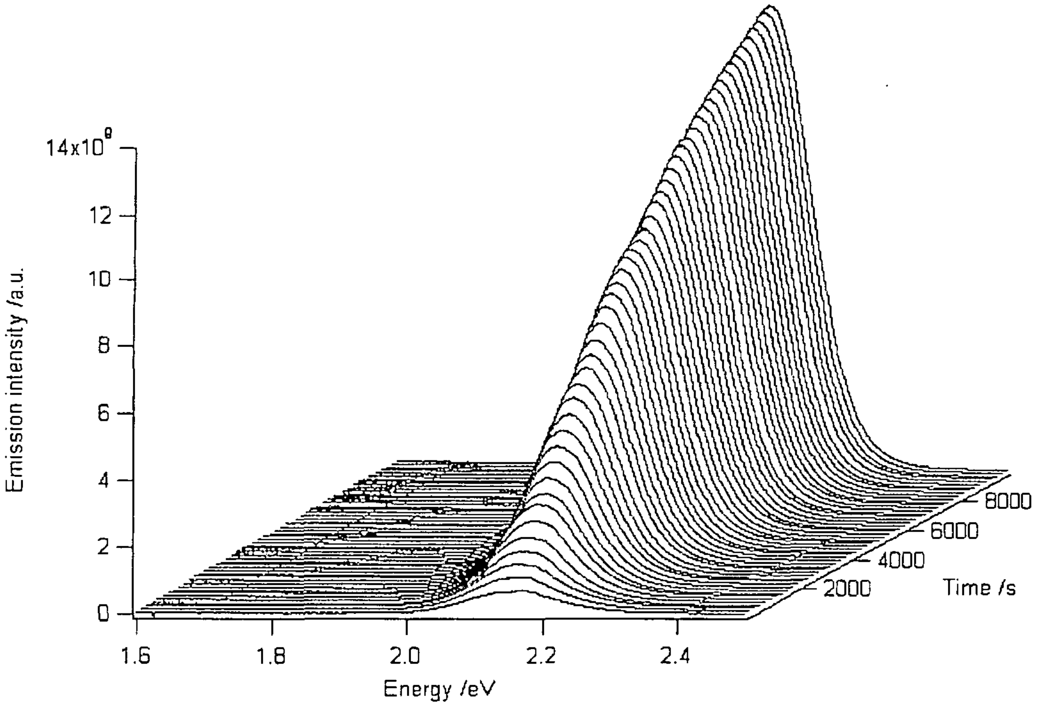

**Figure 1** - A representative series of luminescence spectra from a sample of CdSe/ZnS core/shell quantum dots in a toluene/TOPO solution illuminated by an $Ar^+$ laser outputting 13.5mW of 488nm light.

# SPECTROSCOPY AND DYNAMICS OF GaSe NANOPARTICLES AND NANOPARTICLE AGGREGATES

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The spectroscopy and time-resolved dynamics of GaSe nanoparticles and nanoparticle aggregates are presented here. The nanoparticles are synthesized using variations of previously reported methods. These synthetic methods allow for the focusing or defocusing of the particle size distributions. These particles are two-dimensional disks, having diameters ranging from 2.5 to 9 nm and are a single tetralayer (Se-Ga-Ga-Se) thick. By focusing the size distribution, it is possible to obtain monodisperse samples, with particle diameters controlled to about +/- 10%.

Time-correlated single-photon-counting emission and femtosecond transient absorption results from photoexcited nanoparticles are reported. The emission results are interpreted in terms of electron and hole trapping. The time resolved absorption results indicate the presence of a size-independent transient absorption peak at about 600 nm. Polarization results indicate that the absorption anisotropy is small or negative on the blue edge of the spectrum, and increases with increasing wavelength. The anisotropy reaches a maximum in the 600 nm region, and remains approximately constant out to 700 nm. Smaller particles exhibit smaller (or more negative) anisotropies and a larger wavelength dependence than larger particles. These results are interpreted in terms of a simple effective mass, particle-in-a-cylinder model. This model semiquantitatively predicts the absorption maximum at 600 nm and qualitatively predicts the wavelength and particle size dependence of the absorption polarization. Consistent with previous assignments based on quenching studies, this model shows that the 600 nm absorption peak may be assigned to a z-polarized hole intraband transition.

We show that the largest (9 nm) GaSe nanoparticles form strongly interacting aggregates. The spectra indicate that the interparticle interaction energies are on the order of 1000 $cm^{-1}$. The extent of this interaction is orders of magnitude greater than in other semiconductor nanoparticles, making this type of nanoparticle unique. This strong coupling behavior is due to the two-dimensional nature of the particles. These aggregates are spectroscopically reminiscent of three-dimensional molecular aggregates (so-called JJ-aggregates) and therefore exhibit unusual spectroscopic properties. These properties may be understood in terms of dipolar coupling of the localized excitons.

# RESONANCE RAMAN AND TIME-RESOLVED RESONANCE RAMAN SPECTRA OF MONOMERIC AND DIMERIC COMPLEXES OF 2,3-DIPYRIDYLPYRAZINE

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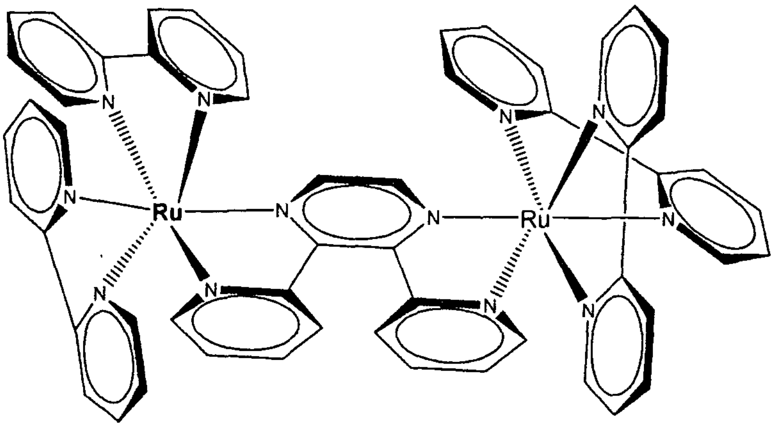
The electronic absorption, resonance Raman (RR) and time-resolved resonance Raman (TR$^3$) spectra of the monomeric and dimeric complexes of Ruthenium(II) with 2,3-bis(2-pyridyl)pyrazine (dpp) were measured; i.e., $Ru(bpy)_2dpp^{2+}$ and $Ru(bpy)_2dppRu(bpy)_2^{4+}$, where bpy is 2,2′-bipyridine. In addition, in order to facilitate definitive assignments of the observed RR spectral parameters, the corresponding selectively labeled complexes employing perdeuterated bpy (d8bpy) were also prepared and studied. It is shown that using judiciously chosen excitation lines to acquire the RR spectra permits selective enhancement of vibrational features associated with specific molecular fragments of the complexes, facilitating structural characterization of ground states of each complex.



In addition, the TR$^3$ spectrum of the monomeric complex yields vibrational signatures of its $^3$MLCT state, which is consistent with polarization of electron density towards the pyrazyl fragment; corresponding studies of the dimeric complex failed to provide conclusive evidence for modes attributable to an anion radical fragment, presumably due to lack of effective enhancement with the excitation lines available. Further studies, in collaboration with Professor John Endicott and his group, involving asymmetric complexes bearing $Ru(NH_3)_4^{2+}$ and $Ru(bpy)_2^{2+}$ units are currently underway.

# PHOTOISOMERIZATION AND INCLUSION COMPLEX FORMATION OF CAROTENOIDS

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Carotenoids (Car) are known to have two major functions in photosynthesis: light-harvesting and photoprotection. The all-*trans* configuration of Car is selected by the light-harvesting complexes, whereas the 15-15'-*cis* configuration is selected by the bacterial reaction centers (RCs). Previous studies on the isomerization of Car were carried out in various solvents, which provided an environment that is totally different from the rigid protein environment of RCs. Numerous cis isomers are formed in solution, with little apparent selectivity. Recently, HYSCORE studies of $Car^{\bullet+}$ formed by oxidation of Car on silica-alumina showed that the di-*cis* isomerization on the solid support is selective, indicating that isomerization of Car in rigid environment is different from that in solvents.

In the present study, MCM-41, Ti-MCM-41 and Fe-MCM-41 molecular sieves were chosen as hosts to study the isomerization of Car in the presence of light or by chemical oxidation. Previous studies in our lab have shown that MCM-41 materials provide an appropriate microenvironment to retard back electron transfer (ET) which increases the lifetime of the photoproduced radical ions and provides some insight into isomerization selectivity. Introduction of $Ti^{4+}$ into the MCM-41 framework was found to significantly enhance the photoinduced ET efficiency of Car due to the strong electron-accepting ability of $Ti^{4+}$. Car imbedded in Fe-MCM-41 can also be oxidized to produce $Car^{\bullet+}$. A very high isomerization efficiency of Car was found in these solid hosts. Strong selective formation of 13-*cis* was found for the isomerization of all-*trans*-*β*-carotene, but no such selectivity was found for canthaxanthin. These phenomena are attributed to different orientations of the two compounds in these hosts. Molecular mechanics calculations show that formation of 13-*cis* isomer of β-carotene is more favorable than other *cis* isomers in the MCM-41 host.

The first direct evidence of carotenoid/cyclodextrin inclusion complex formation was obtained for the water soluble sodium salt of 8'-carotenoic acid by using $^1H$ NMR and UV-Vis absorption spectroscopy. It was shown that this carotenoid forms a stable 1:1 inclusion complex with β-cyclodextrin. All other carotenoids under study in the presence of cyclodextrins (CDs) form large aggregates in aqueous solution as demonstrated by very broad absorption spectra and considerable change in color. By using EPR spin-trapping, the scavenging ability of 8'-carotenoic acid towards OOH radicals was compared to that in an organic solvent and the CD complex in $H_2O$. A considerable decrease of PBN/OOH spin adduct yield was detected in the presence of uncomplexed carotenoid but no decrease occurred in the presence of the CD complex. Instead a significant pro-oxidant effect (increase of spin adduct yield in the presence of carotenoid) was observed. Because Fenton reagents were used for radical generation, we suggest that the pro-oxidant effect is due to the reaction of carotenoid with $Fe^{3+}$ to regenerate $Fe^{2+}$, which in turn regenerates $^{\bullet}OOH$.

# THE EFFECT OF DOPING ON TRANSPORT AND RECOMBINATION IN DYE-SENSITIZED NANOCRYSTALLINE $TiO_2$ SOLAR CELLS

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The effect of doping on the transport dynamics and recombination kinetics in dye-sensitized $TiO_2$ solar cells is studied by time-resolved photocurrent and photovoltage techniques. It is shown for the first time that electron transport limits recombination with the redox electrolyte in a working cell. The doping is found to slow down both transport and recombination. A simple model is presented that accounts for these results. A multiple electron-trapping model involving an exponential density of localized states is also invoked to explain the dependence of the electron diffusion coefficient on photoinduced charge density at various doping densities. The implications of doping of $TiO_2$ on the solar cell performance are also discussed.

Poster # 24

# PHOTOACTIVATION OF COVALENTLY ANCHORED Ti CENTERS IN MESOPOROUS SILICATE SIEVE BY VISIBLE LIGHT, AND RELEVANCE FOR $CO_2$ PHOTOREDUCTION

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A major challenge of light-induced carbon dioxide reduction to a fuel is to engage visible instead of UV photons. We are pursuing this goal by elucidating the detailed mechanism of UV light-induced $CO_2$ reduction by $H_2O$ in MCM-41 silicate sieve containing framework or grafted tetrahedral Ti centers so as to gain insight of how activated Ti centers react with $CO_2$. In parallel, methods are being developed for the synthesis of metal-to-metal charge-transfer (MMCT) redox sites in silicate sieves that afford photoactivation of Ti centers under visible light.

While the final products $CH_3OH$ and $CH_4$ of UV light-driven $CO_2$ reduction by $H_2O$ have been reported by Anpo and coworkers, the sequential 2-electron transfer intermediates under reaction conditions, or the number of photons consumed for the generation of the 6-electron reduction product $CH_3OH$ are not known. Using in-situ FT-IR spectroscopy, we have found that excitation of the $Ti^{+IV}$-$O^{-II}$ → $Ti^{+III}$-$O^{-I}$ ligand-to-metal charge-transfer transition (LMCT) of the sieve loaded with 10 Torr $D_2O$ and 1 atm $^{13}CO_2$ at room temperature results in the formation of gaseous $^{13}CO$ within minutes. Photolysis power dependence studies revealed that CO is a single photon, 2-electron reduction product. The appearance of CO as the main product when using water as electron donor (in contrast to $HCO_2H$ when using methanol as donor) is in agreement with our previously proposed reaction mechanism of $CO_2$ photoactivation at Ti centers.

In order to shift Ti activation in silicate sieve from UV to visible wavelengths, one needs to replace framework oxygen by a stronger electron-donating moiety. MMCT transitions typically lie at visible energies and give rise to broad and fairly intense absorptions. The main task is to develop synthetic methods for assembling and covalently anchoring bimetallic moieties on the pore surface that allow free choice and control of the oxidation state of each metal. $Cu^{+I}$ and $Sn^{+II}$ metal centers were covalently attached to the MCM-41 pore surface employing precursor complexes with labile $CH_3CN$ ligands. Using this method, we have assembled visible light-absorbing $Ti^{+IV}$-O-$Cu^{+I}$ and $Ti^{+IV}$-O-$Sn^{+II}$ redox centers. MMCT chromophores were clearly revealed by difference diffuse reflectance spectra recorded before and after in-situ oxidation of $Cu^{+I}$ or $Sn^{+II}$. Photoreduction of the Ti center to $Ti^{+3}$ upon MMCT excitation was demonstrated by EPR spectroscopy when irradiating the bimetallic sieve at cryogenic temperature. FT-IR spectroscopy showed absorptions characteristic of residual $CH_3CN$ ligands bound to isolated $Cu^{+I}$ centers, $Cu^{+I}$-O-Ti moieties, or $Cu^{+II}$, respectively. Intensities of these bands indicate that as much as half of the grafted $Cu^{+I}$ of TiCuMCM-41 is oxo-bridged to Ti. These results open up a general method for assembling bimetallic redox centers that allow activation of Ti by visible light.

Poster # 25

# SYNTHESIS AND PHOTOCHEMICAL PROPERTIES OF A TRIAD COMPRISED OF A SELF-ASSEMBLED CHROMOPHORE LINKING TWO PORPHYRINS

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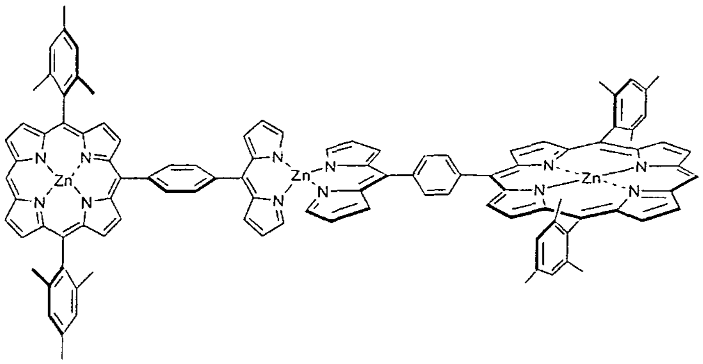
Our long-term goal is to be able to create, in a rational manner and with modest effort, arrays comprised of >100 porphyrinic pigments that collect solar radiation and funnel energy to one site in the array with quantum efficiency >95%. Toward this goal, we have been examining approaches for the synthesis of various types of multiporphyrin arrays. Distinct approaches include (1) stepwise synthesis, and (2) polymerization yielding covalently linked arrays. The former affords well-defined architectures but remains laborious, while the latter is quick but affords complex mixtures. Yet another approach entails the self-assembly of defined architectures from discrete precursors. A major issue in the design of a self-assembling architecture is the choice of unit that engenders the self-association process. We have focused on metal-dipyrromethene complexes (to be exact, bis(dipyrrinato)metal(II) complexes), which are actually quite old motifs in porphyrin chemistry, dating to the time of Hans Fischer (ca. 1924).

Metal-dipyrromethene complexes absorb green light quite strongly ($\varepsilon_{482\ \mathrm{nm}} = 10^5\ \mathrm{M}^{-1}\mathrm{cm}^{-1}$) and, as such, have the potential to serve not only as self-assembling motifs but also as accessory pigments for porphyrins. However, metal-dipyrromethene complexes have very low fluorescent yields (and are often thought to be non-fluorescent). Such excited-state quenching may partly explain why these common structures have never been examined as light-harvesting entities.

We developed methodology for the synthesis of porphyrin–dipyrrins and found that these ligands undergo self-assembly upon adding zinc acetate to give the corresponding bis(porphyrin–diyrrinato)zinc complex. The absorption spectrum is essentially the sum of the spectra of the component parts. The bis(dipyrrinato)zinc complex alone in toluene has $\Phi_f \sim 0.005$ and $\tau = 95$ ps. In the array, the complex has $\tau = 1.3$ ps corresponding to a transfer rate of $\sim(2.6\ \mathrm{ps})^{-1}$ given that there are two acceptors. The quantum efficiency of energy transfer is about 97%. Thus, the bis(dipyrrinato)zinc complex provides the joining unit in a self-assembly process and constitutes an effective accessory pigment for a metalloporphyrin. Application of this self-assembly approach with bis(dipyrrinato)metal(II) complexes to create more elaborate light-harvesting architectures is being contemplated.



# EVIDENCE FOR DIRECT CAROTENOID INVOLVEMENT IN THE REGULATION OF PHOTOSYNTHETIC LIGHT HARVESTING

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Nonphotochemical quenching (NPQ) refers to a process that regulates photosynthetic light-harvesting in plants, as a response to changes in incident light intensity. By dissipating excess excitation energy of chlorophyll molecules as heat, NPQ process balances the input and utilization of light energy in photosynthesis and protects the plant against photo-oxidative damage. The major, rapidly reversible component of NPQ is the so-called feedback de-excitation or energy-dependent quenching (qE). While it has been discovered that qE correlates with the xanthophyll cycle, the change of trans-membrane proton gradient and the PsbS protein, a fundamental understanding of its physical mechanism remains elusive [1].

We performed femtosecond transient absorption experiments on intact thylakoid membranes isolated from spinach and transgenic *Arabidopsis thaliana* plants [2]. These plants have well-characterized qE capabilities and a distinct composition of xanthophyll cycle carotenoids. Upon optical excitation of the chlorophylls in the $Q_y$ band at 683 and 664 nm with sub-100 fs pulses, we monitored the change of absorbance as a function of time delay between pump and probe pulses at different probe wavelength. The kinetics probed in the spectral region of the $S_1 \rightarrow S_n$ transition of xanthophylls (530-580 nm) were found to be markedly different under the quenched and unquenched conditions, corresponding to maximum and no qE, respectively. The magnitude of the kinetic difference was enhanced considerably when the pump wavelength was tuned to 664 nm, the blue edge of the $Q_y$ band, with respect to the results obtained by exciting at 683 nm, the absorption maximum. Measurements using various *Arabidopsis thaliana* mutants further show that the kinetic differences are proportional to the amount of qE and require the presence of zeaxanthin, a specific xanthophyll cycle carotenoid produced by wild type green plants under excess light conditions. Detailed analysis of the transient absorption kinetics allowed us to resolve an additional decay component that exists solely under the quenched conditions. The lifetime of the new quenched component is ~10 ps, a value which is approximately identical to the intrinsic $S_1$ lifetime of zeaxanthin. In addition, the reconstructed spectrum from the kinetic difference measured in spinach thylakoids at a given delay time of 1 ps shows reasonable similarity with the experimental transient absorption spectrum of zeaxanthin in a variety of solvents. The lifetime and the spectral characteristics indicate that the kinetic difference originates from the involvement of the $S_1$ state of zeaxanthin in the quenched case.

1. Müller, P., Li, X.-P. & Niyogi, K. K. (2001) *Plant Physiology* 125, 1558-1566.
2. Ma, Y.-Z., Holt, N. E. Li, X.-P. & Niyogi, K. K. & Fleming, G. R. (2003) *Proc. Natl. Acad. Sci. USA* 100, 4377-4382.

# TEMPLATE SYNTHESIS AND PHOTOELECTROCHEMISTRY OF SEMICONDUCTOR NANOCRYSTAL ARRAYS

Thomas E. Mallouk, Diane E. Wilson, Lara I. Halaoui, Bradley A. Lewis,
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We are investigating the synthesis, photochemistry, and photoelectrochemistry of semiconductor nanowire arrays grown in anodic aluminum oxide (AAO) templates. The goal of this work is to study photochemical charge separation and photochemical water splitting in arrays of semiconductor nanocrystals. Because these arrays consist of individual single crystals wired together at the back contact, we anticipate that the effects of grain boundary electron-hole recombination will be reduced relative to polycrystalline photoelectrochemical cells. The porous template also allows us to create interesting "totem pole" structures in which composition and doping are controlled along the length of the semiconductor nanowires. These structures have the potential to act as multi-junction and tandem solar cells. They also allow us to study some of the effects of reduced dimensionality and quantum confinement on electron-hole recombination and photocurrent.

AAO membranes with pore diameters in the range of 30-300 nm, pore densities of $10^8$-$10^9$/cm$^2$, and thicknesses of 60 µm were obtained commercially or made by anodization of high purity aluminum foil. Catalyst nanoparticles were introduced into the pores by electrodeposition, and the position of the catalyst could be controlled by electrodepositing a prescribed length of a backing metal such as Ag. Several strategies were investigated for growing n-CdSe and Si nanowires in the pores. These included (for CdSe) simple sublimation under vacuum, physical and chemical vapor transport, single source metal-organic chemical vapor deposition, vapor-liquid-solid (VLS) growth using Au, Ag, and $Ag_2Se$ as catalysts, and laser-assisted VLS growth using a Nd:YAG laser and Au catalysts. Of these, the VLS methods proved most effective, and gave nanowire growth with little or no spontaneous nucleation on the outer surface of the membrane at 700-720°C. p-type Si nanowires were grown by VLS at 500°C from Au catalyst particles in the pores, using $SiH_4$ and $B(CH_3)_3$ as the sources of Si and B atoms, respectively. Boron doping levels between $10^{17}$-$10^{19}$/cm$^2$ were measured, and p-type conduction was verified by releasing individual wires from the membranes, trapping them in a lithographically defined FET structure, contacting the two ends of the wire with Au, and gating the central part of the wire through an $SiO_2$-coated buried gate lead. Lithographic structures have also been made for four-point conductivity measurements.

With Si made by the VLS method, we found that single crystal nanowires can be grown symmetrically in the pores (resulting in Au particles at both ends) from individual Au catalyst nanoparticles. Polar growth, which is more useful for photoelectrochemical studies and for water splitting with multi-junction wires, can be achieved by partially filling the pores with a back-contacting metal, such as Rh or Ni, which does not alloy substantially with Au. Using this technique we have fabricated p-Si nanocrystal array electrodes and have conducted preliminary studies of their photoelectrochemistry in non-aqueous solutions containing different redox couples. So far small photocurrents and photovoltages have been obtained using methylviologen. We are currently optimizing the surface pretreatment of the nanowires (through chemical etching and photoetching). We are also synthesizing n-type Si nanowire arrays, using $PH_3$ as the dopant, and p-n junction multilayer wires. The characterization of these nanowire arrays will be reported at the meeting.

Poster # 28

# SOLVATION AND ELECTRON TRANSFER IN ROOM-TEMPERATURE IONIC LIQUIDS

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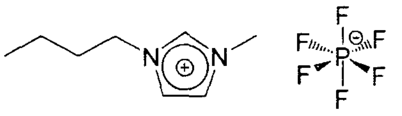
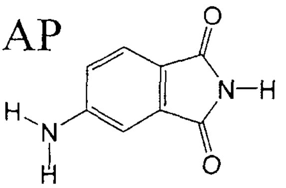
Room-temperature ionic liquids are being intensively studied as possible "green" replacements for volatile organic solvents as well as for their distinctive solvating properties compared to conventional polar solvents. Most room temperature ionic liquids are composed of large asymmetrically shaped cations and large anions, which decrease the strength of ion-ion interactions compared to inorganic salts and frustrate crystallization to the extent that they remain liquid near to room temperature. Solvation of a dipolar solute in ionic liquids results largely from ion-dipole type interactions (and dispersion interactions) and so is distinct from solvation in polar organic solvents where the dominant "polar" interaction is of the dipole-dipole type. For this reason, it is expected that the understanding of polar solvation we have built from experience with dipolar solvents will need to be substantially revised in ionic liquids.

We have begun exploring steady-state solvatochromism, solute rotation, and solvation dynamics in several room-temperature ionic liquids. Our main results to date concern one of the most popular ionic liquids 1-*n*-butyl-3-methylimidazolium hexafluorophosphate ($[\text{bmim}^+][\text{PF}_6^-]$).



$[\text{bmim}^+][\text{PF}_6^-]$

4-AP



Steady-state spectra of a variety of probes show that solvation energetics in $[\text{bmim}^+][\text{PF}_6^-]$ is comparable to that in a conventional polar solvent with solvatochromic parameters $\pi^* = 0.86$; $\alpha = 0.40$; $\beta = 0.18$. Time-resolved measurements of the solute 4-aminophthalimide (4-AP) as well as coumarin probes show that the rotational dynamics of such solutes are typical of what would be expected for a highly viscous solvent (~200 cP at 25 °C). Time-dependent emission spectra, recorded with an instrumental response of 25 ps, indicate that solvation dynamics in $[\text{bmim}^+][\text{PF}_6^-]$ occur in two well-separated time regimes. Near to room temperature, the observable response takes place in the 0.1-2 ns time range. This component can be described by a stretched exponential time dependence with an exponent of 0.6-0.7, indicative of strongly non-exponential relaxation. The integral time of the observed component of solvation is found to be proportional to the rotation time of 4-AP and to solvent viscosity, suggesting the involvement of substantial solvent rearrangement. In addition to this relatively slow component, more than half of the solvation response in $[\text{bmim}^+][\text{PF}_6^-]$ is faster than can be detected in these experiments, i.e. takes place in <5 ps. We are currently working on verifying the presence of this fast component using a Kerr-gated emission experiment and other means. Our poster will include the results of these further experiments, as well as preliminary results on electron transfer in ionic liquids.

**Poster # 29**

# INTERACTIONS AT THE INTERFACES OF METALLIC NANOPARTICLES

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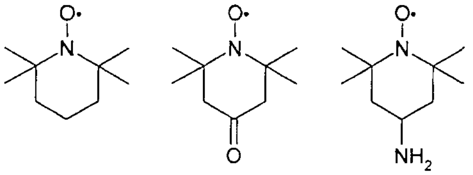
University of Notre Dame, Notre Dame, IN 46556

Metallic nanoparticles are of intense interest in contemporary physical chemistry because of their unusual spectroscopy and their potentially enhanced catalytic activity. In the context of this workshop, metallic nanoparticles are often invoked as redox catalysts in the photochemical conversion of solar energy. We, therefore, are studying the interactions that molecular species, other metallic or semiconductor particles, and radicals may experience at the surface of the particles. Last year we showed that the interface between the core and the shell in metallic nanoparticles disappears when the particles sizes drop below 10 nm (for Au-Ag). Here we report our recent studies on the interaction of radicals with the metallic particles.


TEMPO TEMPONE TEMPAMINE

Scheme I

EPR spectroscopy was used to study the interactions between stable free radicals and gold nanoparticles. To separate the catalytic hydrogen evolution reaction from the interactions with the metal we used the thoroughly characterized nitroxyl free radicals TEMPO, TEMPAMINE, and TEMPONE as spin-probes (Scheme I). These radicals were adsorbed onto Au particles of 15 nm to 2.5 nm in diameter. We find that the EPR signal of all of these probes disappears upon adsorption of the radicals on the particles. Several mechanisms were considered to rationalize this observation. Chemical destructive reaction is not the source of this effect since the radical signal recovers upon exchange with ethanolamine at the surface. Loss of free tumbling is not the cause either because the rotation-correlation time of the particles is fast enough to allow its observation even if the radical is completely immobilized on the surface. The charge density in the particle hardly changes and the radicals do not affect the plasmon band. Thus, charge transfer to the particles is not the major reason for the loss of the signal. Spin-spin exchange was excluded at very low coverage of radicals per particle. Thus, we propose that the reduction in signal intensity arises from exchange interaction between the unpaired electrons of the adsorbed radicals and conduction band electrons of the metallic particles. We also discovered accidentally that in the presence of oxygen adsorbed TEMPAMINE radicals are catalytically oxidized to the carbonyl derivative, TEMPONE (Figure 1). A mechanism for this unexpected catalytic reaction is proposed.

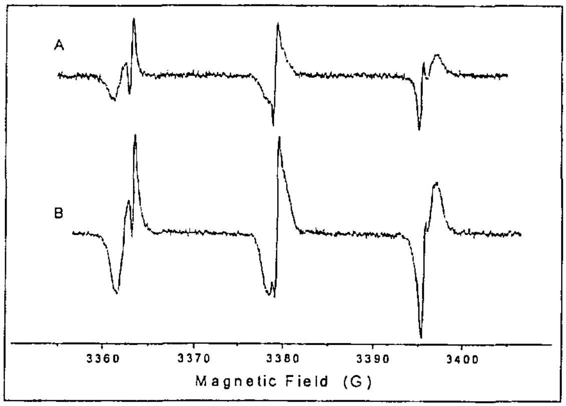


Figure 1: EPR spectra of samples containing: A. Air saturated solution, containing 15 μM TEMPAMINE and 2.3 mM of 15 nm Au particles; B. Air saturated solution of 15 μM TEMPAMINE and 1.5 μM TEMPONE (no gold).

# SYNTHESIS AND CHARACTERIZATION OF COLLOIDAL InP QUANTUM RODS

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Colloidal InP quantum dots have been the subject of intensive experimental and theoretical study during the past decade due to their rich phenomena associated with quantum confinement. The shape effect, on the other hand, has received much less attention because colloidal synthetic methods of quantum rods have not been available until recently. For semiconductor nanowires, diameter and shape control their electrical and optical properties. The rod architecture exhibits potential technological advantages over spherical quantum dots in improved photocell performance, linearly polarized emission and lasing action. We have synthesized quantum rods of InP by colloidal chemistry method. A solution-liquid-solid mechanism with metallic indium nanocrystals as catalyst was used to synthesize InP rods. This approach to rod growth is particularly important for materials with a zinc-blende cubic lattice. We grew soluble nanorods in a liquid medium of melted $In^{0}$ droplets. $In^{0}$ droplets are a crystallization medium for growing InP. Quantum rods were grown by controlling the size of metal In droplets in the presence of a strong organic stabilizer. We used a linear long chain amine as the stabilizer. Organic In-P compounds $(t\text{-}Bu)_2InP(Si(Me_3)_2$ or $(Me_3)_2InPSi(Me_3)_2$ were used to initiate nanowire growth. These organic compounds partially decompose into In metal, which are strongly implicated in the InP crystal-growth process. We have added a mixture of $InCl_3$ and $P(SiMe_3)_3$ to increase precursor concentration, and this leads to an increase in the $InP/In^{0}$ ratio. The size of the melted $In^{0}$ droplet (b. p 157° C) controls the wire diameter, while the length is controlled by the amount of $(InCl_3)$ and $P(Si(Me_3)_3$ added. InP quantum rods in the diameter range of 30–200 Å and 100–1000 Å in length were synthesized. Quantum rods with a high degree of crystallinity are grown along the (111) crystallographic planes. The absorption spectrum of InP nanorods with diameters of about 30 and 100–300 Å in length is in the visible spectral regime, suggesting a substantial blue shift with respect to the bulk (band gap 1.35 eV) that is due to size confinement. Moreover, the Stokes shift of the emission band in the quantum rods is substantially larger than the shift in the corresponding quantum dots.

# MIMICKING THE PHOTOSYNTHETIC FUNCTIONS OF CAROTENOID POLYENES

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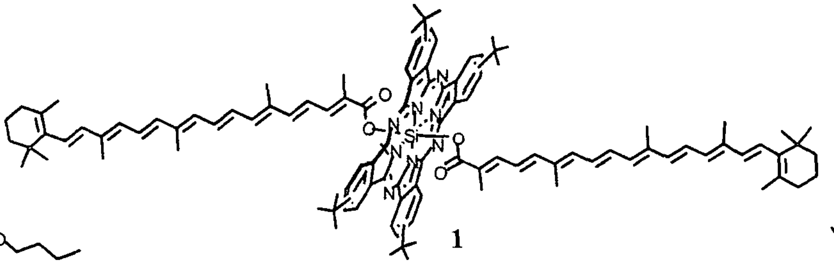
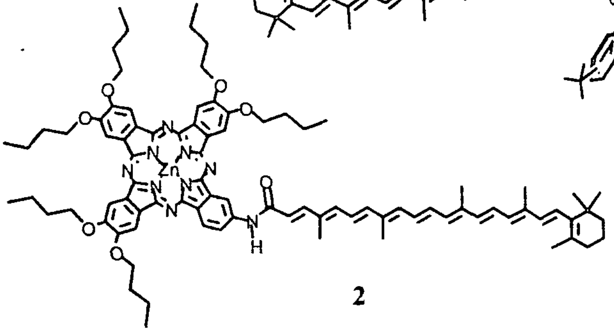
Carotenoid polyenes carry out various functions in photosynthesis, acting as antennas, as switches to limit the accumulation of excess excitation energy, as molecular wires connecting redox centers and as photoprotective agents. Modeling these functions in synthetic systems has proven challenging due to the unusual photophysical properties of carotenoids. Light absorption to generate the carotenoid first excited singlet state, $S_1$, is an electric-dipole forbidden process, and is not observed. The transition to an upper excited singlet state of $B_u^+$ symmetry ("$S_2$") is allowed, leading to strong absorption in the 480-nm region. The $S_2$ state relaxes to $S_1$ in a few hundred fs. The $S_1$ state decays by internal conversion to the ground state in a few ps; both fluorescence and intersystem crossing are negligible. In spite of these limitations, carotenoids function well as antennas in natural photosynthetic membranes, absorbing light and transferring singlet excitation energy to chlorophylls with quantum yields that sometimes approach unity.

The molecules below exemplify synthetic systems prepared in order to study the details of singlet-singlet energy transfer from carotenoids to macrocyclic tetrapyrroles. Spectroscopic investigations of a variety of molecules show that energy transfer occurs from the carotenoid $S_2$ and in some cases $S_1$ states, depending upon the structural details of the donor and acceptor moieties and the nature of the linkage joining them. Overall singlet energy transfer quantum yields approaching 1.0 have been observed in cases where both $S_2$ and $S_1$ levels act as energy donors (triad **1**). Because the $S_1$ states of the carotenoids and tetrapyrroles are of similar energies, dramatically different energy transfer behavior can result from minor structural changes.

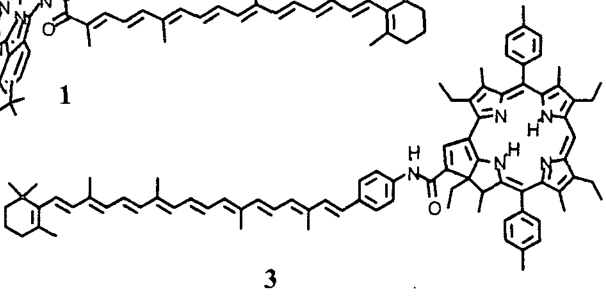
The mechanisms of ultrafast singlet energy transfer of this type are not fully understood. Both coulombic and electron-exchange mediated transfer may be important. In order to investigate the time scale for exchange-mediated energy transfer, ultrafast triplet-triplet energy transfer, presumably by the exchange mechanism, has been studied in similar molecules featuring gold porphyrins. Subpicosecond intersystem crossing in the tetrapyrrole moieties of such dyads allows, for the first time, direct observation of triplet-triplet energy transfer.



**1**



**2**



**3**

# ARE LHCB PROTEINS NECESSARY FOR REGULATION OF PHOTOSYNTHETIC LIGHT HARVESTING BY FEEDBACK DE-EXCITATION?

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[c]Ecosystem Dynamics, Research School of Biological Sciences, Australian National University, Institute of Advanced Studies, Canberra, ACT 0200, Australia

Energy-dependent nonphotochemical quenching (qE), also known as feedback de-excitation, is a process that dissipates excess absorbed light energy as heat in the light-harvesting antenna of photosystem II (PSII) to protect plants from photoinhibition and photo-oxidation. The 22-kD PSII protein (PsbS) is necessary for qE, and its level can determine the capacity of qE. However, the antenna proteins of PSII with which PsbS interacts remain unknown. Here we tested the hypothesis that peripheral PSII light-harvesting complex (Lhcb) proteins, either the major Lhcb complex (LHCIIb, containing Lhcb1, 2, and 3) or the minor Lhcb complexes (CP29, CP26, or CP24, containing Lhcb4, 5, or 6, respectively), are also required for qE in the model plant *Arabidopsis thaliana*.

Because the accumulation of Lhcb proteins is affected in mutants lacking chlorophyll (Chl) *b*, we constructed a series of *Arabidopsis* mutants and transgenic plants that lack Chl *b* but have varying levels of PsbS. The *npq4-2* and *npq4-3* mutants lack both the *psbS* gene and the gene encoding Chl *a* oxygenase (*CAO*), which is needed for Chl *b* synthesis. These genes are located approximately 20 kb from each other on chromosome I, and both genes are eliminated by large deletions in *npq4-2* and *npq4-3*. The *CAO* single mutant *ch1-3*, which lacks Chl *b* but has wild-type *psbS* gene dosage, was used as a control. We also transformed *npq4-2* and *npq4-3* with the wild-type *psbS* gene, yielding transgenic plants that are Chl *b*-less but contain more PsbS than *ch1-3*. Lines #5 and #8 were generated from the *npq4-2* background with two homozygous insertions of *psbS*. Line #2 was generated from the *npq4-3* background with one homozygous insertion of *psbS*.

All Lhcbs, PsbS, qE, and Chl *a* fluorescence lifetime distributions were analyzed in the mutants and transgenics. Using specific antibodies, the major Lhcbs (Lhcb 1, 2 and 3) and CP24 were undetectable in all of these Chl *b*-less mutants. No clear cross-reacting bands were detected when using antibodies against CP29 and CP26, but there were faint, smeared bands migrating at the position near CP29 that cross-reacted with the CP26 antibody. The qE levels were directly proportional to the amount of PsbS in each of the Chl *b*-less lines, which was as follows, line#8 > line#5 = line#2 > *ch1-3* > *npq4-2* = *npq4-3*. The fractional intensities of short fluorescence lifetime components (<0.75 ns) under steady-state illumination conditions (with PSII photochemistry uninhibited) were also directly proportional to the amount of qE and PsbS. These results suggest that Lhcb proteins are not necessary for the PsbS-dependent nonphotochemical quenching of Chl *a* fluorescence in *Arabidopsis*.

# ELECTRON TRANSFER DYNAMICS FROM QUANTUM DOTS TO $TiO_2$ NANOCRYSTALS

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The dynamics of electron transfer (ET) from photoexcited InP and CdS quantum dots (QDs) adsorbed to $TiO_2$ nanocrystals (in the form of both nanocrystalline films and colloidal solutions) have been investigated using time-resolved transient absorption (TA) spectroscopy and photoluminescence (PL) spectroscopy. Experiments were also conducted with QDs adsorbed to nanocrystalline $ZrO_2$ films, where no ET is expected because of the large bandgap of $ZrO_2$. Electron transfer from the QDs to the $TiO_2$ films was confirmed by observing photocurrent in a photoelectrochemical cell. When InP QDs are in contact with $TiO_2$ nanocrystalline films or colloids, the steady state PL from InP QDs shows quenching of the red, deep trap emission, but not of the LUMO-to-HOMO bandedge emission. This suggests ET occurs only from occupied QD surface states and not from the quantized core states. Neither the steady state deep trap nor band edge emission from InP QDs is quenched when they are adsorbed on $ZrO_2$, as expected. TA measurements of the LUMO population confirm that the photoinduced ET is from surface states and not from the QD core. TA measurements also show that ET does not occur from higher excited (hot) quantized electron states of the InP QDs. Time-resolved PL measurements show that the PL lifetime (multi-exponential decay) does not change whether the InP QDs are in solution or adsorbed on either $TiO_2$ or $ZrO_2$ nanocrystalline films. This result is interpreted by a model where a distribution of InP QDs exists in the ensemble, such that some QDs have radiative surface states that are statically quenched by $TiO_2$ but do not allow ET, and other QDs have radiative surface states that are statically quenched and allow ET. Initial results of TA measurements for CdS QDs show different behavior compared to InP QDs; the TA dynamics show a large difference in the LUMO population decay time between $TiO_2$ and $ZrO_2$ nanocrystalline films and indicate that ET occurs from the QD core.

**Poster # 34**

# STUDIES OF TWO-SITE DYE ADSORPTION ON SINGLE CRYSTAL SUBSTRATES: MONTE CARLO SIMULATIONS AND EXPERIMENTAL PHOTOELECTROCHEMICAL RESULTS

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Departments of Computer Science[1], Mathematics[2] and Chemistry[3]
Colorado State University, Fort Collins, CO 80523

Dye sensitized solar cells, using dyes attached to more than one binding site on a metal oxide surface, have shown promising solar energy conversion efficiencies. We have been studying the adsorption of dye molecules that attach to a surface via two adsorption sites. The "chelate effect" enhances the dye binding to the surface and potentially restricts the geometry of the 2D surface phases. We have been using both photoelectrochemical experiments on single crystal metal oxide surfaces and Monte Carlo simulations to begin to understand the special features of this adsorption situation.

So far the photoelectrochemical experiments have surveyed the adsorption and sensitization of a variety of dicarboxylated cyanine dyes on natural anatase (101), Nb-doped rutile and Nb-doped (100) strontium titanate single crystals. Results of the quantum yields for photocurrent from four dyes on these substrates are given in Table 1.

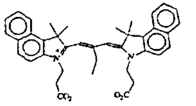
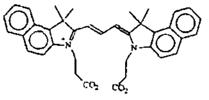
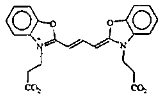
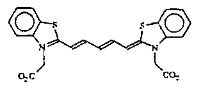
| Substrate |  |  |  |  |
|---|---|---|---|---|
| Anatase (101) | 0.012% | 0.02% | 0.046% | 0.052% |
| Rutile-Nb | 0.023% | 0.013% | 0.048% | 0.0032% |
| $SrTiO_3$-Nb (100) | ~ 0 | ~ 0 | 0.035% | ~ 0 |

Table 1 Quantum yield per incident photon at the sensitization maximum for the dyes and substrates shown. Spectra were measured in acetonitrile solution with either hydroquinone or iodide added as a regenerator. (Dyes provided by Dr. Mark Spitler, ChemMotif Inc.)

The quantum yields are interpreted by considering the geometric arrangement of five-fold Ti bonding sites on the various surfaces. In some cases the photocurrent spectrum showed evidence for both monomer and aggregate formation on the surface. We will also present AFM images of dye structures adsorbed onto terraced metal oxide surfaces and the correlation of these structures with the photocurrent spectra.

Monte Carlo simulations have initially focused on successfully reproducing published simulations of adsorption to two adjacent sites of a square lattice. We then studied the dynamics of dye ordering on the surface via "walking" surface diffusion, where desorption of one end of the molecule is followed by reattachment at a nearby site. Ordering of a random surface into several low-energy ordered structures can be observed in the simulations. We will be extending these calculations to two nonadjacent site adsorption that is characteristic of the dye/oxide surfaces described above.

# SPIN LABELING STUDY OF THE STRUCTURE, DYNAMICS, AND ENERGETICS OF THE PHOTOSYNTHETIC BACTERIAL REACTION CENTER PROTEIN

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Protein conformational dynamics play an important role in controlling the functional activity of biological systems. It is well documented that a number of charge transfer reactions in proteins are gated by conformational transitions. Thus, studies of the dynamical structure of proteins are necessary for understanding the function of biological supramolecular assemblies.

We have investigated the dynamics of the photosynthetic reaction center (RC) protein. By employing a multifrequency EPR approach, we have demonstrated that the cysteine specific nitroxide methanethiosulfonate spin label, MTSL, can be covalently bound to the bacterial RC protein. Inspection of the *Rhodobacter sphaeroides* RC structure reveals five native cysteine residues. We suggest that the MTSL nitroxide is bound to an accessible cysteine residue, H156, which is located on the surface of the protein H-subunit. The four remaining cysteines are located in the protein interior, more than 10 Å from the surface.

Analysis of the multifrequency EPR spectra obtained for spin labeled RC suggests the complex dynamics of spin labeled proteins, which includes overall isotropic tumbling of the globular protein, fluctuation of specific protein side chains, and spin label reorientation with respect to alkyl side chains. Dissecting these types of complex dynamic modes from EPR spectra poses quite a challenge. We demonstrate that simultaneous fitting of multifrequency EPR spectra of spin-labeled proteins is crucial for discriminating between different dynamical modes of motion. The motion of the nitroxide bound to the RC can be described as a very fast libration (restricted reorientational motion) with a correlation time faster than $10^{-9}$ s. We have also followed the dynamics of the protein by monitoring the temperature dependent EPR spectra of paramagnetic species situated at various locations on the RC protein: primary donor cation radical, secondary acceptor anion radicals, as well as $Cu^{2+}$-ions bound at the Fe-binding site and at the surface metal binding site.[1] Thus, we were able to monitor the protein dynamics at different locations of the RC protein. In each case, similar dynamics were observed suggesting the importance of the collective motion of the entire protein. We expect that these data will be helpful in the analysis of the light-induced charge transfer reactions that are gated by conformational changes. Preliminary analysis of the correlations of the observed dynamics with photosynthetic electron and proton transfer events are discussed.

1. L.M.Utschig, Y.Ohigashi, M.C.Thurnauer, D.M.Tiede, Biochemistry 37 (1998) 8278

# ELECTROSYNTHESIS, CHARACTERIZATION, AND DEVICE APPLICATIONS OF COMPOSITE OXIDE FILMS

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Oxide semiconductor films are important in a variety of solar applications related to heterogeneous photocatalysis, photoelectrochromic windows, sensors, and solar cells. This paper describes our recent efforts to develop new electrosynthetic approaches for oxide films and composites for ultimate use in such applications. In particular, we have focused on cathodic electrosynthesis methods based on the electrochemical reduction of precursor species on targeted supports such as transparent conducting glass. Two such methods based on the occlusion of semiconductor oxide particles (e.g., $TiO_2$, $WO_3$) in a matrix of the same material and pulsed electrodeposition of $WO_3$-$TiO_2$ composite films, will be presented. The occlusion approach has the advantage that the semiconductor particle preparation and immobilization/deposition process steps are separated so that, in principle, any targeted morphology for the semiconductor particles (e.g., quantum dots) can be exploited in a film configuration. Similarly, the pulsed electrosynthesis approach that we have developed, is versatile for preparing a wide range of oxide film compositions so that their optoelectronic properties can be tuned for a given application.

We will present morphology/composition/photoactivity data for the above films derived from photoelectrochemical experiments, optical analyses, X-ray photoelectron spectroscopy, electron microscopy, and scanning probe microscopy. The performance of these films in electrochromic and dye-sensitized solar cell devices, will also be described. In particular, our electrosynthesized films have yielded 4% solar-to-electrical efficiencies, photovoltages of ~ 690 mV, and short-circuit photocurrents of ~ 10 mA/cm$^2$ – performance parameters that are among the best, to our knowledge, reported for electrosynthesized device components in a solar energy conversion environment.

# INTERPLAY OF AXIAL LIGATION, HYDROGEN BONDING AND CONFORMATIONAL LANDSCAPES IN Ni(II) PORPHYRINS

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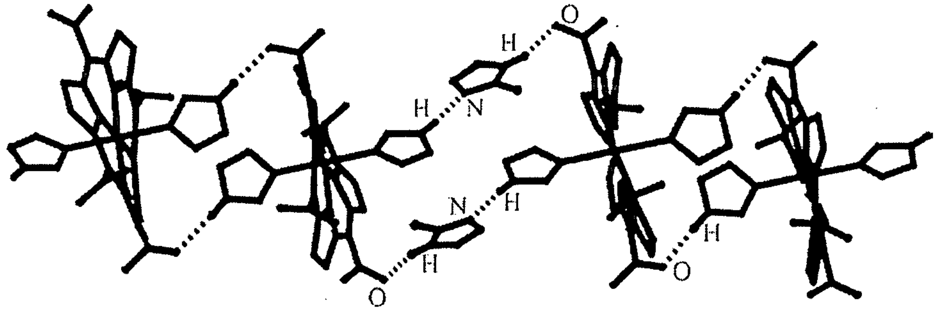
Porphyrin macrocycle distortions are increasingly implicated as contributing factors to the electronic properties of porphyrins in photosynthesis and enzymatic catalysis. Photosynthetic reaction centers and heme proteins have recently been reconstituted with Ni (bacterio)chlorophylls and porphyrins which 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 bacterial tetrapyrrole to contain Ni. The cofactor mediates the final stages of the conversion of $CO_2$ to hydrocarbons in methanogenic bacteria.

To model the interplay between nonplanarity, axial ligation and the ubiquitous hydrogen bonding observed in proteins, the molecular structures of four bis-ligated high spin Ni(II) complexes of the sterically crowded, nonplanar 5, 10, 15, 20-tetranitro-2, 3, 7, 8, 12, 13, 17, 18-octaethyl porphyrin (NiOETNP) were determined. The ligands are imidazole (Im), imidazole plus 2-methyl imidazole (2-MeIm) in the crystal lattice, 1-methyl imidazole (1-MeIm), and 2, 1, 3-benzoselenadiazole (BSeD). Extensive intermolecular hydrogen bonding is observed in the three imidazole-ligated structures consisting of $NH\cdots O$ and $CH\cdots O$ bonding from the imidazoles to neighboring nitro groups, and of $NH\cdots N$ interactions to a nearby 2-MeIm. The different modes of hydrogen bonding, typical of those frequently observed in proteins, mediate the formation of discrete porphyrin dimers as well as more extensive two and three-dimensional arrays. Only the bis-BSeD complex remains monomeric. The presence or absence of the different types of hydrogen bonds controls the orientations of the axial ligands. This combination, in turn, modulates the conformations of the porphyrin skeletons. This interplay further illustrates the multiconformational landscapes that porphyrins can access. Such nonplanar deformations have been shown to significantly affect the optical, redox, magnetic, radical and excited state properties of porphyrin derivatives. That hydrogen bonding can influence ligand orientations and macrocycle conformations with their concomitant consequences on physical and chemical properties may thus be particularly relevant to the bioenergetic roles of porphyrin in vivo. These results also raise the question whether point mutations near porphyrins in vivo are structurally, and consequently functionally, innocent.



**Poster # 38**

# PROGRESS TOWARD CREATION OF A PHOTOSYNTHETIC POLY(LIPID) MEMBRANE COUPLED TO A SEMICONDUCTOR

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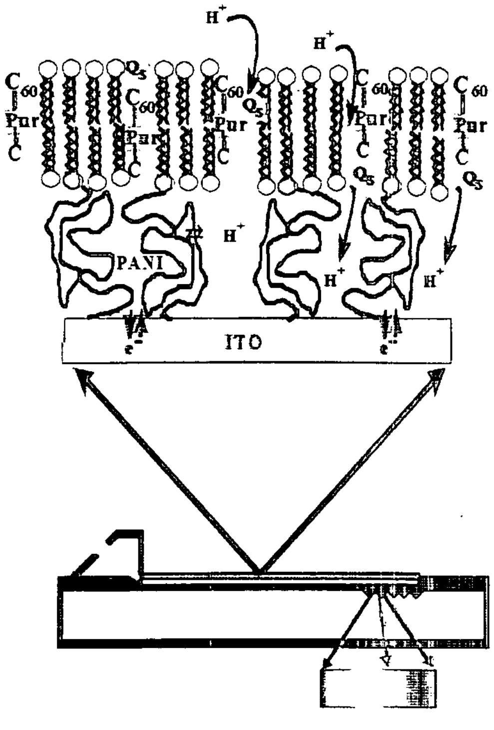
We have initiated a collaborative research program to develop a polymeric, lipid membrane-based, supramolecular assembly that uses photon energy to drive a biomimetic energy transduction process, specifically vectoral proton pumping. The creation of a light-driven proton pump interfaced to an electrically active support is a necessary first step toward efficient coupling of these types of photosynthetic processes to useful molecular devices, e.g. biosensors and energy conversion devices.

The overall design of the assembly is illustrated below. The membrane is composed of synthetic lipids self-assembled into a bilayer, then chemically cross-linked to provide chemical and physical stability. Artificial photosynthetic reaction centers, being developed in the laboratories of Tom Moore, Ana Moore, and Devens Gust at Arizona State University, will be incorporated into the stabilized bilayer. The membrane will be tethered to a planar semiconductor, e.g. a thin indium tin oxide (ITO) layer, via a thin, conductive polymer film (e.g. polyaniline), which will provide a water-swollen "cushion" for accumulation of translocated protons and transduction of the light-driven pmf into a change in interfacial potential. The ITO layer functions as the working electrode in a spectroelectrochemical planar waveguide device, which will allow simultaneous electrochemical and optical characterization. Recent progress toward creation of the individual components of this device will be presented.



Proposed energy transduction system composed of a planar ITO electrode is modified with a ca. 3-10 nm thick hydrophilic, conductive polymer cushion (e.g. polyaniline), which in turn supports a planar lipid bilayer (5 nm thick) that has been stabilized by cross-linking polymerization, and incorporates an artificial photosynthetic reaction center (C-Pur-$C_{60}$). Upon light absorption, the C-Pur-$C_{60}$ undergoes charge separation and electron transfer to produce $C^+$-Pur-$C_{60}^-$, which reduces the diffusive quinone ($Q_s$) at the outer interface and oxidizes it at the inner interface. Thus $Q_s$ shuttles protons from the outer medium across the membrane to the water-swollen space occupied by the polymer cushion. The ITO film (ca. 25-100 nm thick) is the upper layer of a spectroelectrochemical, single-mode planar waveguide. Broadband, polarized planar waveguide ATR spectroscopy, performed under potential control or during potentiometric characterization of the biomimetic process, is used to initiate nanometer-scale proton pumping, quantitatively determine its efficiency, and characterize key structural and functional properties of the multilayer architecture.

Poster # 39

# VIBRATIONAL DYNAMICS IN PHOTOINDUCED ELECTRON TRANSFER

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

We have re-examined our earlier report of electron transfer (ET) in the radical pair $[Co(Cp)_2|V(CO)_6]$ using ultrafast infrared transient absorption spectroscopy, and in this presentation we will focus on interpretation and modeling of geometric structure. One emphasis is to understand the geometric relaxation effects in the $V(CO)_6$ radical, which is Jahn-Teller unstable and capable of inter-converting between multiple geometries. Our experimental data measured a time of 200 fs for relaxation into a stable geometry when there is extra vibrational energy in the system, and we seek to computationally model all of the possible geometries. A second emphasis is to relax all geometric constraints in the ion pair and radical pair, which should also determine if the $Co(Cp)_2$ radical can confer extra stabilization to a particular geometry.

We previously identified a second geometry for the $V(CO)_6$ radical with a $D_{2h}$ symmetry instead of a $D_{3d}$ symmetry of the lowest state, and it was +205 $cm^{-1}$ higher energy and had one imaginary vibration so that it was actually a saddle point. The method of Density Function Theory (DFT) with both B3LYP and BP86 was used in our recent work, and we have found a $C_{2h}$ stable geometry near the prior $D_{2h}$ geometry that is +130 $cm^{-1}$ higher in energy and another $D_{2h}$ geometry of +580 $cm^{-1}$ (in B3LYP, 6-311G*). The relative ordering and existence is independent of DFT method and basis set, so we feel that the main Jahn-Teller geometries have been found. More importantly to our experiments, the IR vibrational frequencies of the two lowest geometries are only 5-10 $cm^{-1}$ different from the lowest energy. The observation of uncertainty broadening in the experiment for 200 fs suggests that there might be some interactions with the paired radical that stabilize the geometry, and the results of our current studies will be reported at the meeting. We find that the metal-metal distance decreases when the radicals can relax, and we are now studying the geometry sensitivity to distortion and relative stabilities.

We have also been studying models of methyl quinolinium cation and the $Co(CO)_4$ anion, and the related radical pairs. Experimental work has begun on this system and we will be trying measurements in glassy, thin film and crystalline environments to see the effect on electron transfer rates.

Poster # 40

# CHARGE ATTACHMENT TO CONJUGATED MOLECULES IN SOLUTION

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Long conjugated organic molecules have potential application for solar energy conversion processes as charge transport material or molecular wires. Information about charge injection into long molecules should provide a basis for studying the charge transport properties of molecular wires. Electron and hole attachment to oligomers and polymers of thiophenes (nT) and poly(phenyleneethynylene) (PPE) in organic solvents were studied by pulse radiolysis. Radical anions of polymers and oligomers studied showed optical absorption bands in vis-NIR region. Electron attachment rates of ~1x $10^{11}$ $M^{-1}s^{-1}$ found for thiophene oligomers (n= 2~4) in THF were similar to the diffusion-controlled rate for electron capture by molecules such as biphenyl. On the other hand, the observed rate for regioregular poly(3-decylthiophene) (P3DT) was only about ten-fold faster than that for oligomers despite its much bigger size ($M_n$ ~30,000; n ~135). The result could indicate that the polymer geometry in solution is distorted from a linear conformation or that aggregation is significant. Theories that describe diffusion-controlled reactions to long chains of n reacting sites predict that for very long molecules (large n) the rate constants increase as ~n/ln(n). In view of this theory, the rates suggest that the polymer is more linear and not extensively aggregated.

Rates at which charge is removed from the polymer by reaction with small molecules also provide information about the state and delocalization of charge in the conjugated polymer. These rates are much more like those for diffusion-controlled reaction of two small molecular species and the reactions can also provide a measure for the redox potential of the polymer.

Poster # 41

# CHROMOPHORE-CORED DENDRIMERS WITH AN ENERGY GRADIENT FOR LIGHT HARVESTING

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Light harvesting devices in biological systems are based on the relative spatial organization of the functional units to direct the charge migrations. The unique macromolecular architecture of dendrimers presents new avenues to control the spatial placement of functional moieties and thus control electronic motions within a macromolecule. Therefore, opportunities to design molecular-scale devices and carry out fundamental studies on the factors that affect light initiated processes such as photoinduced charge migrations are available. Compared to their linear chain counterparts that afford control in one dimension, dendrimers present more compact spatial arrangements in higher dimensions. Moreover, as the charge separates from the core to the periphery, the number densities of the CT units double with each layer of the dendrimer. Therefore, the charge separation could be expected to be more favorable in the compact three-dimensional dendritic macromolecules than their one-dimensional linear counterparts.

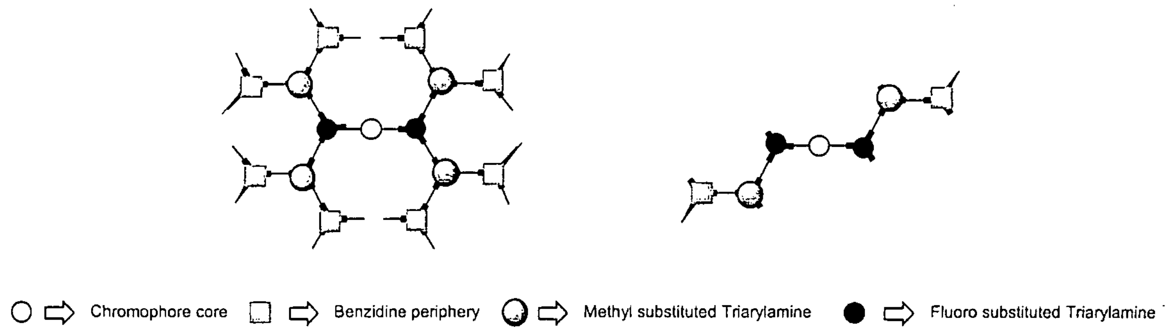

**Figure**. Schematic representation of a charge transport dendron and linear analog

Dendrimers have been designed and synthesized that contain a chromophore core and two hole-transporting (HT) dendrons. Last year, the development of synthetic methodology for achieving tryiarylamine-based dendrons was reported. In this poster, the syntheses of dendrimers with a triarylamine backbone, quinacridone core, and benzidine periphery will be described. Since the radical ion spectra of triarylamines is sufficiently different from benzidines, these moieties serve to identify the location of the positive charge with time. Also, the substituents in the triarylamines are varied in order to build a redox gradient within the dendrimers and thus guide the charge towards the periphery. In order to perform the control studies, the corresponding linear molecules also have been synthesized. The poster will also outline the electrochemical studies of the redox gradient dendrons and some of the preliminary steady-state photophysical studies of these dendrimers and the corresponding linear molecules. The photophysical studies indicate that the chromphores at the core in a second-generation dendrimer is encapsulated and possibly solvent-excluded. This feature will have implications in the efficiency of photoinduced charge separations. Therefore, in order to further investigate this possibility, dendrimers with charge transport units only in the periphery and dendrimers with charge transport units only in the core are being synthesized. Progress in these approaches will also be reported.

Poster # 42

# LOOKING FOR PHOTOOXIDATION OF A Ru(II) POLYPYRIDINE AQUA COMPLEX AS A FIRST STEP IN WATER DECOMPOSITION

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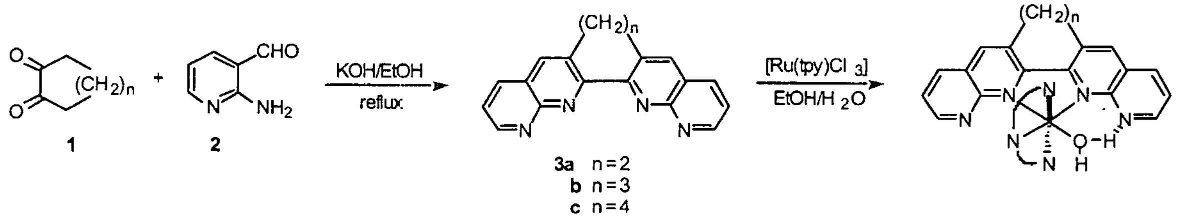
We are interested in exploiting the metal-to-ligand charge transfer character of the excited state of a Ru(II) complex to assist deprotonation, and ultimately oxidation, of a metal bound water molecule. A series of 3,3'-bridged 2,2'-bi[1,8]naphthyridines was synthesized by the Friedländer condensation of 2-aminonicotinaldehyde with cyclic 1,2-diketones. Complexation with [Ru(tpy)Cl3] followed by hydrolysis leads to the aqua-complexes which have been thoroughly characterized by NMR, IR, optical spectroscopy, and x-ray.



X-ray analysis of the aqua-complex where n = 2 reveals that the coordinated water molecule is hydrogen-bonded to the uncomplexed nitrogen of the binaphthyridine ligand. Solvation kinetics demonstrate that displacement of water by acetonitrile is more difficult for the more planar system (n = 2). While solvent exchange of the trimethylene bridged system (n = 3) is complete in about 90 minutes (Fig. 1), the dimethylene-bridged system requires more than 24 hours. In dichloromethane all three complexes oxidize at about +1.06 V (vs. SCE) while pH dependent CV measurements show more variation. A terpyridine ligand analogous to 3 has been prepared as an alternative probe to ligand-assisted deprotonation.

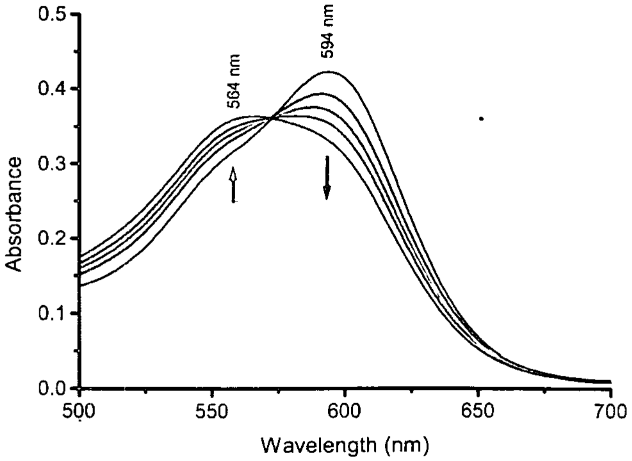


Figure 1. Change in the MLCT absorption of $[Ru(3c)(tpy)(H_2O)]^{2+}$ with added acetonitrile.

**Poster # 43**

# ANALYZING STRUCTURE AND DYNAMICS OF SELF-ASSEMBLED MOLECULAR SYSTEMS FOR PHOTOCHEMICAL ENERGY CONVERSION USING HIGH-ANGLE X-RAY SCATTERING

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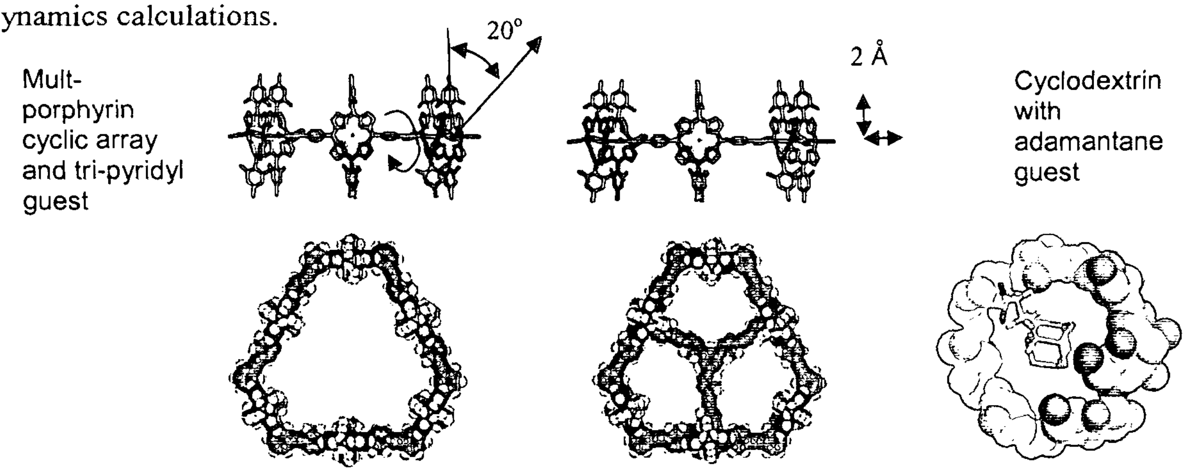
Tremendous advances have been made in the development of synthetic approaches for the creation of molecular assemblies for photochemical energy conversion based on hierarchical design, building block architectures, and controlled self-assembly. While there is an excellent database on building block structures such as porphyrins and organometallic complexes, a critical need exists for the development of *in situ* techniques for structural resolution of complex molecular assemblies in liquids and other disordered media, and to explore the structural basis for function based on time-resolved molecular structure. We have found that a combination of synchrotron measurements (SAXS, WAXS, XAFS) provides a high-resolution, highly sensitive approach for resolving the structure and structural dynamics of complex molecular assemblies under conditions directly relevant to function. We are developing approaches for quantitatively analyzing wide-angle scattering data in terms of time-averaged atom position, temperature factors, and rigid-body motions. We have measured X-ray scattering to a resolution of 2.5Å for a variety of assemblies in solution, including a light-harvesting hexameric porphyrin array, the porphyrin array guest-host assembly, and a series of cyclodextrin-based guest-host complexes that are being developed as linkers for bio-inorganic photochemical assemblies. This resolution was found to be sufficient to resolve configurational states relevant to function, and that the scattering data can be used to "refine" crystallographic or other molecular models to fit structures and dynamics in solution. For example, WAXS measurements for the cyclic porphyrin array discriminated between different energy-minimized conformers and demonstrated a slight 0.2 Å contraction upon tri-pyridyl guest inclusion. Rigid body conformational flexibility was characterized by 20° rms dispersion in the porphyrin plane orientation, and 2 Å rms dispersion in porphyrin positions. The WAXS measurements are being used as a direct test of molecular dynamics calculations.



# PROTEIN CONFORMATIONAL CHANGES CORRELATED TO ELECTRON TRANSFER PROCESSES IN THE BACTERIAL REACTION CENTER

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Proteins fluctuate between different conformational substates at physiological temperature. This intrinsic flexibility is often intimately coupled to protein reactivity, such as electron transfer reactions. The photosynthetic bacterial reaction center (RC) provides an important system for addressing basic questions regarding the nature of conformational changes coupled to biological electron transfer. In RCs, electron transfer occurs sequentially after photoexcitation of a bacteriochlorophyll dimer (P), through one set of cofactors, terminating in the electron transfer between two quinone cofactors, $Q_A$ and $Q_B$. Our work has been focused on the $Q_A^-Q_B \rightarrow Q_AQ_B^-$ electron transfer step. This reaction is temperature activated, coupled to proton movement, modulated by metal ions, and rate limited by conformational changes. As a result of necessary conformational changes, $Q_A^-Q_B \rightarrow Q_AQ_B^-$ electron transfer is not observed at low temperature for RCs frozen in the dark. However, electron transfer between the quinones does occur below 40 K for RCs frozen under illumination in the $P^+Q_B^-$ state and then allowed to return to the ground state. These observed alterations of reaction kinetics by illumination while cooling have been linked to trapping the RC in altered conformations induced by charge separation. We have initiated a detailed spectroscopic study of the heterogeneous polypeptide environments surrounding the redox cofactor sites of *Rb. sphaeroides* RCs to elucidate the light-induced protein conformational changes necessary for low temperature $Q_A^-Q_B \rightarrow Q_AQ_B^-$ electron transfer. High-frequency pulsed D-band (130 GHz) EPR spectral results show that it is possible to distinguish the $P^+$, $Q_A^-$ and $Q_B^-$ radical species in Fe-removed/Zn-replaced RCs substituted with deuterated quinones. Hence, we have used these native RC cofactors as spectroscopic probes of both the low temperature electron transfer kinetics and the structure of trapped conformational substates. Results from pulsed D-band EPR and ENDOR spectroscopies provide structural details of the radicals $Q_A^-$ and $Q_B^-$ and their surrounding protein environments when frozen under different light conditions. Three distinct conformational substates are trapped when the RC is frozen under red light or continuous laser flashing. We have obtained the first high-frequency matrix ENDOR spectrum of $Q_B^-$ for these states. No structural differences at $Q_B^-$ or in the protein structure near $Q_B^-$ were observed for different trapping conditions. We are currently extending these studies to examine the light-induced response of the polypeptide environments surrounding $P^+$ and $Q_A^-$. These experiments will lead to a better understanding of the protein conformational changes necessary for efficient photosynthetic electron transfer.

Poster # 45

# NEW APPROACHES FOR THE COMPUTER SIMULATION OF ELECTRON TRANSFER REACTIONS

Gregory A. Voth
University of Utah

Much of our DOE-funded research[1-5] has been devoted to exploring the fundamental assumptions underlying electron transfer (ET) theory. This body of work has led us to conclude that existing computational approaches for calculating ET rates constant are inadequate. In general, these approaches are missing one or more key features, all of which involve *electronic* and *quantum* effects. In particular, the roles of electronic polarizability (of both the ET complex[1,5] and the solvent[6]), electronic delocalization,[1,2] conformational (non-Condon) effects on the donor-acceptor electronic couplings, and quantization of the nuclear motion are not fully incorporated into the standard computational framework. In this poster, new theoretical methods will be described which promise to greatly expand the range and accuracy of computer simulation in the field of ET. The first such method is a new approach to *ab initio* Molecular Dynamics called Atom-Centered Density Matrix Propagation (ADMP) which will allow us to more accurately describe electronic polarization and delocalization effects in ET reactions. The second method is non-adiabatic Centroid Molecular Dynamics (nCMD) in which *nuclear* quantum effects can be incorporated into ET simulations for realistic condensed phase systems. Results will also be given on *ab initio* MD simulations of semiconductor/electrolyte interface systems,[4] which further reveal the importance of both electronic delocalization and polarization effects, thus highlighting the overall theme of this research.

1. D. V. Matyushov and G. A. Voth, "Reorganization Parameters of Electronic Transitions in Electronically Delocalized Systems: I. Electron Transfer Reactions," J. Phys. Chem. A **104**, 6470 (2000).
2. D. V. Matyushov and G. A. Voth, "Reorganization Parameters of Electronic Transitions in Electronically Delocalized Systems: II. Optical Spectra," J. Phys. Chem. A **104**, 6485 (2000).
3. D. Matyushov and G. A. Voth, “Modeling the Free Energy Surfaces of Electron Transfer in Condensed Phases,” J. Chem. Phys. **113**, 5413 (2000).
4. G. Narayanan, S. Izvekov, and G. A. Voth, "*Ab initio* Molecular Dynamics Simulation of the H/InP(100)–Water Interface," J. Chem. Phys. 117, 872 (2002).
5. D. W. Small, D. M. Matyushov, and G. A. Voth, "The Theory of Electron Transfer Reactions: What May Be Missing?" J. Am. Chem. Soc. (in press).
6. J. Jeon, A. E. Lefohn, and G. A. Voth, "An Improved Polarflex Water Model," J. Chem. Phys. (in press).

**Poster # 46**

# NANOPARTICLE-CORED DENDRIMERS: SYNTHESIS AND CHARACTERIZATION

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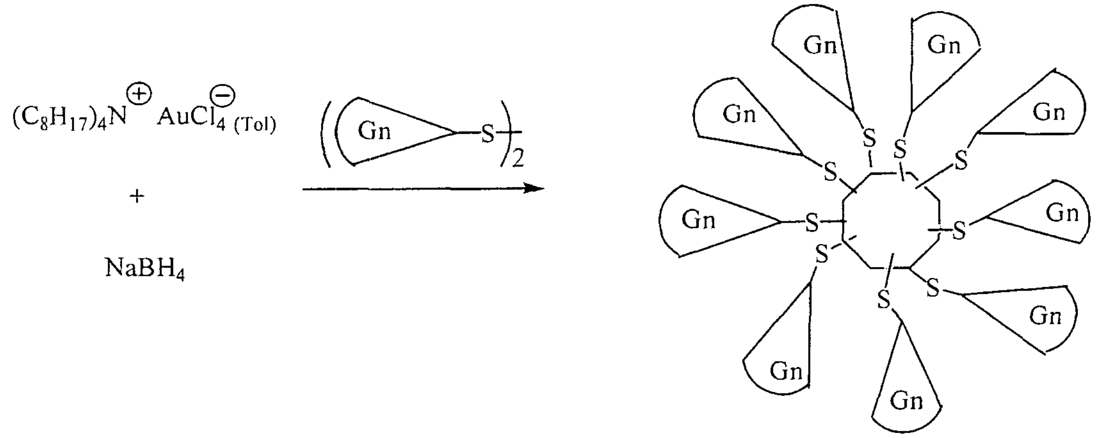
A family of nanoparticle-cored dendrimers has been obtained by the reduction of hydrogen tetrachloroaurate phase-transferred into toluene in the presence of Frechet-type polyarylether dendritic disulfide wedges of generation 1-5, as shown below. These materials possess nanometer-sized gold clusters at the core and dendritic wedges radially connected to the core by gold-sulfur bonds. Analyses by TEM, TGA, UV, IR, and NMR spectroscopies show that the number of branching units connected to the core decreased with the increasing size (generation) of the dendritic wedge. The surface density of the outer shell ranged from 2.18/nm2 for Au-G-2 to 0.27/nm2 for Au-G-5. In the higher generation dendrimers, a large fraction of the metal surface is not passivated and is therefore available for catalytic activity. Thus, NCDs can act as nanoreactors with potential applications in catalysis.



References

"Metal Core—Organic Shell Dendrimers as Unimolecular Micelles," K.R. Gopidas, James K. Whitesell, and Marye Anne Fox, *Chem. Mater.* **2003**, submitted.

"Photophysical Behavior of Variously Sized Colloidal Gold Clusters Capped with Monolayers of an Alkylstilbenethiolate," Jian Zhang, J.K. Whitesell, and Marye Anne Fox, *J. Phys. Chem.* **2003**, in press.

"Energy Transfer from a Surface-bound Arene to the Gold Core in w-Fluorenylalkane-1-thiolate Monolayer Protected Gold Clusters," Tao Gu, James K. Whitesell, and Marye Anne Fox, *Chem. Mater.* **2003**, *15(6),* 1358-1366.

"Nanoparticle-Cored Dendrimers: Synthesis and Characterization," K.R. Gopidas, J.K. Whitesell, and Marye Anne Fox, *J. Amer. Chem. Soc.* **2003**, in press.

# SINGLE-MOLECULE PROTEIN DYNAMICS ON MULTIPLE TIME SCALES PROBED BY ELECTRON TRANSFER

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The conformational dynamics of biomolecules is crucial to their biological functions. Recent advances in room-temperature single-molecule fluorescence spectroscopy allow for real-time observations of conformational motions of individual biomolecules, in particular those on the nanometer scale through fluorescence resonance energy transfer (FRET). Here we demonstrate a new experimental approach to conformational dynamics through photoinduced electron transfer (ET), which sensitively probes the distance between a donor-acceptor (D-A) pair within a protein on the angstrom scale. We report a new observation that a single flavin enzyme molecule undergoes spontaneous D-A distance fluctuation at a broad range of time scales spanning from hundreds of microseconds to seconds. This results from the interconversion among a distribution of conformers, the rate of which is inaccessible from nonequilibrium relaxation experiments on large ensemble of molecules. Our direct measurement of the equilibrium fluctuation of a single protein molecule reveals rich information regarding the energy landscape and dynamics of protein, in particular the potential of mean force for the D-A pair and the anomalous diffusion within. The long-lived conformers might be responsible for the fluctuating catalytic reactivity.

1. Haw Yang, Guobin Luo, Pallop Karnchanaphanurach, Tai-Man Louie, Luying Xun, and X. Sunney Xie, "Single-Molecule Protein Dynamics on Multiple Time Scales Probed by Electron Transfer," submitted to *Science*.
2. Xie, X. Sunney "Single-molecule approach to dispersed kinetics and dynamic disorder: Probing conformational fluctuation and enzymatic dynamics," *J. Chem. Phys.* **117**: 11024 (2002).
3. Yang, Haw; Xie, X. Sunney "Probing Single Molecule Dynamics Photon by Photon," *J. Chem. Phys.*, **117**, 10965 (2002).
4. Sánchez, Erik J.; Krug, John T. II; Xie, X. Sunney "Ion and electron beam assisted growth of nanometric $Si_mO_n$ structures for near-field microscopy," *Rev. Sci. Instr.*, 73, 3901 (2002).
5. Louie, Tai Man; Yang, Haw; Karnchanaphanurach, Pallop; Xie, X. Sunney; Xun, Luying "FAD is a Preferred Substrate and an Inhibitor of Escherichia coli General NAD(P)H: flavin Oxidoreductase," *J. Biol. Chem.*, **277**, 39450 (2002).
6. Yang, Haw; Xie, X. Sunney "Statistical Approaches for Probing Single-Molecule Dynamics Photon-by-Photon," *Chem. Phys.*, **284**, 423 (2002).
7. Krug, John T. II; Sánchez, Erik J.; Xie, X. Sunney "Design of near-field optical probes with optimal field enhancement by finite difference time domain electromagnetic simulation," *J. Chem. Phys.*, **116**, 10895 (2002).

**Poster # 48**

# COMPUTATIONAL STUDIES OF BIOMOLECULE INTERACTIONS WITH TITANIUM OXIDE NANOPARTICLES

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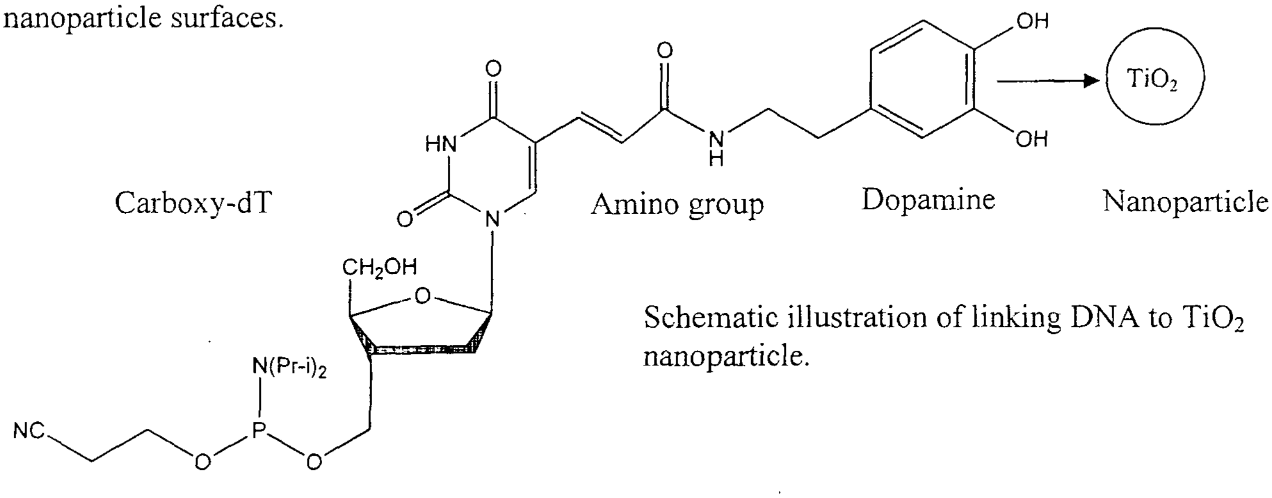
Bio-inorganic interfaces for energy conversion involve charge transfer from a biomolecule to a nanoparticle. The goal of computational studies is to help understand experimental observations and to guide experimental studies to find conditions for more efficient charge transport. Computational studies involve modeling of nanoparticle surface structure and its electronic structure; modeling chemical binding and charge separation between organic linkers and the nanoparticle; and modeling of charge transfer between the linker and the biomolecule such as DNA.

Anatase nanoparticles show a large red shift of about 1.6 eV in the optical spectra when their surface is modified by catechol. A suggested explanation involves under-coordinated corner defects having Ti=O double bonds, which are reactive towards these ligands and result in bidentate dissociative bonding. We have expanded our previous calculations of the interaction of catechol and water with titanium oxide nanoparticles using *ab initio* molecular orbital theory and density functional theory and taking into account possible surface relaxation. We found that a bridging bidentate structure of catechol is strongly stabilized by the surface relaxation while other structures are not strongly affected.

Carboxy-dT, which is used in experiments to help covalently bind DNA to surfaces, was used in the modeling of linker charge transfer properties. Photoexcitation in a DNA-nanoparticle system leads to a hole transport through linker and DNA. Charge transfer rates are related to oxidation potentials. Density functional calculations have been undertaken to study electronic properties of isolated and base-paired carboxy-T without/with an amino group in the gas phase and in solution. It was found that electron donating properties of thymine are increased by consecutive addition of carboxyl and secondary amide functional groups. In aqueous solution, this modification leads to the thymine ionization potential becoming close to that of adenine in the base pair.

Future work will concentrate on the goal of obtaining a realistic description of charge transport and electronic properties of DNA-$TiO_2$ systems. Quantum chemistry methods will be used to calculate oxidation properties of dopamine linking isolated and base-paired carboxy-T to nanoparticle surfaces.



Schematic illustration of linking DNA to $TiO_2$ nanoparticle.

**Poster # 49**

# DETERMINING DNA STRUCTURE IN SOLUTION BY WIDE ANGLE X-RAY SCATTERING

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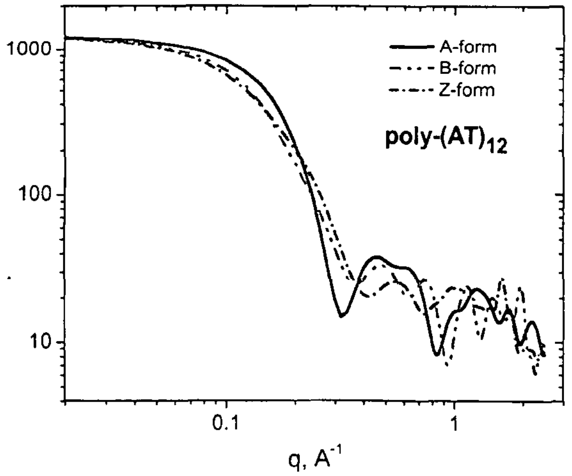
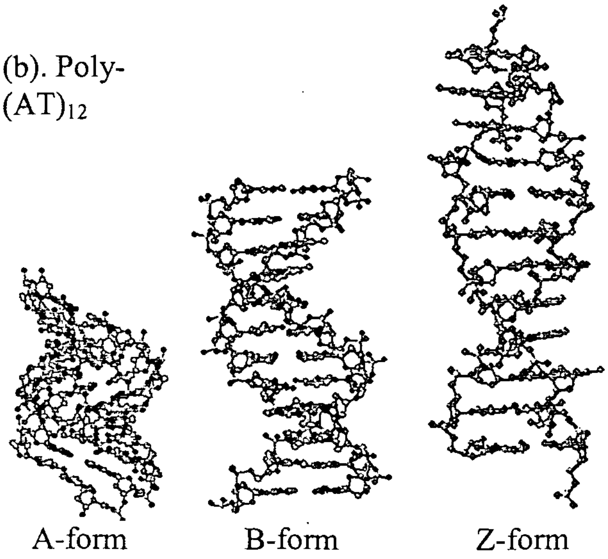
DNA is widely explored as a building block for molecular electronics, recognition, and as a linker for light-activated donor/acceptor assemblies. Information on the structure of DNA in liquids and other noncrystalline media is essential for fully understanding electron transfer, exciton coupling, and self-assembly/molecular recognition processes taking place within DNA. Crystallography and NMR are the two frequently used methods for obtaining the DNA structure. DNA in solution may not necessarily adopt the conformation in crystal. NMR methods are indirect, typically require long acquisition times, and are not readily amenable for ps time-resolved structure resolution. In this project, we are investigating synthetic DNA structure and structural dynamics in solution using synchrotron wide angle X-ray scattering. Calculations show that high-angle scattering patterns are particularly rich, and can readily distinguish DNA with different forms (Fig 1). Calculations also show that the phosphate backbone of DNA dominates the X-ray scattering. However, in peptide nucleic acids (PNA) X-ray scattering will provide more information on the alignment of base pairs. The structure of DNA in solution is dynamic, which was experimentally observed in the wide angle X-ray scattering pattern, indicated by the peak broadening and attenuation. In order to understand the structural dynamics, temperature dependent scattering and molecular dynamic simulations will be carried out. This project is establishing the foundation for the application of time-resolved scattering techniques to analyze conformational states of DNA linked to electron transfer processes.

Figure 1(a). Calculated scattering pattern.



(b). Poly-(AT)$_{12}$



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