

Proceedings of the
Forty-Seventh
DOE Photochemistry and
Radiation Chemistry
P.I. Meeting

Bethesda North Marriott
Rockville, Maryland
June 1-3, 2026

Chemical Sciences, Geosciences, and Biosciences Division
Office of Basic Energy Sciences
Office of Science
U.S. Department of Energy

FOREWORD

The 47th Department of Energy Photochemistry and Radiation Chemistry Principal Investigators' Meeting, sponsored by the Chemical Sciences, Geosciences, and Biosciences Division of the Office of Basic Energy Sciences (BES), is being held June 1-3, 2026, at the Bethesda North Marriott in Rockville, Maryland. These proceedings include the meeting agenda as well as abstracts of the formal presentations and posters.

Solar Photochemistry supports fundamental, molecular-level research on photochemistry and radiation chemistry in the condensed phase and at interfaces. This annual conference is intended to facilitate the exchange of scientific ideas and foster collaboration among researchers.

During the past few decades, the Solar Photochemistry PI meeting has primarily featured projects focused on photochemical phenomena. The meeting this year also includes PIs from radiation chemistry projects. Solar Photochemistry has provided robust support for radiation chemistry research since its inception in the mid-1970s, but PIs in that area have traditionally attended the Condensed Phase and Interfacial Molecular Sciences PI meeting. That arrangement has yielded valuable outcomes and is likely to continue in the future. However, a strong connection between photochemistry and radiation chemistry efforts also offers scientific benefits and opportunities, so PIs from both communities have been invited to participate in this year's Solar Photochemistry meeting.

We would like to express our thanks to Kerry Hochberger of Basic Energy Sciences, as well as Paul Hudson and his colleagues at the Oak Ridge Institute for Science and Education for their assistance with meeting logistics. Finally, we are grateful to all of the participants in this meeting who have contributed so much to the continued success of the Solar Photochemistry Program.

Chris Fecko and Jennifer Roizen
Chemical Sciences, Geosciences,
and Biosciences Division
Office of Basic Energy Sciences

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**47th DOE PHOTOCHEMISTRY AND RADIATION CHEMISTRY
PI MEETING**

June 1-3, 2026

Bethesda North Marriott, Rockville, MD

PROGRAM

Monday Morning, June 1

7:30 a.m. Breakfast

**SESSION I
Opening Session
Jenny Roizen, Chair**

8:30 a.m. News from DOE-BES Chemical Sciences, Geosciences, and Biosciences Division
Gail McLean, DOE Office of Basic Energy Sciences

9:00 a.m. Examining Catalysts at Solution-Catalyst Interfaces
Dan Nocera, Harvard University

9:30 a.m. Electric and Chemical Potentials in Driven (Photo)electrochemical Systems:
Heterogeneity, Dynamics, and the Connection to Interfacial Structure and
Reactivity
Shannon Boettcher, Lawrence Berkeley National Laboratory

10:00 a.m. Break

**SESSION II
Radiation Chemistry
Chris Fecko, Chair**

10:30 a.m. Radiation Effects in Nuclear Reactors: Speciation and Redox Reaction Rates in
High-temperature Water
Dave Bartels, Notre Dame University

11:00 a.m. Non-equilibrium Actinide Radiation Chemistry—From Radiation Tracks to Bulk
Homogenous Phenomena
Greg Holmbeck, Idaho National Laboratory

- 11:30 a.m. Radiation Chemistry Capabilities at Brookhaven National Laboratory and Recent Studies on Radiolytic Transients in Ionic Liquids
Jim Wishart, Brookhaven National Laboratory
- 12:00 p.m. Working Lunch (*Discussions about synergies between photochemistry and radiation chemistry*)

Monday Afternoon, June 1

SESSION III
Proton Transfer with an Electron or Two
Kara Bren, Chair

- 3:30 p.m. Computational Modeling of Concerted Proton-Electron Transfer and Hydride Transfer Reactions
Zahid Ertem, Brookhaven National Laboratory
- 4:00 p.m. Understanding Transition Metal Hydride Intermediates for Selective Electrocatalytic Reduction Reactions
Jenny Yang, University of California, Irvine
- 4:30 p.m. Redox-Active Ligands for Rapid Reductive PCET Mediation
Pat Holland, Yale University
- 4:45 p.m. Break

SESSION IV
Ultrafast Photochemical Processes
Renee Frontiera, Chair

- 5:00 p.m. Elucidating Photoinduced Bond Formation/Cleavage Pathways in Dimeric Pt Complexes by Time-Resolved Wide-Angle X-ray Scattering
Michael Mara, Argonne National Laboratory
- 5:30 p.m. Charge Transfer from Electrochemically Controlled Colloidal Nanoparticles
Tim Lian, University of Pennsylvania

Monday Evening, June 1

- 6:00 p.m. Working Dinner (*Program comments, Chris Fecko and Jenny Roizen*)
- 7:30 p.m. Posters (*Odd numbers*)

Tuesday Morning, June 2

- 7:30 a.m. Breakfast

SESSION V **Macromolecular Organic Photochemistry** Julia Kalow, Chair

- 8:30 a.m. Design, Structure Analyses, and Catalytic Mechanism of Covalent Organic Framework based Photocatalysts
Jier Huang, Boston College
- 9:00 a.m. Understanding Local Nanoenvironments Driving Charge Transfer in Conducting Polymer (Photo)anodes
Erin Ratcliff, Georgia Institute of Technology
- 9:30 a.m. Protonic Diodes and Amplified Electrochemical Cell Potentials: Ion-exchange Membranes Can Do Far More Than Simply Conduct Ions and Separate Reaction Products
Shane Ardo, University of California, Irvine
- 10:00 a.m. Break

SESSION VI **Influencing Reactivity at Photoelectrochemical Interfaces** Kyoung-Shin Choi, Chair

- 10:30 a.m. Probing Water Oxidation Mechanisms on Heterogeneous Catalysts with Atomically Defined Active Sites
Dunwei Wang and **Matthias Waegle**, Boston College
- 11:00 a.m. Tuning Semiconductor, Catalyst, and Electrolyte to Direct Reactivity at PEC Interfaces
Ann Greenaway, National Laboratory of the Rockies

11:30 a.m. Light-Controlled Multi-Electron Catalysis coordinated across Time and Space
Junko Yano and **Joel Ager**, Lawrence Berkeley National Laboratory

12:00 p.m. Working Lunch (*Discussions about formulation of a Data Management Plan*)

Tuesday Afternoon, June 2

SESSION VII **Exploiting Charge Transfer in Molecules** Jeff Blackburn, Chair

3:30 p.m. How Can We Make Better Use of the Inverted Region? A Pulse Radiolysis Study
Matt Bird, Brookhaven National Laboratory

4:00 p.m. Electrostatic Effects in Proton-Coupled Electron Transfer
Ana Moore, Arizona State University

4:30 p.m. Developing the Photocatalytic Workforce
Kristy Mardis, Chicago State University

4:45 p.m. Break

SESSION VIII **Leveraging Two-Dimensional Semiconductors** Prashant Kamat, Chair

5:00 p.m. Bandgap Renormalization and Hot-carrier Photoelectrochemistry at 2D
Semiconductor Electrodes
Justin Sambur, Colorado State University

5:30 p.m. Versatility of Transition Metal Chalcogenides for Durable Photoelectrodes,
Ammonia Generation, and Long-lived Carriers
Elisa Miller, National Laboratory of the Rockies

Tuesday Evening, June 2

6:00 p.m. Working Dinner (*Program comments, Chris Fecko and Jenny Roizen*)

7:30 p.m. Posters (*Even numbers*)

Wednesday Morning, June 3

7:30 a.m. Breakfast

SESSION IX
Organic-Inorganic Interfaces
Mike Therien, Chair

8:30 a.m. Photoinduced Charge and Energy Transfer in Hybrid Donor-Acceptor Systems
Oleg Poluektov, Argonne National Laboratory

9:00 a.m. Controlling Correlated Triplet-Pair Dynamics at Two-Dimensional van der Waals Interfaces
Libai Huang, Purdue University

9:30 a.m. Templating Organic Semiconductors on Silicon for Enhanced Singlet Fission Photophysics
Bobby Jacobberger, University of Wisconsin-Madison

9:45 a.m. Break

SESSION X
Analyzing Semiconductor Photoelectrodes
Mike Mirkin, Chair

10:15 a.m. Description and Application of a Quantitative Model for Voltammetry of Freely Diffusing Redox Species at Semiconductor Photoelectrodes
Stephen Maldonado, University of Michigan

10:45 a.m. Hybridized Semiconductor|Molecule Platforms to Understand Charge-Separation & Charge-Transfer at Interfaces
Mike Rose, University of Texas at Austin

11:15 a.m. Photovoltage Generation at Junctions in Heterogeneous Solar Fuel Photocatalysts and Photoelectrodes
Frank Osterloh, University of California, Davis

11:45 p.m. Working Lunch (*Discussions about new directions for the field*)

Wednesday Afternoon, June 3

SESSION XI
Inorganic Molecular Photosensitizers and Photocatalysts
Jillian Dempsey, Chair

- 1:00 p.m. Heteroleptic Copper(I) Photosensitizers with Long Excited-State Lifetimes
Tom Teets, University of Houston
- 1:30 p.m. Photocatalytic H₂ Production: Investigation of New First-Row Transition Metal Complexes
Claudia Turro, Ohio State University
- 2:00 p.m. Striking While the Fe is Hot: Spin-state and Reorganization Energy Considerations and Anti-Kasha Reactivity in the Photophysics and Photochemistry of Iron(II) Complexes
Jim McCusker, Michigan State University
- 2:30 p.m. Closing Comments
Chris Fecko and Jenny Roizen, DOE Office of Basic Energy Sciences
- 2:45 p.m. Adjourn

Examining Catalysts at Solution-Catalyst Interfaces

Daniel G. Nocera

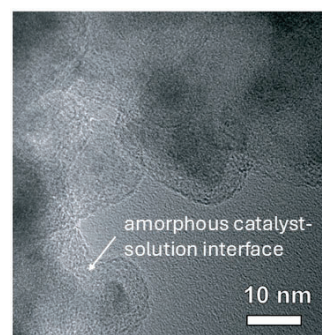
Department of Chemistry and Chemical Biology

Harvard University

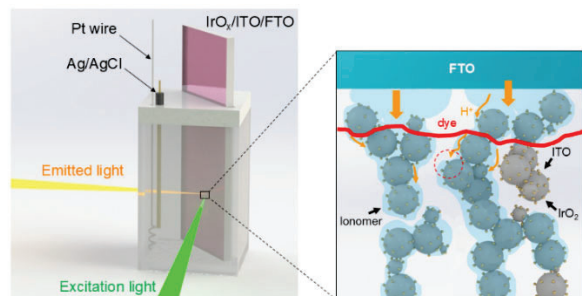
Cambridge, MA 02138

Energy conversion reactions comprise proton-coupled electron transfer (PCET) steps that occur at the interface between the catalyst surface and solvent. It is the interfacial environment that supplies the solvation to enable the coupling of the electron to the proton, providing an imperative for understanding the nature of the interface during catalysis. Recent efforts have focused on how interfacial properties control catalytic reactions.

Performance metrics for catalysts typically report the current density at a given overpotential. Increased performance is ascribed to superior catalytic design. However, this assumption of an intrinsically better catalyst (OER rate constant) in the working environment is not complete as a higher current density at a lower overpotential may arise from a higher concentration of active sites. This assumption in catalyst performance is especially problematic if the crystalline lattice of the catalyst in the working environment is prone to deconstruction and amorphization, thus increasing the number of active sites in the interfacial region. We show this to be the case for first-row, mixed-metal oxide OER catalysts using lanthanide-incorporated cobalt/nickel oxides.



HRTEM image of La^{3+} incorporated Co_3O_4 .



Operando method to determine local pH within a porous electrode microenvironment

In addition to the catalyst interface, it is also helpful to probe the solvent at the catalyst interface. The production and consumption of protons by electrocatalysts that drive the energy conversion reactions can generate localized microenvironments with properties distinct from those of the bulk solution. These local properties are particularly impactful to reactions involving PCET, where the generation of locally basic or acidic environments may significantly influence the energy efficiency and reaction selectivity of

the electrocatalysis. We report an operando method employing polymer bound fluorescent sensors to directly quantify the internal proton gradient in a porous electrode for the OER. Accompanying these measurements is a model that relies only on the straightforward parameters of bulk pH, buffer composition and pK_a , and mass-transport to describe local pH as a function of current density, regardless of the microscopic details of the mechanism. We have shown that local pH considerations can explain the catalytic enhancements observed for reactions at nanostructured electrodes.

In summary – a pristine catalyst in a bulk solution may significantly diverge from the catalyst-solution interface ... where catalysis occurs in the working environment.

DOE Solar Photochemistry Sponsored Publications 2023-2026

1. Operando pH Measurements of OER Within a Porous Oxygen Evolving Electrode. Zhifei Yan, Daniel M. Loh, Rui Sun and Daniel G. Nocera, submitted for publication.
2. Ambient-Pressure X-ray Photoelectron Spectroscopy of the Water Interface of Lanthanum-Modified Cobalt-Oxide Electrocatalysts. Alaina C. Hartnett, Ethan J. Crumlin and Daniel G. Nocera, submitted for publication.
3. Lanthanum-Promoted Electrocatalyst for the Oxygen Evolution Reaction: Unique Catalyst or Oxide Deconstruction? Alaina C. Hartnett, Ryan J. Evenson, Agnes E. Thorarinsdottir, Samuel S. Veroneau and Daniel G. Nocera, *J. Am. Chem. Soc.* **2025**, *147*, 1123–1133.
4. Single Crystal and Magnetic Characterization of Iodobarlowite, $\text{Cu}_4(\text{OH})_6\text{FI}$, A Kagomé Lattice Synthesized from a 2-D Triangular Precursor. R. J. Evenson, X. Feng, M. I. Gonzalez, A. Rogalev, R. Clérac, D. G. Nocera, *Chem Mater.* **2025**, *37*, 8870–8878.
5. Straightforward Model for Quantifying Local pH Gradients Governing the Oxygen Evolution Reaction. Samuel S. Veroneau, Alaina C. Hartnett, Jaeyune Ryu, Hyukhun Hong, Cyrille Costentin and Daniel G. Nocera, *J. Am. Chem. Soc.* **2024**, *146*, 28925–28931.
6. Realizing Ciamician's Energy Future. Daniel G. Nocera, *La Chimica e L'Industria* **2024**, *8*, 58–62.
7. Oxidation Chemistry of Bicarbonate and Peroxycarbonate: Implications for Carbonate Management in Energy Storage. Zhifei Yan, Kristopher G. Reynolds, Rui Sun, Yongjin Shin, Agnes E. Thorarinsdottir, Bryan Kudisch, Giulia Galli and Daniel G. Nocera, *J. Am. Chem. Soc.* **2023**, *145*, 22213–22221.
8. Electrolyte-Induced Restructuring of Acid-Stable Oxygen Evolution Catalysts. Samuel S. Veroneau, Agnes E. Thorarinsdottir, Daniel M. Loh, Alaina C. Hartnett, Thomas P. Keane and Daniel G. Nocera, *Chem. Mater.* **2023**, *35*, 3218–3225.
9. Sustainable Energy Production and Manufacturing Using only Sunlight, Air, and Water. Daniel G. Nocera in *Chemistry Challenges of the 21st Century - Proceedings of the 100th Anniversary of the 26th Solvay Conferences on Chemistry*, K. Wüthrich, B. Feringa, L. Rongy, A. De Wit (eds), World Scientific Publishing: Singapore, **2023**, Ch 4.1.

Electric and Chemical Potentials in Driven (Photo)electrochemical Systems: Heterogeneity, Dynamics, and the Connection to Interfacial Structure and Reactivity

Shannon W. Boettcher, Ethan Crumlin, Sarah Berlinger, Jin Qian

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The long-term objective of this program is to advance the atomic/molecular-level understanding of electric and chemical potential distributions across interfaces in driven, non-equilibrium (photo)electrochemical systems. These interfacial potential landscapes govern charge separation, recombination, and reaction kinetics, therefore largely determine the efficiency and selectivity of electrochemical and photoelectrochemical systems. The program aims to: *i*) understand how semiconductor interfacial oxides and their dynamics influence selective carrier collection; *ii*) define cooperative adaptive versus buried-junction behavior at catalyst-semiconductor interfaces; and *iii*) elucidating how nanostructured catalyst architectures couple to electric double-layer structure. The team combines capabilities uniquely available at Berkeley Lab, including *operando* ambient-pressure X-ray photoelectron spectroscopy (AP-XPS), advanced electrochemical methods, and complementary computational modeling. The goal is to develop and apply these new tools to probe nanoscale interfacial electric and chemical potentials under operating conditions, interpret measurements through predictive simulations, and establish design rules for efficient and selective (photo)electrochemical interfaces.

A central recent result is demonstration that *cooperative adaptive* electrocatalyst–semiconductor (cat|sem) junctions, are key drivers of charge separation in overall water-splitting photocatalysts.¹ We use single-crystal SrTiO₃ semiconductor photoabsorbers as a model system. Dual-working-electrode measurements on Pt|SrTiO₃ and CoO_x|SrTiO₃ interfaces reveal that as Pt is driven to more negative potential, particularly approaching HER, its apparent electron barrier decreases, consistent with the formation of a more ohmic, electron-selective contact. In contrast, as CoO_x is driven to more-positive potential into the OER regime, its apparent barrier increases, consistent with increasing hole selectivity. These results show that both the metal HER catalyst (Pt) and the oxide OER catalyst (CoO_x) dynamically alter their junction properties with the semiconductor under operations. *Operando* AP-XPS (Figure 1), as a wireless element-

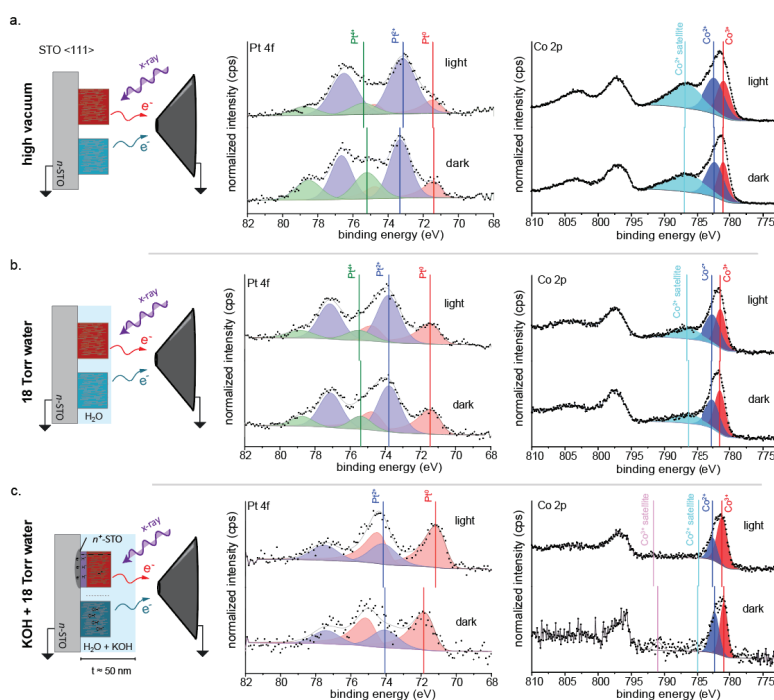


Figure 1. Adaptive junction and photovoltage measurements by AP-XPS. The left-most diagrams on panels (a), (b), and (c) respectively illustrate high-vacuum AP-XPS conditions, 18 Torr water vapor, and 20 μ L 0.013 M KOH in 18 Torr water vapor.¹

specific potential probe, shows that this behavior depends critically on the environment. Under high vacuum or water vapor alone, Pt does not exhibit the expected electron-collecting behavior under illumination. However, when KOH and water are both present, illumination drives a chemical transition in which Pt functions as an electron-collector while CoO_x oxidizes from a Co^{2+} -rich state toward Co^{3+} hole-collecting state. Together, these data establish design principles for overall water splitting electrocatalyst contacts and are applicable to lower-band gap photocatalysts that can achieve high solar-conversion efficiency once their interfacial selective hole and electron contacts are improved.

Corresponding computational studies of adaptive junctions have been initiated using Pt nanoparticle/ SrTiO_3 as a model system. The goal is to evaluate both the ground-state and the charge-accepted states using constrained density functional theory (CDFT) to understand what defines an effective electron sink on the Pt side. We constructed three systems to probe environmental effects: bare Pt/ SrTiO_3 , Pt/ SrTiO_3 with water, and Pt/ SrTiO_3 with water and KOH (Figure 2). This configuration enables a systematic assessment of solvation effects on interfacial charge transfer.

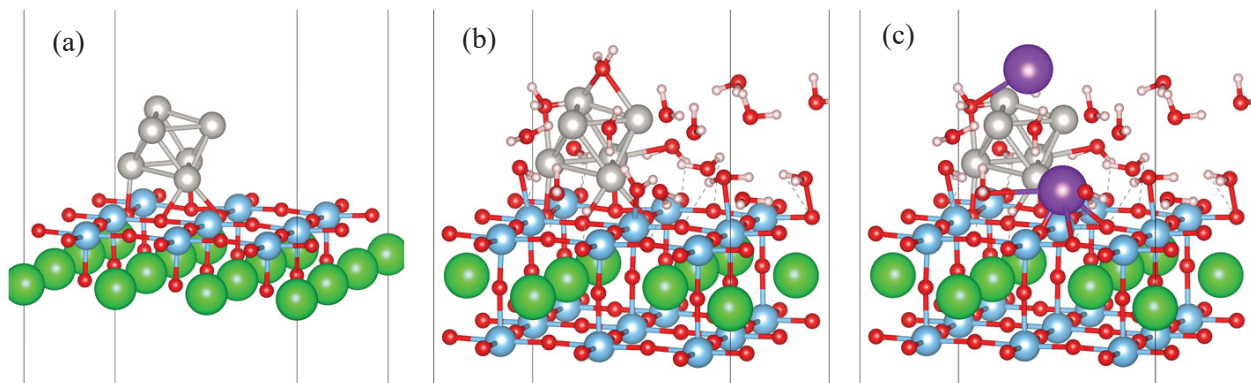


Figure 2. Computation: (a) Bare Pt/ SrTiO_3 , (b) Pt/ SrTiO_3 with water, and (c) Pt/ SrTiO_3 with water and KOH.

Ongoing and future work includes extending this adaptive-junction framework from Pt to other metals like Pd and alloys, where surface- and bulk-hydride formation is hypothesized to dynamically tune the metal work function and barrier height, probed by dual-working-electrode Schottky analysis together with *operando* AP-XPS now equipped with a ~ 10 ns snapshot detector to resolve transient photovoltage decay and *time-resolved charge-dissipation dynamics under reactive environments*. In parallel, we are defining how spatial confinement in meso- and nanoporous electrodes restructures the electrochemical double layer and alters ion dynamics. We synthesize model mesoporous thin films with tunable pore sizes and vary the electrostatic screening length through electrolyte concentration to tune degree of spatial confinement and characterize dynamic behaviors with *in situ* techniques such as XPCS, EIS, ATR FTIR, and XAS.

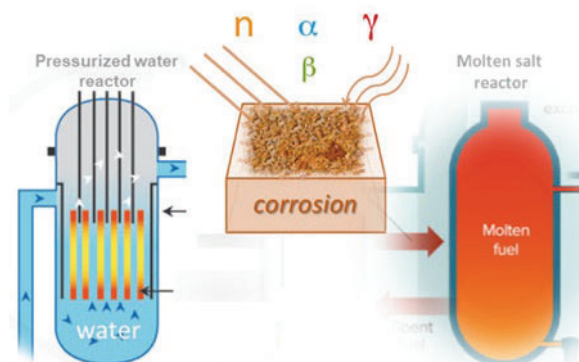
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- (1) Kaufman, A.; Wheeler, K.; Crumlin, E. J.; Boettcher, S. W. Cooperative Adaptive Junctions Govern Overall Photoelectrochemical Water Splitting. Revised manuscript at *Nature Catalysis* **2026**, pre-print available at *ChemRxiv*: <https://doi.org/10.26434/chemrxiv-2025-sd6mj>.
- (2) Kaufman, A. J.; Nielander, A. C.; Meyer, G. J.; Maldonado, S.; Ardo, S.; Boettcher, S. W. Absolute band-edge energies are over-emphasized in the design of photoelectrochemical materials. *Nat. Catal.* **2024**, 7 (6), 615-623. DOI: 10.1038/s41929-024-01161-0.

Radiation effects in nuclear reactors: speciation and redox reaction rates in high-temperature water

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Notre Dame University
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If there is an obvious application area for Radiation Chemistry, the cooling loops of nuclear reactors have to be near the top of the list. All owners and vendors of water-cooled nuclear reactors carry out extensive modeling of the cooling loop chemistry in order to predict problems with material degradation and corrosion. This is an essential task if the lifetime of the current reactor fleet is to be extended. The intense radiation field in the high-temperature water dramatically alters the corrosion environment and reliable predictions require a fundamental knowledge of both multi-length and multi-time-scale mechanisms.



Fundamental action of ionizing radiation is to separate both charge and spin, producing ions and free radicals. The Notre Dame Radiation Laboratory has a nearly unique set of tools able to study such chemistry at high temperature, allowing us to address important knowledge gaps. These tools include electron pulse radiolysis with subnanosecond (to seconds) time resolution using a unique transient absorption detection system covering a wide spectral range in single shot events (see figure 1). Transient conductivity signals can be simultaneously captured for the study of ionic reactions. Other electron accelerators are dedicated to time-resolved EPR and time-resolved resonance Raman detection methods adapted to study free radical chemistry at high temperatures and pressures.

In the last several years we have focused on the unexpected radiation chemistry of concentrated borate buffers, used in pressurized water reactor cooling loops. For decades it was believed that borate and boric acid were inert toward the primary radicals of water radiolysis, OH, H, and $(e^-)_{aq}$. However, we discovered that OH radicals do indeed react with borate anion, $B(OH)_4^-$, though not boric acid $B(OH)_3$. Initially we thought the transient absorbance we found in N_2O -saturated solutions of borax could be described simply in terms of a first-order reaction of OH with $B(OH)_4^-$, followed by second order recombination of the $^{\bullet}BO(OH)_3^-$ radicals. However, the second order decay rates

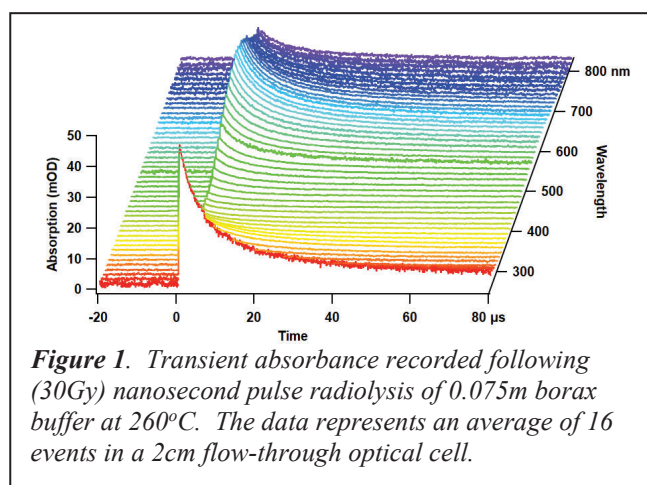
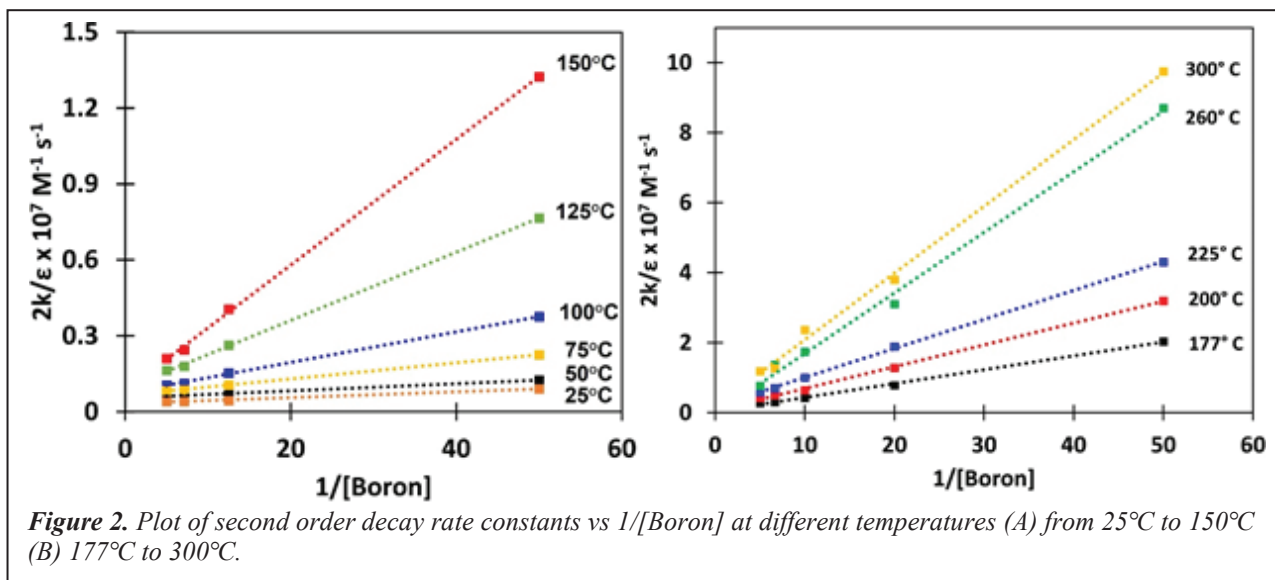


Figure 1. Transient absorbance recorded following (30Gy) nanosecond pulse radiolysis of 0.075M borax buffer at 260°C. The data represents an average of 16 events in a 2cm flow-through optical cell.



($2k/\epsilon$, where ϵ is radical extinction coefficient) depend on the INVERSE of borate concentration, as shown in figure 2.

In order to explain this behavior we are forced to define an equilibrium complexation reaction: $R + B = X$, where R is the initial radical anion whose identity is undetermined; complexant B might be boric acid or borate ion; and X is the final complex. The equilibrium constant for the complex radical formation is $K_{eq} = [X]/[R][B]$. Now if we assume $K_{eq}[B] \gg 1$ -- in other words, most of the radicals are complexed -- then following some algebra we obtain

$$2k_r = 2k_{RR} / K_{eq}^2 [B]^2 + k_{RX} / K_{eq} [B] + 2k_{XX} \quad (1)$$

where k_r is the overall second-order decay rate constant, k_{RR} and k_{XX} represent the self-recombination decay of the initial radical and the complex radical respectively, and k_{RX} is the decay by cross-recombination between the complexed and uncomplexed radicals. We can ignore the first term of equation (1) since $K_{eq}[B] \gg 1$, and then the plot of $2k_r$ vs. $1/[B]$ will be linear with intercept $2k_{XX}$ and slope k_{RX}/K_{eq} . This behavior of the second order decay vs. inverse borax concentration conforms to our observation in figure 2.

When we investigated the behavior of second order decay at very different ratios of borate ion/boric acid, we were able to clearly show the complexant “B” is borate anion, and not boric acid. This result is very profound, because the monomer radical anion $\text{BO}(\text{OH})_3^-$ has sp^3 hybridization at boron, and it can only readily complex with (sp^2 -hybridized) boric acid to form a sp^3 - sp^3 dimer. The dimer can dehydrate to form a more stable sp^3 - sp^2 dimer. The equilibrium involving borate must be $R(\text{=dimer}) + B(\text{=borate}) = X(\text{=trimer})$. Most of the transient absorbance we see is therefore due to borate trimer di-anion radical absorbance.

The final piece of this puzzle, is that the radicals show no evidence of ionic strength dependence of their recombination reactions. We carried out ab initio simulations of all the dimer and trimer anions to estimate which are most stable. To our surprise, the calculations suggest that borate trimer dianions will readily ion pair with two sodium ions, producing essentially a zero-charge species. With this result we can qualitatively explain the experimental results. Much further work is in progress, to isolate spectra of the various species, determine equilibrium constants, and explore reactivity of the borate radicals with impurities like peroxide and carbonate.

DOE Photochemistry and Radiation Chemistry Sponsored Publications 2023-2026

1. Conrad, J.K.; Lisouskaya, A.; Barr, L.; Stuart, C.R. and Bartels, D.M.
High temperature reaction kinetics of e_{aq}^- and $HO_2^\bullet$ radicals with aqueous iron (II) ions
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2. Conrad, J.K.; Lisouskaya, A.; Mezyk, S.P. and Bartels, D.M.
Kinetics of the temperature-dependent e_{aq}^- and $^\bullet OH$ radical reactions with Cr(III) ions in aqueous solutions
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4. Lisouskaya, A.; Tarábek, P.; Bartels, D.M. and Carmichael, I.
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6. Neupane, P.; Bartels, D.M. and Thompson, W.H.
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15. Das, L.; Guerin, S.J.; Bruggeman, C.; Carmichael, I. and Bartels, D.M.
Unexpected radiation chemistry of borate buffer: II. Second order decay
J. Phys. Chem. B **2026** submitted

Non-equilibrium actinide radiation chemistry—from radiation tracks to bulk homogenous phenomena

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Actinides are inherently unstable elements frequently encountered alongside other radioisotopes, creating intense, multicomponent ionizing radiation fields that drive the formation of non-equilibrium actinide species.^{1,2} These short-lived intermediates, formed within radiation tracks and propagated into bulk solution, play critical mechanistic roles in oxidation, ligand degradation, and metal-ion speciation. Despite their importance, the fundamental kinetics and molecular-level pathways governing their formation and decay remain poorly defined, yet such insight is essential for advancing actinide science and accurately predicting radiation-driven behavior.

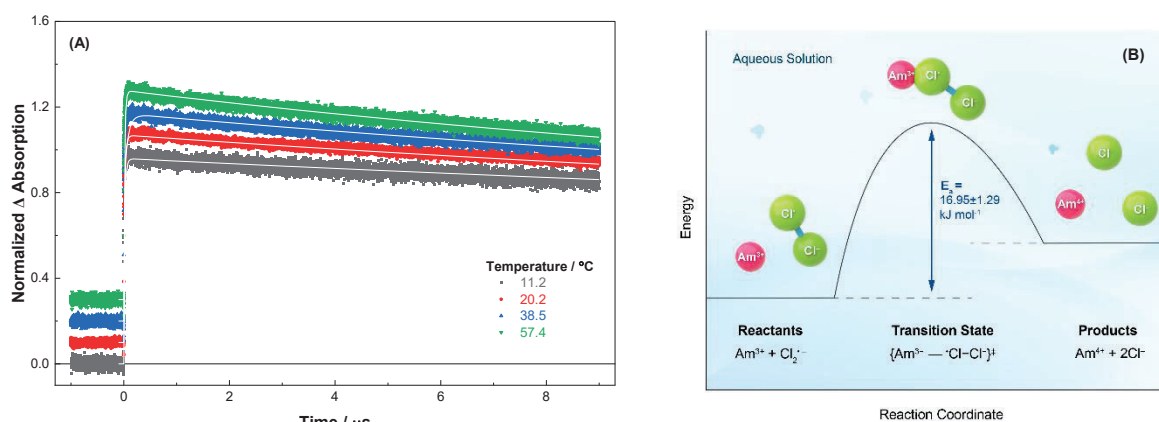


Figure 1. (A) Dose-normalized $\text{Cl}_2^{\bullet-}$ growth and decay traces measured at 350 nm after the electron pulse-irradiation of 1.68 mM Am(III) in aqueous 3 mM HCl, 1.4 M NaCl, and 0.6 M $\text{Na}_2\text{S}_2\text{O}_8$ solutions at 11.2 °C (**black**), 20.2 °C (**red**), 38.5 °C (**blue**), and 57.4 °C (**green**). Solid white lines are global model fits to data. Traces staggered by 0.1 for clarity. (B) Reaction coordinate schematic highlighting the associative mechanism in which $\text{Cl}_2^{\bullet-}$ undergoes coordination to form an americium–radical adduct as inferred from Arrhenius and Eyring kinetic activation parameters.

This presentation highlights recent progress from two complementary efforts (DE-AC07-05ID14517 and DE-SC0024191) that utilize time-resolved electron pulse radiolysis

and temperature-controlled radical kinetics to investigate radiation-induced chemistry across the actinide series. Using americium as a model redox-active center, we quantify the temperature-dependent oxidation of Am(III) by the dichlorine radical anion ($\text{Cl}_2^{\cdot-}$), revealing activation parameters that support an associative, inner-sphere pathway for Am(IV) formation under chloride-rich conditions (**Figure 1**).^{3–7} Parallel studies of actinyl organic complexes uncover dramatic, actinide-specific enhancements in ultrafast electron–hole transfer kinetics, demonstrating that heavier actinides fundamentally reshape early-time radical chemistry.

Together, these findings establish a coherent framework linking track-structure processes to homogenous bulk solution behavior, providing evidence for how initial charge-transfer pathways dictate both transient speciation and long-timescale radiolytic stability. These insights provide molecular-level handles for designing next-generation extractants, predicting radiation-driven evolution in actinide systems, and ultimately improving the performance and resilience of advanced nuclear fuel cycle technologies.

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DOE Solar Photochemistry Sponsored Publications

DE-AC07-05ID14517 (2025–2026)

1. Kruse, S. J.; Kynman, A. E.; Mezyk, S. P.; Grimes, T. S.; Layne, B.; Grills, D. C.; Horne, G. P. Temperature-Controlled Radiation-Induced Americium Redox Chemistry in Aqueous Chloride Media. *Inorganic Chemistry* **2026**, *in preparation*. (DE-AC07-05ID14517)

DE-SC0024191 (2023–2026)

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Radiation Chemistry Capabilities at Brookhaven National Laboratory and Recent Studies on Radiolytic Transients in Ionic Liquids

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The BNL Accelerator Center for Energy Research (ACER) provides sophisticated tools for the application of radiation chemistry to problems relevant to energy production, storage and utilization, as well as the development of new, advanced materials and devices, improving the nuclear fuel cycle and mitigating its environmental consequences, developing principles for the design of massive particle detectors, and investigating charge transfer and transport mechanisms in molecular systems. ACER provides rare capabilities to the chemical research community, and we promote the value of radiation chemistry over a broad range of science as we participate in meetings and exchange information with our fellow researchers and sister laboratories.

The principal elements of ACER are the Laser-Electron Accelerator Facility (LEAF),^A the Van de Graaff electron accelerator (VdG), and two ⁶⁰Co gamma sources. LEAF is based on an RF photocathode electron gun, which uses a laser and the photoelectric effect to generate picosecond electron pulses inside a high-field microwave cavity that accelerates them to ~8.7 MeV. The 2 MeV electron VdG is a versatile instrument for kinetics on microsecond and longer timescales and can deliver larger radiolytic doses than LEAF. Both accelerators include capabilities for UV-VIS-NIR transient absorption measurements using lamps and transient digitizers, and a unique, structure-specific vibrational spectroscopy capability using a mid-IR laser-based time-resolved infrared (TRIR) detection system.^B The VdG also supports a broadband, nanosecond time-resolved step-scan FTIR spectroscopic pulse radiolysis system that allows TRIR spectra to be rapidly recorded over wide regions of the mid-IR to locate radiolytically-induced transient IR bands.^C The design of LEAF provides synchronized laser probe beams to stroboscopically measure kinetics down to the 5-10 picosecond time scale, faster than can be measured with detectors and digitizers. LEAF's unique and innovative Optical Fiber Single-Shot (OFSS) detection system^D multiplexes the laser stroboscopic method to simultaneously measure absorbances at 142 time delays after a single electron shot at tunable wavelengths between 500-1600 nm. This allows us to study very fast radiolytic processes using only sub-mL sample quantities per experiment. We have two ⁶⁰Co sources (2760 and 237 Gy/hr) that are important resources for radiolysis product studies examining the effects of radiation on materials and for competition kinetics.

Our accelerators and ⁶⁰Co sources are easy for experimenters to use with a modest amount of training that, in the case of LEAF, is truly remarkable for a picosecond accelerator. In addition, we have technical assistance at LEAF to support end users who just wish to collect data and do not need to be trained on the machine. We prioritize our development projects to expand experimental capabilities by their potential to enable new science for our chemistry programs. At the same time, we work constantly to make the more sophisticated parts of our experimental systems increasingly user friendly.

Fundamental Radiation Chemistry of Ionic Liquids

Radiation is called “ionizing” when it has sufficient energy to completely eject an electron from an atom or molecule that it impinges on. It produces a “hole”, or electron vacancy, where the electron came from, and an excess electron where the ejected electron came to rest. Holes and electrons are thus the initial products of radiolysis and they are usually very reactive in whatever medium they have been formed. Our work in fundamental ionic liquid (IL) radiation chemistry focuses on how the speciation and reactivity of electrons and holes depends on the chemical natures of the cations and anions that make up the liquid.

In a recent pair of studies conducted in collaboration with the groups of David Blank (U. Minn.) and C. Margulis (U. Iowa), who are both supported by the CSGB CPIMS Program, we explored the behavior of electrons and holes in the ionic liquid 1-butyl-1-methylpyrrolidinium dicyanamide ($\text{Pyrr}_{14} \text{N}(\text{CN})_2^-$). We sought to resolve the enigma that despite the excess electron’s thermodynamic instability towards dissociative attachment to dicyanamide or bis(trifluoromethylsulfonyl)imide (Tf_2N^-) anions, which constitute half of a given IL, pulse radiolysis experiments in many ILs that contain $\text{N}(\text{CN})_2^-$ and Tf_2N^- anions clearly show large yields of excess electrons that behave like the “cavity” or “solvated” electrons found in molecular solvents and persist for hundreds of nanoseconds. A series of *ab initio* molecular dynamics simulations⁵ showed that, while *delocalized* electrons can quickly “search and find” ionic targets that are lower in SOMO energy than a cavity electron, electrons that do manage to localize and become solvated need to climb and cross barriers to escape their local cationic environment. Thus, solvated electrons may not be the most energetically favorable states, but when they form, they are kinetically metastable.

While holes represent an equally important side of the radiolysis “coin” in ILs, they tend to be less well understood because they often manifest poorly observable optical transitions. Such is not the case with dicyanamide ILs, where holes have strong and characteristic optical signatures. Using pulse radiolysis measurements and first-principles calculations in the bulk and gas phases, we showed that the most likely hole species in $\text{Pyrr}_{14} \text{N}(\text{CN})_2^-$ is a dimer radical anion that, somewhat surprisingly, has similar spectral features to the excess electron, including a broad near-infrared absorption band.⁶

Ionic liquids containing aromatic cations such as imidazolium and pyridinium (RPy^+) are the subjects of a substantial fraction of the research in the IL field. Radiolysis of these ILs results in extremely rapid electron capture by the aromatic cations. In the case of imidazolium, this results in ring deformation and radical chemistry that we are presently investigating. In contrast, most RPy^+ cations form a relatively stable electron adduct that can undergo reversible electron transfer reactions. We investigated what happens to the structural, physical and radiolytic properties of RPy^+ ILs when a dimethylamino group is attached at the *para* position (making RDMAP^+), with Tf_2N^- as the counterion.⁹ The influence of the electron-donating dimethylamino substituent is evident in the differences in the electronic density of states between the RDMAP^+ and RPy^+ ILs. This leads to substantial changes in the radical transients observed in pulse radiolysis of the neat ILs. While RDMAP^+ is an electron acceptor like RPy^+ , it can also be easily oxidized by the holes, resulting in a characteristic strong absorption feature at 470 nm. When benzyl substituents are used, forming $\text{BzDMAP}^+ \text{Tf}_2\text{N}^-$ and $\text{BzPy}^+ \text{Tf}_2\text{N}^-$ ILs, holes are trapped by charge resonance dimers of the benzyl groups in $\text{BzPy}^+ \text{Tf}_2\text{N}^-$, but remain cation-centered in $\text{BzDMAP}^+ \text{Tf}_2\text{N}^-$.

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Computational Modeling of Concerted Proton-Electron Transfer and Hydride Transfer Reactions

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The goal of our research in the Artificial Photosynthesis Program at Brookhaven National Laboratory (BNL) is to gain a fundamental understanding of processes involved in the chemical conversion of solar energy. We perform coordinated experimental and theoretical studies to address the scientific challenges associated with efficient coupling of light absorption, photo-induced electron-transfer processes, and chemical transformations, together with managing proton movement and charge leveling in catalysts. The first part of the talk will highlight our detailed kinetic studies on concerted proton-electron transfer (CPET) reactions, and the second part of the talk will focus on our efforts to decipher the correlation between thermodynamic and kinetic hydricities of transition metal hydrides.

Computational Modeling of Concerted Proton-Electron Transfer

Concerted proton-electron transfer (CPET), where simultaneous proton (H^+) and electron (e^-) motion occurs in a single chemical step, is ubiquitous in both biological and chemical energy transduction processes. Yet, a fundamental understanding of the behavior of CPET over a wide range of driving forces (ΔG^0) extending into the Marcus inverted region is lacking due to the limited free energy window accessible by conventional techniques. Pulse radiolysis (PR), a unique capability at BNL, is a powerful method for rapidly preparing and directly monitoring the reactivity of a wide variety of redox species which could enable access to a wide free energy range, up to and including, the inverted region to study CPET reactions in organic solvents. In this part of the talk, I will present our recent computational results on modeling the temperature dependent kinetics of CPET of organic molecular systems initiated by PR in dichloroethane solvent media (Fig. 1a). The computations indicate the importance of employing explicit solvation for accurate description of the thermodynamics and kinetics of the CPET components in PR media and the role of the geometric features of the CPET components in theoretical modeling of the temperature dependent kinetics of CPET via nonadiabatic PCET theory (Fig. 1b).

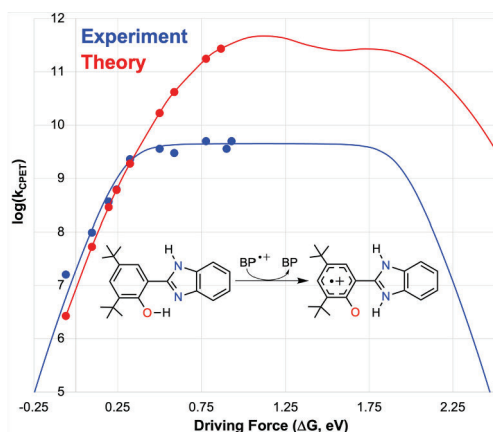
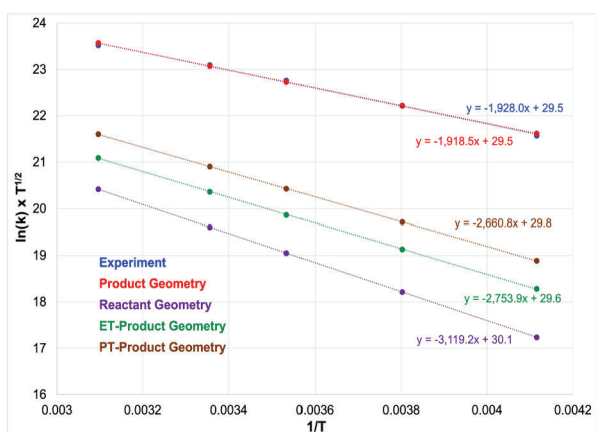


Figure 1. (a) Driving force dependence of CPET rates



(b) Temperature dependence of CPET rates

Marcus Relationships for Hydride Ion Transfer (HIT) Reactions

Transition metal hydrides are essential intermediates in a wide range of catalytic reactions including those relevant to energy storage applications. In many of these reactions, hydride transfer is the rate limiting step. Thus, a detailed fundamental understanding of HIT with transition metals as either the hydride donor or acceptor is critical for the rational design of efficient catalysts. The ability of a transition metal hydride to donate a hydride ion can be depicted by (i) thermodynamic hydricity, defined as the free energy required to release a free hydride ion, H^- , from a species in solution ($\Delta G^\circ_{\text{H}^-}$), and by (ii) kinetic hydricity, which is related to the free energy of activation ($\Delta G^\ddagger_{\text{H}^-}$) and provides information on the rate of HIT.

As part of our programmatic research on the reactivity of transition metal hydrides, we assess the feasibility and limitations of the Marcus model for describing the rates of HIT reactions of transition metal hydrides. Previously we showed that reactions between $(^R\text{bpy})\text{Ir}(\text{CO})_3\text{H}$ (^Rbpy = 4,4'-R-2,2'-bipyridine; R = OMe, ^tBu, Me, H, Br, CO_2Me , CF_3) and 5 different hydride acceptors were sensitive to the steric properties of the acceptor which prevented accurate analysis of the data using Marcus theory. In our recent work, we reported the rate of HIT from three Ir hydride complexes of the type $\text{Cp}^*\text{Ir}(^R\text{bpy})\text{H}^+$ (Cp^* = C_5Me_5 ; ^Rbpy = 4,4'-R-2,2'-bipyridine, R = OMe, H, CO_2Me) to six *N*-methylacridinium ($^R\text{Acr}^+$) acceptors with electronically different substituents in the 2- or 2,7-positions (Fig. 2). In this part of my talk, I will present the computational analysis for the concerted hydride transfer mechanism for the three Ir complexes and determination of reorganization energies for the hydride transfer reactions using the Marcus model.

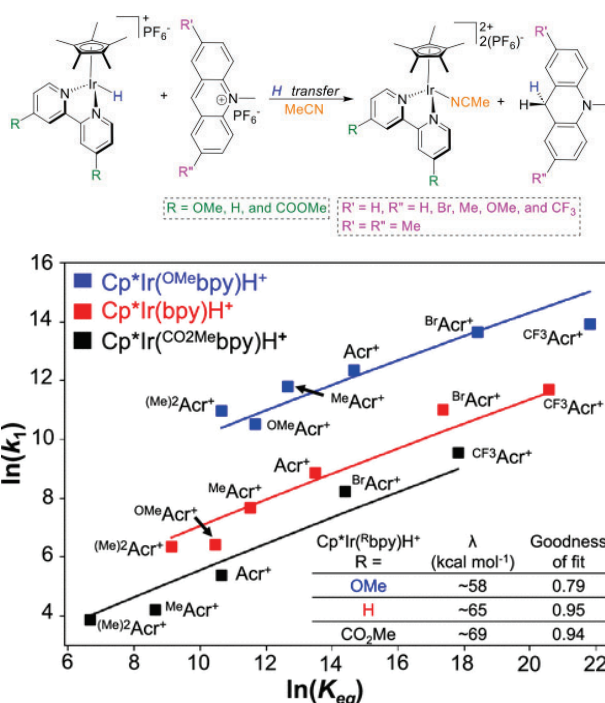


Figure 2. Elucidation of Marcus relationships for hydride transfer reactions involving transition metal hydrides.

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Understanding Transition Metal Hydride Intermediates for Selective Electrocatalytic Reduction Reactions

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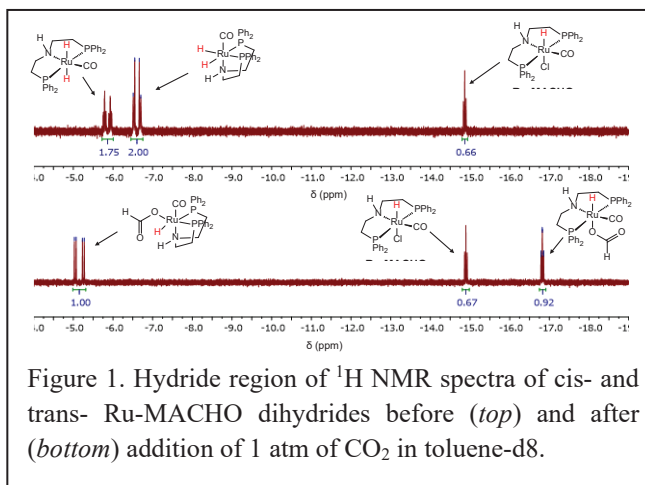
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Our work is broadly focused on developing selective electrocatalysts for hydride transfer reduction reactions.² The scope of work includes new transition metal ligand development, synthesis and characterization, reactivity studies, and thermochemical measurements.

One area of focus has been understanding the hydride transfer intermediates in hydrogenation catalysts. There are many more examples of hydrogenation catalysts than reductive electrocatalysts for challenging substrates, including more examples with earth-abundant elements. Understanding the properties and characteristics of the hydride intermediates of known hydrogenation catalysts facilitates translation of their reductive activity to electrocatalysis.

Our initial work focused on aqueous hydride chemistry of $[\text{Co}(\text{dmpe})_2](\text{BF}_4)_2$. Successful electrocatalytic generation of the corresponding dihydride with 40-70% Faradaic efficiency for CO_2 reduction to formate in water was achieved by quantifying the redox properties and acidity of the hydride intermediate.¹

We also investigated Ru-MACHO ($\text{Ru}(\text{HN}(\text{CH}_2\text{CH}_2\text{PPh}_2)_2)(\text{H})(\text{Cl})(\text{CO}))$, a widely used and commercially available homogeneous hydrogenation catalyst. This catalyst has also demonstrated high activity towards the challenging hydrogenation of CO_2 to CH_3OH . Despite its widespread use, key questions about the catalytic mechanism remain unresolved, particularly regarding the identity and reactivity of the reductive dihydride intermediate formed under catalytic conditions. While the trans-dihydride has long been proposed as the catalytically relevant intermediate, we performed the first structural characterization of the cis-dihydride isomer of Ru-MACHO by single-crystal X-ray diffraction. We demonstrate that both the cis- and trans- dihydride are competent hydride donors capable of reducing CO_2 and the ester 4-fluoromethylbenzoate.⁵ To



further demonstrate the relevance of these results, we performed high-pressure, high-temperature operando NMR spectroscopy in collaboration with A. Appel, R. Trevino, and J. Linehan (PNNL) under catalytic conditions and observed both isomers. These results indicate that the cis-dihydride, previously overlooked, is a likely catalytic intermediate, and should be incorporated into mechanistic models and computational studies of the Ru-MACHO catalyst family.

More recently, we have initiated studies into $[\text{Fe}(\text{PP}_3)(\text{CH}_3\text{CN})](\text{BF}_4)_2$ where $\text{PP}_3 = \text{tris}[2\text{-(diphenylphosphino) ethyl}]$ phosphine, a rare example of an earth abundant metal-based catalyst that can hydrogenate CO_2 to CH_3OH . We have characterized the corresponding mono-hydride and cis-dihydride by NMR spectroscopy and X-ray crystallography. We are currently investigating the reactivity and thermochemical properties of these species, including their hydricities, as few of these values have been measured for iron complexes.

Homogeneous CO_2 hydrogenation chemistry is most frequently studied in aqueous solution. Our interest in these catalysts have also led to the synthesis of new water-soluble ligands. To enable water solubility, we synthesized diphosphine and terpyridine derivatives with cationic functionalities (Figure 2). The corresponding complexes have already demonstrated unusual pH-dependent activity (Figure 2, top).³ Additional studies on the photo-catalytic and -chemical properties of the $\text{Ru}(\text{II})(\text{terpy})(\text{bpy})$ complexes (Figure 2, middle, bottom) are being carried out in collaboration with G. Manbeck (BNL).

Some of the work with hydride transfer in my research group is inspired by formate dehydrogenase (FDH), which performs reversible hydride transfer between CO_2 and formate at high rates near the thermodynamic potential. Preliminary studies on a structural mimic of the active site demonstrates the importance of the secondary structure. However, we noted the potential importance of bidirectional hydride transfer for operation at mild potentials. In an effort to mimic this reaction architecture, we have synthesized a series of heteroleptic bis-NHC bis-phosphine complexes with Pd and Pt. We expect these complexes will be strong hydride donors, and the modular ligands can be modified to incorporate weakly acidic sites to promote bi-directional hydride transfer.

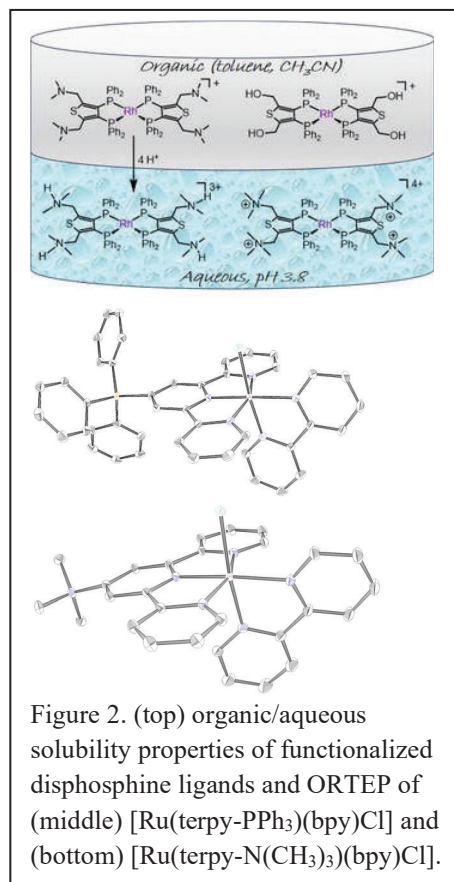


Figure 2. (top) organic/aqueous solubility properties of functionalized diphosphine ligands and ORTEP of (middle) $[\text{Ru}(\text{terpy-PPh}_3)(\text{bpy})\text{Cl}]$ and (bottom) $[\text{Ru}(\text{terpy-N}(\text{CH}_3)_3)(\text{bpy})\text{Cl}]$.

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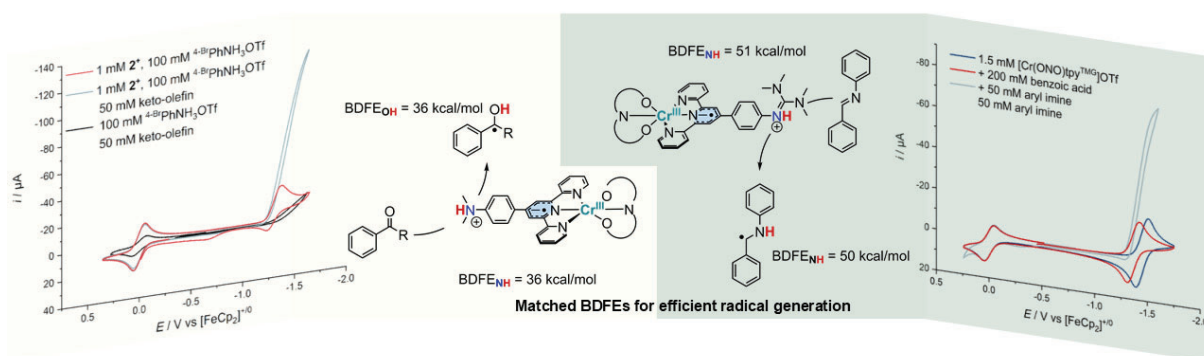
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Redox-Active Ligands for Rapid Reductive PCET Mediation

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Reductive proton-coupled electron transfer (PCET) is a method for forming weak X–H bonds in energy-storing molecules.[1] A particular challenge is forming X–H bonds of <52 kcal/mol because of competition with hydrogen evolution (HER). A recently developed strategy [2] is to use molecular mediators with spatially separated cobaltocenium sites for redox and aniline sites for proton transfer; this was demonstrated for electrocatalytic reductions but the rates were slow. Here, we show that heteroleptic chromium-terpyridine complexes mediate rapid electrocatalytic PCET to organic substrates. The fast rates are attributed to the use of redox-active terpyridine ligands, which can form a stabilized radical anion in the reduced form, while the chromium(III) scaffold is redox-inert. The transient intermediate species, in which the mediator is reduced *and* protonated, show characteristic UV/Vis transitions and are accessible using pulse radiolysis or spectro-electrochemistry. By changing the Brønsted-basic substituent on the terpyridine ligand, the thermodynamic properties of the mediator can be modified and matched to different substrate classes. The modular design enables the fast, energy-efficient and selective generation of radicals from substrates with C=O, C=N and C=C multiple bonds. Mechanistic studies indicate that the delivery of H⁺/e[−] to the substrates is concerted, and goes through a transition state that builds up negative charge on the substrates. The rates follow the driving force for PCET, which allows a predictive approach to the design and optimization of catalytic protocols.



Electrochemical methods have been used to optimize these methods and test mechanistic details. However, in the long run, these scaffolds are intended for coupling to light-driven reduction methods, which will take advantage of the fast rates and redox-active ligand scaffold.

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Elucidating Photoinduced Bond Formation/Cleavage Pathways in Dimeric Pt Complexes by Time-Resolved Wide-Angle X-ray Scattering

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Charge transfer states in transition metal complexes are instrumental in the conversion of light energy to charge or fuels in photosynthetic systems. Excitation of these states is often accompanied by bond formation/breaking processes, affecting excited-state energies and dynamics. Because these atomic displacements can couple directly to electronic dynamics, it is vital to quantify the motion of nuclei and correlate these motions to excited-state dynamics. Pt dimer complexes are useful models for investigating how these atomic motions ultimately affect ultrafast electronic dynamics and excited-state trajectories. Excitation of a metal-metal-to-ligand charge transfer (MMLCT) band can drive bond formation/photolysis, depending on the bridging ligands and oxidation state of the Pt centers. The excited-state dynamics are strongly correlated to the electronic and atomic structure of the ground state, particularly the occupation of the Pt 5d_{z²} orbitals, i.e. the Pt oxidation state, and the Pt-Pt distance, which is a function of the organic linker used to bridge the two Pt centers. Pt(II) dimers have been studied most extensively, exhibiting Pt-Pt bond formation upon MMLCT excitation by the creation of a hole in the Pt-Pt antibonding orbital which enables formal Pt-Pt bonding character. In contrast, Pt(III) dimers have empty Pt-Pt antibonding orbitals, resulting in a formal Pt-Pt bond in the ground-state which is weakened, or broken altogether, upon MMLCT excitation. Thus, the Pt-Pt distance has been identified as a key reaction coordinate that influences intersystem crossing and photoinduced electron transfer in Pt dimer complexes. While ultrafast optical techniques can infer changes in atomic structure,

primarily through detecting coherent vibrational wavepackets (CVWPs) and relating their vibrational frequencies to specific nuclear motions, these methods cannot directly quantify the structural distortions. Using time-resolved wide-angle X-ray scattering (TR-WAXS) at an X-ray free electron laser, we can quantify the structural evolution in the Pt dimer MMLCT state to ascertain the interplay between electronic and atomic motions.

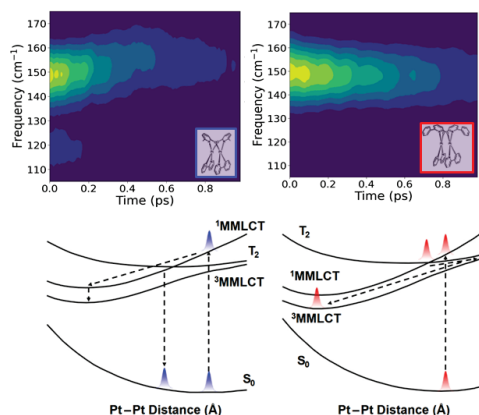


Figure 1: Coherent vibrational wavepackets are observed in the TR-WAXS signals of methylpyridine (left) and phenylpyridine (right) bridged Pt(II) dimers, indicating the nature of vibronic coupling effects in mediating ISC rates in these complexes.

In addition to providing time-dependent positions of individual atoms, TR-WAXS can also monitor CVWPs; in the case of Pt dimers, these are typically encoded in the Pt-Pt distance. While TR-WAXS is a purely structural measurement, indirect electronic state trajectories can be obtained through analysis of

the interference between CVWPs. We demonstrated this for Pt(II) dimers utilizing methylpyridine and phenylpyridine bridging moieties (Figure 1). The methylpyridine-bridged dimer exhibits two CVWPs whose frequencies represent Pt-Pt vibrations in the ground- and excited-state geometries. The CVWP on the ground-state surface is phase-shifted relative to the excited state. The phase relationship reveals trajectory crossing between electronic excited states, specifically the absence of vibronic coupling in the methylpyridine-bridged dimer. Alternatively, for the phenylpyridine-bridged dimer, where strong vibronic coupling facilitates intersystem crossing (ISC), only one vibrational frequency is observed. These results show the role that the Pt-Pt contraction plays in mediating efficient, ultrafast ISC pathways.

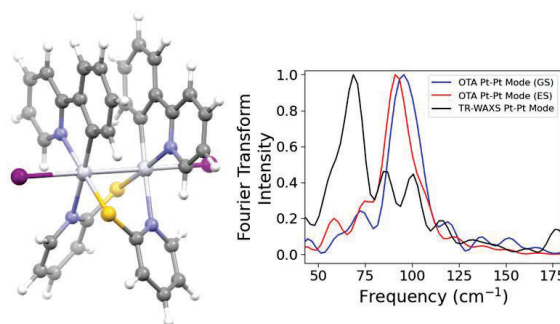


Figure 2: TR-WAXS (black) indicates a CVWP that does not correspond to Pt-Pt modes detected by OTA (blue, red). What role does this vibrational mode play in ultrafast bond photolysis/ISC?

In comparison, the Pt(III) dimers with pendant halogen atoms (Figure 2) have a ground-state Pt-Pt bond with trans-axial halogens. In principle, changing the trans-axial halogens can tune the Pt-Pt bond strength and the dynamics of Pt-Pt bond cleavage. A series of the Pt(III) dimers were investigated using TR-WAXS and complementary ultrafast optical spectroscopy. CVWPs are observed by broadband transient absorption spectroscopy, with frequencies that reflect the ground and excited-state Pt-Pt distances (confirmed by DFT). TR-WAXS of the -I and -Br Pt(III) dimers reflects expansion in the Pt-Pt bond distance, and weak, quickly dephasing CVWPs are observed. Typically, the CVWPs from TR-WAXS match the frequencies from those obtained from optical measurements, but here we observed a peak shifted nearly 30 cm^{-1} to lower frequency, suggesting an additional component to the structural evolution in the MMLCT state.

The TR-WAXS work discussed here focuses exclusively on Pt-Pt dimers. This is in large part due to the flexibility in the design of these complexes afforded by the rather large Pt 5d orbitals. However, MMLCT bands can also be observed for dimers of Ni(II) and Pd(II), given a judicious choice of bridging ligands that enforce a suitably short metal-metal distance for d orbital overlap. Ni(II) dimers have shown catalytic activity towards the oxidation of cyclo-dienes upon MMLCT excitation. While the Ni(II) dimer should exhibit similar interplay between nuclear degrees of freedom and ultrafast ISC pathways observed in Pt(II) dimers, it will likely introduce low-lying metal-centered states that rapidly depopulate the MMLCT state. Future work will involve a new series of Pt(II), Pd(II), and Ni(II) dimer complexes, which will be investigated using TR-WAXS and metal K-edge X-ray spectroscopy. TR-WAXS will interrogate the structural evolution with specific emphasis on the metal-metal contraction and Ni-ligand expansion in the MMLCT and d-d states, respectively. CVWPs are expected to appear in the metal-metal contraction, with frequencies predicted by DFT, and the electronic structure, including the nature of a potential metal-centered state in the Ni(II) species, will be determined using Ni K-edge X-ray absorption spectroscopy.

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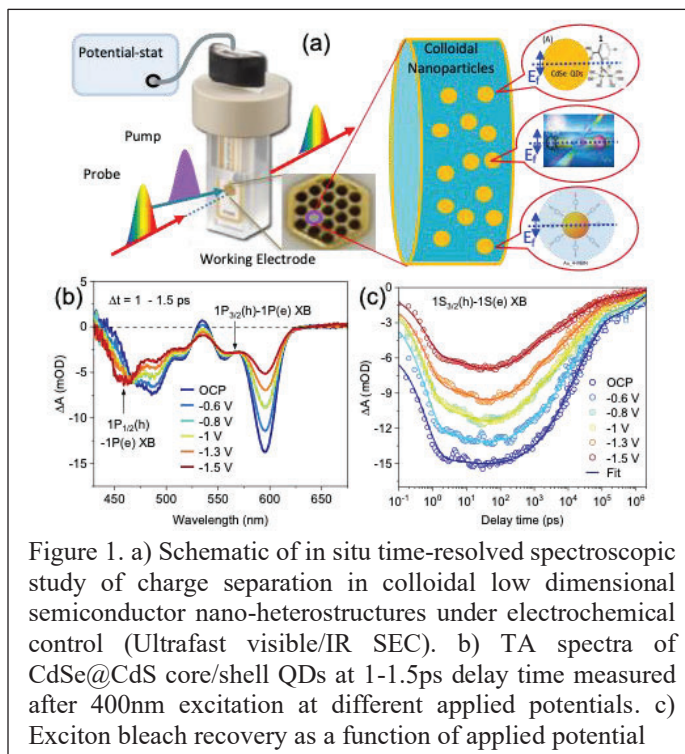
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Charge Transfer from Electrochemically Controlled Colloidal Nanoparticles

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The long-term goal of our research program is focused on detailed mechanistic understanding of *colloidal nano-heterostructures* for solar fuel generation. These nano-heterostructures are ideal model systems for particle-based photocatalysts because elementary charge transfer and catalytic reactions in these systems can be carefully examined by *operando* time-resolved spectroscopic tools. In principle, the study on colloidal NP solutions can also provide important insight into interfacial charge transfer (CT) processes of bulk photoelectrodes. In bulk electrodes, their Fermi level, one of the most important properties, is known and tuned by an external potential-stat, while in NP systems, their Fermi level is often unknown and/or difficult to adjust. To bridge this “Fermi level gap”, we initiate a new research program to combine electrochemical control of colloidal solution and time-resolved spectroscopy, i.e. ultrafast spectro-electrochemistry (**ultrafast SEC**), to study charge separation processes in colloidal NPs with known and controllable Fermi levels (Figure 1a). In this talk, I will report our progress in three specific aims of the proposed research program.



1) *Exciton dynamics of charged colloidal CdSe/CdS core/shell quantum dots (QDs).* The application of QDs in optoelectronic devices and photocatalysis inevitably involves them in charged states, whose carrier and exciton dynamics remain poorly understood. Herein, the electrochemical charging effects in colloidal CdSe/CdS core/shell quantum dots are systematically investigated using static spectro-electrochemistry and in situ transient absorption spectroscopy. Static SEC reveals the presence of in-gap trap states from 0.9 eV below the conduction band edge. Negligible changes of transient absorption spectra and kinetics were observed from OCP to more anodic potentials within the QD band gap (result not shown). At more cathodic potentials, the TA spectra and kinetics show strong dependence on the potential (Figure 1b&c), caused by charging of trap and band edge states. The negatively charged QDs show band edge trion decay with a lifetime of 690 ± 31 ps, and slower 1P to 1S electron relaxation with time constants of 12.4 ± 0.8 ps assigned to the spin blockade effect and 316 ± 35 ps assigned to phonon bottleneck effect (Figure 1c). Our study reveals rich effects of charging on QD excited state.

2). Concerted proton-coupled electron transfer (PCET) of QD/anthraquinone(AQ) complexes.

Although PCET reactions of molecular catalysts have been studied in recent years, much less is known about photoinduced PCET in QD-catalysts systems despite their important roles in solar fuel generation. Using QD-AQ as a model system, we study photoinduced PCET by transient absorption spectroscopy (Figure 2). TA spectra reveal that semiquinone radicals ($AQH^\bullet$) form on the picosecond timescale at pH 6.30, while no anthraquinone radical anions ($AQ^{\bullet-}$) are detected (Figure 2b). The direct generation of $AQH^\bullet$ indicating a concerted transfer of electron and proton (Figure 2c). The formation of $AQH^\bullet$ depends sensitively on the pH of the solution. Additionally, the kinetic isotope effect is investigated in this system. From the weight-averaged lifetime the KIE values were calculated to be 6.9 ± 1.5 at pH 6.30, supporting the concerted PCET pathway. This work provides a detailed mechanistic understanding for PCET in QD-Molecule systems.

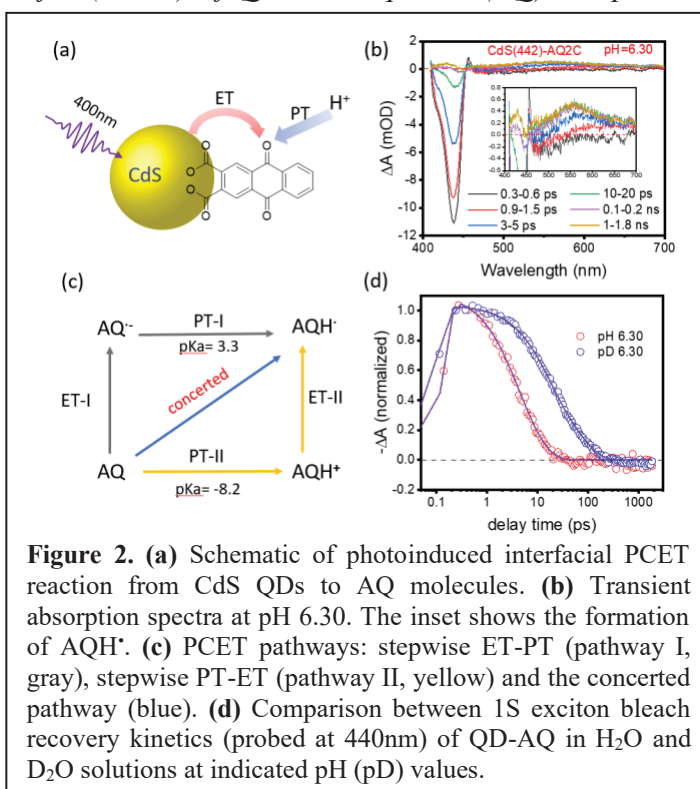


Figure 2. (a) Schematic of photoinduced interfacial PCET reaction from CdS QDs to AQ molecules. (b) Transient absorption spectra at pH 6.30. The inset shows the formation of $AQH^\bullet$. (c) PCET pathways: stepwise ET-PT (pathway I, gray), stepwise PT-ET (pathway II, yellow) and the concerted pathway (blue). (d) Comparison between 1S exciton bleach recovery kinetics (probed at 440nm) of QD-AQ in H_2O and D_2O solutions at indicated pH (pD) values.

3). Plasmonic driven adsorbate vibrational dynamics of colloidal 4-mercaptobenzonitril (4-MBN) capped Au nanoparticles.

Plasmon photocatalysis is often hypothesized to proceed through plasmon driven selective excitation of adsorbate electronic or vibrational excitation, although direct experimental evidence is often lacking. We have carried out time-resolved IR study of 4MBN-capped Au NPs (Figure 3a). Upon 500nm excitation of the Au plasmon band, the adsorbate CN stretching mode is redshifted (Figure 3b). About 50% of the adsorbate vibration excitation shows an instrument response limited rise, indicating hot electron transfer induced adsorbate vibration spectral change. The remaining excitation grows in on the few picosecond time scale, indicating hot phonon induced adsorbate heating. Ongoing study and detailed analysis are aimed at understanding the mechanism of hot carrier induced vibrational mode excitation on plasmonic metals.

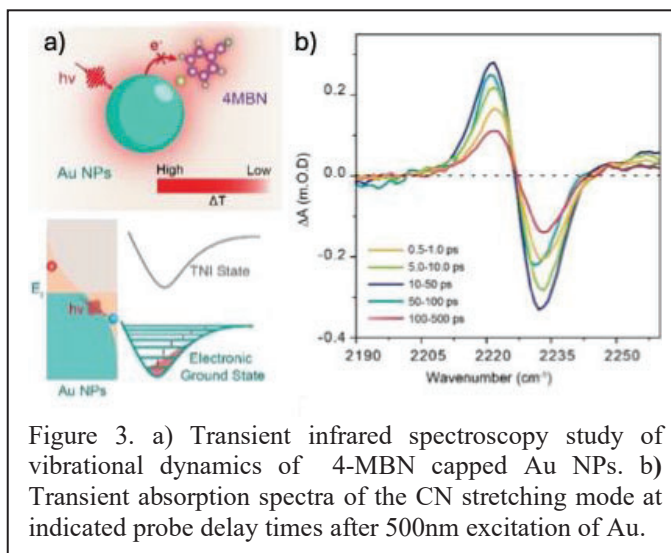


Figure 3. a) Transient infrared spectroscopy study of vibrational dynamics of 4-MBN capped Au NPs. b) Transient absorption spectra of the CN stretching mode at indicated probe delay times after 500nm excitation of Au.

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Design, Structure Analyses, and Catalytic Mechanism of Covalent Organic Framework based Photocatalysts

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Artificial photosynthesis through CO₂ reduction to generate chemical fuels has gained increasing attention as an attractive strategy for energy conversion. In these systems, oxygen evolution reaction (OER) provides the necessary electrons and protons for driving the overall reaction, but represents the rate-limiting step due to its inherently sluggish kinetics. Therefore, efficient overall artificial photosynthesis requires photocatalysts that can drive both the oxidation and reduction half-reactions at balanced rates, which places stringent demands on catalyst design.

Covalent organic frameworks (COFs) are a novel class of crystalline porous materials constructed from organic building blocks linked by robust covalent bonds. They have been demonstrated as remarkable photocatalytic materials owing to their π -conjugation that often allows absorption of visible light in addition to their inherent porosity and large surface area. Moreover, the wide availability of diverse building blocks, including monomers and linkages, offers great opportunities to fine-tune the structure of COFs. This enables the design of diverse tailor-made COF photocatalysts with integrated photosensitizers and catalytic sites in a single material, while also allowing tuning their photophysical properties to optimize their functionality for catalysis.

For these reasons, COFs provide a powerful platform for the systematic optimization of structure and photophysical properties to achieve efficient CO₂ reduction, OER, and ultimately, overall artificial photosynthesis. Consistent with this premise, we synthesized two structurally isomeric imine-linked COFs with reversed imine bond directions (Figure 1), i.e., f-COF (CHO-BPY + NH₂-TTA) and r-COF (CHO-TTA + NH₂-BPY). We found that reversing the imine linkage flips the charge transfer (CT) direction and exciton delocalization, where f-COF forms a delocalized hole with a BPY-localized electron, and r-COF generates the opposite, namely a localized BPY-hole and delocalized electron (Figure 2a). Upon incorporating Re(BPY)(CO)₃Cl molecular catalyst onto the COF backbone (Re-COF), these differences translate into sharply contrasting CO₂ photoreduction activity, with Re-f-COF active and Re-r-COF inactive (Figure 2b). These discoveries not only suggest that the chemistry of imine linkage should be a primary focus when developing imine-

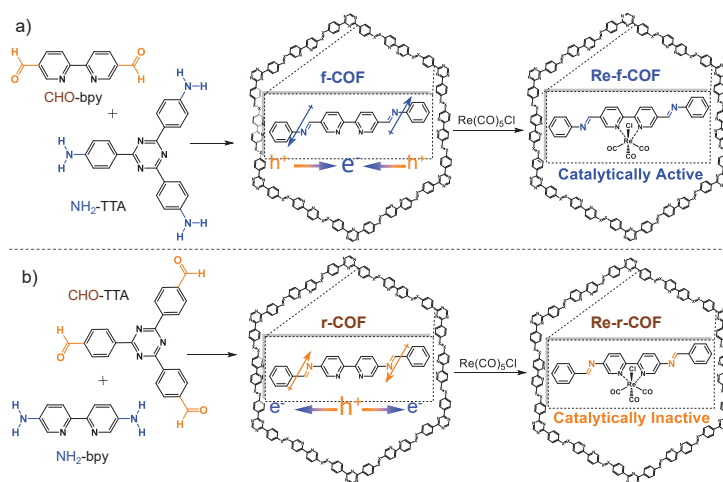


Figure 1. Synthetic scheme of (a) f-COF and Re-f-COF and (b) r-COF and Re-r-COF. They are built from COF monomers in which the amine and aldehyde functional groups are switched.

linked COFs for photocatalytic applications but also highlight the potential to advance COFs as OER catalysts as hole density can be directed toward the targeted OER catalytic site.

An intuitive takeaway from these studies is to use r-COF as the platform for OER after incorporating water oxidation sites. However, the practical value of r-COF is limited by the difficulty of obtaining highly crystalline materials and by low synthetic yield. We therefore instead opt to develop f-COF as the photooxidation platform by deliberately exploiting the imine linkage as a catalyst chelating motif. Our central hypothesis is that anchoring metal centers directly to the hole-proximal imine N will shorten charge-carrier migration distance, enabling more efficient hole collection and thereby enhancing photocatalytic water oxidation. To test this idea, we designed a TTA-IPY COF in which 3,3'-BPY ([3,3'-bipyridine]-6,6'-dicarbaldehyde) replaces 2,2'-BPY ([2,2'-bipyridine]-5,5'-dicarbaldehyde) in f-COF (hereafter TTA-BPY COF), thereby enabling conjunction with adjacent imine N atoms to install two imine-pyridine (IPY) chelation sites (Figure 3), in contrast to the single catalytic site available in TTA-BPY COF. In this way, TTA-IPY can possess both a higher density of metal coordination sites and a shorter CT pathway, which are expected to enable effective capture of photogenerated holes localized at the IPY coordination sites (catalyst chelating site) before they can recombine with their corresponding electrons localized at the 3,3'-BPY unit. We show that, upon coordination with CoCl_2 , Co-TTA-IPY achieves an O_2 evolution rate of $3102.8 \mu\text{mol g}^{-1}\text{h}^{-1}$ with a turnover frequency (TOF) of 6.17 h^{-1} per Co atom, which is significantly higher than that of Co-TTA-BPY ($961.2 \mu\text{mol g}^{-1}\text{h}^{-1}$ and 2.61 h^{-1} per Co atom). The combination of time resolved and in situ spectroscopy, including In situ X-ray absorption spectroscopy, In situ ATR FTIR, and femtosecond transient absorption spectroscopy, confirmed that the significantly enhanced OER activity in Co-TTA-IPY can be attributed to more efficient hole collection and utilization, and accelerated rate-determining conversion from Co=O to Co-OOH compared with Co-TTA-BPY. Collectively, this study not only provides a new design strategy for effective hole collection to facilitate OER efficiency in COF-based photocatalysts but also demonstrates the key role of charge separation mechanism play in photocatalytic water oxidation.

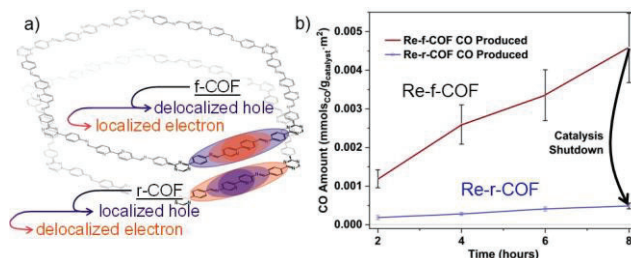


Figure 2. (a) Pictorial scheme of exciton localization in f-COF and r-COF; (b) Time profile of CO production from CO_2 by Re-f-COF and Re-r-COF per gram of COF catalyst.

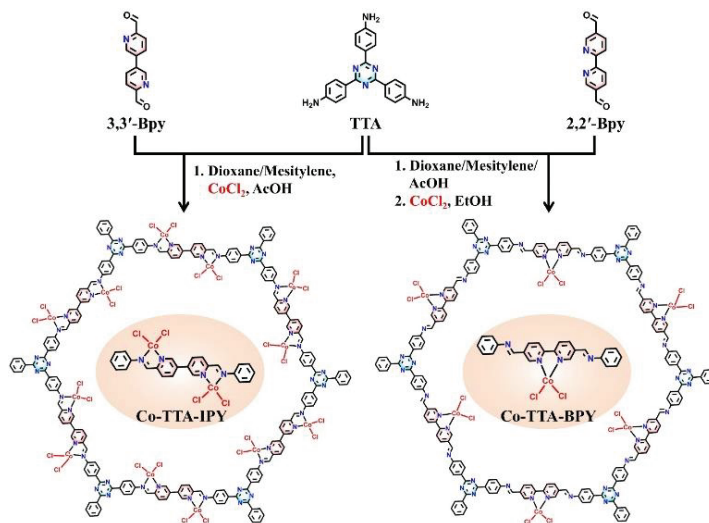


Figure 3. Synthetic routes for Co-TTA-IPY featuring double imine-pyridine (IPY) chelation sites and Co-TTA-BPY incorporating a single bipyridine (BPY) chelation site.

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Understanding local nanoenvironments driving charge transfer in conducting polymer (photo)anodes

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The long-term vision of this new BES effort is the use of low-cost, scalable organic semiconductors oxidative chemical conversions. To achieve this vision, the goal of this effort is to seek fundamental understanding of mechanisms that govern electron transfer in prototypical soft material/electrolyte anodic interphases (Figure 1), specifically dark and light-driven electrochemical reactions, which underpin the development of new molecular catalysts and generation of chemical energy carriers.

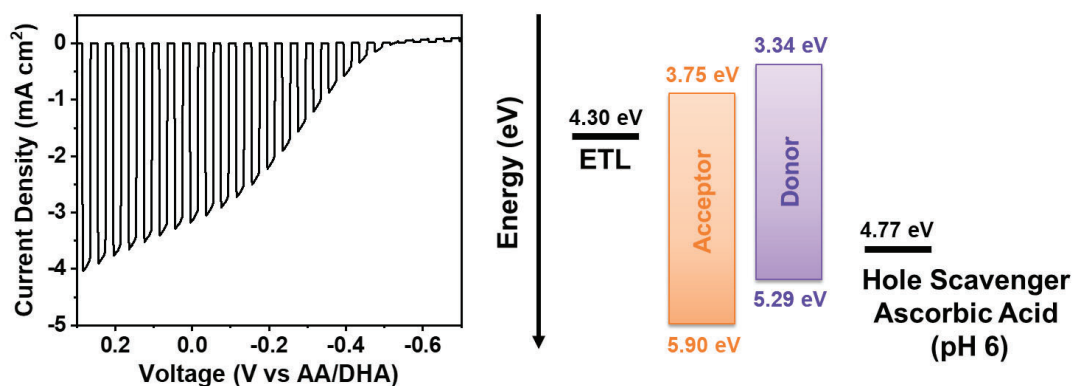


Figure 1. Soft photoanode demonstration. (left) Chopped (i.e., light on/off) current density versus voltage, where the onset of ascorbic acid oxidation occurs approximately 500 mV more cathodic than the Nernst potential (0.0 V vs. AA/DHA). (right) Schematic energy band diagram of the electron donor and electron acceptor materials used for the light-driven process, relative to the hole-extracting electrolyte (here, ascorbic acid at pH ~ 6).

Across materials systems, electro-synthetic reactions are known to be affected by the chemical composition, structure, and energetics of the electrode/solution interface at nanometer length scales and the transport of charges to/from the interface. This work is investigating the knowledge gap of the fundamental metrics driving redox reactions at soft material/electrolyte interphases beyond length scales of discrete interfaces of metal catalyst/electrolyte interactions and/or the standard band bending framework developed for inorganic semiconductor/electrolyte interfaces.

Soft materials lack mid-gap surface states arising from chemical reactions compared to conventional inorganic semiconductors; when polymers contact the electrolyte, these organic semiconductors do not undergo band bending but instead dope volumetrically (10^{15} to 10^{21} carriers/cm³) due to combined electronic-ionic transport across extended length scales. However, soft materials also have a lower density-of-states than conventional inorganic electrodes, which suggests intrinsically that electron transfer rates could be slower. Charge transport predominantly follows a hopping mechanism, resulting in carrier percolation pathways through the organic materials.

In this talk, we focus on recent efforts by the group to track the number of charges that participate in redox reactions, starting first with single component soft electrodes and model redox probes as a function of differences in free energy. We can visualize these charge carriers using voltage- and frequency-dependent spectroelectrochemical capabilities, which allow us to compare between different microstructures, architectures, and/or electrolyte effects to better understand charge transfer mechanisms. The results are coupled with scanning electrochemical cell microscopy (SECCM), which uses a nanocapillary pipette to evaluate local rates of electron transfer and provides histogram analysis of the impacts of local disorder on macroscale electrode performance. New capabilities and efforts towards operando near-ambient pressure-X-ray photoelectron spectroscopy (NAP-XPS) will also briefly be discussed.

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Nothing to report at this time; grant started October 2025.

Protonic diodes and amplified electrochemical cell potentials: ion-exchange membranes can do far more than simply conduct ions and separate reaction products

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Junctions formed at semiconductor interfaces generate space-charge regions. These can result in rectifying diode behavior, which is a predictor of efficient electronic charge separation and photoconversion. Space-charge regions also form at ion-exchange-membrane interfaces. We are working to design them for efficient energy conversion, in particular protonic charge separation as motivated by our light-driven proton-pump platform.

To achieve rectifying diode behavior from ion-exchange membranes we have developed (i) room temperature solution-phase diffusion-reaction doping of cationic anion-exchange membranes with (tri)anionic dopants in an H-cell to form monolithic protonic pn-homojunction bipolar membranes; (ii) protonic recombination/generation junctions based on state-of-the-art water formation/dissociation catalysts for low-impedance back contacts; and (iii) four-composite-layer membrane-electrode assemblies with gas-fed H₂ (for reversible H₂ redox) and water vapor (for adequate membrane hydration). Via a combination of these innovations, we were able to measure, using electrochemistry, highly rectifying behavior (*Fig. 1*) and remarkably low-impedance space-charge regions whose capacitive built-in electric potentials measured under reverse bias are consistent with a protonic pn-homojunction.

We are also continuing to develop a platform whereby a single polymer film can be covalently modified post-synthetically to convert regions of it at different depths into a cation-exchange membrane, anion-exchange membrane, or hydrated uncharged polymer. We have already demonstrated the ability to use diffusion-reaction doping to modify brominated polyphenylene polymers with trimethylamine to form cationic fixed charges as anion-exchange membrane regions. We also suspect that dimethylamine impurities generate fixed protonatable groups that serve as undesired recombination/generation sites. Via this platform we aim to use diffusion-reaction doping to generate the first monolithic protonic pin-junction bipolar membranes, which we hypothesize will have near-optimal rectification and electrostatic properties

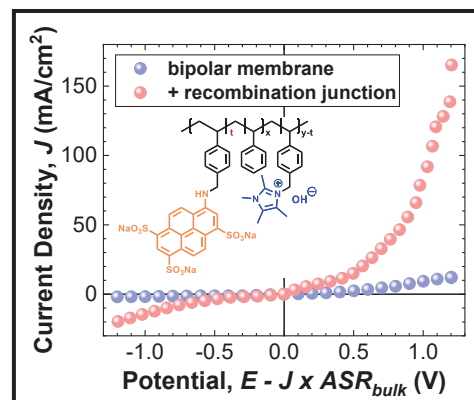


Fig. 1 | Monolithic protonic pn-homojunction bipolar membranes formed by diffusion-reaction doping of X37 anion-exchange membrane with APTS³⁻ (orange). When reversible H₂ redox was designed to occur in each of acidic and alkaline conditions, electrochemical response was poor (blue) in comparison to when reversible H₂ redox was designed to occur only in acidic conditions via addition of a low-impedance recombination/generation junction.

that we plan to characterize using KPFM. Introduction of custom excited-state photoacid or photobase molecules to these materials will advance light-to-protonic energy conversion science.

During our analysis of the above multilayer constructs, we discovered a process whereby use of an inherently leaky ion-exchange membrane wetted by simple aqueous monovalent electrolytes, can boost cell potentials to values beyond those expected based on simply Nernst and Donnan theories. This occurs due to a liquid-junction potential that forms within the ion-exchange membrane (Fig. 2A). We first observed this phenomenon experimentally and later supported it using a straightforward analytical model of steady-state ion crossover that was able to replicate time-dependent cell potentials (Fig. 2B,C). Moreover, nonlinear least-squares best fits of these data revealed the approximate diffusion coefficient of minority coions. We are not aware of another way to extract this value with such accuracy, yet it is critical because minority coions gate overall ion crossover flux. The only adjustable parameters in our model based on a linearized version of Fick's first law of diffusion are the mass-transfer coefficients of each species in each phase – as the ratio of its diffusion coefficient to its transport distance – meaning that these properties can be used to amplify electrochemical power output from charged membranes.

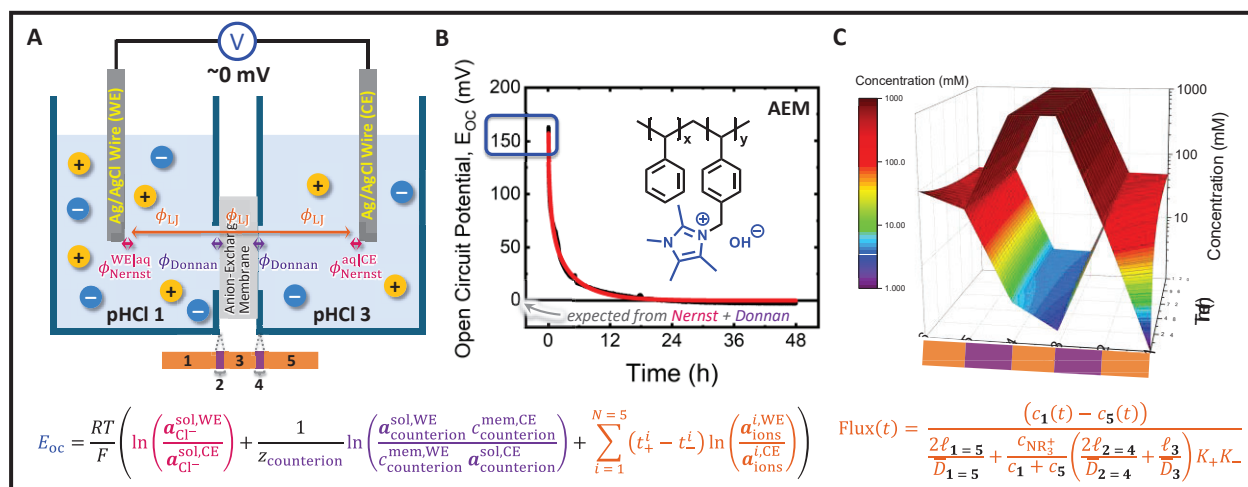


Fig. 2 | Single ion-exchange membrane electric potentials and ionic fluxes. (A) Depiction of the experimental electrochemical H-cell and relevant electric potential differences that result in observed cell potentials based on the indicated equation, which includes **Nernst potentials**, **Donnan potentials**, and **liquid-junction potentials**. **(B)** Measured open-circuit potential over time across X37 anion-exchange membrane (AEM) (black) and nonlinear least-squares best fits (red) to an equation based on both shown, which includes contributions due to the five regions shown in panel A. **(C)** Simulated spatiotemporal concentration profiles of counterions and coions, based on the best fit from panel B.

The impact of this discovery is that the energy output from differences in the concentration of aqueous salt, acid, or base across an ion-exchange membrane can be larger than previously thought. This information provides new design principles for tuning the degree of electrolyte crossover, which even though it inherently dissipates stored energy, in fact can generate net electrical energy that exceeds that possible from a system consisting of leak-free membranes. This unexpected discovery defines a pathway to overcoming the persistent issue of low energy output from flow batteries based on salinity, acid, or base gradients, while also providing guidance for how to boost light-to-ionic energy conversion.

Collectively, these results remind us that ions, and ionically conductive phases, provide a huge parameter space to innovate in photoelectrochemical devices.

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4. Tang, D.; *et al.*, *in preparation*.
5. Keskin, D.; *et al.*, *in preparation*.

Probing Water Oxidation Mechanisms on Heterogeneous Catalysts with Atomically Defined Active Sites

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Water oxidation, a multistep proton-coupled electron transfer (PCET) process, represents a technologically important model reaction for understanding complex catalytic chemistry. The high oxidizing potentials required to drive this reaction create a fundamental challenge in catalyst design: how to achieve high activity while maintaining structural durability. Under photochemical conditions, this challenge becomes even more intricate because the supply of oxidizing equivalents is governed by photon absorption, making the generation of photogenerated charges and the catalytic deprotonation steps mutually dependent. Despite its importance, the interplay between charge supply and catalytic turnover remains insufficiently understood, particularly for heterogeneous systems. Progress has been slow due to limited molecular-level knowledge of surface structures, obscuring quantitative insight into active-site densities and the identities of key intermediates.

To address this gap, our project introduces two key innovations: 1. A heterogeneous catalyst with atomically defined active centers, derived from a high-performing Ir-based molecular catalyst. Heterogenization preserves molecular-level atomic arrangement while enabling studies under realistic interfacial conditions. 2. Time-resolved spectroscopic characterization of reaction intermediates using surface-enhanced infrared absorption spectroscopy (SEIRAS), which provides the sensitivity needed to probe water-oxidation intermediates in aqueous environments.

In this talk, we present recent advances along two fronts. First, we reveal how surface catalytic kinetics and photogenerated charge supply are tightly coupled. On bare metal-oxide photoelectrodes, distinct temperature-dependent behaviors emerge: TiO_2 exhibits a positive temperature dependence across a broad potential range, whereas Fe_2O_3 shows inverse temperature dependence at low potentials and positive dependence at higher potentials. These trends highlight how surface reaction steps regulate charge accumulation. Upon introducing the Ir catalyst, the system displays a more complex relationship between surface charge concentration and active-site density. We further show that the electrolyte plays an essential role: both cations and anions exert strong, previously underappreciated influences on water-oxidation kinetics.

Second, we demonstrate the utility of phase-sensitive SEIRAS for resolving water-oxidation intermediates. This approach dramatically improves signal-to-noise ratios, enabling detection of transient species against the strong infrared background of aqueous media. Applied to the Ir molecular catalyst, SEIRAS reveals two distinct intermediates depending on applied potential: $\text{Ir}=\text{O}$ dominates below 1.8 V vs RHE, while $\text{Ir}-\text{O}-\text{O}$ emerges at higher potentials. By applying a simple adsorption-kinetic model, we extract semi-quantitative rate information about the associated interfacial catalyst dynamics. These results establish a foundation for time-resolved SEIRAS studies of heterogeneous catalysts, which will guide our next phase of work.

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Tuning Semiconductor, Catalyst, and Electrolyte to Direct Reactivity at PEC Interfaces

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The research in my group focuses on directing photoelectrochemical (PEC) reactivity and charge transfer from light-absorbing semiconductor, through a catalyst, to reactants in the electrolyte. We are particularly interested in using non-traditional strategies, such as strain in the semiconductor or catalyst, unique light-matter interactions in molecular modifiers, and high-pressure electrochemical environments to tune reactivity. This presentation will reflect progress in work on both the oxygen evolution reaction (OER) and carbon dioxide reduction reaction (CO₂R), moving from a focus on the semiconductor to the catalyst and then electrolyte.

Semiconductor focus: We investigated the role of mechanical strain on the reactivity of TiO₂ semiconductors for OER. While many PEC studies use prototypical semiconductors such as TiO₂, absent compositional characterization techniques with sufficient interface sensitivity, PEC performance can be misinterpreted in the context of near-surface properties. TiO₂ thin films grown by air-annealing the superelastic alloy Nitinol were found to crack under mechanical strain, increasing electrochemically active Ni sites density. Correspondingly, trends in OER kinetics and fill factors followed Ni site density, with overpotentials slopes decreasing for Ni site densities > 10¹³ Ni/cm²_{geo} (Fig. 1a, b). However, spectroscopic near-surface-sensitive probes

of composition predicted a surface concentration of Ni nearly an order of magnitude higher than that revealed electrochemically; these characterization methods struggle to identify where the Ni signal originates in the several nm near the surface (Fig. 1c). This result highlights the challenge of correlating PEC kinetic performance with intrinsic surface properties of electrochemical interfaces in the presence of near-surface compositional heterogeneity. In the future, work on strain will be transferred to III-V semiconductors to investigate the role of strain on reduction reactions.

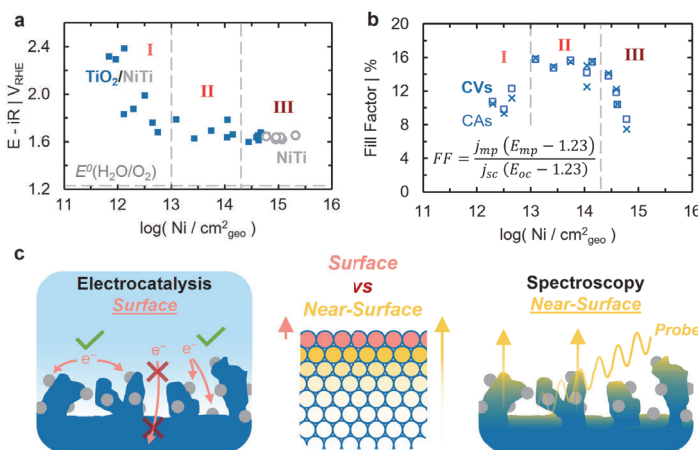


Figure 1: Impact of Ni site density on strained TiO₂ a) overpotential and b) fill factor where vertical grey dashed lines delineate distinctions between (I) low ($< 10^{13} Ni/cm^2_{geo}$, pink), (II) critical ($\sim 10^{13}$ to $2 \times 10^{14} Ni/cm^2_{geo}$, red), and (III) roughening regimes ($> 2 \times 10^{14} Ni/cm^2_{geo}$, dark red). c) Compositional information derived from surface- (left, electrochemical) and near-surface-sensitive probes (right, spectroscopic) in the presence of near-surface compositional heterogeneity (Ni gray spheres in the blue TiO₂ matrix).

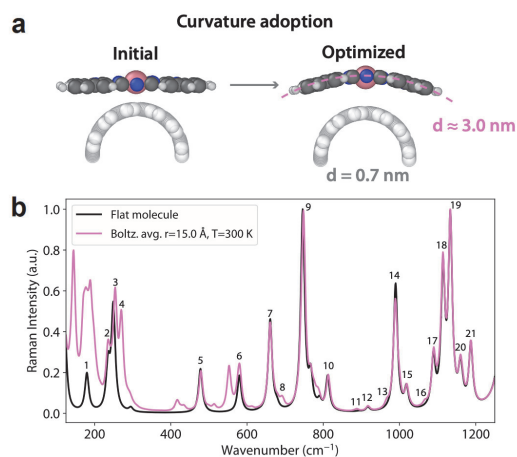


Figure 2: a) Side view of CoPc adsorbed on a (6,5) SWCNT fragment showing the initial (left) and optimized, curved (right) structures. b) DFT calculated Raman spectra for flat CoPc (black) and the optimized CoPc curvature (pink).

out-of-plane molecular vibrational modes, but that CoPc bends around, but does not fully conform to, the nanotube surface (Fig. 2). In the next phase of this project, we will study the impact of these CoPc/s-SWCNT interactions on electrochemical CO_2R and determine the role of photo-induced charge transfer from the nanotube to the catalyst.

Second, the chiral-induced spin selectivity (CISS) effect has emerged as a strategy for improving electrochemical reactions with spin-dependent elementary steps by selectively populating the spin states of reaction intermediates. However, there is a significant gap in experimental data to guide the design of chiral molecular photocatalysts for spin-selective photoinduced charge transfer. Toward this goal, we synthesized two atropisomers of torsionally-restricted biphenyls (BBPs) that exhibit thermally stable axial chirality; these chiral BBPs serve as molecular bridges for probing how optical activity and CISS emerge through electronic coupling with a perylene absorber on a mesoporous metal oxide scaffold. We employ steady-state and time-resolved spectroscopies to interrogate how chirality is communicated between layers through chiral imprints in circular dichroism spectra and how photo-excited energy is transferred to spin selectively within the system through hopping or tunneling mechanisms. Next, we will incorporate molecular OER catalysts with the BBP units on mesoporous metal oxide surfaces to probe OER.

Electrolyte focus: While the properties of the light-absorbing semiconductor and electrocatalyst strongly influence PEC reactivity and selectivity, the electrolyte environment where PEC reactions take place is equally important. Aqueous PEC CO_2R studies are limited by the poor solubility of CO_2 in water and competition with the more facile hydrogen evolution reaction. In contrast, high-pressure, non-aqueous environments provide a route to understand the durability and selectivity of CO_2R catalysts in a controlled environment not limited by substrate starvation and competing reactions. We will describe the initial certification of a high-pressure electrochemical reactor for investigation of CO_2RR in non-aqueous environments up to supercritical pressures. This pilot reactor is being used to establish electrochemical baselines for CO_2RR on metallic surfaces (Cu, Ag/Au) with controlled H^+ concentrations, with future work focused on investigating elemental reaction steps under illumination.

Semiconductor/catalyst interface focus: First, we are studying the interactions of molecular catalysts with semiconducting single-walled carbon nanotubes (s-SWCNTs). We used cobalt phthalocyanine (CoPc) to deeply probe nanotube-catalyst interactions using absorption and Raman scattering spectra, which show that CoPc molecules adsorb onto the SWCNT scaffolds as a mixture of monomers and aggregates. The monomer absorption features are shifted and/or broadened relative to monomers isolated in solution, indicating π - π stacking and electronic coupling of the CoPc to the s-SWCNTs. Raman spectroscopy of these hybrids, taken in regions devoid of aggregates, reveals rich spectral changes for SWCNT-adsorbed molecules relative to CoPc thin films. DFT vibrational analysis for curved CoPc confirm that the curvature imposed by adsorption can lead to increases in intensity for several

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Light-Controlled Multi-Electron Catalysis coordinated across Time and Space

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This program seeks to use bio-inspired approaches to control the efficiency and selectivity of multi-step electrochemical reactions, with a specific focus on artificial photosynthesis. In biochemical catalysis, signaling, feedbacks, allostery and compartmentalization enable precise control over spatial and temporal flows of charges and reactants, yielding highly selective chemical transformations. We translate these concepts into artificial systems through strategies that constitute a paradigm shift in artificial photosynthetic system design. A primary focus is the introduction of time as a design parameter, moving away from steady-state reactions toward transient injection of charges to catalytic centers, operating in concert with regulated substrate delivery. Time-resolved spectroscopy, guided by theory and stochastic kinetics simulations, enables operando characterization of these bio-inspired constructs. Our goal is to understand the factors governing (photo)electrochemical reactivity, establishing a foundation for solar energy conversion via cascaded catalytic sequences involving multiple electron and proton transfers. The fundamental questions are (1) how molecular-level processes initiated by multiple energy carriers can be tightly coordinated, and (2) how photo-driven catalytic sequences can be controlled to ensure only desired products are formed. In this period, we made progress in the following areas (**Figure 1**).

Detecting chemical changes with temporal and spatial sensitivity:

We have developed X-ray spectroscopy methods with modulation excitation with both electrochemical bias (Energy Environ. Sci., 2025) and light to significantly increase the detection efficiency, and for the purpose of controlling chemical processes. Currently, we used the water oxidation reaction with IrO_2 (*manuscript to be submitted*) and the CO_2 reduction reaction with Cu films to show the effect of modulation frequency.

Designs of catalytic cascades using biological principles: We have performed a computational study examining substrate channeling in enzyme systems as a paradigm for improving the

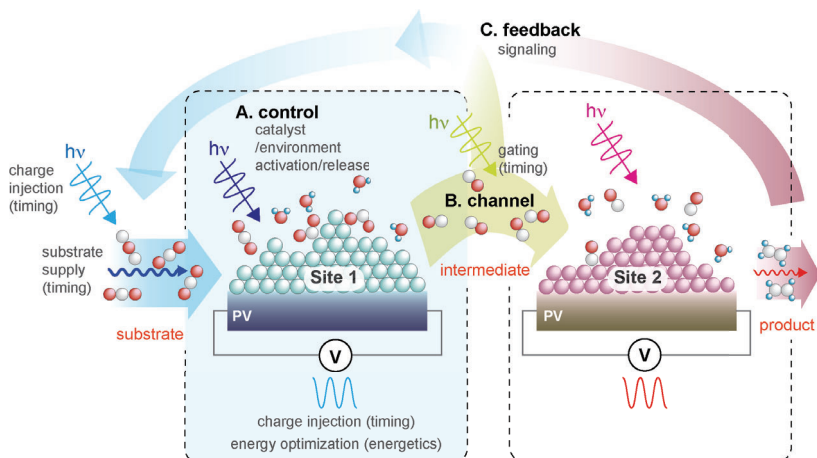


Figure 1: Controlling cascaded artificial photosynthetic systems. Improved catalytic cascade needs controlled charge injection, substrate channeling and feedback signaling, for synchronizing different reaction sites.

efficiency of catalytic cascades in artificial photosynthesis. The results show that a substrate channeling path is not enough: catalyst confinement, directional motion control and timing control are also required. This work provides our foundation for studies of how to incorporate signaling and feedback for autonomous catalytic control (Chem. Sci. 2025).

Modulated charge injection with controlled waveforms: By introducing pulsed resistive-capacitive (RC) circuits, we achieve time-domain control over electrochemical reactivity, a degree of freedom unavailable under steady-state conditions. External RC circuits govern both the characteristic timescale (decay constant, $1/RC$) and total duration of charge injection at electrocatalyst sites, analogous to how biological systems regulate reactivity through the timing of substrate and electron delivery at enzyme active sites. We demonstrate how this temporal control influences selectivity in CO_2 reduction, with reactivity modeled using stochastic kinetics simulations accounting for Au-catalyzed CO_2 reduction mechanisms under RC-controlled pulsed polarization (manuscript to be submitted). This approach opens a path toward artificial catalytic systems that exploit time as an explicit variable in controlling chemical outcomes.

Controlled storage and release of reaction intermediates: Controlled storage and release of reaction intermediates from reservoirs would be highly beneficial in realizing cascade catalysis. To this end, we have focused on CO_2/CO reduction Cu electrocatalysts, motivated by its complex reaction network and high selectivity to ethylene (C_2H_4) formation. Our new mass spectrometry methods achieve sub-second time resolution, allowing real-time evaluation of the carbon mass balance. Potential step experiments for CO reduction reveal that initial CO consumption is fast (< 1 s), but C_2H_4 appearance can be 10 times slower, attributed to the time required for C_1 intermediate storage and subsequent reconstruction into the active, C_{2+} -forming, configuration. Critically, isotopic-labeled gas switching ($^{12}\text{CO}_2$ - ^{13}CO) experiments yield compelling evidence that CO_2 preferentially reacts with this C_1 reservoir, in contrast to prior reaction networks that assumed CO_2 solely forms C_1 intermediates, as evidenced by the temporal observation of the mixed isotopologue $^{13}\text{C}^{12}\text{CH}_4$ (manuscript to be submitted). Towards control of intermediate storage, we have demonstrated potential-controlled "catch and release" of CO from Pt, Au, and Ag surfaces, with our approach allowing measurement of the CO adsorption energy under aqueous electrocatalytic conditions, analogous to temperature-controlled desorption in thermal catalysis.

Future plan:

- Development of data acquisition and analysis methods of modulation-excitation methods with higher chemical sensitivity.
- Combination of voltage and light to control reaction kinetics, and therefore the directionality of chemistry.
- Use light to mediate the release of CO from Pt, Au, and Ag reservoirs, potentially aided by plasmonic effects; demonstrate transport and reaction of this species at a second site in the cascade.
- Use temporal modulation of CO, CO_2 , and possibly other substrates to control the formation of the C_1 reservoir and its non-steady-state chemistry.
- Develop designs for signaling-feedback strategies to control the chemistry timing of two catalysts operating as a cascade and demonstrate their properties by reaction-diffusion simulations.

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How can we make better use of the inverted region? A pulse radiolysis study

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Scope

Our research centers on leveraging the unique capabilities of pulse radiolysis (PR) to study fundamental processes relevant to photochemistry and radiation chemistry. Our core effort focuses on the role of delocalization and low polarity in charge transfer, transport, escape and recombination reactions as well as the use of pulse radiolysis to complement electrochemistry (e.g. nonpolar media, no electrolyte, short-lived species, irreversible behaviors). Emerging interests include developing the capabilities and expertise to use PR to study radiation-induced chemistry in EUV resists for microelectronic applications, spatially separated spin-correlated radical ion pairs for quantum information science, radiolytic conversion of small molecules, mechanisms of photoredox catalysis, and “forever chemical” destruction.

Pulse radiolysis has been an important technique in fundamental studies of electron transfer, historically revealing the Marcus inverted region for the first time using D-B-A intramolecular electron transfer,¹ and more recently in bimolecular reactions.^{2,3} These recent approaches overcame challenges of diffusion-limited observed rates by reducing electronic coupling and reorganization energy through charge delocalization in one case² and raising the diffusion-controlled limit and pressure-tuning the free energy driving force for electron transfer, ΔG_{et} , using solvent-phase electrons in another.³ We seek to better understand the interplay between delocalization and polarity to enable the powerful inverted region effect to be fully exploited in real-world energy applications.

Recent results

Figure 1 summarizes some relevant measured electron transfer rate constants involving delocalized charge and/or nonpolar solvents.¹⁻⁴ Extrapolating these rate constants to energies relevant to solar energy conversion ($\Delta G_{\text{et}} \sim 1\text{-}2$ eV) predicts much larger values than reported “CT state” lifetimes seen in nonpolar donor-acceptor films of highly conjugated molecules ($\sim 10^8\text{-}10^{10} \text{ s}^{-1}$).^{5,6} The exact reason for this discrepancy is unclear. It could relate to disorder in the film that enables charges to separate, or to greater delocalization of both donor and acceptor species.

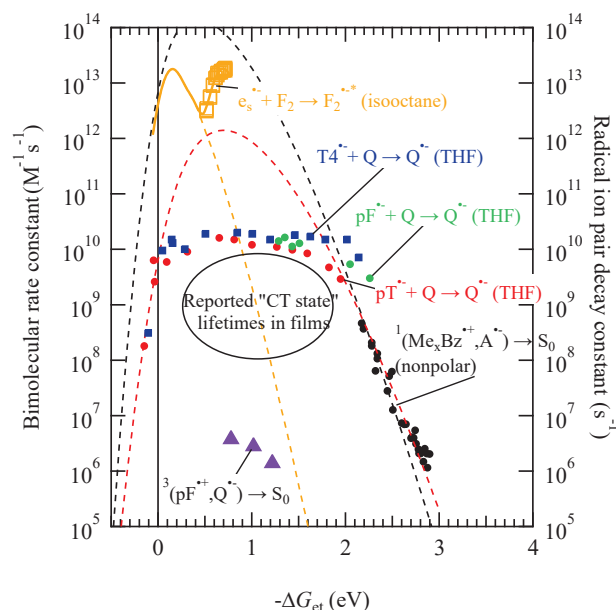


Figure 1. Compilation of observed electron transfer rate constants between molecules in low-polarity solvents from various sources (see text).

Extrapolations in Fig. 1 are based on data from Gould⁴ on non-radiative recombination of small molecule ion pairs in low-polarity solvents (black dots), as well as electron transfer reactions from delocalized radical anions of oligo/polythiophene² (blue,red) and polyfluorene (green) to benzoquinones in THF using PR (note diffusion limit at $\sim 10^{10} \text{ M}^{-1}\text{s}^{-1}$). While not a direct measurement, fitted parameters for bimolecular electron transfer from the highly mobile isooctane solvent-phase electron to an oligofluorene (F₂, orange points) suggest that rate constants of $\sim 10^8$ - $10^{10} \text{ M}^{-1}\text{s}^{-1}$ may be observable in delocalized systems at moderate ΔG_{et} . However, observation of such slow rate constants is hindered by the low-lying excited state of the F₂ radical anion, which lies in the normal regime where the rate constant increases as ΔG_{et} becomes more negative.

None of the data in Figure 1 show electron transfer between *two* highly delocalized states in nonpolar solvents that would correspond best to the film data.

We have compiled a large dataset of electron transfer reactions involving delocalized charges, including both recombination reactions and radical anion electron transfer processes using PR. Some examples of these, such as those shown in Fig. 2, involve triplet radical ion pairs, where a complex interplay between spin, electronic coupling and local triplet excited states governs the lifetimes.

We will present these results along with electron transfer between delocalized radical anions in nonpolar solvents xylene and isooctane, and compare this behavior to that observed in the more polar environment of THF.

Future Plans

A significant challenge in exploiting the inverted region is that excited states of the product of electron transfer in delocalized systems are typically low in energy (e.g. local triplets or radical anion excited states). These states provide electron transfer pathways with small ΔG_{et} , masking inverted region effects. We are particularly interested in how emerging classes of materials, such as multiple resonance thermally activated delayed fluorescence (MR-TADF) molecules and expanded libraries of stable radicals, may provide opportunities to minimize the impact of these excited product states. These fundamental studies will help guide the development of strategies to mitigate energy-loss pathways in photoconversion systems, whether for electricity generation or chemical transformation.

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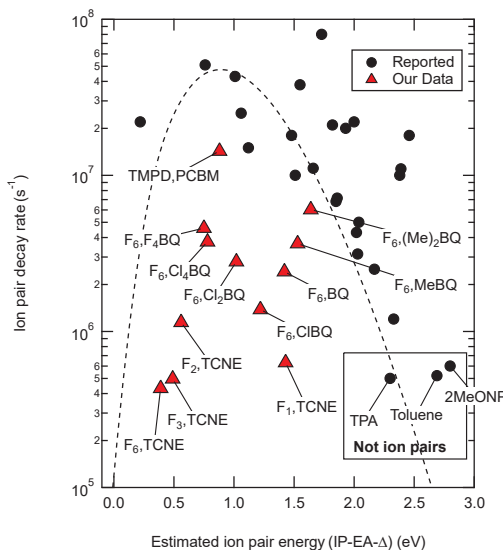


Figure 2. Representative first order decay rate constants for radical ion pairs in xylene/benzene.

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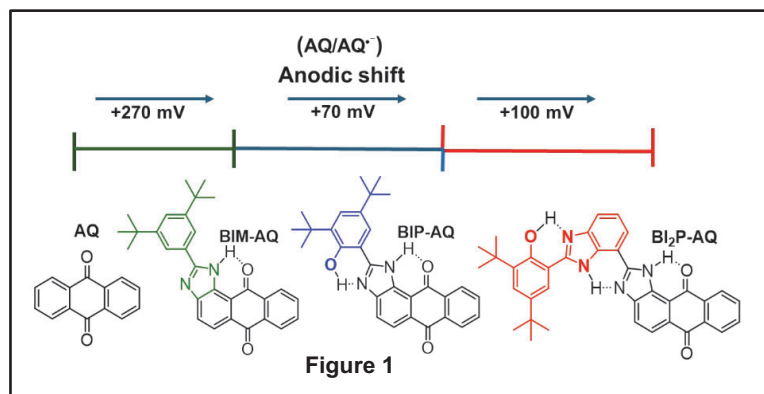
Electrostatic Effects in Proton-Coupled Electron Transfer

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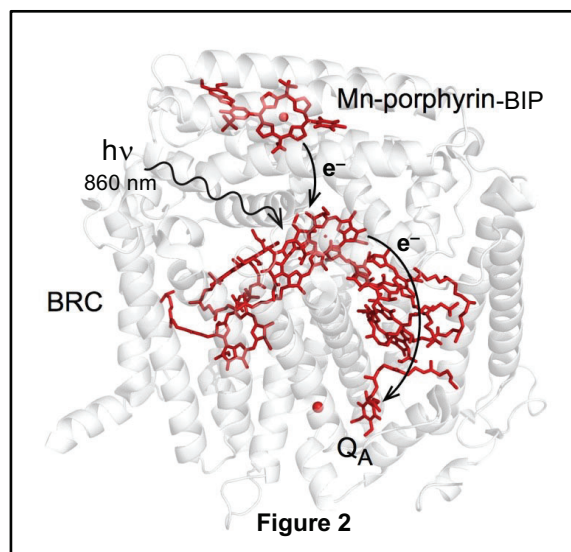
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Our model systems have expanded the PCET concept to include Multiproton-Coupled Electron Transfer (MPCET) as a mechanism for transporting protons away from the electron-transfer redox site. In addition to delivering proton chemical potential to distant locations for catalysis, MPCET can be involved in the generation of proton motive force (proton chemical potential – the organizing principle of bioenergetics) in reengineered photosynthesis. In some of our systems, the redox process can be either electrochemically or photochemically driven, involving the one-electron oxidation of a benzimidazole phenol (BIP) coupled to a variable-length Grotthuss-type polybenzimidazole-based proton wire capable of translocating protons up to ~ 16 Å. Our results provide no indications that this distance is the limit.¹⁻⁴



Currently, we are designing and synthesizing push-pull systems in which oxidation of a phenol (as in BIPs) “pushes” a proton along a Grotthuss-type proton wire, and an anthraquinone bearing a hydrogen-bonded substituent located at the distal end of the wire would, upon reduction, “pull” the proton towards itself. Expanding on this theme, the hydrogen-bonded network of the **BIM-AQ** was extended, as seen in

BIP-AQ and **BI₂P-AQ** in Figure 1. Cyclic voltammetry in dichloromethane reveals a systematic anodic displacement of the AQ/AQ^{•-} couple as the relay is extended, progressing from $E_{\text{mid}} \approx -1.10$ V for **AQ** to -0.83 V for **BIM-AQ**, -0.76 V for **BIP-AQ**, and -0.66 V for **BI₂P-AQ**, corresponding to a cumulative +440 mV increase in E_{mid} for the semiquinone-radical anion species. Visible (VIS) and infrared (IR) spectroelectrochemistry (SEC) data under negative polarization are consistent with the formation of a hydrogen-bonded semiquinone-radical anion in **BIM-AQ**, **BIP-AQ**, and **BI₂P-AQ**. The VIS and IR SEC data do not establish the role of the distal hydrogen bonds of the hydrogen-bonded framework in the increase of E_{mid} . To address this issue, conventional DFT and Nuclear-Electronic Orbital (NEO-DFT, which treats the hydrogen nuclei of the hydrogen-bonded framework quantum mechanically) show that the proton donor-acceptor distance of the hydrogen bond proximal to **AQ** decreases by up to 0.09 Å upon one electron reduction of **AQ**. NEO-DFT convincingly shows that the effect propagates along the hydrogen-bonded network: the hydrogen bonds farther from the reduction center (**AQ**) also contract. Indeed, the proton nuclear quantum effect is significant. Encouragingly, it appears that “pulling” protons along the hydrogen-bonded network is a viable strategy to increase the E_{mid} , which can be attributed to the electrostatic effect of AQ^{•-} causing the proton(s) to move closer to it.⁵



In another project, we have been experimenting with PCET in protein environments. Constructs consisting of a four-helix bundle enclosing a high-potential Mn-porphyrin docked to a high-potential bacterial reaction center (**BRC**) have been assembled.⁶ Exciting the **BRC** at 860 nm reversibly oxidizes **Mn(II)**-porphyrin to **Mn(III)**-porphyrin as detected by the characteristic shift of the absorption band from 430 nm to 451 nm (similar changes were observed when Mn(II) was oxidized to Mn(III) electrochemically with the Mn-porphyrin dissolved in dichloromethane). The charge-separated state involving the **Mn(III)**-porphyrin and **Q_A** of the BRC returns to the ground state in ~1-2 min, and no change in pH is detected in the bulk solution using cresol red as the pH

indicator. We regard this as a control experiment. However, a very different result was observed when the simple Mn-porphyrin in the four-helix bundle was replaced by an analog where a BIP is covalently attached to the *meso*-position of the Mn-porphyrin, forming a dyad, that was attached to the **BRC** (see **Figure 2**). Illumination of the **BRC** in this construct resulted in band shifts similar to those above, indicating the oxidation of **Mn(II)** to **Mn(III)** and the pH indicator showed a decrease in the pH. As with the simple **Mn(II)**-porphyrin, the process is reversible but on a very different time scale. Recovery occurs in 1-2 h. To identify the site of deprotonation, a BIP phenol was protected as a methyl ether, but a similar reduction in pH upon irradiation of the BRC was observed, thus eliminating the phenol as the source of deprotonation; instead, the imidazole is a likely candidate. At this point, new reference compounds lacking the phenol are being prepared in parallel with comparative testing of redox-inactive **Zn(II)**-porphyrin derivatives. Our current working hypothesis is that under ambient proton activity in the unbuffered aqueous solution, the imidazole is protonated, and the generation of **Mn(III)** by the photochemically activated reaction center results in an electrostatic effect that lowers the pK_a of the dyad's imidazole. That causes it to deprotonate into the solution, lowering the pH. This effect is interpreted as an electrostatically induced PCET process. Such processes are observed in natural systems, for example, around **Q_B** of Photosystem II. These are promising results for developing hybrid artificial photosynthetic constructs in which energy-conserving processes could be redesigned and optimized.

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Developing the Photocatalytic Workforce

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This project has two aims: 1) increase the number of undergraduate and early career graduate students engaged in high impact research and 2) investigate transition metal molecular catalysts through a combined approach using computational, spectroscopic, and synthetic techniques leading to the design of new biohybrid complexes for light driven fuel production. Nickel, cobalt, and copper molecular catalysts offer a promising opportunity for understanding the primary mechanisms of photochemical energy conversion as they are inexpensive, readily synthesized, and can be chemically modified to tune their properties. Density Functional Theory (DFT) techniques are being utilized to understand the effect of structural changes on the electronic and catalytic properties of the molecular catalysts. Electron Paramagnetic Resonance (EPR) spectroscopy is used for characterizing the charge-transfer events and electronic structure of the transition metal complexes and the biohybrid complexes. Protein biochemistry techniques are being utilized to develop new biohybrid assemblies consisting of a photosensitizer protein linked to a molecular catalyst.

Furthering our goal to increase the number of students engaging in high impact research in photochemistry, in the first full year of the grant, 16 students participated in the research program across the three academic institutions (CSU, EU, NSU). Of these, nine students participated in summer research which provided greater opportunities for engagement with PIs and the project. Biweekly virtual group meetings were attended by all the students supported by the program and all four PIs; these meetings are a critical piece of training. Students learn to present their research results from the past two weeks, allowing them to engage in interdisciplinary thinking and participating in larger group dynamics than would be possible at the individual primarily undergraduate institutions. Furthermore, they have received professional development training in resume preparations, AI tools with a focus on prompt writing through tools provided by IBM SkillsBuild, and presentation skills. Thirteen student posters were presented at several undergraduate research symposiums in 2025-2026 at Elmhurst University, University of Illinois Champaign Urbana, and Chicago State University. Three trainees graduated in December 2025 with another four graduating in May 2026.

The PIs have led the student trainees into

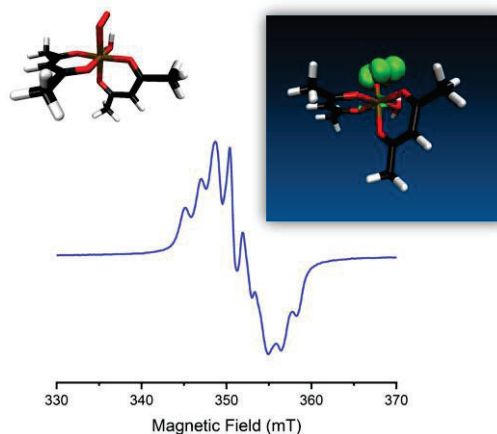


Figure 1. Experimental continuous wave X-band EPR spectrum and calculated spin density isosurface of Co(III)-superoxo complex obtained during photo-redox cycles of the catalytic Co(II)/Co(III) pair.

investigating several nickel and cobalt molecular catalysts both experimentally by EPR spectroscopy and computationally with geometry optimizations and calculations of magnetic resonance parameters such as anisotropic electronic g-tensors and hyperfine interaction tensors (**Fig. 1**). For the cobalt structure, bis(acetylacetonato)cobalt(III) bound to a dioxygen radical (upper left Fig 1), the agreement between calculated and experimentally determined magnetic resonance parameters (g-tensor, ^{59}Co hyperfine tensor) allowed differentiation between competing structures.

To advance the biohybrid portion of the project, where the catalysts are integrated into the protein, students utilized various molecular and biochemical techniques for the development of an *E. coli* overexpression system for a Photosensitizer Protein (PSP) which mimics the natural photosystem I (PSI) reaction center. Biohybrid complexes will be developed through site-specific linkages of transition metal catalysts (cobaloxime and copper-based complexes as examples) for light-driven hydrogen generation. Several copper (II) catalysts were synthesized at Elmhurst University and will be studied by EPR spectroscopy at Norfolk State University. Molecular dynamics (MD) simulation of the protein with the attached catalyst will be used to explore the conformational space followed by DFT geometry optimization of the catalyst with its relevant microenvironment including near amino acids, and computation of magnetic resonance parameters such as g- and hyperfine-tensors will continue at Chicago State University with the larger MD simulations and hyperfine coupling calculations being performed using the Laboratory Computing Resource Center (LCRC) computing facilities at Argonne National Laboratory. We will also use pulsed X-band and High Frequency/High Field D-band EPR at Argonne for increased spectral resolution to resolve the anisotropic g-tensor and hyperfine tensors permitting a better characterization of the binding of the catalyst in the biohybrid. In addition, a molecular linker has been designed and synthesized at Elmhurst University and will be used for the site-specific attachment of the PSP to a copper (II) catalyst (**Fig. 2**) leading to a new biohybrid complex for light-driven hydrogen production. Future work in the biohybrid portion of the project will focus on the characterization of the PSP-catalyst complexes using EPR, DFT analysis, and hydrogen evolution assays.

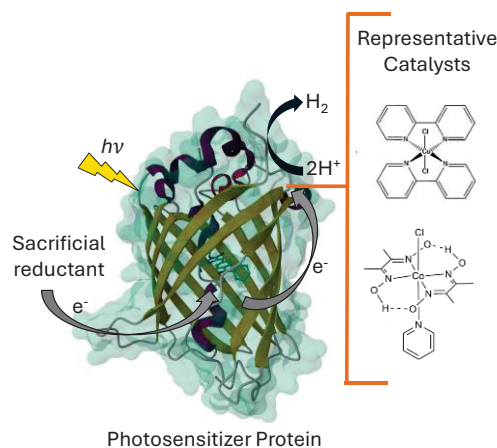


Figure 2. Photosensitizer Protein harboring a benzophenone chromophore based on PDB 6L02 linked via the newly included site-specific linker to copper or cobalt catalysts.

Bandgap renormalization and hot-carrier photoelectrochemistry at 2D semiconductor electrodes

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Two-dimensional (2D) transition metal dichalcogenide (TMD) semiconductors such as monolayer (ML) MoS₂ and WS₂ are under active investigation for hot-carrier photoelectrochemistry because their atomically thin geometry places photogenerated hot carriers directly at the electrode/electrolyte interface before their excess energy is lost. Harvesting that energy for fuel-forming reactions requires the hot-carrier extraction rate to exceed the cooling rate, which in turn demands energy level overlap between occupied hot-carrier states and unoccupied electronic states of acceptor molecules in solution. A defining and underexplored feature of these materials is the giant band gap renormalization (BGR) effect, in which many-body Coulomb interactions cause the electronic band gap (E_g) to shift dramatically (~ 0.5 eV) with free carrier concentration n . The BGR effect creates a fundamental complication that is unique to 2D semiconductor photoelectrodes because n is a direct function of E_{app} and light intensity, and therefore the BGR effect necessarily alters the energy level alignment between semiconductor conduction band states and molecular redox levels in solution during photoelectrochemical cell operation. Yet no existing electrochemical model integrates this potential-dependent E_g into the current–voltage (J – V) response (Figure 1), leaving the field without quantitative tools to predict or control hot-carrier-driven reactivity. This talk presents three interconnected advances addressing this gap.

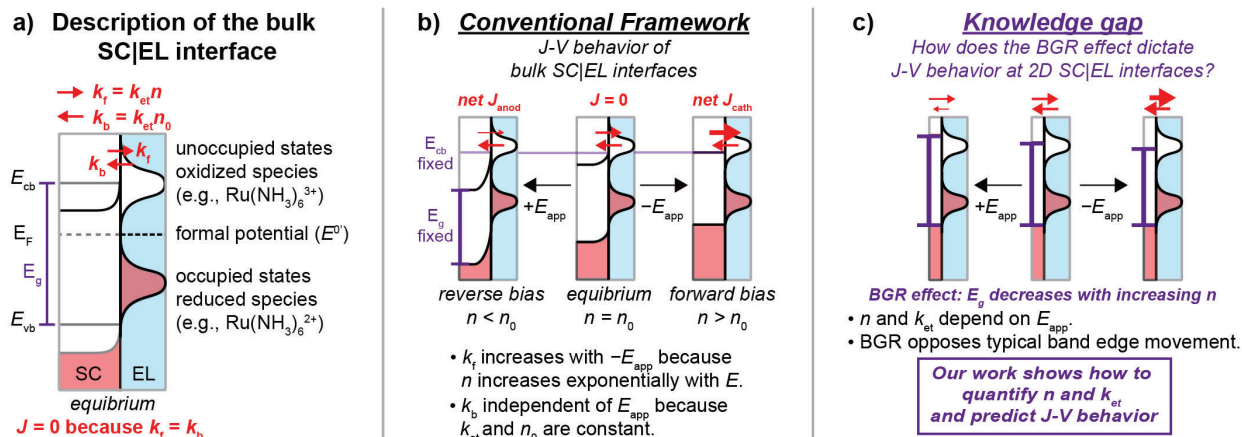


Figure 1. The conventional Marcus–Gerischer framework (a, b) describes bulk semiconductor|electrolyte interfaces in which band edges remain fixed with applied potential. For 2D semiconductors (c), the BGR effect causes E_g to decrease with increasing E_{app} and, therefore, carrier density, opposing typical band edge movement and introducing a fundamental knowledge gap in predicting J – V behavior.

Using in situ absorbance micro-spectroscopy and many-body theory, we quantify a >200 meV shift in E_g over a narrow potential range and demonstrate that redox couples modulate E_g equivalently under open-circuit conditions — an effect with no analogue in bulk electrodes. Across 11 ML-MoS₂ electrodes, we observe three reproducible sub-populations of J – V responses ranging from reversible to fully irreversible (Figure 2). Marcus–Gerischer simulations incorporating BGR

reproduce all three response types; models that omit BGR fail. These results establish BGR as a new mechanism for band edge movement in 2D electrodes and open a route to voltage-tunable redox selectivity. Separately, by varying the solvent dielectric constant, we show that Coulomb screening directly controls the magnitude of the BGR effect and tunes exciton binding energies — establishing solvent choice as a handle for controlling interfacial energy level alignment. Finally, bis(trifluoromethane)sulfonimide acid surface treatment produces >30-fold photocurrent enhancements in ML-TMD photoelectrodes. Ongoing pump-selective femtosecond transient absorption measurements will determine whether this reflects increased hot-carrier extraction, suppressed surface recombination, or both.

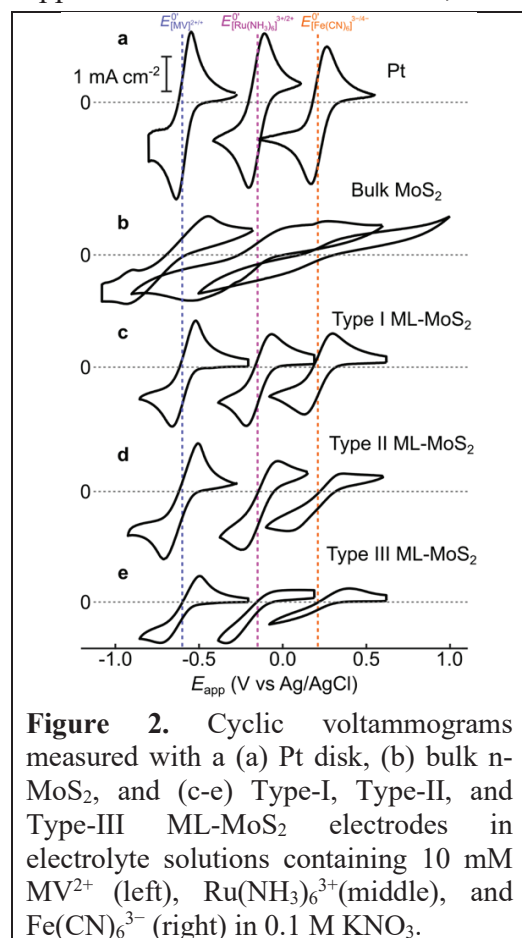


Figure 2. Cyclic voltammograms measured with a (a) Pt disk, (b) bulk n-MoS₂, and (c-e) Type-I, Type-II, and Type-III ML-MoS₂ electrodes in electrolyte solutions containing 10 mM MV²⁺ (left), Ru(NH₃)₆³⁺ (middle), and Fe(CN)₆³⁻ (right) in 0.1 M KNO₃.

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Versatility of Transition Metal Chalcogenides for Durable Photoelectrodes, Ammonia Generation, and Long-lived Carriers

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The research in my group focuses on tuning optoelectronic properties of 2D transition metal dichalcogenides (TMDCs) and other semiconducting materials towards various applications, such as energy conversion processes microelectronics, and sensors. In the past three years, we have leveraged unique interfaces to create long-lived carriers and durable photoelectrodes as well as transformed TMDCs into vacancy rich transition metal chalcogenides to electrochemically generate ammonia (NH₃) over hydrogen (H₂) evolution. In addition to this work, we have evaluated how 2D TMDCs and other semiconductor thin film properties change with strain, focused on MoS₂ monolayers, GaAs, and nitinol with a TiO₂ top layer. Below three research directions are detailed with future directions discussed.

The first research direction focuses on photoelectrode protection using monolayers of MoS₂. Specifically, gallium indium phosphide (GaInP) is a large-bandgap semiconductor and a promising candidate for the top cell in a tandem cell for photoelectrochemical (PEC) water splitting. GaInP has been reported in the literature to degrade during PEC hydrogen evolution reaction (HER), and buried junctions, p-n junctions, surface functionalization, and metallic interfaces have been shown to prevent GaInP degradation. We are taking a different approach with monolayer MoS₂. Our

preliminary data suggests that a single monolayer of MoS₂ reduces photodegradation under acidic conditions, for 100-h of ~1 sun conditions (Figure 1a). This builds on previous work from other groups that have created a buried heterojunction with 5-10 nm MoO_xS_y thin films to prevent photodegradation. With thorough pre- and post-surface characterization, we determine that a small

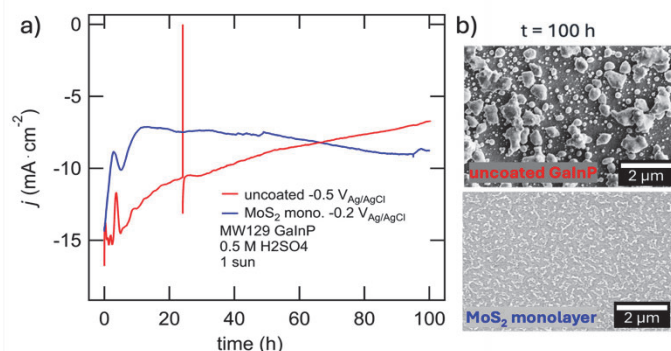


Figure 1. GaInP photoelectrodes for H₂ generation perform better over 100 hours when a monolayer of MoS₂ and small amounts of Cu are present. (a) Photoelectrochemical current measured over 100 hours for GaInP with and without a monolayer of MoS₂. (b) Scanning electrochemical microscopy images showing how the GaInP surfaces are different with and without MoS₂ monolayer.

amount of Cu metal is needed, and we hypothesize that this Cu acts like a “pin-cushion” to tack the MoS₂ monolayer to the GaInP photoelectrode during PEC HER. Post 100-h PEC HER scanning electron microscopy (SEM, Figure 1b), Raman, and XPS show differences in the surface chemistry, specifically compositional changes that yield In metal buildup as is typical with unprotected GaInP photoelectrodes. The goal of this project is to demonstrate how a monolayer of MoS₂ can prevent or decrease photodegradation of GaInP and can likely be extended to other photoelectrodes. In the future, we plan to understand how additional stacking of monolayers will impact charge separation and therefore photoelectrode protection.

The second research direction investigates the electrochemical nitrate reduction reaction (NO₃RR) as a sustainable pathway for NH₃ synthesis under neutral pH conditions using a polycrystalline vanadium sulfide (VS_x) electrocatalyst derived from annealed vanadium disulfide (VS₂). The research demonstrates that VS_x outperforms its precursor, VS₂, in terms of activity and Faradaic efficiency toward NH₄⁺ (69% at -0.69 V_{RHE}) in phosphate-buffered neutral electrolyte. Detailed characterization reveals that the annealing of VS₂ enhances crystallinity, reduces surface oxidation, and alters local bonding environments, possibly introducing sulfur vacancies (S_v) or undercoordinated vanadium sites that act as active binding sites for nitrate. Density functional theory (DFT) calculations confirm that S_v sites energetically favor nitrate binding over proton adsorption, and all reaction steps toward NH₄⁺ production are thermodynamically downhill, while kinetic isotope effect (KIE) experiments suggest a non-proton-coupled first electron transfer as the kinetic rate-limiting step. In future work, we will investigate how the VS_x nanomaterials electrocatalytically generate urea from NO₃⁻ and CO₂ reduction. We developed a protocol for quantifying urea by NMR and are exploring experimental parameters for urea generation. From here, we will determine how VS₂ grows on other nanomaterials such as MoS₂ and carbon

nanotubes (CNTs). This new interface will be characterized for charge transfer from the light absorbing nanomaterial (MoS₂ or CNTs) to the VS_x, where we hypothesize electrocatalysis will occur at a lower potential.

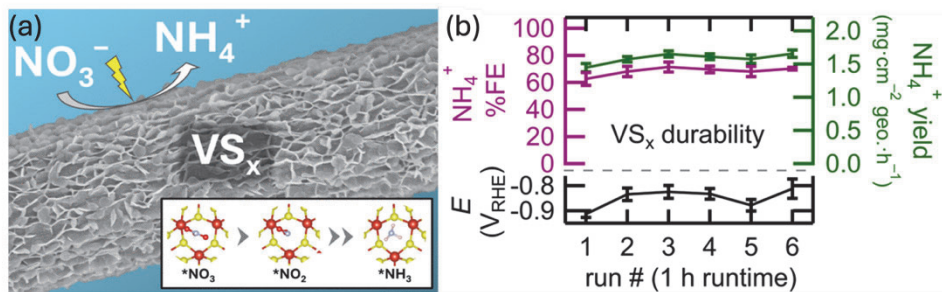


Figure 2 (a) Electrochemical nitrate reduction reaction (NO₃RR) depicted as a pathway for ammonia (NH₃/NH₄⁺) synthesis using a polycrystalline vanadium sulfide (VS_x) electrocatalyst. The inset shows theoretically calculated steps of VS₂ for NO₃RR with sulfur vacancies that thermodynamically favors NH₄⁺ generation. (b) Experimental results of a 6-hour electrochemically active VS_x catalyst for NO₃RR.

Finally, the third research direction demonstrates precision doping of 2D monolayers of MoS₂. By leveraging interface chemistry with the oxide substrate and visible light exposure under ambient conditions, this study demonstrates a robust and scalable photo-dedoping process for monolayer MoS₂. The mechanism involves the oxide layer trapping photoexcited holes, leaving long-lived electrons to drive surface reactions at sulfur vacancies, leading to stable dedoping. The stability of this process, which withstands high temperatures and vacuum conditions, demonstrates suitability for commercial semiconductor fabrication. Next steps include tuning the underlying oxide for further mechanistic control as well as extending beyond MoS₂ to other TMDCs.

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Photoinduced Charge and Energy Transfer in Hybrid Donor-Acceptor Systems.

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The overarching goal of our research is to develop a fundamental understanding of the mechanisms, (supra) molecular architectures, and design principles required for efficient coupling of light-generated excited states to multielectron, proton-coupled water-splitting and fuel-forming catalysis. Molecular systems, with their atomic-scale precision, provide an unparalleled opportunity to examine how even subtle structural changes influence photochemical and catalytic activity. A hallmark of this program is the close integration of synthesis with high-resolution physical characterization of both ground and excited states using a range of techniques, including multifrequency, pulsed, and time-resolved EPR spectroscopic approaches. Specifically, advanced EPR methods including ENDOR, ESEEM, and DEER spectroscopy are applied to provide deep insight into molecular and electronic structure as well as charge and spin dynamics following photoexcitation, allowing us to understand photochemical energy conversion systems in detail. A specialty of our group is time-resolved multifrequency EPR spectroscopy at X-band (9 GHz), Q-band (34 GHz), and D-band (130 GHz), using *in situ* pulsed laser excitation. This talk will discuss recent results uncovering photoinduced charge and energy transfer mechanisms in hybrid systems composed of inorganic quantum dots (QDs) conjugated to organic dye molecules.

Photochemical charge separation in organic donor-acceptor systems and photosynthetic reaction-center proteins can produce spin-correlated radical pairs (SCRPs). These entangled spin pairs are formed in well-defined spin states and provide an exceptionally sensitive platform for probing electron- and energy-transfer dynamics. Although SCRPs in organic donor-acceptor systems and photosynthetic reaction centers have been extensively studied, only a very limited number of EPR investigations of light-induced SCRPs in inorganic photocatalytic systems have been reported.

Hybrid conjugates of organic chromophores and ZnO QDs are emerging as model systems for generating and controlling photoinduced spin states relevant to quantum information science, spintronics, photocatalysis, and triplet-sensitization applications. In these systems, photoexcitation of the molecular dye is followed by charge separation to the ZnO QD, forming SCRPs (Fig. 1). These are especially attractive as spin-based qubit pairs (SQPs) because they are generated in well-defined, nonthermal, spin-polarized states and can evolve into highly-polarized molecular triplet states through charge recombination. We've been investigating a variety of tunable ZnO QD-molecule conjugates incorporating chromophores such as D131, 9,10-bis(phenylethynyl)anthracene (BPEA), and perylene derivatives, while systematically varying QD size and donor-acceptor linker length. The

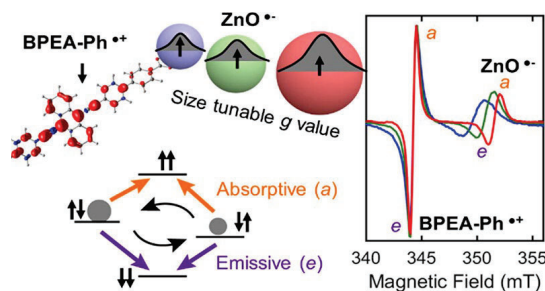


Figure 1. Light-induced Spin-Correlated Radical Pair (SCRPs) formation in hybrid organic dye/inorganic ZnO Quantum Dot (QD) conjugates.

QDs provide a flexible platform for studying charge-separation and charge-recombination dynamics because their electronic and spin properties are size-tunable and their surfaces are readily functionalized. In addition, the spin states in QDs can exhibit g-values far outside the range typical of organic molecules, enabling detailed characterization of each spin within the SCRP. The broad choice of organic dyes makes it possible to tailor optical absorption, energetics, kinetics, and the interaction strength between electron spins on donor and acceptor. Optical spectroscopy demonstrates efficient and reversible photoinduced charge separation and the formation of long-lived charge-separated states, with charge-transfer rates and SCRP lifetimes strongly dependent on electronic coupling, linker length, and driving force. Time-resolved continuous wave and pulsed EPR measurements reveal the generation of singlet-born SCRPs, followed by spin mixing that populates the T_0 triplet manifold, and the formation of highly spin-polarized triplet states localized on the molecular dye. In some of these conjugates, back transfer from the triplet charge-separated state generally dominates over direct singlet recombination. The spin properties are highly tunable: the ZnO QD anion g-value depends on QD size through the quantum size effect, linewidths reflect radical-pair separation, and spin polarization is well described by existing SCRP theory. Pulsed microwave experiments show that these photogenerated spin states can be selectively accessed and manipulated, representing an important step toward applications in quantum sensing. The temperature-dependence of SCRPs life-time indicates that charge recombination occurs with low activation barriers, while differences between transient SCRPs and stable photoreduced ZnO states suggest distinct regimes of electron delocalization. Together, these results establish ZnO QD-molecule conjugates as highly tailorable hybrid nanostructures in which interfacial chemistry, charge dynamics, and spin polarization can be systematically engineered to achieve spin-selective addressability, long-lived excited states, and controlled triplet generation.

Among QD-based hybrid materials, conjugates of organic molecules with Si QDs have demonstrated efficient triplet energy transfer (TET). To date, most understanding of these systems has come from optical methods such as time-resolved photoluminescence and transient optical absorption spectroscopy. However, direct experimental insight into the spin-dependent mechanisms of energy transfer remains limited. Recently, we have performed the first time-resolved EPR study of TET in dodecane-capped

Si QDs conjugated to one of three anthracene-based organic dye molecules: 9EA, 9VA, and BPEA (Figure 2). We monitor triplet formation and spin dynamics using time-resolved EPR techniques, revealing Dexter-type TET from the Si QDs to the anthracene moiety. The spatial extent of the triplet wavefunction tracks the aromatic character of the anthracene derivative, as determined by both molecular structure and the bridge to the QD. The electron spin polarization patterns observed in these conjugates are unusually fully emissive, which reflects complex exciton dynamics in the Si QDs, and cannot be explained by conventional spin-orbit or radical-pair mechanisms associated with purely organic donor-acceptor systems. This work identifies Si QDs as efficient triplet donors for tailoring spin polarization and highlights the potential of these hybrid materials for photochemical energy transformation, photon upconversion, and optoelectronic technologies.

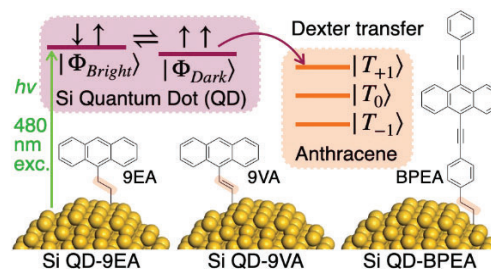


Figure 2. Light-induced Triplet Energy Transfer (TET) in hybrid Silicon Quantum Dot (QD)-Anthracene conjugates results in selective population of Anthracene triplet spin energy levels.

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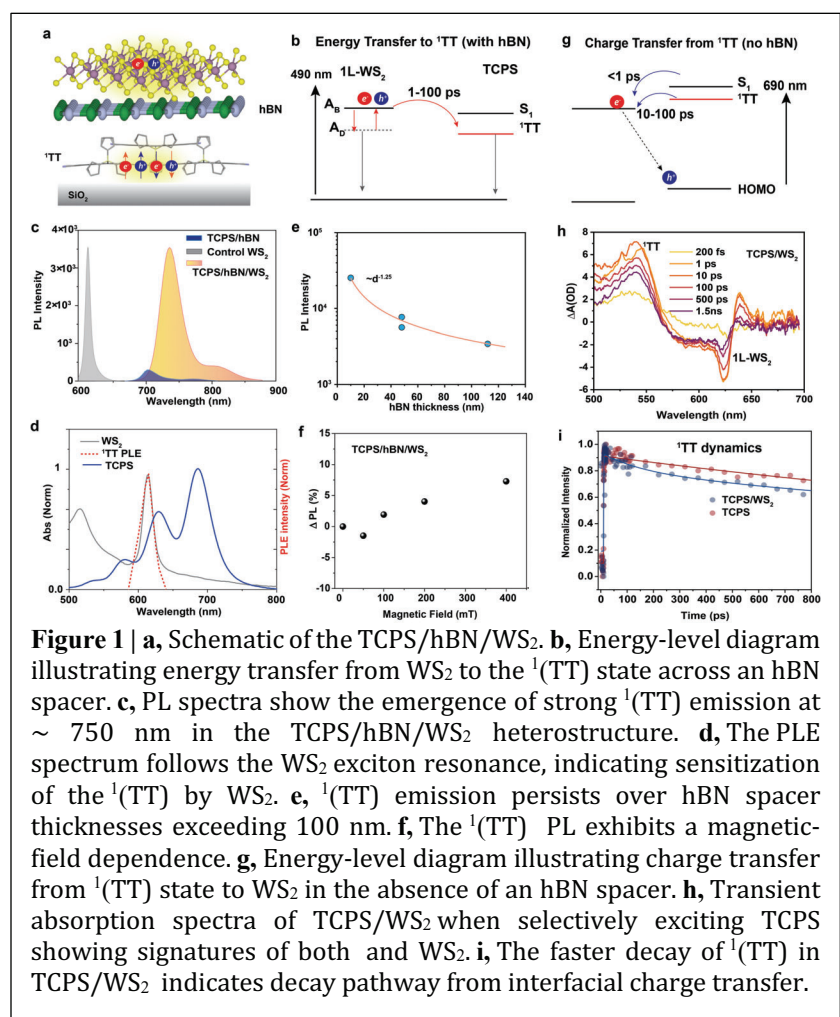
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Controlling Correlated Triplet-Pair Dynamics at Two-Dimensional van der Waals Interfaces

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Scope of the Project: The overarching goal of this project is to control the dynamics and coherence of correlated triplet-pair states through the design of molecular/two-dimensional (2D) van der Waals interfaces. We address two complementary challenges. For energy applications, the goal is to promote charge-transfer and decoherence pathways that enable efficient charge separation from triplet-pair states. For quantum information applications, the goal is instead to preserve coherence and enable optical readout of these correlated states. To achieve these objectives, the project combines singlet-fission molecules with transition metal dichalcogenides (TMDCs) and hexagonal boron nitride (hBN), using ultrafast spectroscopy and microscopy to probe charge transfer, energy transfer, spin coherence, and optical emission with high temporal and spatial resolution.



Long-Range 2D Exciton Sensitization of Triplet-Pair Emission:

We have demonstrated that monolayer WS₂ can act as an efficient and long-range sensitizer of correlated triplet-pair emission (**Figure 1a-b**). We constructed heterostructures from 6,13-bis(triisopropylsilyl)ethynyl-tetramethyl tetracene (TCPS) with long-lived bound ¹(TT). An hBN spacer with thicknesses ranging from 3 to 100 nm is inserted to suppress charge transfer. A new emission band near 750 nm emerges in WS₂/hBN/TCPS

heterostructures, and the integrated photoluminescence increases by more than two orders of magnitude compared with hBN/TCPS controls (**Figure 1c**). Spectral analysis, energetic considerations, and magnetic-field dependence support assignment of this new emission to the correlated triplet-pair $^1(\text{TT})$ state rather than to singlet emission, excimer emission, or interfacial charge-transfer excitons. Photoluminescence excitation measurements further show that this emission follows the WS_2 A-exciton resonance, demonstrating that energy absorbed in the TMDC is efficiently transferred into the molecular triplet-pair manifold (**Figure 1d**). The sensitization was found to persist over remarkably long distances. By inserting hBN spacers of controlled thickness between WS_2 and TCPS, we show that efficient triplet-pair sensitization remains observable even for separations exceeding 100 nm. The measured distance dependence follows an approximate power law of $d^{-1.25}$, which is far shallower than expected for conventional Förster-type dipole-dipole transfer (**Figure 1e**). This behavior indicates that radiative, photon-mediated energy transfer plays a major role, enabled by the exceptionally large optical dipole and strong excitonic response of monolayer WS_2 . The resulting $^1(\text{TT})$ emission exhibits a clear magnetic-field dependence (**Figure 1f**), highlighting its potential for optical readout of triplet spin states.

Charge Separation from Triplet Pairs at WS_2 Interfaces: We have also demonstrated charge separation directly from the correlated triplet-pair state $^1(\text{TT})$, by leveraging strong interfacial coupling between $^1(\text{TT})$ and TMDCs. When TCPS is selectively excited, the $^1(\text{TT})$ dynamics in the TCPS/ WS_2 heterostructure show an additional decay channel with a characteristic timescale of 10s to 100s ps, accompanied by a WS_2 bleach and signatures of long-lived charge-separated states (**Figure 1g-i**). These observations support direct electron transfer from the correlated triplet-pair manifold into WS_2 . We also clarified the kinetic relationship between singlet transfer, triplet-pair formation, and charge recombination. Ultrafast singlet transfer to WS_2 occurs on the sub-picosecond timescale.

Temperature-dependent measurements showed little change in the $^1(\text{TT})$ charge transfer dynamics, arguing against a thermally activated hopping process. In addition, transfer was found to depend strongly on the electronic character of the acceptor. In multilayer WS_2 , where the conduction-band minimum shifts and energetic driving force should in principle improve, triplet-pair transfer is nevertheless suppressed. Similarly, comparison with MoS_2 -based structures supports the conclusion that interfacial orbital overlap and acceptor-state character play a crucial role. These findings refine the design rules for future interfaces: resonance, electronic coupling, and acceptor-state wavefunction overlap are essential for extracting charge from correlated multiexciton states.

Future Plans: Future work will build on these recent results by further establishing 2D van der Waals interfaces as a platform for controlling triplet-pair dynamics, coherence, and optical spin readout. We will pursue the two pathways identified here: direct charge extraction and optical spin readout of triplet-pair states. In particular, we plan to perform optically detected magnetic resonance (ODMR) measurements on the $^1(\text{TT})$ emission in $\text{WS}_2/\text{hBN}/\text{TCPS}$ heterostructures. We also plan to explore the use of hBN surface to isolate triplet pairs. The next phase of the project will focus on systematically tuning interfacial coupling, extending this approach to additional TMDC and molecular systems, and investigating coherent optical control and nanoscale interactions of triplet-pair states.

DOE Solar Photochemistry Sponsored Publications 2023-2026

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Templating Organic Semiconductors on Silicon for Enhanced Singlet Fission Photophysics

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Project Scope

Singlet fission (SF) is a carrier multiplication process, exhibited by select organic semiconductors, in which a single photon is transformed into two triplet excitons. It has the potential to significantly increase the efficiency with which optoelectronics convert sunlight into electricity and to enable quantum technologies in which long-lived, optically addressable spin qubits are generated on demand at controlled locations, even at room temperature. Integrating SF films onto state-of-the-art semiconductors, such as Si, is important for realizing the full potential of SF in device-relevant architectures and understanding photophysics in hybrid organic/inorganic heterostructures.

In this project, we aim to elucidate the fundamental design principles required to efficiently harvest triplet excitons generated in SF films on Si. We plan to achieve this goal by interfacing SF films to Si using a novel class of interlayers based on atomically thin two-dimensional (2D) materials (**Fig. 1c**). The 2D interlayers promise to afford precise control over the photophysical, structural, interfacial, electronic, and energetic factors required to understand and enhance triplet generation in SF films, triplet diffusion in SF films to Si, and triplet transfer from SF films to Si (**Fig. 1a**).

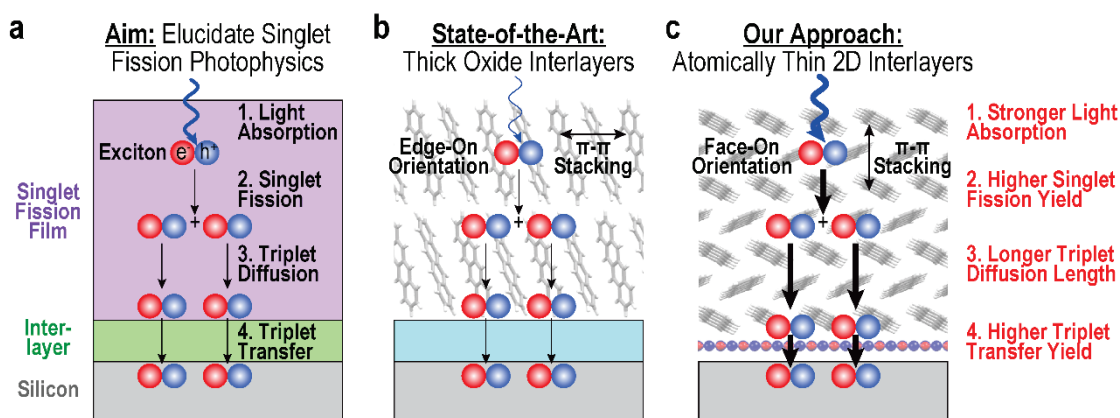


Figure 1. Schematic diagrams of SF films on Si depicting (a) basic photophysical mechanisms we aim to elucidate, (b) state-of-the-art thick oxide interlayers, where SF films have undesirable π - π stacking orientation, and (c) our atomically thin 2D interlayers, where SF films have desirable π - π stacking orientation. Arrow thicknesses in (b,c) indicate yield of processes (1)–(4) shown in (a).

First, due to π - π interactions, 2D interlayers are expected to epitaxially align SF molecules into the unconventional “face-on” orientation, where π - π stacking is perpendicular to the Si surface. Face-on molecular orientations will improve light absorption and triplet generation, diffusion, and transfer because of enhanced light-dipole and orbital overlap interactions. Second, due to their atomic thinness, lack of dangling bonds, low charge disorder, and high crystallinity, 2D interlayers are expected to be ideal tunneling barriers for triplet transfer. Third, due to their exceptional

diffusion barrier properties, 2D interlayers are expected to preserve Si surface passivation and, therefore, enhance triplet transfer. In contrast, state-of-the-art oxide interlayers used in previous work (**Fig. 1b**) yield undesirable “edge-on” orientations, where π - π stacking is parallel to the Si surface, require relatively thick films to passivate the Si surface, and are highly disordered.

Recent Progress

In the first eight months of this project, we have primarily focused on producing SF films on Si with ideal molecular orientation and packing for triplet exciton harvesting. Notable results include:

(1) Epitaxially Controlling Molecular Orientation. We have discovered that 2D interlayers based on hexagonal boron nitride (h-BN) and graphene can epitaxially align several SF chromophores, including tetracene, perylene diimide, and anthracene derivatives, in desirable face-on orientations. X-ray diffraction (XRD) and grazing-incidence wide-angle scattering (GIWAXS) indicate that for most of these molecules, >90% yield of face-on orientations is achieved on the 2D interlayers. In all cases, undesirable edge-on orientations form with ~100% yield on bare Si or oxide substrates that are not coated with 2D interlayers.

(2) Engineering Novel Polymorphs that Enhance SF Dynamics. By tuning the interlayer properties, the uncommon but highly desirable Tc II polymorph of tetracene can be achieved with high yield. Preliminary ultrafast transient absorption (TA) spectroscopy studies indicate that the SF rate is enhanced in films with large Tc II concentration. Tc II is also expected to enhance triplet transfer to Si compared to the common Tc I polymorph of tetracene.

(3) Passivating Semiconductor Surfaces with 2D Interlayers. We have demonstrated that h-BN interlayers grown directly on Ge, a group-IV semiconductor similar to Si, effectively passivate the Ge surface, preventing its oxidation in air for several weeks. In contrast, Ge surfaces that are not coated with h-BN oxidize within minutes. Moreover, we have found that h-BN interlayers transferred (as opposed to grown directly) on Si and Ge exhibit degraded passivation performance.

Future Plans

We aim to establish molecular and interfacial design rules to enhance triplet exciton dynamics in SF + Si systems. For example, we are currently utilizing ultrafast spectroscopy to investigate the effects of π - π stacking orientation, molecular packing, molecular composition, and interface composition on the SF rate, triplet lifetime, and triplet transfer yield.

Description and Application of a Quantitative Model for Voltammetry of Freely Diffusing Redox Species at Semiconductor Photoelectrodes

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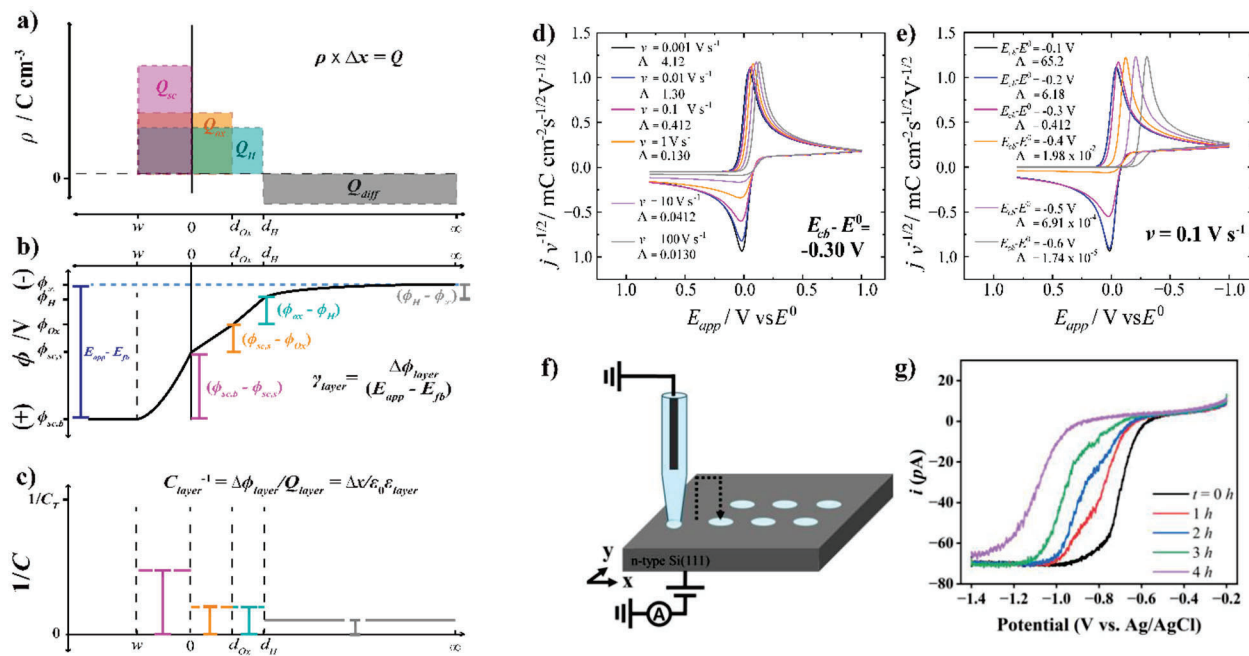


Figure 1. a-c) Graphical summary of the Gauss's Law model used to describe the potential-dependent operation of a semiconductor electrode. Briefly, (a) the injected charge is calculated across the semiconductor/electrolyte contact comprising the semiconductor space charge, surface oxide, Helmholtz, and diffuse layers. The corresponding partitioning of the applied potential is calculated based on (c) the relative dielectric properties of each layer. d) An example set of model results calculated in conjunction with a semi-integral algorithm that describes planar diffusion at a semiconductor macroelectrode. These data show the expected voltammetric data responses as a function of scan rate for a redox species with a standard potential 0.3 V more positive than the conduction band edge of an n-type semiconductor. e) An example set of calculated voltammograms measurements of redox couples with different standard potentials relative to the conduction band edge but measured at the same scan rate. f) Graphical depiction of a scanning electrochemical cell microscopy experiment. g) Set of steady-state voltammograms for aqueous $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ measured at a freshly etched n-Si substrate exposed to ambient conditions as a function of time.

This presentation will advance the premise that semiconductor voltammetry has significantly more quantitative information about semiconductor surface and bulk properties than understood in the extant literature. A quasi-analytical model for understanding and assessing voltammetric data collected with freely diffusing redox species and semiconductor electrodes operating in the dark or under illumination will be presented. This model is based on a Gauss's Law description of how an applied potential and injected charge is distributed across the semiconductor/liquid junction. A key advancement of this present work is the inclusion of both equilibrium and kinetic calculation stages that collectively describe dynamics of a

semiconductor/electrolyte interface when a *time-dependent* waveform is applied. The use of this refined model with two different current expressions that describe diffusion at macro- and microelectrodes will be presented. First, the model will be discussed in conjunction with a semi-integration algorithm that describes diffusion to a planar surface. Some basic predictions from this form of the model will be discussed to calibrate the audience on how to interpret common voltammetric data shapes as a function of parameters of interest including scan rate, dopant density, presence of a surface oxide, and the density & energy of surface states. This model also will be discussed to address poorly understood factors in semiconductor electrochemistry: a dependence of the Helmholtz layer on the interfacial electric field at a semiconductor electrode and the impact of surface states with different charges. The prevalence of these factors will be articulated by describing data features in the semiconductor voltammetry literature that have previously been undecipherable.

Second, results from the same model in conjunction with a current expression that describes radial diffusion to a point electrode will be introduced. Voltammetric data of this form will be shown from scanning electrochemical cell microscopy measurements of model semiconductor electrode materials. Time permitting, two examples will be shown that illustrate the capacity of voltammetry to be used as a spatially-dependent probe of surface properties. The first example will show how scanning electrochemical cell microscopy can be used to map the chemical properties of Si electrodes under ambient conditions. The second example will highlight the capacity of scanning electrochemical cell microscopy to probe spatially the electrical properties of two dimensional semiconductors like MoS₂.

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Hybridized Semiconductor|Molecule Platforms to Understand Charge-Separation & Charge-Transfer at Interfaces

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Our goal is to combine our hybridized interface molecular orbital (HYIMO) theory and synthetic chemistry of semiconductor surfaces to understand and modulate charge-transfer phenomena across electrode interfaces. Unfortunately, the well-known Gerischer model of photo-electrochemistry does *not* account for *beneficial* surface states that reside outside the bandgap and within the conduction band (CB) or valence band (VB), most notably near-edge-energy states at which charge-transfer reactions occur. Such beneficial surface states could modulate (i) charge-separation after photo-excitation, (ii) charge-transfer events (blocking/promoting electrons/holes), and (iii) the energies at which charges enter/exit the semiconductor to/from the contacting phase.

We hypothesize that these processes are influenced by the interaction of the installed MO's with the electronic structure of the semiconductor. There is an intellectual challenge to synergistically describe the electronic structure of both an attached molecule and the semiconductor. Such a framework will be broadly useful to researchers studying molecular interactions with electrode interfaces — from organic molecules to catalysts to polymers; from single-molecule junctions to qubits to PEC platforms; and from semiconductors to semi-metals to metal electrodes. Crossing results from our publications, we report 3 progress points and 2 points of ongoing study:

Three Main Points of Progress

(A) Re-conceptualizing Hybridization of Surface Molecular Orbitals & Semiconductor Wavefunctions. The descriptions of both solid-state electronic structure and molecular orbital theory are fundamentally grounded in combining atomic orbitals to produce delocalized bulk or molecular wavefunctions that obey the same fundamental laws of energy and symmetry. However, because their detailed descriptions emerged from different fields (solid-state physics vs molecular chemistry), their nomenclature and ‘working space’ are orthogonal. To this end, we have described the 17 common Group IV, III-V and II-VI semiconductors in the symmetry language of chemistry to canonize how and why molecular orbitals can hybridize (or not) with semiconductor band structure. The information is translatable to nanocrystal and thin-films, and will provide researchers with more precise language and rationale to describe hybridization schemes across platforms both ‘on-paper’ and in computations.

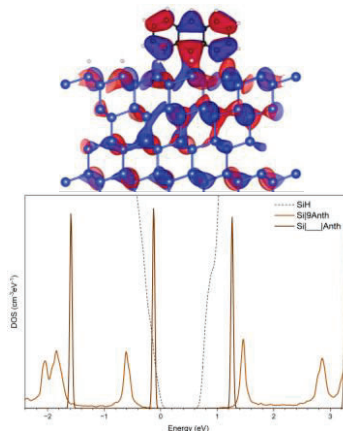


Figure 1 | (Top) Calculated phased orbitals of hybridized Si(111)–Anthracene VB|HOMO; (bottom) corresponding DOS plot.

(B) Atomistic Structural & Spectroscopic Characterization of Functionalized Surfaces. We have been queried for many years regarding the exact chemical structure and attachment geometry of molecules attached to silicon surfaces. We thus visualized the structure of an Si(111)–Anthracene motif at the atomic level using STM and surface DOS (STS). The STM proved the

expected upright binding geometry, and the STS spectroscopy proved hybridization of the anthracene molecular orbitals with the silicon electronic substructure: the molecular anthracene band gap decreased from ~ 3.3 eV to ~ 2.5 eV due to hybridization. The results were corroborated by ensemble-level measurements of UPS, LEIPS and EIS.

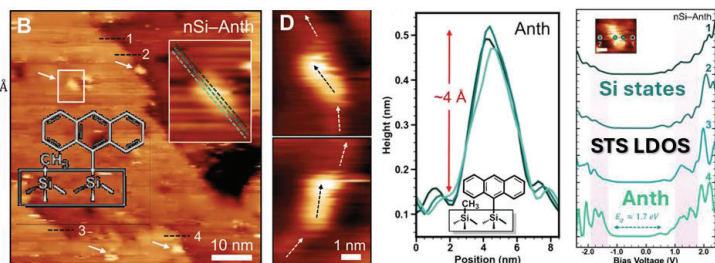


Figure 2 | STM/STS characterization of Si(111)-Anthracene.

(C) Modulation of Photo-electrochemical & Charge-Transfer Operating Parameters. We demonstrated that installing near-band-edge states using Si-Tetracene (*cf* anthracene) moved the ‘molecular acceptor’ states closer to the CB edge and improved photovoltage in both vacuum surface photovoltage and PEC liquid contacts. How? (*see Future Study*). Our finding was paradoxical because although Tetracene did install surface MO’s closer to the band-edge, its LUMO proved *unhybridized* (unlike hybridized anthracene) with the Si CB wavefunction.

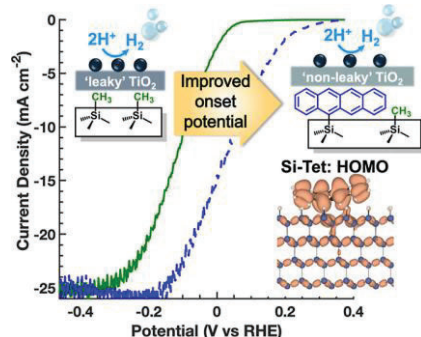


Figure 3 | Si-Acene hybridization Scheme & photovoltage results.

Ongoing work is poised to untangle the effects of orbital energy and symmetry on charge-transfer parameters. We also demonstrated control over the interfacial potential drop using molecular interface chemistry. A model system comprised of methyl, 1- vs 2-point attachment anthracene, & bi-anthracene provided atomistic understanding of potential drop. For ‘extreme potential’ redox couples outside the band-gap, electronic effects of surface functionalization and hybridization proved negligible (band-bending dominates). But for redox equilibrations *within* the band gap, surface hybridization provides a tunable handle on photovoltage. How? (*see Future study*).

Two Main Points of Ongoing Study

(A) Direct Electron Transfer Rate Determinations in Hybridized Systems. We are transitioning from aggregate photovoltage measurements (a dynamic $\sim K_{eq}$ comprised of individual electron/hole k_{ET} ’s) to measuring elementary electron transfer kinetics. We will better understand the role of (non)hybridized surface orbitals on promoting charge-separation and selectively enhancing (or blocking) electron vs hole. Using the experimental handles of semiconductor identity, crystal facet and MO/spin hybridization, we will demonstrate how to rationally *promote desired* charge-transfer reactions and *suppress undesired* charge-transfer. We will employ SECCM to gain nanoscale resolution on surface functionalization effects: What are the electrochemical effects of molecular functionalizations on terraces vs step-edges vs etch-pits?

(B) Develop a Usable Computational Toolkit for the Field to Evaluate MO|Wavefunction Hybridization. Using a DFT/VASP approach, we are developing a method to not only determine and visualize molecule|semiconductor hybridization in the context of HYIMO, but also the more challenging goal of mapping hybridized MO’s into the k space diagram of the semiconductor electronic structure. This effort intends to answer the question: At which high-symmetry points in k space are the MO’s located? How should we best select orbitals and molecules to achieve hybridization? In concert with experimental data, hybridization with which k points provide the best route to tunable experimental parameters like k_{ET} and charge-separation efficiencies?

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Photovoltage Generation at Junctions in Heterogeneous Solar Fuel Photocatalysts and Photoelectrodes

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The photovoltage defines the energy conversion efficiency of heterogeneous solar fuel photocatalysts and photoelectrodes. It represents the maximum Gibbs free energy (G) that can be extracted from such devices under illumination. However, the terminal photovoltage of solar fuel semiconductor electrodes is not generally accessible through standard three-electrode measurements because charge transfer reactions at solar fuel electrodes have large kinetic overpotentials. This makes it difficult to assess the electrochemical potential of the minority charge carriers and the true energy conversion properties of such electrodes. Here we show that these parameters can be observed in a semi-contactless way with a Vibrating Kelvin Probe (VKP). This is shown for p-GaP hydrogen photocathodes and for n-WO₃, and n-BiVO₄-oxygen evolution photoanodes. We find that the terminal photovoltage of these systems depends not only on the light wavelength, the light intensity and on the electrochemical potential of the electrolyte, but also on the presence of cocatalysts, and the kinetics of the redox couple. The VKP technique also detects sub-band gap defects in transition metal oxynitrides ABO_xN_y (A=Sr, Ba, La, B = Ti, Nb, Ta). These materials are promising semiconductors for the solar water splitting reaction, but their photovoltage is limited by recombination defects. It is shown that such defects can be minimized by synthesizing the oxynitrides from the corresponding metal oxides in *dilute* ammonia gas.

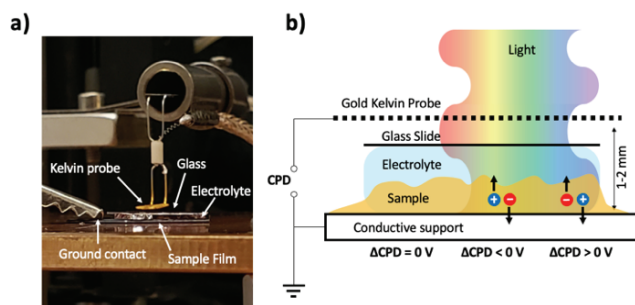


Figure. Vibrating Kelvin Probe Surface Photovoltage (VKP-SPV) Spectroscopy in liquids. a) Photo. b) Schematic of the measurement configuration. Illumination occurs through the 60% semi-transparent KP, placed 1-2 mm above the sample, and through the electrolyte, enclosed by a microscopy glass cover slide. The surface photovoltage signal $SPV = CPD(\text{light}) -$

$CPD(\text{dark})$ is given by the Contact Potential Difference (CPD) change under illumination.

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Heteroleptic Copper(I) Photosensitizers with Long Excited-State Lifetimes

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Earth-abundant photosensitizers that absorb visible light, separate charge, and initiate electron or energy-transfer reactions are critical for the continued development of schemes to capture, store, and convert solar energy. A major challenge with most classes of earth-abundant photosensitizers is achieving sufficiently long charge-separated excited-state lifetimes to allow efficient bimolecular reactivity after excitation. This talk describes our recent progress on heteroleptic copper(I) complexes that exhibit charge-transfer excited states, highlighting complementary strategies to extend their excited-state lifetimes and improve their photocatalytic reactivity.

Sterically driven strategies, in which the physical bulk of supporting ligands restricts deleterious excited-state distortion events, are commonly used to extend lifetimes in copper(I) chromophores. The first part of this talk (Figure 1) describes our efforts to investigate ligand steric effects in heteroleptic copper(I) charge-transfer chromophores. The most in-depth insight has emerged from studies on Cu(β -diketiminate)(isocyanide) complexes. We have established a correlation between percent buried volume ($\%V_{\text{bur}}$) and excited-state lifetime, with the steric profile of the β -diketiminate ligand having a larger

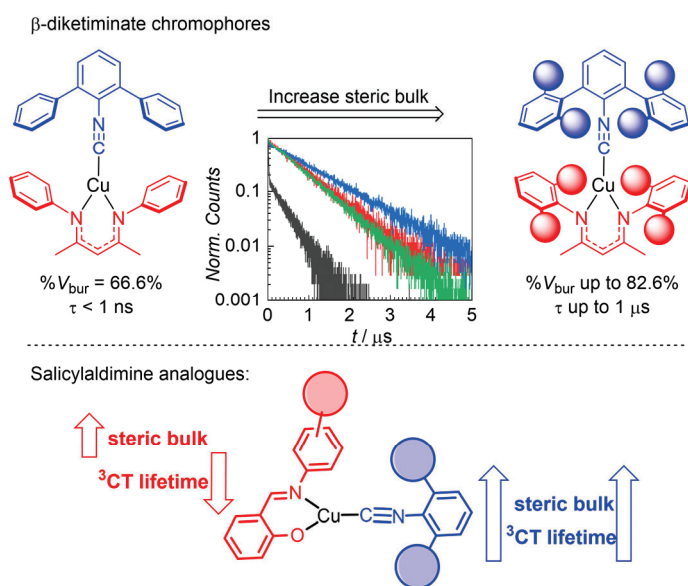


Figure 1. Sterically driven increases in excited-state lifetime.

heteroleptic copper(I) complexes. In this approach, the isocyanide ligand includes a polycyclic aromatic substituent, e.g., pyrenyl, phenanthrenyl, or naphthyl, that has a localized $^3(\pi \rightarrow \pi^*)$ excited state. If this localized state is energetically proximate to the native charge-transfer (^3CT)

diketiminato ligand having a larger influence on these two correlated parameters. In compounds with minimal steric bulk excited-state lifetimes in the low-nanosecond range are observed, but in compounds with encumbered β -diketiminate and *m*-terphenyl isocyanide ligands, lifetimes up to $1 \mu\text{s}$ are obtainable. Ligand steric effects are also effective in a complementary class of Cu(salicylaldimine)(isocyanide) complexes, where in this case the steric profile of the isocyanide is the main driver for extending the excited-state lifetime.

The triplet reservoir effect represents a complementary strategy for achieving long excited-state lifetimes in the above-mentioned class of

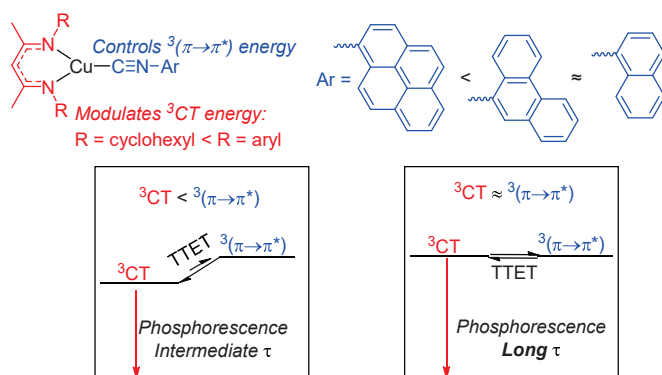


Figure 2. Reversible triplet-triplet energy transfer to increase charge-transfer excited-state lifetimes.

of *N*-substituent on the β -diketiminate ligand. In situations where there is a slight mismatch in the energies of the two excited states, moderate excited-state lifetimes (ca. 250–300 ns) are observed, but in cases where the ${}^3\text{CT}$ and ${}^3(\pi \rightarrow \pi^*)$ states are isoenergetic, an order-of-magnitude increase is observed, with lifetimes in the range of 1.9–3.9 μs .

The last part of this talk describes four-coordinate heteroleptic copper(I) β -diketiminate photosensitizers, replacing the monodentate isocyanide capping ligands with bidentate diisocyanide ligands (Figure 3). Compared to three-coordinate analogues, the four-coordinate compounds have smaller HOMO–LUMO gaps, and their excited-state lifetimes are responsive to the steric profile of the diisocyanide, although increasing the bulk of the β -diketiminate ligand leads to the formation of diisocyanide-bridged dicopper(I) complexes. Most significantly, the four-coordinate complexes outperform a related three-coordinate analogue in photocatalytic redox transformations of benzophenone derivatives. On account of being a slightly stronger photoreductant and having greater photostability due to the bis-chelate structure, the four-coordinate complex results in higher yields of product in visible-light-promoted photohydrogenation reactions.

state of the copper(I) chromophore, reversible triplet-triplet energy transfer (TTET) can occur, lengthening the amount of time the compound resides in the excited state (Figure 2). Our work in this area has clearly established the energetic criteria necessary for this reversible TTET to operate. The energy of the localized ${}^3(\pi \rightarrow \pi^*)$ state is dictated by the choice of polycyclic aromatic triplet acceptor (1-pyrenyl < 9-phenanthrenyl $\approx$ 1-naphthyl), and the energy of the ${}^3\text{CT}$ state can be independently modulated by the choice

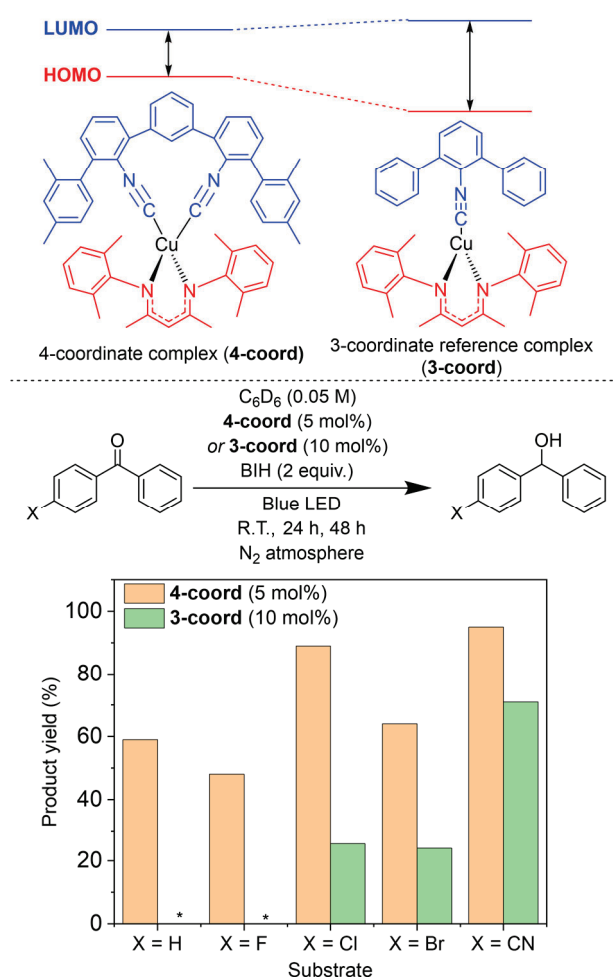


Figure 3. Improved photocatalysis with four-coordinate photosensitizers.

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Photocatalytic H₂ Production: Investigation of New First-Row Transition Metal Complexes

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Dirhodium(II,II) complexes of the type $cis\text{-}[\text{Rh}_2(\text{form})_2(\text{bncn})_2]^{2+}$ (form = formamidinate, bncn = benzo[*c*]cinnoline; Figure 1a, R = -H) have been shown to serve as single-molecule photocatalysts for H₂ production with red light. The Rh₂/form → bncn triplet metal/ligand-to-ligand charge transfer (³ML-LCT) of these complexes generates the corresponding singly-reduced complex, $cis\text{-}[\text{Rh}_2(\text{form})_2(\text{bncn})_2]^+$, where the electron is localized on one of the bncn ligands, when irradiated in the presence of a sacrificial electron donor. The chemical or electrochemical reduction of the complex by two electrons to generate $cis\text{-Rh}_2(\text{form})_2(\text{bncn})_2$, results in the production of H₂ in the presence of acid. In the photocatalytic cycle, $cis\text{-}[\text{Rh}_2(\text{form})_2(\text{bncn})_2]^+$ is able to absorb a second photon and oxidize the sacrificial donor, generating the $cis\text{-Rh}_2(\text{form})_2(\text{bncn})_2$ reactive species.

In order to help elucidate the step in the catalytic cycle that limit reactivity, a series of complexes with electron-donating and -withdrawing substituents on the *para* positions of the *N,N*-diphenylformamidinate (DPhF) ligands, $cis\text{-}[\text{Rh}_2(p\text{-R-DPhF})_2(\text{bncn})_2]^{2+}$ (R = -OCH₃, -CH₃, -H, -F, -Cl, -CF₃; Figure 1a). Although the ³ML-LCT lifetime and driving force of the generation of the singly-reduced complex increases across the series from -OCH₃ to -CF₃, the H₂ production is more efficient for the parent complex, with R = -H. It was found that the lifetime and excited state character of the singly-reduced $cis\text{-}[\text{Rh}_2(\text{form})_2(\text{bncn})_2]^+$ complex plays a critical role in the reactivity. Additional mechanistic experiments using spectroelectrochemistry experiments with mid-IR detection conducted in collaboration with David Grills (Brookhaven) are consistent with H-H bond formation proceeding through one of the formamidinate ligands, as previously calculated.

Electrocatalytic measurements, theoretical calculations, as well as experimental data using complexes with blocked axial ligands point to a mechanism for H₂ formation that is localized on the bncn ligand, instead of proceeding through a Rh-H hydride intermediate. This is an important finding because it may be possible to replace the precious rhodium with abundant, first-row transition metals. Two Cu₂(I,I) complexes with bncn ligands have been synthesized and their photophysical properties investigated (Figure 1b). $[\text{Cu}_2(\mu\text{-bncn})_2(\kappa\text{-bncn})_2]^{2+}$ exhibits a Cu(I) → bncn metal-to-ligand charge transfer (MLCT) absorption at 420 nm that tails to ~500 nm.

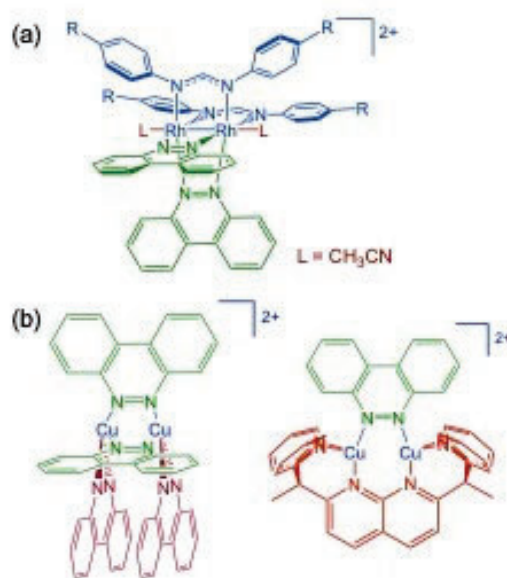


Figure 1. (a) Structure of $cis\text{-}[\text{Rh}_2(p\text{-R-DPhF})_2(\text{bncn})_2]^{2+}$ series and (b) Cu₂(I,I) complexes of bncn.

Excitation of $[\text{Cu}_2(\mu\text{-bncn})_2(\kappa\text{-bncn})_2]^{2+}$ at 400 nm (fwhm = 85 fs) results in the population of the $^3\text{MLCT}$ excited state with lifetime, τ , of 6 ps. The short excited state lifetime is attributed to the fluxional nature of the coordination sphere in the complex.

The coordination of bncn to the $\text{Rh}_2(\text{II,II})$ core shifts the ligand's reduction potential from $-1.9\text{ V vs Fc}^{+/0}$ in the free ligand to $-0.94\text{ V vs Fc}^{+/0}$ in $\text{cis-}[\text{Rh}_2(\text{DPhF})_2(\text{bncn})_2]^{2+}$ in DMF (0.1 M TBAPF_6). It was hypothesized that the more negative bncn reduction potential in the free ligand results in decomposition in the presence of acid, such that electrocatalytic H_2 production is not observed. In order to lower the

reduction potential of a bncn-like ligand, we sought to prepare mononuclear first-row transition metal complexes based to the 1,5,6,10-tetraazaphenanthrene (taph) ligand, two of which are shown in Figure 2. The $\text{Fe}(\text{II})$, $\text{Ru}(\text{II})$, $\text{Cu}(\text{I})$, and $\text{Co}(\text{III})$ metal centers were chosen in an attempt to minimize the presence of low-lying ligand-field states that are known to deactivate $^3\text{MLCT}$ excited states. To date, we have prepared the complexes shown in Figure 2 and began investigating their electrochemistry in the presence of acids and their excited state properties upon excitation with visible light. These results will be presented, along with future plans.

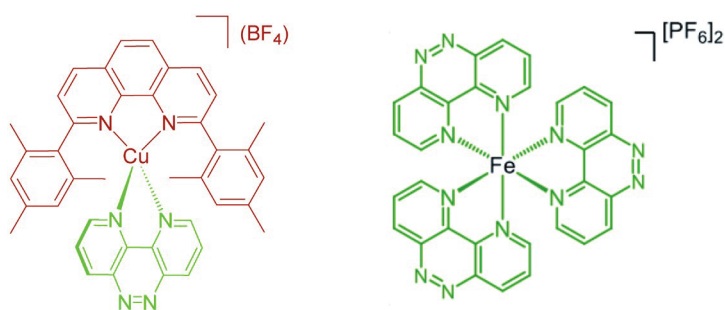


Figure 2. Examples of $\text{Cu}(\text{I})$ and $\text{Fe}(\text{II})$ complexes with taph ligand.

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Striking while the Fe is hot: Spin-state and reorganization energy considerations and anti-Kasha reactivity in the photophysics and photochemistry of iron(II) complexes

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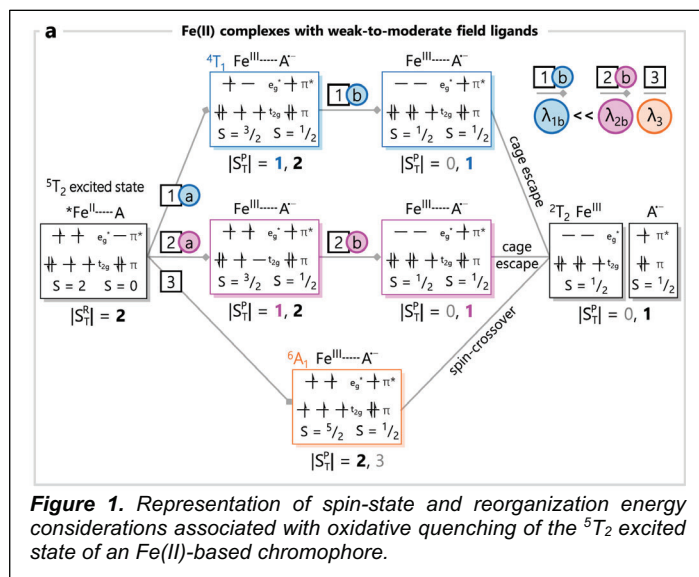
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Our research program focuses on the development of chromophores based on first-row transition metal ions for use as light harvesting components in light-to-chemical energy conversion. The underlying motivation stems from the notion that light capture represents the most material-intensive part of the process coupled with a realization of the limited potential of traditional second- and third-row chromophores to achieve scalable solutions due to their elemental scarcity. A key scientific issue impeding the incorporation of most first-row metal complexes into light conversion strategies is the rapid deactivation of charge-transfer states to lower-lying, metal-centered ligand-field states. This behavior stands in stark contrast to what is observed for their second- and third-row congeners and renders their first-row analogs largely ineffectual for virtually any application reliant on the creation of light-induced chemical potential (at least when viewed through the lens of charge transfer-based reactivity). This issue, which has its origins in the so-called primogenic effect and basic consequences of quantum mechanics,¹ represents a fundamental research challenge that must be addressed if one is to create new paradigms based on earth-abundant transition elements.

Over the past several years, we have focused primarily on first-row metals possessing a d^6 configuration – specifically Fe(II) and Co(III) – to understand reactivity arising from metal-centered, ligand-field excited states. Expanding on our report of oxidative quenching of the 5T_2 high-spin excited state of $[\text{Fe}(\text{tren}(\text{py})_3)]^{2+}$,² we attempted analogous studies on a series of polypyridyl complexes whose excited-state properties should have led to an enhancement of the reactivity exhibited by $[\text{Fe}(\text{tren}(\text{py})_3)]^{2+}$.

Instead, none of these complexes displayed excited-state reactivity of any kind with suitable quenchers. It was determined that previous observations, while based on accurate and reproducible data, was actually due to a sluggish thermal reaction between the quinoidal quenchers and the tertiary amine associated with the $\text{tren}(\text{py})_3$ ligand (the tertiary amine does not contribute to the absorption spectrum of the compound, so this side reaction went undetected in our previous study).



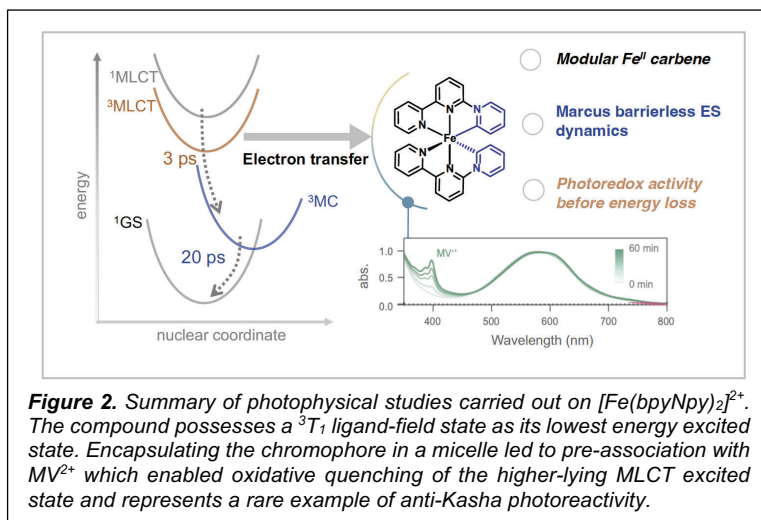
The inability of the 5T_2 state of the Fe(II) complexes to engage in electron

transfer despite having sufficient driving force and lifetime to effect bimolecular chemistry stands in stark contrast to the well documented photoredox activity arising from the 3T_1 ligand-field excited state of analogous Co(III) complexes. Our analysis of this situation allowed us to identify the likely origins of this difference in excited-state reactivity, namely that the combination of large reorganization energies coupled with an absence of low-energy, spin-allowed pathways conspire to suppress the oxidation of the 5T_2 excited state of Fe(II) polypyridyls on a time scale that is kinetically competitive with excited-state relaxation back to the 1A_1 ground state (Figure 1). A similar analysis for Co(III)-based excited-state chemistry revealed that (a) the 3T_1 excited state of Co(III) is well positioned to act as a photooxidant due to the presence of easily accessible spin-allowed pathways and a substantial reduction in reorganization energy, consistent with experimental results, and (b) ligands that can stabilize low-spin Co(II) as the photoproduct of reductive quenching of the 3T_1 excited state of Co(III) should result in highly effective photocatalysts.

The limited prospects for strictly polypyridyl complexes of Fe(II) to act as a conduit for energy conversion strategies compelled us to develop new ligand platforms that could stabilize the 3T_1 state as the lowest-energy ligand-field excited state of an Fe(II)-based chromophore.

[Fe(bpyNpy) $_2$] $^{2+}$ (where bpyNpy is 6-(N-pyridinium)-2,2'-bipyridine) achieves this goal, wherein the combination of a N_4C_2 coordination sphere and a positive charge of the nitrogen of the pyridinium moiety leads to a strongly absorbing chromophore possessing a 3T_1 state as its lowest-energy excited state (Figure 2). The compound has been characterized by steady-state and time-resolved spectroscopies that were used to establish the initially formed $^1,^3MLCT$ state(s) converts to the $S = 1$ ligand-field manifold with

a time constant of ~ 3 ps. This lowest-energy ligand-field excited state then undergoes barrierless relaxation back to the ground state with a temperature-independent time constant of ~ 20 ps. Given the detailed energetic landscape that we were able to construct, we carried out a series of studies wherein the Fe(II) chromophore was encapsulated in a micelle that promoted pre-association between the micellular assembly and the methylviologen dication (MV^{2+}) to circumvent limitations imposed by diffusion. Formation of MV^+ subsequent to MLCT excitation of [Fe(bpyNpy) $_2$] $^{2+}$, coupled with the endothermicity associated with oxidative quenching of the 3T_1 , leads to the conclusion that electron transfer reactivity from a higher lying, non-thermalized excited state of the Fe(II) complex (specifically, the 3MLCT state) has been realized in this system.



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Use of carbonyl as an infrared reporter for probing the nature of charges in oligo(*p*-phenylene)s

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Although a record-high power conversion efficiency of ~21% has been achieved,¹ there is still a long way to go before all-polymer solar cells can be fully commercialized. The bottleneck, in part, stems from a lack of understanding and control over the movement of localized electrons in donor-acceptor-type conjugated polymers.

Based on our prior work of using nitrile functional groups as infrared reporters for probing electron delocalization in ladder-type oligo(*p*-phenylene)s,² we hypothesize that the carbonyl group could be a new infrared reporter for the same purpose, with the advantage that it is more commonly found in the types of polymers that are used in solar cells.³ In this poster presentation, we report the synthesis of ladder-type, carbonyl-functionalized oligo(*p*-phenylene)s, theoretical calculations by density functional theory,⁴ and preliminary results of electron delocalization in these oligomers by nanosecond time-resolved infrared spectroscopy coupled with pulse radiolysis. We thank the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, for financial support under Award #DE-SC0023329.

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Enabling Solar Water Oxidation by BiVO₄ in Strongly Acidic Solutions

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The overall objective of our project is to understand and control the factors that affect the photoelectrochemical properties of multicomponent and multilayer oxide photoelectrodes for use in photoelectrochemical cells to produce fuels and chemicals. Our motivation to study multicomponent photoelectrodes is that the structural and compositional diversity of multicomponent photoelectrodes (e.g., ternary or quaternary oxide photoelectrodes) increases the chance of designing a photoelectrode with desired band positions, charge transport properties, and solution compatibility. Our motivation to study multi-layer photoelectrodes is that even when a promising photoelectrode is developed, it needs to be optimally interfaced with appropriate catalyst, buffer, and protection layers to enable the most effective and stable utilization of surface-reaching charge carriers for desired redox reactions.

In this presentation, we discuss the use of Nb₂O₅ as a protection layer, which enables an n-type BiVO₄ photoanode to operate for photoelectrochemical water oxidation in strongly acidic solution. The oxygen evolution reaction (OER) is paired with various electrochemical and photoelectrochemical reduction reactions for fuel and chemical production. As there is strong interest in performing many of these reduction reactions in strongly acidic solutions to increase reaction rates, efficiencies, or selectivities, there is also strong interest in enabling efficient and stable OER in strongly acidic solutions.

We studied Nb₂O₅ as a protection layer on a BiVO₄ photoanode in 0.1 M HNO₃ (pH 1) for photoelectrochemical OER (POER). While Nb₂O₅ has rarely been used as a protection layer for photoelectrodes in the past, our results show its excellent capability to suppress both the chemical and photoelectrochemical dissolution of BiVO₄ at pH 1 (**Fig. 1**). After stabilizing BiVO₄ with Nb₂O₅, we added Co²⁺ ions to the electrolyte as an OER catalyst to enhance POER. We found that Co²⁺(aq) acts as a homogeneous OER catalyst without depositing as a CoO_x solid on Nb₂O₅, owing to the inertness of the Nb₂O₅ surface toward Co adsorption. This study, demonstrating stable POER of BiVO₄ in 0.1 M HNO₃ using a Nb₂O₅ protection layer and Co²⁺(aq) as a homogeneous OER catalyst, highlights promising opportunities for acidic POER and OER.

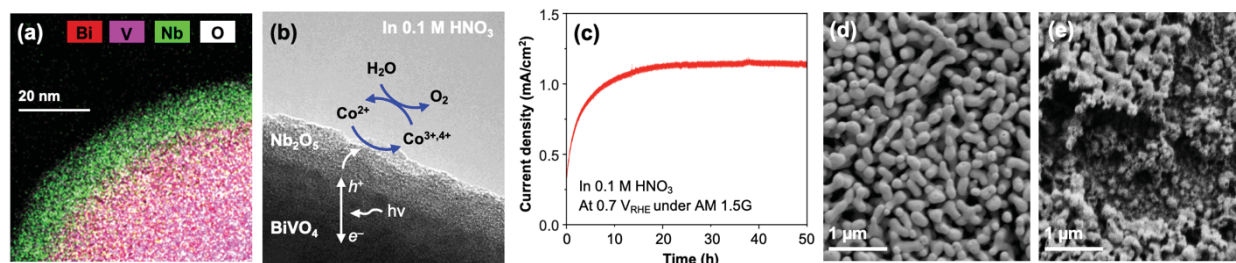


Fig. 1. (a) HAADF-STEM image with corresponding EDS element mapping, (b) a schematic of POER by BiVO₄/Nb₂O₅ and Co²⁺(aq), (c) *J*-*t* plot of BiVO₄/Nb₂O₅ with Co²⁺(aq) for POER, and SEM images of (d) BiVO₄/Nb₂O₅ and (e) BiVO₄ after the *J*-*t* measurements.

Oxynitride photonic glass photoanodes via urea-based chemical transport nitridation

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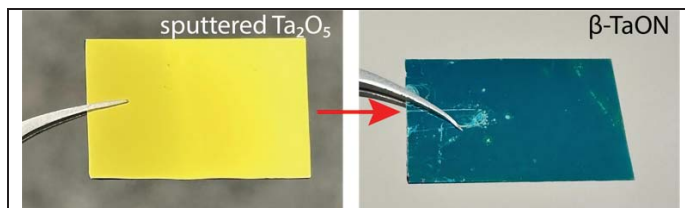


Figure 1 – The color change indicates the transformation of sputtered Ta_2O_5 (left) into the photoactive β -phase of TaON, as confirmed by x-ray diffraction. The process was carried out in a sealed furnace tube via urea decomposition in N_2 .

Metal oxide semiconductors can be modified by nitridation reactions to form oxynitride compounds to improve their utility in solar fuels reactions. The common rationale for this is that the integration of nitrogen into the compound moves the valence band maximum to more negative potentials than in the oxide while preserving the position of the conduction band minimum. As a result, the band gap is reduced in the compound. In some cases, the resulting oxynitride

compound has favorable band edge positions for both half reactions of solar-driven water splitting. A major loss mechanism in these materials is the recombination of photogenerated carriers due to poor minority carrier diffusion/lifetime characteristics of the material. Electrons and holes are generated too far away from the interface to be collected before recombining. A strategy to overcome this is to use thin film materials in coordination with a light-trapping nanostructure to improve carrier collection while maintaining high absorbance.

Here, we describe our recent work towards improving photoelectrochemical yields in oxynitride-based photoanodes. We have utilized a photonic glass electrode structure which facilitates tailorable light trapping in a disordered, scalable photoelectrode nanostructure. Our work to date has used wide band gap ZnO ^[1,2] and TiO_2 ^[3,4] to demonstrate these improvements under UV illumination. We will present our efforts to translate these advances to two visible light-absorbing oxynitrides – TaON and CaTaO_2N – which have favorable band gaps and band edges for solar-driven water splitting. We will show the results of a urea-based chemical transport method for the nitridation of the relevant metals and oxides via in situ ammonia generation. We will also present preliminary results for the water oxidation activity of thin film photoanodes based on this synthesis. Finally, we will describe the design and integration of photonic glass photoelectrodes to enhance the photoactivity of these materials under visible light.

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Modular Nanoscale and Biomimetic Assemblies for Photocatalytic Hydrogen Generation

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The overarching goal of this project is to develop and understand photochemical systems for hydrogen (H_2) production from water using nanocrystalline quantum dots (QDs), which absorb visible light, catalyze H_2 production, and/or transfer electrons to bioinspired cocatalysts. A key objective of this work is to develop structure-function relationships governing system activity.

Effect of CdSe Surface Structure on H_2 Production. We compared the photocatalytic H_2 evolution activity of CdSe QDs synthesized with tetradecylphosphonic acid (TDPA) or with oleic acid (OA) surface ligands, subsequently exchanged for mercaptopropionic acid (MPA). MPA-CdSe QDs generated from TDPA-capped QDs exhibit 5-fold higher activity in comparison to QDs that were originally OA-capped. Interestingly, the relative difference in activity was correlated with cadmium-to-selenium ratios in the QD: TDPA-CdSe QDs are selenium-rich (Cd:Se = 0.87:1), while OA-CdSe QDs are cadmium-rich (Cd:Se = 1.40:1). To test whether stoichiometry has a significant effect on activity, OA-CdSe QDs were synthesized with excess selenium (OA Se), leading to stoichiometric CdSe QDs. It was observed that the stoichiometric QDs generate similar amounts of H_2 to those generated from TDPA-CdSe QDs (Fig. 1). These results support the hypothesis that exposed selenium sites on the surface of CdSe QDs improves their catalytic activity, providing insight into how surface structure relates to photocatalytic activity.

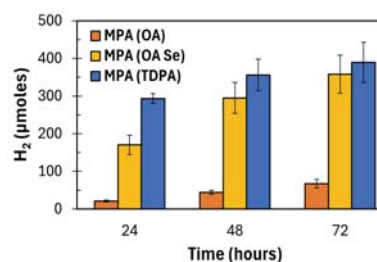


Figure 1. H_2 produced from MPA-capped CdSe QDs synthesized with TDPA, OA or excess Se.

Impact of CdSe Surface Structure on Hole Transfer. We evaluated the effect of the ligands on polyoxovanadate- (POV-) alkoxides on their hole transfer activity with CdSe QDs. Looking at the effect of alkoxide chain length, we found that $[V_6O_7(OCH_2CH_3)_{12}]^{1-}$ displays lower efficiency for hole transfer (HT) in comparison to its methoxide congener. We further demonstrated that capping a POV-alkoxide with a ligand displaying a pyridine moiety improved HT to the nanocrystal due to a stronger QD-cluster association arising from the pyridine derivative.

Pairing Biomolecular Cocatalysts with QDs. Cobalt-porphyrin mini-enzymes such as the cobalt porphyrin peptide CoMP11-Ac (Fig. 2) display excellent activity for catalyzing H_2 evolution from

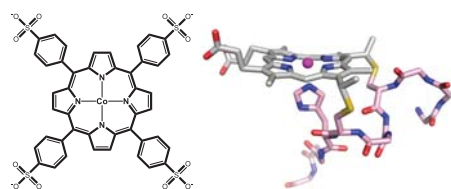


Figure 2. Cocatalysts CoTPPS (left), CoMP11-Ac (right)

water through a wide range of conditions. We are pairing CoMP11-Ac with CdSe QDs and seeing remarkable enhancement of system activity. Notably, CoMP11-Ac enhances activity to a greater extent than the synthetic cobalt porphyrin CoTPPS (Fig. 2), which is attributed to the higher activity of CoMP11-Ac, hypothesized to result from its stable axial ligation.

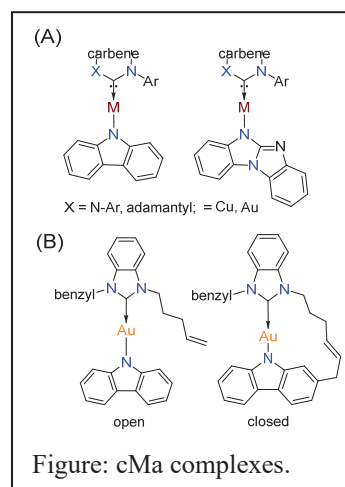
Structural and Electronic Effects on Spin Orbit Coupling and Intersystem Crossing in Group 11 (carbene)metal(amide) sensitizers

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We will discuss work developing sensitizers based on a carbene-metal-amide (cMa, M = Cu(I) and Au(I)) architecture. The solution-phase complexes show long lifetimes ($\tau \sim 0.5\text{--}250\mu\text{s}$) and high reducing potential for the excited states. Together, this makes them potent diffusive sensitizers in homogeneous solution.

We are exploring the role of spin-orbit coupling (SOC) in facilitating intersystem crossing (ISC). The precise contribution of SOC to ISC, and its interplay with TADF, the principal decay mechanism, is not well understood. Here, we have focused on building a way to disentangle SOC and excited state energetics to better understand the ISC and the TADF rates. These are the principal parameters that control the excited state decay rate. Much of this work is tied to cMa complexes that have a minimum energy structure with the carbene and amide ligands coplanar, but with a small barrier to ligand rotation of 3-5 kcal/mol (Figure A). We have also prepared complexes where the carbene and amide ligands are tied together with a covalent strap, fixing their dihedral angles close to 0° (Figure B) Using a combination of transient absorption spectroscopy (TA) and temperature-dependent time correlated single photon counting (TCSPC) we have shown that singlet-to-triplet ISC rates in these systems span a wide range, *i.e.* $(3\text{--}200) \times 10^9 \text{ s}^{-1}$, depending on the metal ion and ligand choices. ISC rates in solution are roughly 10x faster than for doped polystyrene films. Using a combination of Arrhenius and Marcus fitting of the temperature-dependent TCSPC measurements gives us the spin-orbit coupling constants (SOCCs) and reorganization energies (λ) for the exergonic and endergonic ISC processes (ISC^{exe} and ISC^{end} , respectively). We find that the ISC^{exe} rate is directly proportional to SOCC^2 , leading to a 10-fold difference in ISC rate between isostructural Cu- and Au-based cMa complexes ($\tau_{\text{ISC}} = 350, 39 \text{ ps}$, and $\text{SOCC} = 2.1, 6.7 \text{ cm}^{-1}$ for Cu and Au, respectively). The λ values are the same for Cu and Au, but vary significantly with the carbene and amide ligand choices, giving maximum values for SOCC and λ for complexes with the CAAC carbene (Figure A: X = adamantyl).



In the polystyrene films, the carbene and amide ligands are held close to coplanar throughout the excitation and ISC process. Penfold has investigated the SOC process theoretically as function of the interligand dihedral angle and finds a maximum at close to 45° . To investigate this, we have compared open and closed forms of a cMa (Figure B). Here we see that the closed form, which restricts the dihedral angle close to 0° gives an ISC^{exe} rate of $240 \times 10^9 \text{ s}^{-1}$, while the open form gives a rate of $22 \times 10^9 \text{ s}^{-1}$. The ISC^{exe} rate is too fast to study by the TCSPC methods used above to determine SOCC and λ , but the TA and theoretical calculations support large increases in SOC and ISC when ligands are locked in a fixed, near coplanar orientation.

Spin-Vibronic Coherence Emerges in the Intermediate Spin--Orbit Coupling Regime

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Understanding and controlling the interplay between intersystem crossing, internal conversion, and vibrational motion is crucial for engineering photochemical reactivity in transition-metal complexes. In this work, we investigate spin-vibronic coherence driven by the ground state vibrational mode in a series of five structurally tuned, double-bridged Pt(II) dimers using nonadiabatic dynamics incorporating both spin-orbit coupling and derivative nonadiabatic couplings. Across these systems, the variations in cyclometalating and bridging ligands modulate Pt-Pt distances, excited-state electronic structure, and spin-orbit coupling strengths that enable systematic probing of coherence mechanisms. We show that ligand-controlled spin-orbit coupling dictates early-time intersystem crossing behavior. Fourier analysis of time-dependent populations reveals that spin-vibronic coherence arises when the Pt-Pt stretching frequency becomes near-resonant with the spin-orbit coupling between singlet and triplet states. If spin-orbit coupling is too weak, vibrational motion dominates; if spin-orbit coupling is too strong, intersystem crossing and vibration become decoupled. These results establish a clear mechanistic picture and provide molecular design guidelines for modulating spin-vibronic coherence in photoluminescent and photocatalytic Pt(II) systems.

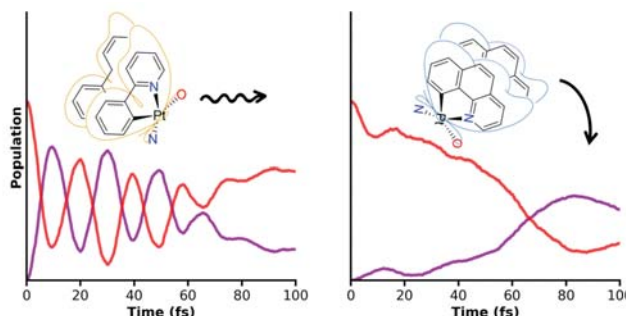


Figure 1. The identity of the cyclometalating ligand plays an important role in controlling the singlet--triplet spin--orbit coupling strength, which in turn governs early-time intersystem crossing kinetics and the emergence of coherent singlet-triplet population oscillations.

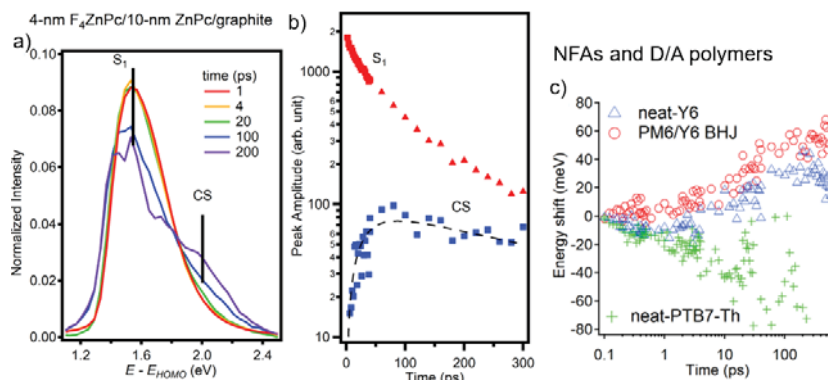
Spontaneous Charge Separation in Non-fullerene Acceptor Materials without an Interfacial Energy Offset

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Our project aims to understand why organic bulk heterojunctions (BHJs) consist of non-fullerene acceptors (NFA) can enable efficient charge separation (CS) despite a very small energy level offset at the donor/acceptor (D/A) interface. In PM6:Y6, the prototype NFA BHJ leading to the recent breakthrough in organic photovoltaic (OPV) efficiency, we found that a significant portion of CT excitons can convert spontaneously (in 10 – 100 ps) into separated carriers despite the CT exciton has a considerable binding energy of 0.15 eV. Using time-resolved two-photon photoemission spectroscopy (TR-TPPE), we directly observed an increase in average electron energy with time. We propose that the enthalpy-uphill CS is driven by entropy, and the entropic driving force is maximized when the delocalized electron and hole in the CT exciton forms a point-like junction (Adv. Mater. 36, 2400578 (2024)). We also found that this enthalpy increase can occur at nearly an order of magnitude faster rate in the PM6:eC9 blend. The eC9 is an improved version of the Y6, and PM6:eC9 OPV efficiency is close to 20%. Hence, the rate of the enthalpy-uphill CS appears to correlate with better OPV efficiencies.

Another important question is whether a D/A interface is needed at all for effective CS. For organic semiconductors, it has been a prevailing assumption that a D/A interface is needed for effective CS. To challenge this presumption, ZnPc molecules with different degrees of fluorination were used to tailor a D/A interface with an interfacial energy offset as small as 0.1 eV. We found that despite the very small energy offset, enthalpy-uphill CS can still occur (Fig. a, b). A multi-scale simulation approach, that combines density functional theory (DFT) calculations and kinetic Monte Carlo (kMC) simulations, shows that the CS can be driven by entropy gain, and that this gain can be further enhanced by a small band bending near the interface (J. Phys. Chem. Lett. 16, 12545-12552 (2025); J. Phys. Chem. C, under review). Our next step is to investigate whether free carriers can still be generated in neat NFA films. Our preliminary measurements show that the average enthalpy of excitons increases with time in neat-Y6 films. However, interestingly, this behavior is not observed in D/A polymers such as the PTB7-Th (Fig. c).

Currently, we are investigating what features in the NFA crystal can allow a spontaneous increase in the exciton enthalpy and whether this enthalpy increase will necessarily lead to free-carrier generation.



a-b) TR-TPPE spectra and temporal dynamics showing spontaneous CS at the ZnPc/F₄ZnPc D/A interface. c) Temporal change in exciton energy for Y6, and PTB7-Th measured by TR-TPPE.

Identification of nuclear coordinates driving solar energy conversion processes using ultrafast Raman techniques

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The overarching hypothesis for our work is that by identifying specific nuclear coordinates and quantum coherences that drive photochemical processes, we can design molecular systems for optimized solar energy conversion. Using molecules to transduce light into chemical or electrical energy involves fast processes occurring on highly multidimensional potential energy landscapes, which are made up of a number of interacting nuclear degrees of freedom. By mapping out the relevant reaction coordinates, and by distinguishing driving from spectator from killer vibrational modes, we aim to guide rational molecular design for improved performance. This fundamental research builds upon our development of advanced Raman spectroscopic techniques to complex systems with multiple nuclear coordinates that contribute to the reaction trajectory.

Our work focuses on three inter-related aims, including (1) Mode-selective FSRS to identify driving nuclear coordinates, (2) Tracking photochemical reactivity in optimized polaritonic systems, and (3) Magnetic field effects in vibrationally-driven photochemistry. We have made progress in all aims, including work quantifying the impact of select vibrational modes on exciton transport,¹ work elucidating how light-matter coupling can steer wavepackets on excited potential energy surfaces with both resonance Raman intensity analysis² and femtosecond stimulated Raman spectroscopic tracking of structural dynamics, and preliminary work showing changes in photochemical reaction outcomes under applied magnetic fields (Figure 1).

Overall, our work seeks to apply Raman spectroscopy to identify key reaction coordinates in solar photochemistry, and to use those insights to design molecules with improved product yields. We focus on the use of advanced Raman spectroscopies to provide synthetic insight on molecular-based solar energy conversion systems, and do so by identifying certain nuclear coordinates and vibrational coherences which can be modified in order to improve function.

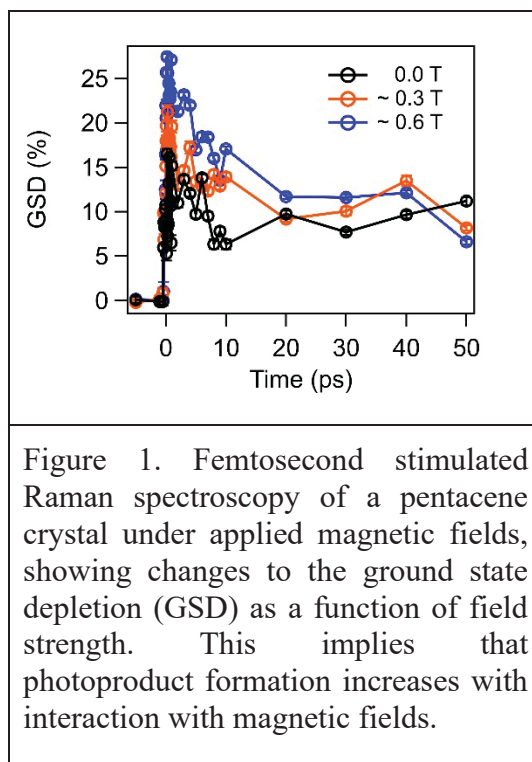


Figure 1. Femtosecond stimulated Raman spectroscopy of a pentacene crystal under applied magnetic fields, showing changes to the ground state depletion (GSD) as a function of field strength. This implies that photoproduct formation increases with interaction with magnetic fields.

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2. Alam, S., Liu, Y., Holmes, R., Frontiera, R. R. <https://arxiv.org/abs/2501.06364>

Stability, Energetics and Kinetics Control of Copper Complexes via Ligand Exchange Reactions

M.D. Adesanya, T.W. Hamann

Chemistry

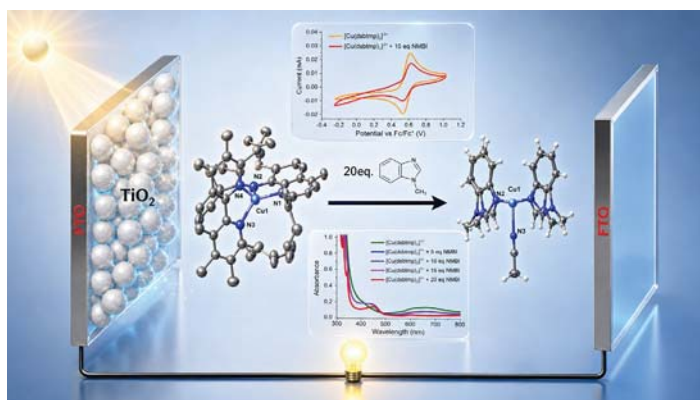
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Photochemical systems that convert sunlight into electricity or chemical fuels rely on a series of electron-transfer steps following light absorption to generate a charge-separated state. In dye-sensitized photoelectrochemical cells, this charge separation typically occurs via two sequential processes: electron injection from the photoexcited dye into the conduction band of a semiconductor, followed by regeneration of the oxidized dye by a redox couple in solution. The goal of this project is to explore the feasibility of achieving a similar charge-separated state using a single chromophore in solution through a single electron-transfer step. Recent work focuses on copper coordination complexes, particularly $[\text{Cu}(\text{dsbtmp})_2]^+$ (dsbtmp = bis(2,9-di(sec-butyl)-3,4,7,8-tetramethyl-1,10-phenanthroline)), due to the long-lived excited state (exceeding 1 μs in various solvents), which is necessary to enable diffusion to the TiO_2 surface and subsequent electron injection.

We have found the presence of an exogenous base, including 4-*tert*-butylpyridine (TBP), 4-methylpyridine (4MP), N-methylimidazole (NMI) and 1-methylbenzimidazole (NMBI), is critical to enable promising photon to electricity conversion. There are several roles of these bases, however, that can have both beneficial and deleterious effects. Although $[\text{Cu}(\text{dsbtmp})_2]^+$ is found to be stable in the presence of the bases investigated, photoluminescence, UV-

Vis titrations, electrochemical measurements and quantitative NMR spectroscopy measurements reveal that these bases substitute one or both of the dsbtmp ligands of the oxidized form, $[\text{Cu}(\text{dsbtmp})_2]^{2+}$. In addition to the exogenous base, coordinating solvents, such as acetonitrile, can also displace a dsbtmp ligand of $[\text{Cu}(\text{dsbtmp})_2]^{2+}$, which is one of the degradation pathways of this as a photosensitizer. Initial investigations in alternative, non-coordinating, solvents will also be presented. Further, a general These results offer insight into the stability and ability to control the behavior of copper photosensitizers. Preliminary efforts to establish a more general relationship between the formal redox potential and Cu^{2+} stability constants as a predictive tool for ligand substitution in copper redox couples / photosensitizers will be presented.



Physics and chemistry of unburied electrocatalyst/semiconductor interfaces in functioning water-splitting photo(electro)catalysts

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Photoelectrocatalysts, including those used for solar water splitting, combine a semiconductor (SC) light absorber with electrocatalyst (EC). SC generates photovoltage that powers electrocatalytic half-reactions at the EC sites. In many cases EC is introduced in the form of metallic nanoparticles, and the SC/EC interface is directly exposed to the reactive chemical environment. These “unburied” interfaces behave very differently from the more studied and better understood thin-film “buried” junctions where the EC/SC interface is protected by a thin and impermeable film of an EC. Fundamental principles governing charge transfer and photovoltage generation in unburied junctions are poorly understood. A key difficulty is that these unburied EC/SC interfaces are highly dynamic under operating conditions, undergoing condition-dependent structural and chemical changes. As a result, accurately describing the operation of these photoelectrocatalysts requires careful consideration of atomistic-level transformations at the interface during reactions. Our work focuses on analyzing the physical and chemical mechanisms underlying the operation of functioning photo(electro)catalysts. We seek to unravel how dynamic reaction environments impact charge carrier selectivity and photovoltage through their interaction with the EC/SC interface.

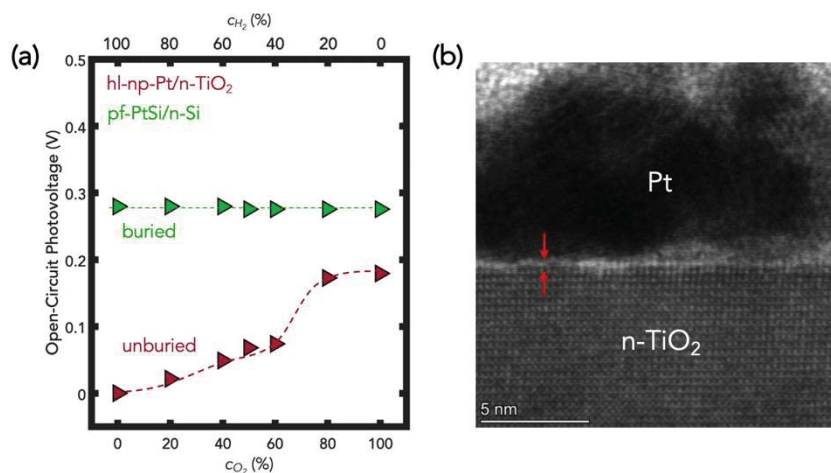


Figure 1. (a) Open-circuit photovoltage of buried and unburied junction model systems as a function of H₂ and O₂ composition in electrolyte. (b) Atomic-resolution cross-sectional HAADF-STEM image of the Pt/n-TiO₂ interface.

I will discuss our recent work on wide band gap n-TiO₂ and n-SrTiO₃ SCs coupled to different metal ECs for the HER and OER half-reactions. The model systems we studied include np-EC/SC (with unburied junctions), flat film EC/SC, and buried EC/SC junctions. These model systems allow us to shed light on the similarities, differences and contradictions involved in the operation of buried and unburied junction photo(electro)catalysts. By comparing the behavior of these model systems under diverse reaction conditions, we uncover how reactive environments impact unburied junctions relative to their buried analogues and drive photoelectrochemical conversion. I will describe physical and mathematical models that we developed allowing us to capture the behavior of these systems.

Radiolysis of nuclear fuel separation systems: room and low temperature EPR studies

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Solvent extraction is a fundamental process in advanced nuclear waste separation. Organic ligands, including phosphates, phosphonates, organic acids, and amides, must maintain high selectivity for fuel components while dissolved in a hydrocarbon matrix, modeled here by n-dodecane. However, exposure to ionizing radiation triggers deleterious chemical transformations. Understanding the radiolytic stability of these systems is critical for optimizing solvent longevity and reducing secondary waste.

This research employs Electron Paramagnetic Resonance (EPR) spectroscopy to provide high-fidelity data on the structure and stability of paramagnetic intermediates. Because radiation-induced intermediates are highly transient, specialized techniques are required to detect them within standard EPR spectrometers. These include the spin-trapping method, which stabilizes radicals by transforming them into more persistent species, and low-temperature stabilization, which prevents diffusion-controlled recombination.

The efficiency of radical formation in tributyl phosphate (TBP) at room temperature was first evaluated using the PBN (N-tert-butyl- α -phenylnitron) spin-trapping approach. The determined G-value for TBP radicals is $0.22 \mu\text{mol J}^{-1}$ (2.1 radicals/100 eV), consistent with literature data for alkanes under similar conditions. A similar approach was applied to 3tBNB (2,4,6-tri-tert-butyl nitrosobenzene) in dodecane. Despite being less efficient than iodine, 3tBNB enabled the differentiation between primary and secondary alkyl radicals and hydrogen adducts.

Low-temperature studies focused on neat ligand radiolysis, the thermal evolution of stabilized radicals, and the characterization of radical cations produced in Freon matrices. We explored the EPR spectra and formation kinetics of radicals generated at 77 K for a specific set of currently used and proposed separation ligands. Experimental signals were assigned using extensive quantum chemical calculations. Our findings suggest that during radiolysis at 77 K, alkyl or amide carbon-centered radicals are predominantly formed, aligning with existing experimental data. Regarding thermal behavior, the estimated energy barriers for radical interconversion are approximately 20 kcal/mol, suggesting that temperature-induced changes primarily involve conformational rearrangements rather than radical transformations.

Ongoing research into radical cations has yielded several outcomes. Phosphate ligands do not produce stable primary radical cations under the experimental conditions, likely transforming into distonic structures. In contrast, the primary DEHBA (N,N-di-(2-ethylhexyl)butyramide) radical cation was observed at 99 K. Its thermal evolution occurs at 133 K, implying a proton transfer and the formation of a mixture of two distonic radical cations.

Ultimately, the studies of radical species and their thermal interconversion provide a fundamental framework for understanding the degradation of complex extraction systems. These mechanistic insights are essential for developing predictive models of solvent longevity and guiding the rational design of the next generation of radiation-resistant ligands for nuclear waste processing.

Photoinduced charge separation and catalysis using Cu-chalcogenide clusters

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A key goal of this research program is to uncover the atomic and electronic structure factors that promote and stabilize multi-electron photoinduced charge accumulation in molecularly defined modular assemblies. To complement our group's work that focuses primarily on mononuclear transition metal coordination complexes as artificial and biomimetic photosynthetic modules, we have recently initiated an effort to investigate the photo- and redox-activity of discrete metal-chalcogenide clusters. These clusters introduce the possibility to leverage the unique cluster electronic structure, specifically multi-metal interactions and metal-ligand covalency, for supporting long-lived photoinduced charge separation and charge accumulation to promote effective photochemical energy conversion. This poster will describe our group's recent efforts to understand how coordinating ligands influence the electro- and photochemical activity of discrete metal-chalcogenide clusters, with a particular focus on clusters based on first row transition metals.

$\text{Cu(I)}_6(\text{pyrimidine-thiol})_6$ clusters exhibit long excited-state lifetimes with NIR emission, and have been investigated as photocatalysts, therapeutic agents, and environmental and molecular sensors. We have synthesized a $\text{Cu(I)}_6(\text{pyrimidine-thiol})_6$ cluster in a fully neutral state and with an overall +2 charge following protonation of two of the pyrimidine ligands. In solution, both clusters have excited state lifetimes in the 1 – 10 microsecond range, with slight variation depending on solvent polarity and ligand protonation state. Time-resolved (TR) optical and EPR spectroscopies confirm photoinduced electron transfer to model electron acceptors, with charge separation stabilized for nearly 100 microseconds (Figure 1, top). TR-EPR experiments and DFT analysis are used to map the extent of Cu(II) localization across the cluster in the charge-separated state. The Cu_6 clusters are highly effective photosensitizers for photocatalytic hydrogen evolution in aqueous media in the presence of a molecular cobalt catalyst and sacrificial electron donor (Figure 1, bottom). Mechanistic analysis suggests that the protonation state of the Cu_6S_6 cluster ligands plays an outstanding role in the observed H_2 generation, and proposed intermediates and mechanistic insight based on computational analysis will be discussed.

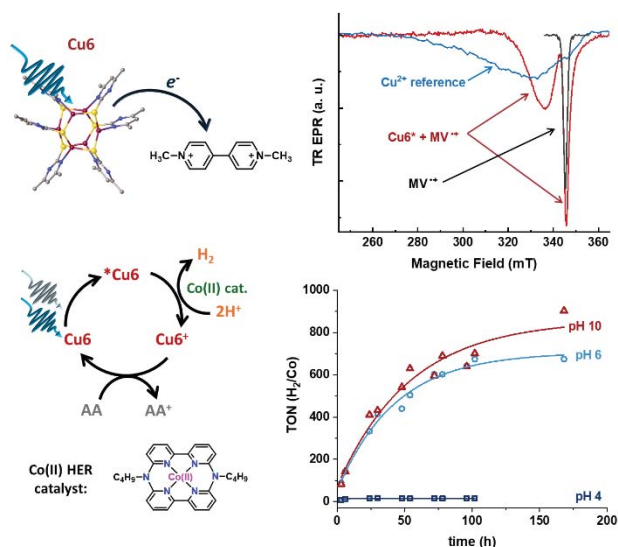


Figure 1. Top: crystal structure of $\text{Cu}_6(\text{pyrimidine-thiol})_6$ cluster and proposed photoinduced charge transfer to methyl viologen. Time-resolved EPR spectra of $\text{Cu}_6 + 10$ equivalents MV^{2+} in 1:1 $\text{CH}_3\text{CN}:\text{C}_6\text{H}_5\text{CH}_3$ at 20K; spectra integrated between 600 – 1500 ns following 420 nm excitation. Bottom: proposed mechanism of photocatalytic H_2 evolution using Cu_6 clusters as photosensitizer; comparison of H_2 TON as a function of pH.

Radiation-Induced Transformations of Sulfur-Donor Ligands Relevant to Actinide–Lanthanide Separation: A Pulse Radiolysis and Computational Study

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Selective separation of trivalent actinides from lanthanides is a critical challenge in advanced nuclear fuel recycling. Sulfur-donor extractants of the Cyanex dithiophosphinic acid class offer exceptional An/Ln selectivity, yet their radiation stability and mechanistic degradation pathways under process-relevant conditions are poorly characterized. This work addresses that gap using structurally tractable model systems: bidentate dithiophosphates, monothiophosphate analogs, and two hydrophilic soft-donor candidates — 2,2'-thiodiacetic acid (TDA) and 2,5-thiophene dicarboxylic acid (TPA) — studied under anoxic aqueous conditions across pH 4–10.

Radiation-induced transformations were investigated by pulse radiolysis with transient absorption (TA), transient conductivity (TC), and time-resolved resonance Raman (TRRR) detection. Second-order rate constants for reactions with hydrated electrons, hydroxyl radicals, and one-electron oxidants were measured by TA kinetics. TC provided pH-dependent protonation equilibria of short-lived intermediates, and TRRR yielded vibrational fingerprints of strongly absorbing transients. Experimental results were interpreted with (TD)DFT calculations at the ω B97X-D/aug-cc-pVTZ/IEFPCM level to assign spectra, characterize intermediate geometries, and evaluate the regioselectivity of OH radical attack.

The results establish the primary oxidative and reductive intermediates formed during the early stages of radiolytic degradation of these ligand classes, providing mechanistic data needed to predict extractant stability and inform the design of radiation-resistant soft-donor systems for the nuclear fuel cycle.

Molecular Catalyst Kinetics dictating Electrochemical CO₂ Reduction Product Selectivity

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Electrochemical reduction of carbon dioxide (CO₂) to value-added chemicals and fuels can be mediated by molecular catalysts. Generally, the two-electron reduction products CO and formate (HCO₂⁻) are first accessed, but these species can serve as intermediates for the synthesis of higher-value and more energy-dense chemicals through multi-catalyst cascade reactions. The majority of known molecular CO₂ reduction catalysts selectively generate CO or are unselective, yielding a mixture of CO and HCO₂⁻, as well as hydrogen (H₂). Because HCO₂⁻ is a particularly attractive synthon for higher value chemicals, design principles for catalysts that selectively reduce CO₂ to HCO₂⁻ are needed.

The imino bipyridine cobalt(II) catalyst is reported to reduce CO₂ to a mixture of HCO₂⁻ and CO.¹ Using a combination of cyclic voltammetry, controlled potential electrolysis, and stopped-flow rapid mixing, we have quantified the kinetics of elementary proton-coupled electron transfer steps, as well as CO₂ binding, associated with the reaction pathways that generate CO, HCO₂⁻, and H₂ (Figure 1). Across these experiments, a range of proton sources are employed to evaluate how pK_a, steric effects, and charge influence elementary proton transfer kinetics and the resulting selectivity of CO₂ reduction products. The relative kinetics of these elementary steps are expected to dictate reaction selectivity.

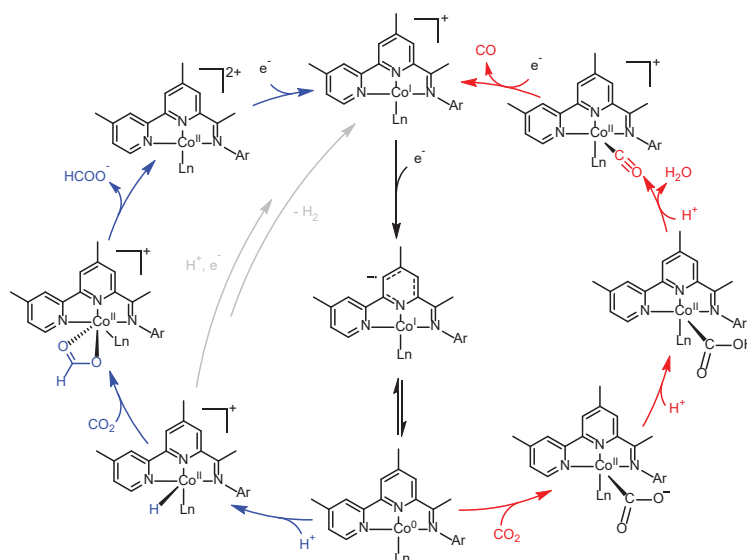


Figure 1. Electrochemical CO₂ reduction mediated by a imino bipyridine cobalt(II) catalyst is hypothesized to operate via two parallel mechanisms to yield CO, HCO₂⁻, and H₂.

By correlating kinetic parameters with catalytic selectivity, this work aims to establish general design principles for catalysts that favor HCO₂⁻ production. These insights will guide the development of next-generation molecular catalysts capable of efficiently converting CO₂ into useful chemical fuels.

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Leveraging Chirality-Induced Spin Selectivity to Enhance the Production of Solar-Driven Radical Intermediates

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Chiral-induced spin selectivity (CISS) enables spin-selective electron transport, facilitating the generation of spin-polarized currents without requiring ferromagnetic materials and external magnetic fields. To date, the CISS effect has emerged as a promising strategy to enhance the efficiency of photoelectrochemical (PEC) water splitting. Although the spin-dependent competition between oxygen (O_2) and hydrogen peroxide (H_2O_2) production has been elucidated, the impact of CISS on the kinetics of one-electron oxidation of water that leads to hydroxyl radicals ($\bullet OH$) remains unclear. To elucidate the role of CISS for $\bullet OH$ generation, chiral molecules (L and

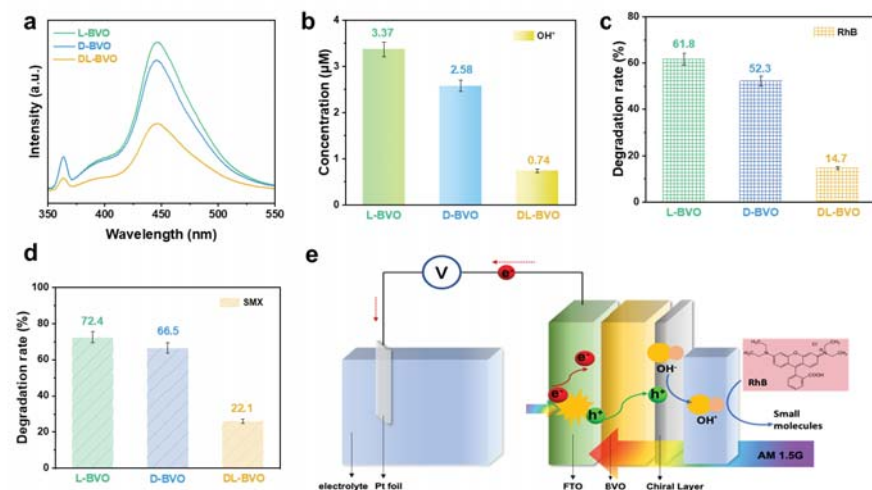


Figure 1: Quantification of hydroxyl radical ($\bullet OH$) (a) Fluorescence spectra of post-reaction OH-CCA solutions on the L-BVO, D-BVO, and DL-BVO under 1.23 V vs. RHE over 24 h. (b) Calculated concentration of $\bullet OH$ on the L-BVO, D-BVO, and DL-BVO after reaction, each experiment is repeated for 3 times. Photodegradation rates of (c)RhB and (d)SMX after 2 h over L-BVO, D-BVO, and DL-BVO (e) Schematic illustration of a chiral layer decorated BVO photoelectrode.

D-methionine) were integrated with $BiVO_4$ (BVO) photoelectrode to construct a BVO-chiral molecule interface. The chiral molecule modified L-BVO and D-BVO exhibited enhanced oxygen evolution reaction (OER) performance when compared to their racemic (DL-BVO) and bare BVO counterparts. In addition, the fluorescence probe strategy was employed to quantitatively measure the $\bullet OH$ yield (Fig 1. a-b). It revealed that in the presence of chiral molecules, L- and D-BVO exhibit 3-4 times higher $\bullet OH$ generation, accompanied by

significantly improved degradation efficiencies for ppm-level organic dyes (Rhodamine B(RhB)) and antibiotics (Sulfamethoxazole (SMX)) compared to DL-BVO (Fig. 1c-e). This study opens new opportunities to advance oxidation processes toward the deep mineralization of organic pollutants by leveraging spin effects.

Radiation Chemistry at the Notre Dame Radiation Laboratory (NDRL)

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Notre Dame Radiation Laboratory
University of Notre Dame
Notre Dame, Indiana, IN 46556

Capabilities available to pursue radiation chemical research at the NDRL are briefly described.

Three pulsed electron accelerators, one LINAC and two van de Graaff generators, initiate the **radiation chemical processes** under investigation.

8 MeV > 100 ps



optical absorbance
conductivity
multichannel acquisition

3 MeV > 10 ns



electron spin resonance
electrochemical impedance

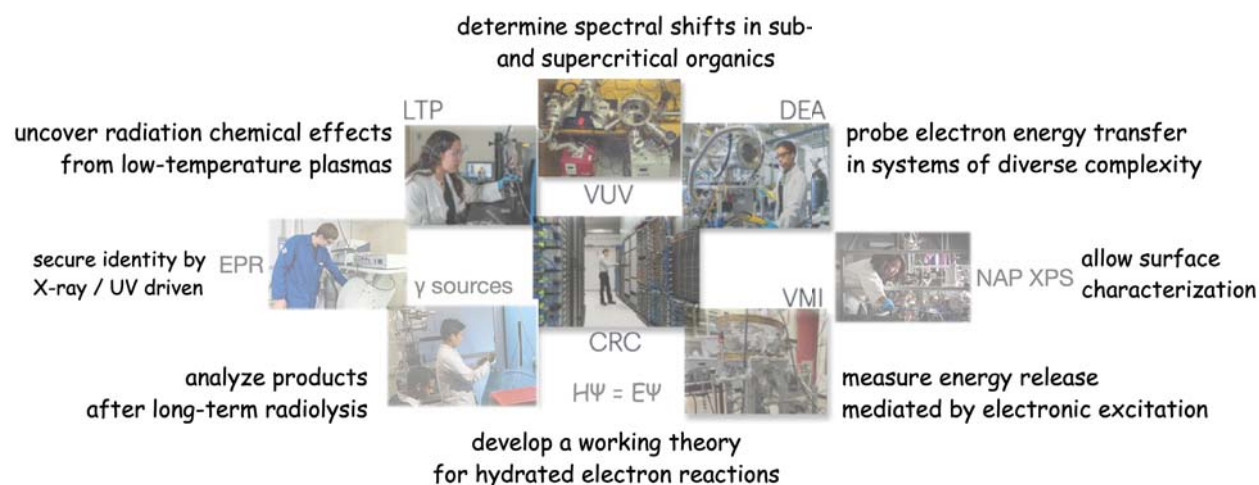
2 MeV > 100 ns



resonance Raman
temperature variability
molten salt capability

Visitors are frequent and we particularly encourage collaborative enterprises.

A wide range of **complementary techniques** is locally available to broaden the impact and enhance the interpretability of those data directly available at the accelerators.



Some are highlighted above. Their use generally requires in house assistance (*collaboration*).

We have recently added actinide-handling capabilities to our suite of techniques and will be reporting initial results on actinide redox chemistry soon.

In-Situ Multi-Probe X-ray Transient Absorption Spectroscopy Captures New Catalytic-Site Intermediates in Iridium Blue Dimer Water Oxidation Catalysts

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Artificial photosynthesis harnesses sunlight to drive proton or CO₂ reduction to chemical fuels, offering a promising route for photocatalytic conversion of small molecules to value-added chemicals. This process relies on the oxygen evolution reaction (OER) to supply the electrons and protons critical for fuel formation; yet OER is the rate limiting step due to its intrinsically sluggish and multistep kinetics. As a result, developing efficient OER catalysts that can substantially accelerate water oxidation is essential for balancing the oxidative and reductive half-reactions. However, progress toward this goal is hampered by the lack of knowledge on the detailed mechanisms of OER, which involves multiple redox events spanning timescales, for which few techniques can capture the full sequence of intermediates.

Multiple X-ray Transient Absorption (MXTA) represents a uniquely powerful technique for probing multi-redox processes involved in OER cycle. MXTA can acquire thousands of time-resolved XAS spectra over a wide time window, from ~100 ps to sub-ms, thereby offering a direct means to map evolution of the catalytic intermediates across a broad time region. In this work, we present our progress in using MXTA to probe the early events in the OER catalytic cycle with an Ir-based molecular catalyst, the Ir blue dimer (Ir-Blue) (Figure 1a), as a prototypical platform. In the presence of [Ru(bpy)₃]²⁺ as the photosensitizer and Na₂S₂O₈ as the sacrificial electron acceptor, the oxidation of Ir-Blue (Ir^{IV,IV}) to a Ir^{V,V} state was observed as a 1.1 eV shift in the Ir-L_{III} edge (Figure 1b). The oxidative shift was accompanied by an increase in coordination number in the first-shell of the Ir center, consistent with the binding of an additional aquo ligand forming a previously unresolved 7-coordinate Ir species. Early time MXTA measurements also captured the rapid formation and decay of a reduced Ir species. This phenomenon was particularly pronounced at low electron acceptors concentrations (Figure 1c) and is attributed to rapid electron transfer from excited [Ru(bpy)₃]²⁺ to Ir-Blue, which directly competes with the intended electron transfer from

excited [Ru(bpy)₃]²⁺ to electron acceptors. Collectively, these results reveal previously unresolved early redox events in the water oxidation catalytic cycle and demonstrate the ability of MXTA to disentangle multiple catalytic intermediates.

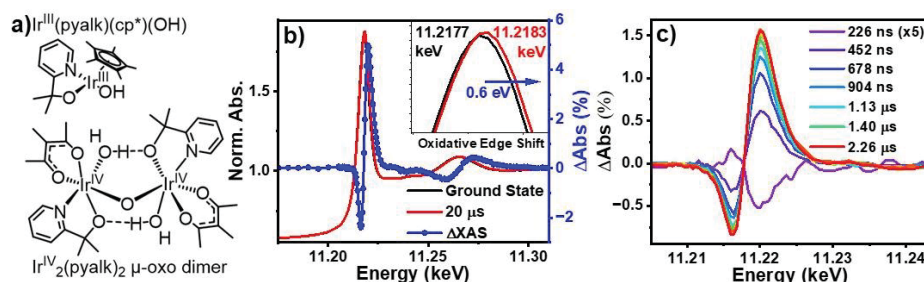


Figure 1. a) Structure of synthesized Ir monomer precursor and Ir-Blue; MXTA spectra of Ir-Blue dimer collected under in situ catalytic conditions (b) and in the absence of electron acceptor (c).

Understanding how nanocrystal and enzyme properties govern binding interactions, charge transfer, and photochemical NH₃ production in nanocrystal-nitrogenase biohybrids

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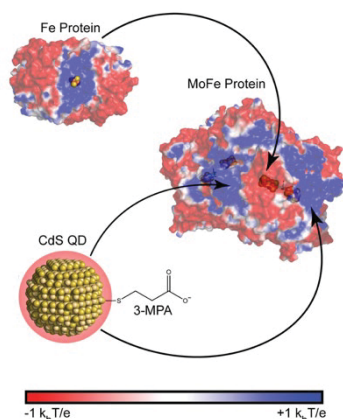
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Our core program investigates the coupling of semiconductor nanocrystals (NCs) with nitrogenase MoFe protein. These systems enable an understanding of how properties of both the NCs and the enzyme control light-driven N₂ reduction to ammonia. In this poster, we focus on understanding the binding interactions between NCs and MoFe protein. We also investigate how the NC surface capping ligands affect hole scavenging and ultimately photochemical N₂ reduction.

To understand the binding between CdS quantum dots (QDs) and MoFe protein, we developed an air-free method for microscale thermophoresis (MST). The NCs are capped with 3-mercaptopropionic acid (3-MPA) so that the carboxylate imparts a negative charge on the QD surface, allowing for an electrostatic interaction with positive charged patches on the MoFe protein surface.



Using MST, we examined the binding as a function of salt concentration and found that higher salt concentrations reduce the strength of binding. This observation supports the hypothesis that the binding interaction between the CdS QD and MoFe protein is electrostatic in nature. We compared the CdS QDs binding to MoFe protein to the binding of the native electron donor, Fe protein. We found that the CdS QDs bind more strongly to the MoFe protein but that binding behavior is different in the two systems, with QDs having positive cooperativity while the Fe protein has negative cooperativity. We then examined how the binding interactions depend on the QD diameter and observed two distinct binding regimes. At lower QD diameters, the dissociation constant scaled linearly with QD diameter, revealing that smallest QDs bind most strongly. QDs

with diameters > 4.0 nm, however, do not show a clear binding signal. We explain these results in terms of the electrostatic landscape at the putative QD binding site on the MoFe protein.

To examine how surface-capping ligands can be used to guide photochemical activity, we changed the surface capping ligand from 3-MPA to 4-mercaptobenzoic acid (4-MBA), replacing the two carbon alkyl chain with a benzene ring. By making this seemingly small chemical change, we noticeably impacted multiple properties of the QD-MoFe protein system. The change in the surface capping ligand increased the QD excited state lifetime as well as the total number of electrons in photochemical products. We also found that the choice of sacrificial electron donor (SED) has a significant impact on the yield of photochemical N₂ reduction, but this dependence is different for 3-MPA and 4-MBA. We attribute this complex behavior to both the interactions of the QDs and MoFe protein and the interactions between the SED and the surface-capping ligands.

A Molecule-Based Approach to Z-Schemes for Visible Light-Driven Water Splitting

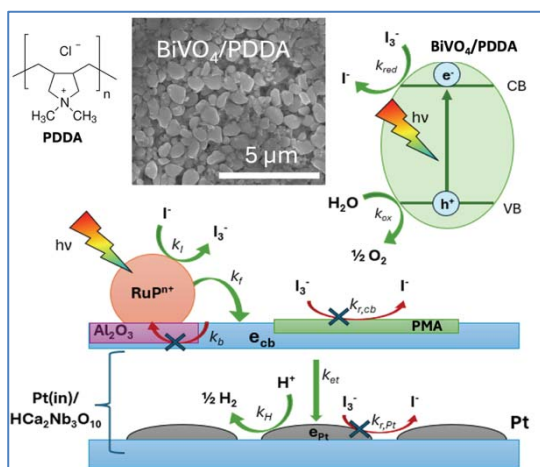
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This project investigates the kinetics of light-driven and dark reactions that underpin the development of molecule-based Z-schemes for splitting water to hydrogen and oxygen. In these systems a wide bandgap semiconductor, typically a layered niobate or titanoniobate, is sensitized with a visible light-absorbing dye, and a reversible redox couple shuttles electrons generated at a colloidal oxygen-evolving photocatalyst. While these dye-based systems are so far less efficient than Z-schemes based on complementary semiconducting light absorbers, the use of molecular dyes, polymers, and redox shuttles provides an opportunity to use the tools of molecular synthesis to control the spatial distribution of components and their electrochemical properties. Light-driven and dark electron transfer rates in the hydrogen- and oxygen-evolving components of these Z-



schemes are measured on timescales of nanoseconds to seconds by a combination of flash photolysis, stopped flow, and electrochemical methods. Polymer adsorption on the oxygen- and hydrogen-evolving particles helps to control the spatial distribution of the oxidized and reduced forms of the redox shuttle, inhibiting charge recombination reactions that shunt the Z-scheme. For example, we have found that adsorption of hydrophilic polyanions (PMA) on the hydrogen-evolving niobate particles inhibits charge recombination by I_3^- , and adsorption of a hydrophobic polycation (PDDA) on $BiVO_4$ particles promotes oxygen evolution by selectively binding I_3^- .

Our recent experiments have focused on problems that limit the efficiency of the Z-scheme shown in the figure above. One is that Ru polypyridyl sensitizers and $BiVO_4$ both absorb at the blue edge of the visible, limiting the spectral utilization. The second is that back electron transfer between the oxide semiconductor and the dye is kinetically competitive with hydrogen evolution at internally sited Pt nanoparticles. To address the first problem, we synthesized Os(II) polypyridyl dyes with singlet-triplet absorbance extending into the red region of the spectrum. Despite their very short excited-state lifetime relative to analogous Ru(II) complexes, electron injection from the excited Os(II) dyes into the layered oxide semiconductor is efficient. Os(II)-sensitized photocatalysts show higher H_2 evolution rates than Ru(II)-sensitized photocatalysts when ascorbate is used as an electron donor. In contrast, negligible H_2 evolution was found with I^- as the redox mediator for water splitting. Transient absorption spectroscopy revealed that the low activity resulted from slow electron transfer from I^- to oxidized Os(II), motivating re-design of the sensitizer and mediator. The second problem is a consequence of hole transfer between sensitizer molecules, which accelerates charge recombination with electrons in the oxide semiconductor. Co-adsorption of octadecylphosphonic acid inhibits cross-surface charge transfer and substantially improves the yield of photogenerated H_2 in model systems with sacrificial electron donors.

Driving Force Dependent Photoinduced Charge Transfer Dynamics in Polymer-Wrapped Semiconducting Single-Walled Carbon Nanotubes

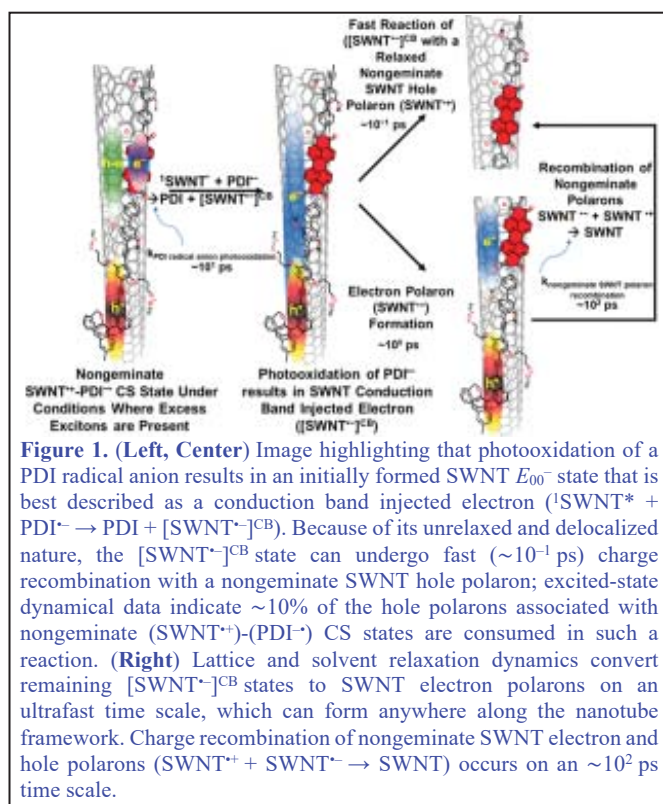
Riley H. Stephenson, James A. Alatis, Alexander C. Wilcox, Francesco Mastrocinque, Zachary X. W. Widel, George Bullard, Ethan Li, Natalia Rae Alatis, John Naquin, Yusong Bai, Peng Zhang, David N. Beratan, and Michael J. Therien

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We investigate the thermodynamic driving-force dependences of photoinduced charge separation (CS) and subsequent charge transfer dynamics in single-walled carbon nanotube (SWNT)–perylene-3,4,9,10-tetracarboxylic diimide (PDI) donor–acceptor (D–A) superstructures. Pump–probe spectroscopy reveals



that $[\text{SWNT}^{(\bullet+)_n}](\text{PDI}^-)_n$ CS states form on an ~ 100 fs time scale following photoexcitation; these dynamics are invariant across an ~ 400 mV driving force range, indicating that SWNT hole polaron formation time scales are determined by nanotube lattice and solvent relaxation. These CS states feature SWNT hole polarons adjacent to (geminate) and nearby (nongeminate) PDI radical anions. Analysis of the free energy dependence for charge recombination (CR) of $[\text{SWNT}^{+\bullet}]^{\text{geminate}}-(\text{PDI}^-)$ CS states highlights an ~ 2 meV value for D–A electronic coupling (H_{AB}) and ~ 0.93 eV for the total reorganization energy (λ_{T}). A corresponding driving force dependence of the CR dynamics for $[\text{SWNT}^{+\bullet}]^{\text{nongeminate}}-(\text{PDI}^-)$ CS states indicates a diminished H_{AB} value (~ 0.6 meV) and a larger λ_{T} (~ 1.1 eV), consistent with larger transfer distances. SWNT excitons that persist following photoinduced CS drive photooxidation of

PDI^- components of $[\text{SWNT}^{(\bullet+)_n}](\text{PDI}^-)_n$ CS states ($^1\text{SWNT}^* + \text{PDI}^- \rightarrow \text{PDI} + \text{SWNT}^-$); this reaction manifests a significantly reduced λ_{T} value (~ 0.67 eV) as the initially prepared SWNT reduced state bears the character of a conduction band injected electron ($[\text{SWNT}^-]^{\text{CB}}$). This reaction thus gives rise to relaxed, nongeminate SWNT electron and hole polarons on the same nanotube; these polarons react on a 10^2 ps time scale independent of the electronic structure of these SWNT-PDI superstructures.

Publications:

(1) *J. Am. Chem. Soc.* **2024**, *146*, 31169–31176; *J. Am. Chem. Soc.* **2025**, *147*, 43822–43830.

Jahn-Teller Distortion Controls Electron Transfer in Photoexcited Cu(I) Donor–Acceptor Systems

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The Jahn–Teller distortion (JTD) in the metal-to-ligand-charge-transfer (MLCT) excited state of Cu(I)-diimine derivatives has been extensively investigated in the literature, including our own work. However, whether the JTD affects photochemical properties of these complexes, such as inter-system crossing (ISC) and photoinduced electron transfer (PET) remains largely unexplored. Here, we demonstrate that the JTD governs charge separation (CS) through a vibronically controlled conical intersection in heteroleptic Cu(I) bisphenanthroline–naphthalene diimide (CuHETPHEN-NDI) donor–acceptor dyads. Using 20-fs broadband transient absorption spectroscopy (BBTA) combined with coherent vibrational wavepacket (CVWP) analysis and quantum chemical calculations, we directly tracked nuclear motions that steer the system from the ¹MLCT state to the CS state through the PET process where the ¹MLCT state is an electron donor and NDI is an electron acceptor. Bulkiness of the pendant groups at the 2,9-positions of the phenanthroline ligands hinders the JTD (decrease of the angle between the two ligand planes) and subsequently slows down the CS state formation. Short-time Fourier transformation and Fourier filtering analyses identified two key vibrational modes: a low-frequency breathing mode ($\sim 100\text{ cm}^{-1}$) via a bond distance change between Cu and ligated N atoms (Cu–N) that modulates the the NDI anion absorption and acts as a vibronic coupling coordinate, and a higher-frequency mode ($\sim 313\text{ cm}^{-1}$) that evolves along the PET trajectory. Normal mode analysis and potential energy surface calculations show that the JTD brings the ¹MLCT and CS states into degeneracy, while the Cu–N breathing motion dynamically modulates donor–acceptor electronic coupling to enable ultrafast nonadiabatic electron transfer. Steric hindrance exerted by the groups at the 2, 9 positions of the phenanthroline ligands suppresses this vibronic coupling, leading to faster CVWP decoherence for the 313 cm^{-1} mode and slower CS. These findings unravel JTD-controlled vibronic coupling at conical intersection as a governing factor for CS and provide insight into designing Cu-based photosensitizers by harnessing structural dynamics to control PET.

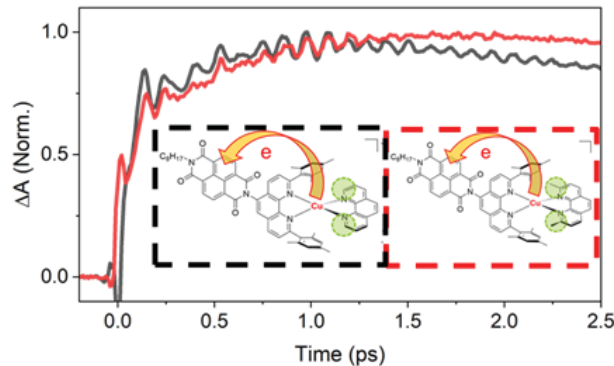


Figure 1. The steric hindered Jahn-Teller distortion of Cu(I) diimine complexes (red) are shown to have slower charge separation rate (1.48 ps) and faster dephasing time for coherent vibrational packet motions compared to less hindered counter part (black)

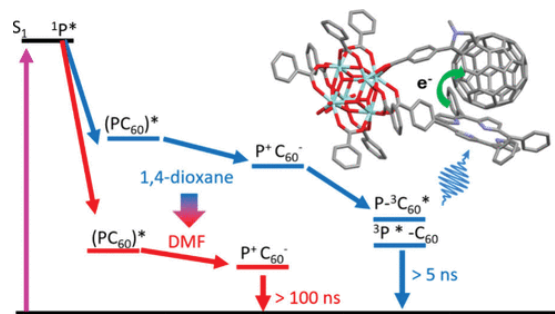
Reference: *Chem. Sci.*, 2026, Advance Article doi.org/10.1039/D5SC10209J

Photoinduced Charge Transfer and transport in donor-acceptor Frameworks

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Engineering efficient photocatalytic materials relies critically on controlling their photoinduced charge transfer and transport behavior. Metal organic frameworks (MOFs), as self-assembled, permanently porous, solid-state polymeric materials, provide a platform for tuning such charge carrier dynamics through framework design and post synthetic modification (PSM). Incorporating photoactive molecular building blocks with electron donor-acceptor properties as framework and/or guest components can lead to long-lived charge-separated excited states with the capacity for charge transport that are required for efficient photocatalysis. As part of our collaborative research project, we focus on a set of MOFs containing photosensitizer/electron donor porphyrin linkers and electron acceptor fullerene guest species. Using solvent-assisted ligand insertion (SALI) and other PSM strategies, the fullerene guest location, loading and solvent environment within the MOF pores are systematically adjusted to tailor the donor-acceptor arrangements and therefore the charge transfer pathway and dynamics. Characterization of these host-guest systems via complementary structural and surface analyses, along with UV-vis titration and fluorescence quenching experiments, reveals the porphyrin-fullerene binding strengths and confirms preferential pore locations. Optical transient absorption (TA) spectroscopy methods reveal sub-picosecond charge transfer with recombination pathways and kinetics exhibiting strong solvent dependence. Fullerene loading further influences these kinetics, with some charge recombination lifetime components in the microsecond range for the highest loading level. The potential for charge delocalization due to fullerene aggregation within the pores is evaluated by using molecular dynamics simulations and its translation to long range charge transport behavior is established through bulk photoconductivity measurements. Future directions for this project include exploring design strategies to incorporate transition metal-based guest complexes or strategic metalation of the porphyrin linkers as potential catalytic sites along with other small molecule guests serving auxiliary electron acceptor/donor roles needed for completing the catalytic cycle.



(1) Arissa, Alison; Rose, Thomas; Leick, Noémi; Kucheryavy, Pavel; Ouyang, Junjie; He, Huixin; Grimme, Stefan; Johnson, Justin C.; Lockard, Jenny V.; Pore-Selective Fullerene Loading in a Porphyrin-Based Metal–Organic Framework Controls Photoinduced Charge-Transfer Dynamics. *J. Phys. Chem. Lett.* **2026**, ASAP. DOI: 10.1021/acs.jpcclett.6c00574

Spin, Chirality, and Carrier Dynamics in Semiconductor Nanocrystals and Photocatalytic Interfaces

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We present advances in controlling and characterizing the electronic, optical, and spin properties of semiconductor nanocrystals and chiral photocatalytic interfaces, unified by the role of surface chemistry in governing bulk and interfacial functionality.

In PbS nanocrystals (NCs), post-synthetic room-temperature cation exchange replaces surface Pb(oleate)₂ with M(oleate)_x (M = Cs⁺, Bi³⁺) via Z-type ligand exchange. The resulting surface M-oleate layer acts as a dopant reservoir, driving metal cation incorporation into the PbS core while preserving colloidal stability. Trion dynamics and first-exciton bleaching confirm doping, with Bi³⁺ and Cs⁺ yielding up to 5.5 and 4 injected carriers per NC, respectively, while retaining colloidal stability. Depth-sensitive synchrotron XPS confirms the surface-reservoir model, with XRD and TEM confirming retention of the rock-salt cubic phase.

In CdSe nanoplatelets (NPLs), we demonstrate a single-step synthesis incorporating chiral aminodecanoic acid ligands directly during growth, bypassing post-synthetic ligand exchange and the solvent incompatibility issues that typically compromise NC quality. The resulting NPLs exhibit photoluminescence quantum efficiencies of 50% and circular dichroism dissymmetry factors $g_{CD} \sim 10^{-4}$.

To probe spin and carrier dynamics, we employ time-resolved Faraday and Kerr ellipticity measurements that simultaneously record transient reflectivity or absorption, enabling correlated characterization of spin and charge dynamics with picosecond resolution. In CdS/CdSe/CdS quantum-shell NCs, hole confinement within the CdSe shell and electron delocalization across the NC produce long biexciton (~10–20 ns) and hole spin (~20 ns) lifetimes, while electron thermalization and spin relaxation occur on ~100 ps timescales. At chiral copper electrocatalytic electrodes, Kerr ellipticity measurements reveal CISS-driven spin polarization via a photoinduced Seebeck current, with ellipticity phase reversing upon switching electrode handedness. At GaAs/chiral interlayer/Pt photoelectrode interfaces, the chiral layer drives preferential transfer of one spin orientation to the Pt catalyst, leaving a net spin-polarized population in the GaAs directly detected by transient Kerr ellipticity.

Exploring the effect of thermal energy on the plasmonic photothermal catalyst in water splitting

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Recently, plasmonic nanoparticles (NPs) have been combined with photocatalysts to improve catalytic performance. However, the fundamental mechanism underlying the enhanced plasmonic photocatalytic performance remains unclear, with debate over whether it arises from plasmonic heating or plasmonic hot-carrier generation. In this project, we aim to explore the mechanism using hybrid thermometry, gas evolution, and ultrafast absorption spectroscopy with a controlled plasmonic nanoarray.

In this fiscal year, the plasmonic nanoarray (Fig. 1A) has been fabricated using e-beam lithography in the CINT integration lab. The dimension and its spectrum are checked to have the maximum electric field strength and absorption. A TiO₂ film in the anatase phase is prepared by atomic layer deposition (ALD) and annealed at 400 Celsius. Raman spectra and XRD analysis were done to confirm the anatase phase of TiO₂. A parametric study of the nanodot size is conducted by varying the diameter and height. A comparative study will be done with thermal energy generation from an electric field.

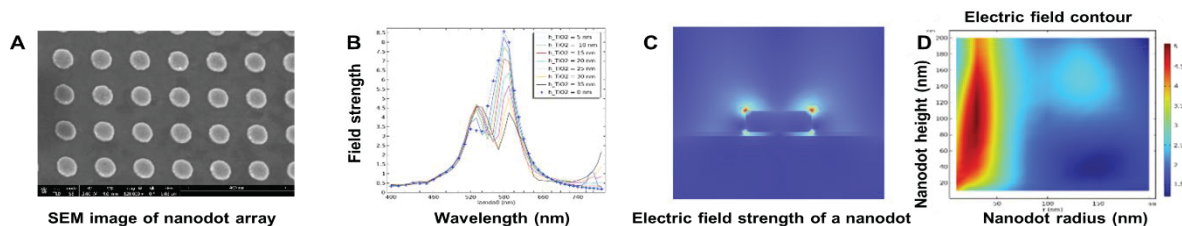


Fig. 1 The nanodot array fabrication (A) and COMSOL FEM simulation (B-D).

A photoelectrochemical (PEC) setup was configured to assess the photocatalytic activity of TiO₂ (ALD film and nanoparticles) using a potentiostat. A PEC cell, consisting of a plasmonic array surface and a glass wall, is mounted on top of the prism in a surface plasmon resonance (SPR) imaging setup to monitor gas evolution and changes in the temperature field. An interference fringe (IF) technique is being employed to experimentally verify the submicron (or nanoscale) thickness of liquids during droplet spreading, enabling monitoring of gas evolution and combining with SPR imaging.

A thermoplasmonic simulation is conducted to relate the two-temperature model to the heat-diffusion equations. The two-temperature model is being verified over ~100 ns for laser heating, using thermorefectance data to confirm its parameters. The electron, lattice, and mean temperatures are calculated as a function of the laser pulse duration (femto, pico, nano), the repetition rate, and the nanodot density. The non-Fourier effect is incorporated into the heat equation to demonstrate its validity on picosecond-to-microsecond times in the nanodot array.

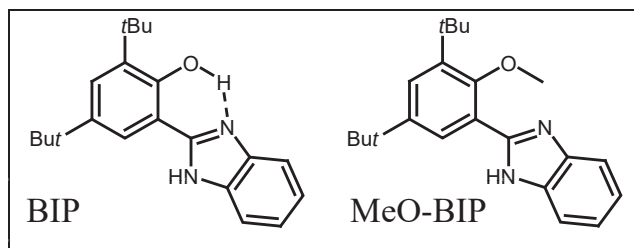
Plasmonic nanodots will be prepared by varying the array density, period, and TiO₂ thickness, and their absorption spectra will be measured. Transient absorption will be measured for the photocatalytic samples with excitation. Simultaneous temperature and gas morphology measurements will be performed in SPR imaging.

Experimental and Theoretical Insights into Concerted Proton Electron Transfer

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Concerted proton-electron transfer (CPET) reactions play an important role in natural and artificial photosynthetic transformations, providing low energy pathways in charge separation, charge transport and redox catalysis. Contrary to electron transfer (ET), for which rigorous theoretical models have been well established, theoretical treatment of CPET is still emerging. One of the challenges in CPET model refinement is the scarcity of experimental data which provides highly accurate values of reaction driving forces, reorganization energies, vibronic coupling and reaction rates. Our approach leverages the ability of pulse radiolysis to rapidly generate highly reactive oxidative radicals with accurately known reduction potentials (ca. 15 mV precision)¹ and follow their reactivity with CPET or ET donors.

The reaction between CPET reagent benzimidazole phenol (BIP) and a series of arylamine and biphenyl radical cations generated radiolytically followed a free energy relationship with experimentally determined reorganization energy $\lambda = 1.1$ eV and vibronic coupling $|V_{elS}| = 200$ cm⁻¹. Interestingly, a structurally similar molecule bearing methyl group in place of acidic proton and incapable of CPET reaction (MeO-BIP) exhibited very small electronic coupling for ET $|V_{el}|$ of only ca. 40 cm⁻¹, which is typical for the type of electron acceptors used in this work. In this poster presentation, we discuss new insights into mechanism of CPET using computational and experimental results and compare it to the ET process.



1. Polyansky, D. E., Transient methods for understanding the properties of strongly oxidizing radicals. *Chem. Commun.* **2025**, 61, 3461-3471.; Polyansky, D. E.; Manbeck, G. F.; Ertem, M. Z., Combined Effects of Hemicolligation and Ion Pairing on Reduction Potentials of Biphenyl Radical Cations. *J. Phys. Chem. A* **2023**, 127, 7918-7927.

Free Carrier Generation in Mixed-Dimensionality Heterojunctions

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Garry Rumbles,¹ Andrew J. Ferguson,¹ Colin Nuckolls,* Obadiah G. Reid¹

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This poster will cover studies aimed at understanding the roles of molecular structure and nanoscale dimensionality in facilitating the directed movement of excitons, charges, and electron spins in mixed-dimensionality donor/acceptor interfaces.

I will discuss the use of photoinduced absorption detected magnetic resonance (PADMR) to measure charge separation in both molecular and hybrid donor acceptor heterojunctions. Distance-dependent magnetic coupling in molecular heterojunctions serves as a ‘ruler’ to measure electron-hole distances following photoinduced charge transfer (CT), and how these connect to the thermodynamic charge transfer driving force (ΔG_{CT}) and free charge yields. These results facilitate the development of a detailed balance model to predict limiting OPV device efficiencies and how they depend on driving force, reorganization energy, interface dimensionality, disorder, and dielectric constant. The second PADMR study explores mixed-dimensionality donor/acceptor heterojunctions between 1D semiconducting SWCNTs and 2D monolayer MoS₂. PADMR reveals large steady-state spatial separation (> 2 nm) between electron and hole spins (CS*, **Fig. 1a**) following interfacial charge separation and reveals a prominent interfacial recombination pathway that populates SWCNT triplet states (T_{a-c} , **Fig. 1a**). Driving the distinguishable magnetic resonance transitions of weakly magnetic dipole-coupled charge separated states versus more localized SWCNT triplet states also demonstrates that the CS states and triplet states have distinct absorption signatures, clarifying prior transient studies.

I will also discuss ultra-fast spectroscopic studies on interfaces featuring chiral donors and acceptors, aimed at probing the impact of chirality on spin-selective photoinduced charge transfer via the chirality-induced spin selectivity effect (**Fig. 1b**). We find a complex dependence on the helicity of electron donor (SWCNT), acceptor (perylene diimide, PDI), and the intervening DNA used to extract the enantiomerically pure SWCNTs. The results suggest potential pathways towards spin-selective photochemical and opto-electronic systems.

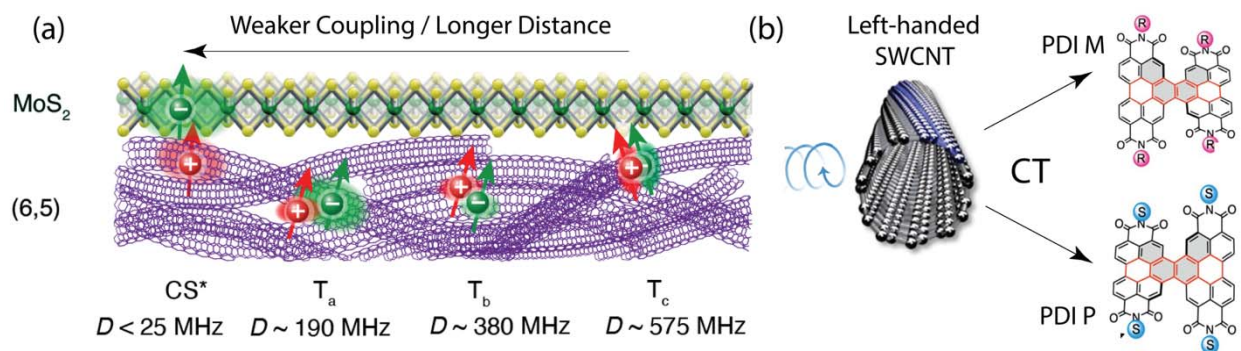


Figure 1. (a) Long-range charge-separated state (CS*) and triplet states (T_a - T_c) identified in SWCNT/MoS₂ heterojunction by PADMR. (b) Chiral/chiral heterojunctions between SWCNT and perylene diimide (PDI) enantiomers.

Radiolysis Studies of Lanthanide and Actinide Diglycolamide Complexes

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Hydrophilic diglycolamides (DGA) have been proposed for use as a holdback reagent of curium from americium, giving potential for easy separation of these two closely related elements. DGA ligands are also being deployed on an industrial scale for lanthanide separations. However, reagents used in reprocessing streams are exposed to intense radiation fields where ionizing radiation can degrade the ligand through radiolysis-induced radical reactions and ultimately compromise its performance. Ionizing radiation can also cause radiolysis-induced transient redox reactions with metal ions in solution. For these reasons, efforts are made to study the chemistry of tetramethyl diglycolamide (TMDGA) to better understand their behavior with the actinides in the understudied field of actinide chemistry.

We have prepared and fully characterized $[M(\text{TMDGA})_3]^{3+/4+}$ complexes (TMDGA = tetramethyldiglycolamide) with all Ln^{3+} cations except Pm^{3+} and with An^{3+} cations from Pu^{3+} to Cf^{3+} , including the rare Bk^{3+} complex as shown in Figure 1 (*left*). Structural characterization and spectroscopic details provide valuable insights into the modes of reactivity of these molecules including that the Pu^{3+} undergoes somewhat rapid oxidation to Pu^{4+} . Moreover, pulsed radiolysis studies of the nitrate radical, $\text{NO}_3^\bullet$, with $[\text{Nd}(\text{TMDGA})_3]^{3+}$ demonstrate that the rate of reaction of uncomplexed TMDGA is not the same as that of $[\text{Nd}(\text{TMDGA})_n]^{3+}$ ($n = 1, 2, \text{ or } 3$) (Figure 1, *right*). Studies are underway to determine if the radiolysis products also differ between DGA ligands that are not complexed by metals versus those that are bound to metal ions and if there are reactivity differences between Ln^{3+} and $\text{An}^{3+/4+}$ complexes.

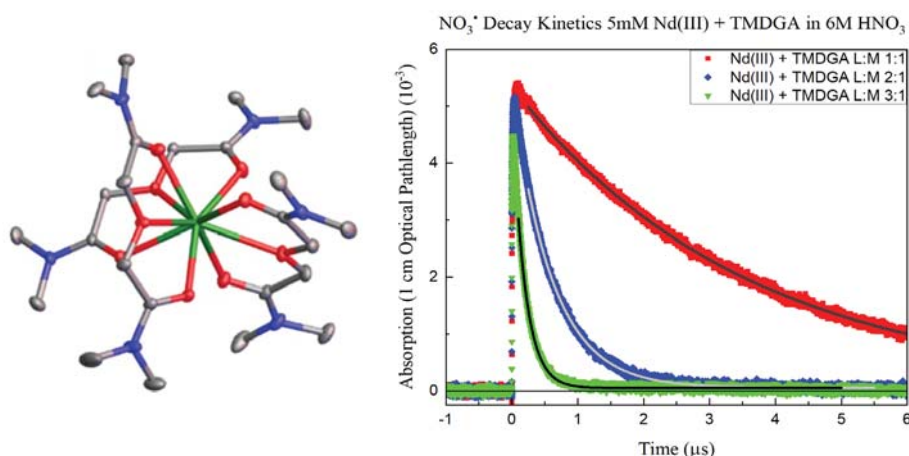


Figure 1. (*left*) Structure of a $[\text{M}(\text{TMDGA})_3]^{3+/4+}$ ($\text{M} = \text{Ln}^{3+}$ or $\text{An}^{3+/4+}$; TMDGA = tetramethyl diglycolamide) complex. (*right*) Radiolysis decay traces of $\text{NO}_3^\bullet$ in the presence of $[\text{Nd}(\text{TMDGA})_n]^{3+}$ ($n = 1, 2, \text{ or } 3$).

Ultrafast Photoreduction Driven by Interfacial Spin-Exchange in Manganese-Doped Quantum Dots

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Project Objective: The work presented in this abstract is part of the project titled “Photoinduced Electronic Dynamics at Chemically Assembled Quantum Interfaces”. In the current project cycle, its focus is on novel approaches to harness the energy of hot, unrelaxed carriers in photochemistry and other photoconversion technologies. In particular, we aim to exploit a recently discovered class of ultrafast spin-exchange (SE) interactions in Mn-doped quantum dots (QDs) for generation, stabilization, and transport of hot carriers, and their utilization in practical chemical reactions. In this abstract, we focus on our recent demonstration of ultrafast photoreduction driven by interfacial spin exchange in manganese (Mn)-doped QDs.

Results & Discussion: Spin-active dopants offer a powerful yet underexplored route to reshape interfacial redox chemistry in quantum-confined semiconductors. Here we show that Mn doping in CdSe QDs enables an ultrafast SE-mediated pathway for electron transfer that allows methyl viologen (MV^{2+}) to be reduced even under conditions where conventional band-edge energetics are unfavorable (Fig. 1a).

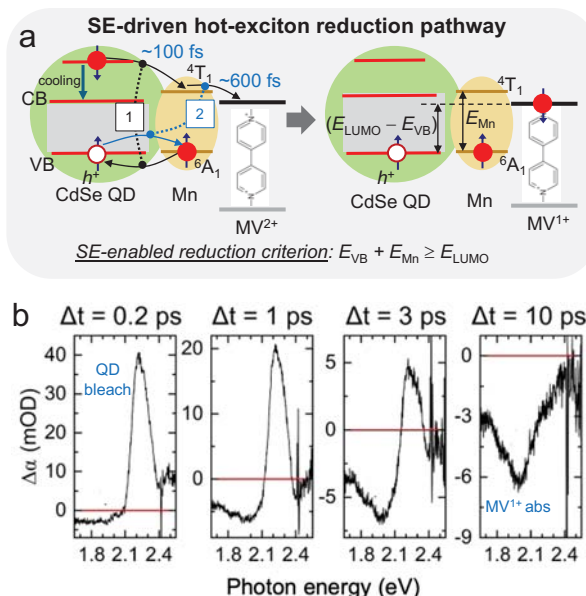


Figure 1. a, Schematic of SE-mediated hot-exciton reduction: ultrafast capture of a hot exciton by a Mn^{2+} ion (~100 fs), followed by spin-flip relaxation via electron transfer to MV^{2+} and compensating hole transfer from the QD (~600 fs), yielding MV^{1+} . **b,** Transient absorption measurements of Mn:CdSe QD- MV^{2+} complexes showing rapid depopulation of the QD electron state (1S bleach) accompanied by the buildup of MV^{1+} absorption.

This mechanism operates across resonant, hot-exciton, and off-resonant (energy-uphill) regimes, underscoring its robustness and identifying SE coupling—not band alignment—as the primary determinant of electron-transfer rates and efficiencies. These findings establish magnetic doping as a viable strategy for harvesting hot carriers and enabling energetically demanding redox transformations in photocatalytic and energy-conversion systems

Future Work: In future research, we will continue exploring SE interactions in the context of SE-enabled photochemistry. We also aim to demonstrate long-range hot-electron transport (sub-millimeter scale) enabled by hot-carrier regeneration via SE-Augur up-conversion.

Energy Capture and Conversion in Self-assembled Chlorophyll Analogues

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Tetrapyrroles – Nature’s chromophores – include the bacteriochlorophylls, chlorophylls, and porphyrins that capture and convert solar energy at a scale sufficient to power most life on Earth. While extensively studied as monomers and within proteins, their properties in synthetic, strongly coupled organizations remain largely unexplored. We focus on engineering novel tetrapyrrole macrocycles for self-assembly into materials that engender energy transport or charge separation. Our integrative program encompasses molecular design, synthesis, spectroscopy, and theoretical simulations that, together, offer insights into how structural organizations drive each photophysical and photochemical processes (**Figure 1**).

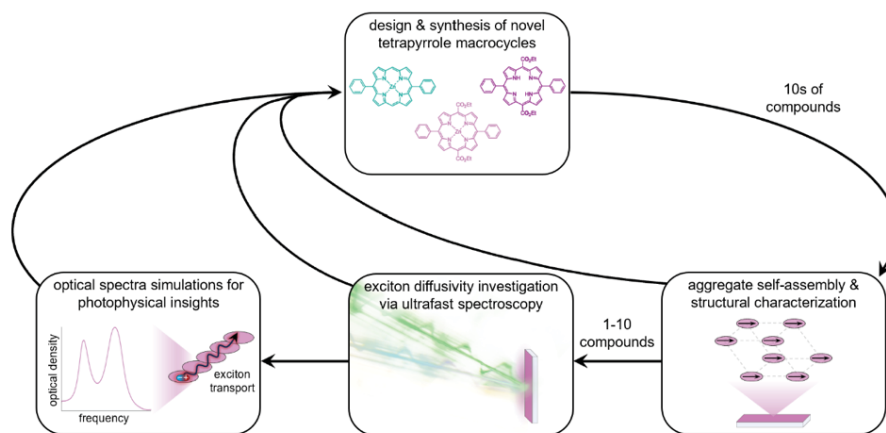


Figure 1. Iterative molecular design of tetrapyrrole supramolecular aggregates.

Application of this workflow identified a zinc porphyrin that assembles in an extended three-dimensional array that supports long-distance exciton transport. We synthesized a zinc(II) 5,15-dicarboethoxy-10,20-diphenylporphyrin and an analogue lacking dicarboethoxy groups. While both porphyrins self-assembled into extended aggregates, fluence-dependent ultrafast exciton annihilation measurements revealed that the porphyrin containing dicarboethoxy groups gave rise to diffusion with a 2-D diffusion length of 39.6 nm and a diffusion constant of $7.1 \times 10^{-3} \text{ cm}^2\text{s}^{-1}$, whereas no diffusion was observed for the porphyrin lacking dicarboethoxy groups. Structural and spectroscopic analysis along with corresponding simulations revealed coordination between the central Zn(II) ion and the carboethoxy groups, generating an extended three-dimensional slipped-stacked organization. In the analogue lacking dicarboethoxy groups, only local organization was observed. This study suggests that synthetic tetrapyrroles can be designed and chemically tuned to produce not just local organization but long-range patterns of assembly that give rise to long-distance exciton transport.

Enhancing the Durability and Efficiency of III-V Photocathodes for Fuels Production

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Nathan S. Lewis

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Although III-V semiconductors can achieve high efficiencies for conversion of visible photon energy to chemical bond energy, III-V photocathodes exhibit poor stability in highly acidic or alkaline electrolytes. We pioneered the use of inert yet conductive metal oxide protection layers to stabilize III-V photoanodes. We have recently extended this metal oxide protection layer strategy to III-V photocathodes, primarily focusing on the protection of p-InP as an example material. We have spectroscopically elucidated the electronic band structure at the interface between p-InP and several candidate protection layers (TiO_2 , Nb_2O_5 , HfO_2 , or Ta_2O_5) as well as developed electrochemical protocols to evaluate the effectiveness of these oxides as protection layer materials for p-InP photocathodes. These analyses link the electronic structure to photoelectrochemical performance, allowing for effective protection layer materials to be predicted via known material properties. In contrast to all other known metal oxides, Nb_2O_5 uniquely conducted photogenerated electrons, blocked interfacial transfer of holes, and exhibited both thermodynamic and kinetic stability in acidic aqueous electrolytes. The interfacial behavior was characterized fully by surface science and electrochemical techniques, including the dual working electrode method.

We have also explored the synthesis of woodpile mesostructures via inorganic phototropic growth. Photoelectrochemical deposition of semiconducting Se-Te using spatially uniform, linearly polarized illumination produced arrays of lamellae oriented parallel to the optical polarization direction. Continued deposition in conjunction with an orthogonal polarization shift produced aligned bridging features that spanned the void space between, and were orthogonal to, the preexisting lamellae. The height and pitch, respectively, in each layer of the woodpile were a function of the charge density and illumination wavelength during deposition. These structures provide a scalable, flexible platform that is amenable to spatially controlled decoration with electrocatalysts and may be tuned to optimize light collection as well as product ingress/egress.

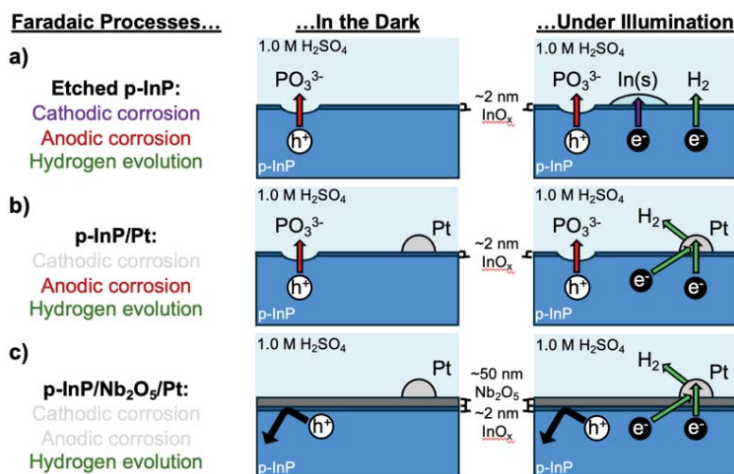


Figure 1. Corrosion processes of etched p-InP (a), platinized p-InP (b), and Nb_2O_5 -coated p-InP with a Pt catalyst (c) in acidic media with and without, respectively, illumination. With a Pt catalyst, cathodic corrosion due to In plating is suppressed in favor of hydrogen evolution, but anodic corrosion continues. With a Pt catalyst and Nb_2O_5 protection layer, both cathodic and anodic corrosion processes are suppressed.

Stepwise ET-HAT for Selective CO₂ Conversion and N₂ Reduction

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Brookhaven National Laboratory
Upton, NY 11973-5000

The catalytic activation and conversion of small molecules in air such as CO₂, N₂, H₂O and O₂ involves multi-electron, multi-proton processes. As a result, many challenges arise regarding catalyst efficiency, durability and selectivity. In the case of CO₂ conversion using molecular catalysts, a two-electron reduction is typically required that leads to either CO₂ binding to generate a metallocarboxylate or protonation to generate a metal hydride. Competition among these pathways leads to a variety of products such as CO, H₂ and formate. In dinitrogen reduction the situation is even more complicated and low temperatures and insoluble proton sources are typically needed to inhibit competing HER. We have developed a new strategy to tackle these issues. It involves sequential electron transfer (ET) and formal hydrogen atom transfer (HAT) steps that avoid the need for two-electron reduced species and/or proton sources, Figure 1.

We have successfully used this strategy for selective and efficient *photochemical* CO₂ conversion to formate. A saturated coordination environment around the transition metal enhances catalyst stability and enables access to first-row transition metal-based catalysts. In this approach, the redox chemistry takes place at the ancillary ligands while the thermally activated processes required for catalysis take place at another ligand (for example, CO). The use of molecular photosensitizers enables the stepwise ET-HAT process in a controlled fashion avoiding HER and CO generation while CO₂ conversion to formate is achieved with over 95% selectivity. The same ET-HAT strategy has been used to achieved, for the first time, catalytic *chemical* conversion of CO₂ to formate and formic acid.

In the case of N₂ reduction strong reductants are typically combined with strong and insoluble acids to achieved reduction of end-bound N₂ or M≡N after N₂ cleavage. In addition, the catalysis is carried out at low temperature. Our stepwise ET-HAT process enables fast reduction of metal-nitridos to ammonia at room temperature and with high selectivity as demonstrated by a combination of XAS (NSLS-II), high resolution mass spectrometry, single-crystal X-ray crystallography and DFT calculations.

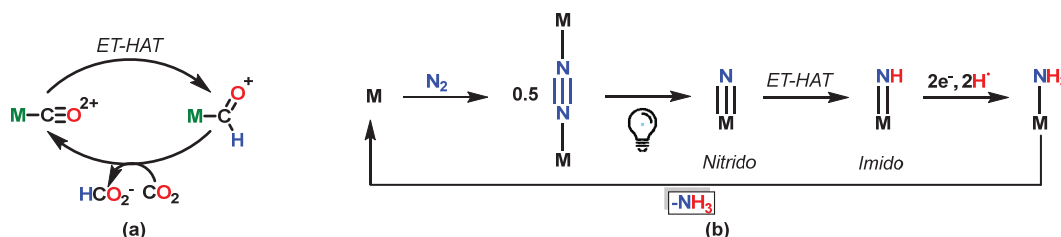


Figure 1. Strategies for selective CO₂ conversion and N₂ reduction with stepwise ET-HAT.

Collapse of the State Vector and Nonlocal Correlations in Quantum Mechanics

Alfy Benny, Yuanheng Wang, Ian Lim, Gregory D. Scholes

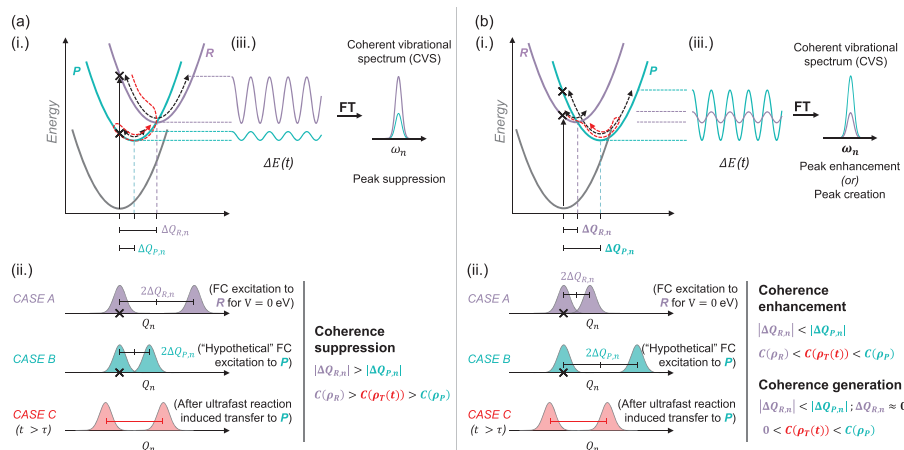
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The measurement postulates of quantum mechanics imply the ‘collapse’ rule, which intuitively resolves the problem of obtaining a physical measurement outcome from a superposition state. Further, it guarantees that a subsequent measurement on the state also gives an eigenvalue. Researchers have sought a microscopic explanation for collapse of the state vector for a century. For example, Omnès in Chapter 2.6 of his book discusses reduction of the wavepacket, also known as collapse of the wavefunction and concludes that “... reduction appears as one of the major problems in the theory [of measurement]”. Dickson, Chapter 2.2 of his book, who criticizes the supposition of collapse, writes “What is it about *measurement*, or *observation* (as opposed to other physical processes), that causes such a collapse?”

Yet, if a plausible mechanism for collapse can be found, it would enable perplexing question about measurement to be answered intuitively based on the postulates. I will propose a resolution of the problem for the case of separated subsystems associated with an entangled state. Further, it will be shown why the collapse of a state vector for one subsystem in a composite state is correlated with the collapse of the state vector of the other subsystem, without the need for any kind of inexplicable long-range interaction after the subsystems separate. That ensures correlations in the measurement outcomes of the separated subsystems. These nonlocal correlations arise without any kind of ‘spooky action at a distance’.



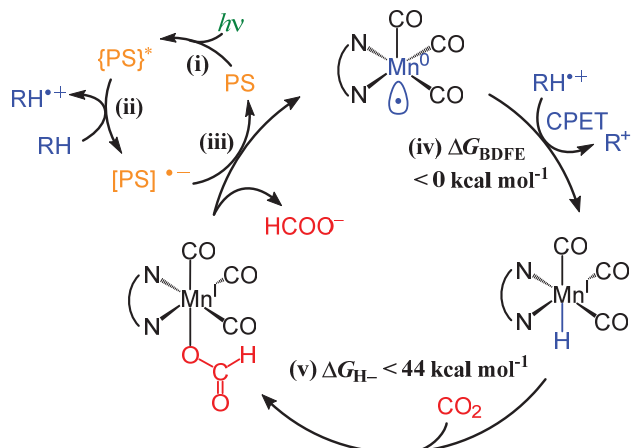
The poster will also include a highlight summary of recent work studying how vibrational wavepackets evolve in systems undergoing ultrafast electron transfer reactions. Using numerically exact quantum dynamics, we show that quantum quench effects significantly impact the final vibrational coherence observed in ultrafast excited-state proton and electron transfer reactions. We find that the multidimensional quantum dynamics provide microscopic insights to prior experimental observations, such as selective suppression or amplification of coherent vibrational spectra, peak intensities, phase-shifts, and damped oscillations of vibrational beats. A summary of planned experiments will be given.

Radiation Chemistry as a Tool to Decipher CPET Pathways in Manganese-Mediated CO₂ Reduction to Formate

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Earth-abundant, homogeneous manganese-based catalysts have received intense interest in recent years in both electro- and photocatalytic conversion of CO₂. Most of these catalysts produce CO with high selectivity, while conversion to formate is less common, in some cases requiring exotic solvent mixtures. The development of catalysts that are selective for formate is beneficial, since formic acid is a commodity chemical with a wide range of uses. The key to generating formate as a product is the efficient production of a metal-hydride intermediate that reacts with CO₂ to produce formate. A promising strategy for making Mn–H intermediates under mild conditions during electrocatalysis utilizes concerted proton-electron transfer (CPET) mediators, resulting in significantly enhanced efficiency for CO₂ electroreduction to formate.

We hypothesize that in photocatalytic applications, selective CO₂ to formate conversion can be achieved by harnessing CPET from appropriate H-atom donors, for the generation of one-electron reduced metal hydride (M–H) intermediates (see Figure). This bypasses the two-electron reduced form of the catalyst, avoiding competing CO and H₂ evolution pathways. Pulse radiolysis (PR), which is a radiation chemistry tool, is a powerful way to rapidly and cleanly produce one-electron reduced species for mechanistic investigations by time-resolved spectroscopy, thus making it ideally suited to the study of CPET-mediated Mn–H formation. Our initial focus is on the application of PR coupled with time-resolved infrared spectroscopy (PR-TRIR) to characterize the formation of Mn–H intermediates with model systems, such as Mn(dppf)(CO)₃Br (dppf = 1,1'-bis(diphenylphosphino)ferrocene), and determine the kinetics of key reaction steps. Here, we present the results of these PR studies, together with steady-state IR spectroscopy and electrocatalysis.



We thank our collaborator, Prof. Jonathan Rochford (U. Mass Boston), for the synthesis and electrochemical characterization of the manganese complexes.

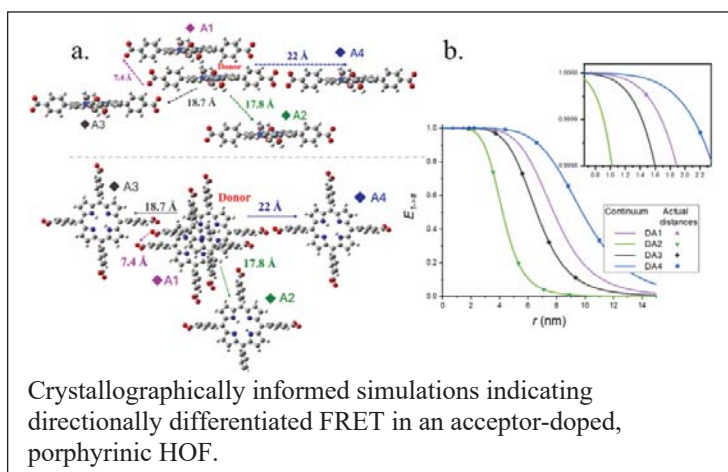
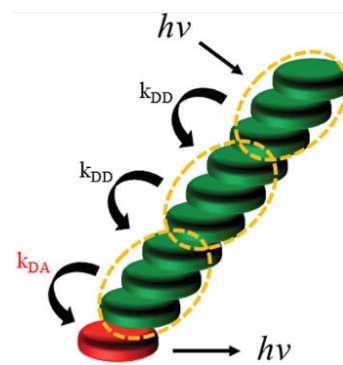
‘Antenna-Like’ Light-Harvesting in Partially Metalated Porphyrin Hydrogen-bonded Organic Frameworks

Alice Li, M. Irfan¹, Subhadip Goswami, Lucas Besteiro¹, Richard Schaller, Joseph Hupp

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Arrays of light harvesting molecules with long-range order hold promise as materials capable of efficient collection of photons as well as rapid transport of captured solar energy to chemical catalysts. Hydrogen-bonded organic frameworks (HOFs) could be promising artificial light-harvesting platforms, due to their crystalline nature, their molecular-scale porosity, and their comparative ease of synthesis. HOFs containing both zinc-metalated tetrakis(4-carboxyphenyl)porphyrin (Zn-TCPP; energy donor) and corresponding free-base porphyrin (FB-TCPP; energy acceptor) units have been examined and found to display ‘antenna-like’ light harvesting behavior. Using steady-state and time-resolved emission spectroscopy, energy transfer from zinc porphyrin to free-base porphyrin was assessed. We find that, in the limit of high dilution of the acceptor, energy can be transferred from any of ~70 donor chromophores. Application of Förster resonance energy transfer (FRET) theory and time-dependent density functional theory to a simplified model of the HOF, suggests that Coulomb coupling can account for energy transfer from ~30 Zn-TCPPs. Closer examination of FRET modeling indicates a strong bias for transfer along the direction of porphyrin stacking. We speculate, by analogy to the behavior of related MOFs (metal-organic frameworks), that rapid transport of molecular excitons (via donor-to-donor FRET) accounts for participation of Zn-TCPP units beyond the ca. 30 expected from simplified FRET modeling. Measurements at comparatively high acceptor concentrations indicate a limiting energy-transfer efficiency of ~95%, with a limiting time of roughly 20-50 ps. These findings suggest that stacked chromophores within HOFs can act as light harvesting ‘antennae’ and may offer prospective application as photochemical energy-conversion systems.

Experiments with a related HOF show that light harvesting and energy transport can be exploited to sensitize the catalytic reduction of unbuffered water by a Keggin-like polythiometalate cluster present at low loading within HOF channels.



Crystallographically informed simulations indicating directionally differentiated FRET in an acceptor-doped, porphyrinic HOF.

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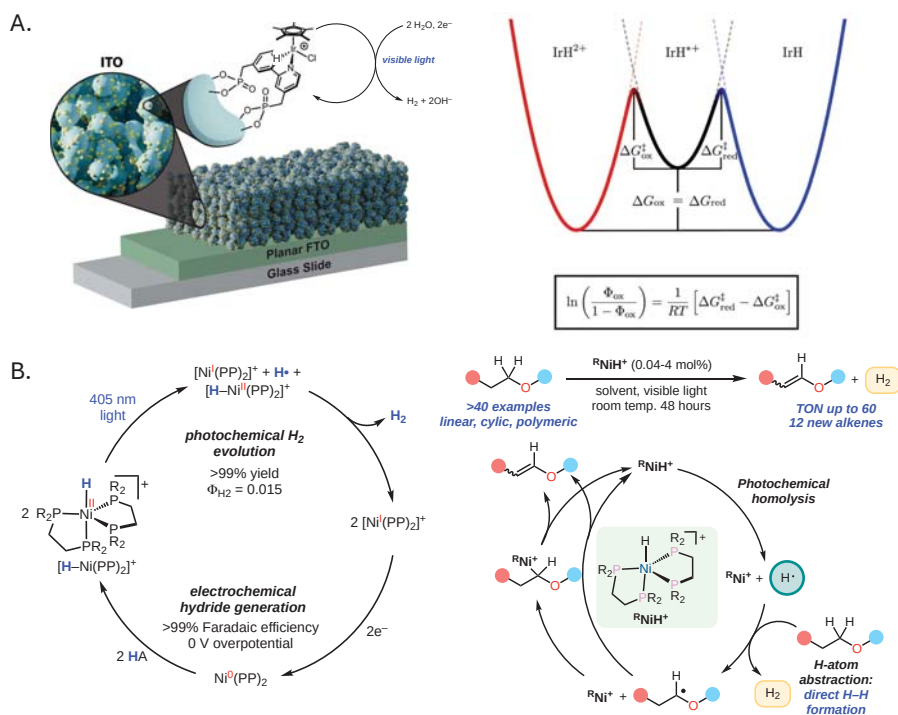
Metal Hydride Photochemistry for H₂ Evolution in Solution and at Interfaces

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The goal of this project is to learn from photophysical and mechanistic studies of isolable metal hydride complexes to develop of photocatalytic fuel-forming reactions. Progress on the light-driven generation of H₂ mediated by molecular photoelectrocatalysts in solution and attached to electrode surfaces will be presented.

Archetypal molecular photoelectrocatalysts for H₂ evolution related to [Cp*Ir(bpy)H]⁺ undergo bimolecular excited-state electron transfer followed by rapid H–H coupling when dissolved in solution. When attached to a conductive metal oxide electrode, however, unimolecular kinetics indicate excited-state electron transfer from the electrode to the Ir hydride. A Marcus-type analysis was developed to better understand the operative pathways during photoelectrochemical H₂ evolution (Panel A).



Nickel hydrides of the type [HNi(diphosphine)₂]⁺ are another promising class of complexes for photochemical H₂ evolution. The nickel complexes produce H₂ via Ni–H homolysis (Panel B). Systematic ligand variations have led to improved quantum yield for H₂ evolution in these complexes, and time-resolved spectroscopic studies have been carried out to understand the origin of the improved efficiency. Reasoning that photogenerated hydrogen atoms could be harnessed for other reactions, we developed the first acceptorless catalytic dehydrogenation of ethers. This photosynthetic reaction is amenable to a wide range of ethers, as well as other molecules with aliphatic functionality. Thermodynamic and kinetic analyses provide insight into the mechanism and point to potential applications.

Understanding causes and effects of hole scavenging on reactivity and efficiencies of nanocrystal-nitrogenase photochemical ammonia production

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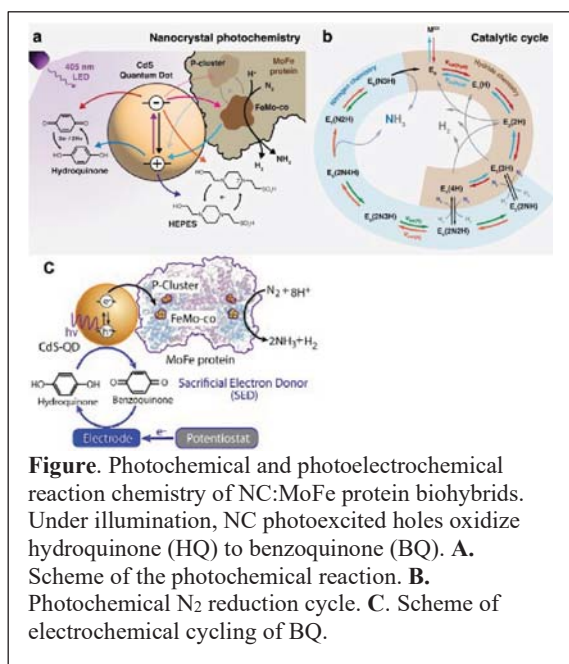
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Our core program investigates the coupling of semiconductor nanocrystals (NCs) with nitrogenase MoFe protein. These systems are enabling an understanding of the parameters and reaction steps that control rates and efficiencies of light-driven N_2 reduction to ammonia (Figure A). A critical aspect is that conditions are dynamic, and changes profoundly affect durations and product yields. Here we focused on the sacrificial electron donor (SED) reaction kinetics, which together with photoexcited electron transfer is essential to regeneration of the NC ground state that sustains catalytic turnover (Fig. A).

We report on two approaches for elucidating the role of SED. One involves explicit calculations of quantum efficiencies and charge separation rates into a kinetic modeling framework for the NC:MoFe protein catalytic cycle (Fig. B). The model enabled simulation of catalytic rates and accounting of the dynamics in reactant and product concentrations, and from NC variability.



Model validation included fits to experimental product formation kinetics under various SED (hydroquinone, HQ) concentrations. Refinements included fits to independent experimental datasets on product formation kinetics, pN_2 dependence, H_2 inhibition, and the time-resolved populations of MoFe protein intermediates obtained from photo-driven, electron paramagnetic resonance spectroscopy. Our results revealed that the oxidized donor product, benzoquinone (BQ) becomes a scavenger of photoexcited electrons, leading to MoFe protein oxidation by photoexcited CdS NC holes. The model also provided a detailed evaluation of the photochemical mechanism of MoFe protein, suggesting that the key N_2 activation step can occur at any one of three catalytic intermediates after accumulation of three, four, or five electrons and protons (Fig. B).

The second is an electrochemical system (Fig. C) designed to reduce BQ to HQ and used to investigate the hole-scavenging reaction via chronoamperometry. A continuous, real-time readout of the SED dynamics under variation in light intensity and SED concentration revealed that rates of hole-scavenging scale with photon flux and exhibit non-linear dependence on SED concentration, enabling a quantitative understanding of hole-scavenging in biohybrid systems.

Photocatalytic Reduction of CO₂ to Formate: Catalysis and Mechanism

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Metal carbonyl clusters (MCCs) have long been recognized as models for the study of heterogeneous surface processes. This project uses MCCs to model nanoparticle and heterogeneous photocatalysis. Recent progress has focused on 1) using electrochemically-derived mechanisms to develop photocatalytic CO₂ reduction to formate, and 2) on time-resolved measurements of fluxional ligand behavior that impacts catalyst performance, and product selectivity. Future plans will expand on the substrate scope and cluster catalyst scope for photocatalytic hydride transfer (HT) reactions.

Several challenges remain in photocatalytic formate formation from CO₂, including the selective generation of a single product along with the requirement for a catalyst that is stable in water. Using guiding data that had been obtained in prior mechanistic electrocatalysis studies of kinetics and mechanism, we developed a CO₂-to-formate reduction using [Fe₄N(CO)₁₂][−] (**1**[−]) as a HT photocatalyst, Ru(bpy)₃Cl₂·6H₂O as the visible-light photosensitizer, and sodium ascorbate as the sacrificial reductant in phosphate-buffered water at neutral pH. Under visible-light excitation, we observed a turnover number of 416 for formate production with > 99% product selectivity and minimal decomposition of **1**[−]. Stern–Volmer analyses of the mechanism indicated that a reductive quenching mechanism is operable, where reduction of [Fe₄N(CO)₁₂][−] is performed by [Ru(bpy)₃]⁺.

Substrate migration is common on the surfaces of heterogeneous and atomically precise cluster photocatalysts. Information can be obtained about these fluxional processes under catalytic conditions using solution-based techniques of molecular photochemistry and using a soluble model photocatalyst such as **1**[−], which is known to convert CO₂ into formate *via* a HT mechanism (Figure 1). In a collaborative study with Brookhaven National Laboratory, we used time-resolved infrared spectroscopic detection to interrogate transient intermediates. The initiation of the reaction was performed either with pulse radiolysis, with a photosensitizer [Ru(bpy)₃]²⁺, or an applied potential, in various experiments. These combined results enabled observation of CO₂ binding to **1**^{2−} and we further deduced that formation of a (CO₂-**1**)^{2−} adduct does not result in CO formation. In addition, migration of the hydride ligand of the intermediate (H-**1**)[−] was observed, and the data are consistent with initial generation of a terminal hydride (H-**1**)[−] that accesses a more thermodynamically stable μ²-bridging hydride with rate of 14.3 s^{−1} and equilibrium constant ~28.6. The μ²-bridging hydride resting state returns to the terminal hydride with rate of 5 s^{−1}. The gated formation of terminal (H-**1**)[−] is likely important in the observed selectivity of HT to CO₂ without H₂ evolution.

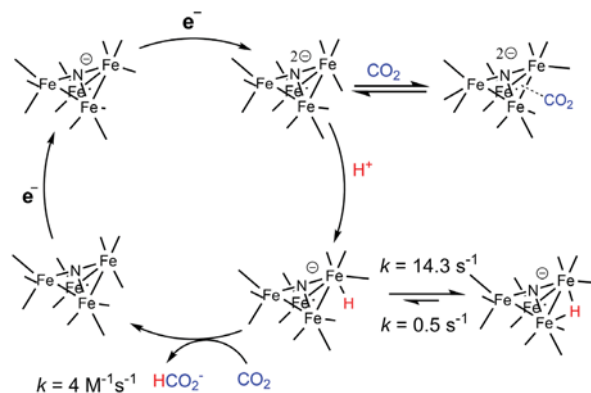


Figure 1. Proposed catalytic cycle, including off-cycle intermediates (CO₂-**1**)^{2−} and (μ²-H-**1**)[−].

Achieving Long-Lived Charge Carrier Formation using Photo-driven Symmetry-Breaking in Tetrachloro-perylenediimide Single Crystals

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Symmetry-breaking charge separation (SB-CS) has often been proposed to improve the efficiency of organic photovoltaics (OPVs) due to the possibility of generating high energy charge carriers that minimize energy loss in the generation of the ion pair state by maximizing the open-circuit voltage. One challenge with utilizing chromophores that undergo SB-CS in the past has been photogenerating a charge-separated state that lives long enough to allow the formation of free charge carriers that can be harvested. In most cases, the ion pairs generated by photo-driven SB-CS are strongly coupled electronically, so that the charges recombine quickly. Our goal is to discover the fundamental design principles that will allow photo-driven SB-CS to quickly and efficiently generate ion pairs that produce long-lived, mobile free charge carriers.

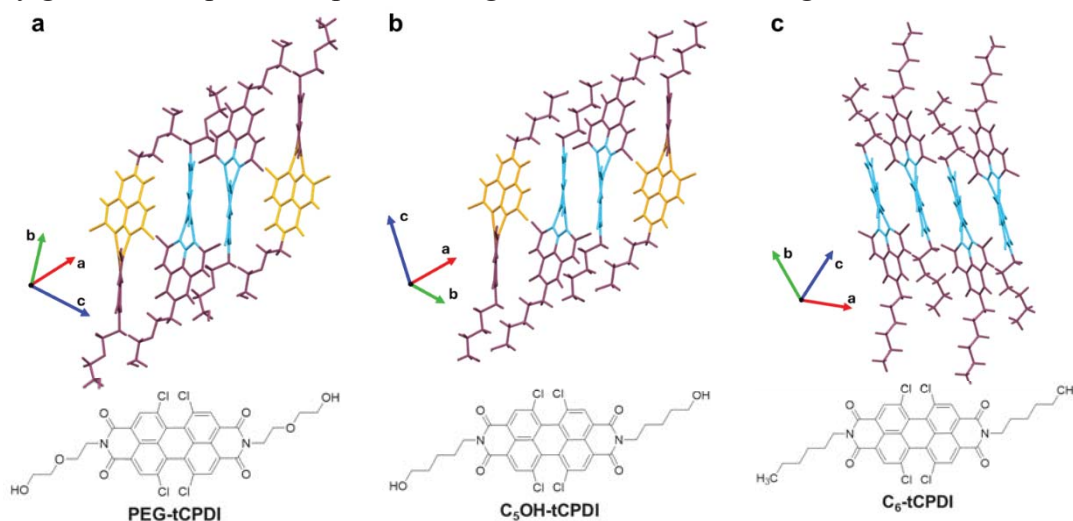


Figure 1: Crystal structures for (a) PEG-Cl₄PDI, (b) C₅OH-Cl₄PDI, and (c) C₆-Cl₄PDI as viewed from the side of a stack of two repeating unit cells in the direction of the a-axis.

We have discovered that controlling the crystal morphology of robust tetrachloro-perylenediimide (Cl₄PDI) single crystals results in ultrafast SB-CS to generate free charge carriers in the crystals. We used polyethylene glycol-based tails (PEG-Cl₄PDI, Figure 1a) and pentanol tails (C₅OH-Cl₄PDI, Figure 1b) to grow crystals whose structure is controlled by hydrogen bonding between the terminal alcohol groups. Photoexcitation of these crystals results in ultrafast SB-CS to produce long-lived (~1 ms !) charge carriers as determined by time-resolved microwave conductivity, while eliminating the terminal alcohol groups (C₆-Cl₄PDI, Figure 1c) results in a structure that yields only excimer trap formation. The identity of the tails do not have a chemical or electronic effect on the Cl₄PDI crystals, yet they control both the crystal packing and electrostatic environment to elicit photophysics that produce long-lived charge carriers. Future plans will include determining how charge carrier formation and mobilities depend on the electronic interaction of the chromophores as determined by the crystal morphology.

Uncovering the Density of States for Quantum Confined Materials by Electrochemical Impedance Spectroscopy

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In this paper, we present a new method to measure the density of states and energy levels for quantized nanomaterials such as semiconductor quantum dots and other low-dimensional systems such as 2D semiconductors, as well as surface bound molecular species such as catalysts through electrochemical impedance spectroscopy. We adsorb or chemically bind these systems to a relatively chemically inert semiconductor and measure the capacitive impedance response in a nonaqueous electrolyte. Through modeling the measured capacitance can be directly related to the density of states of the adsorbed quantum species and we can estimate the energy offset between quantum dot levels and the substrate semiconductor. We demonstrate the method using PbS quantum dots of varying sizes – thereby shifting their energy levels – adsorbed on a SiC substrate. The method was inspired by results from the Rose group that showed that electrochemical impedance can be used to measure the density of states in doped semiconductors such as n- and p-type silicon (J. Am. Chem. Soc. 2024, **146**, 18989). The extension of these results is to treat the adsorbed quantum nanomaterials as surface states and, as long as the dots can exchange carriers with the semiconductor surfaces, they can be described using an extra capacitance in the effective electrical circuit that represents the complex semiconductor/quantum dot/electrolyte interface. By separately measuring and modeling the response of the SiC substrate depletion region capacitance and the electrolyte double layer capacitance, we can then isolate the chemical capacitance that is due to the presence of the quantum dots. When comparing the results with literature data from scanning tunneling spectroscopy (STS), we find good agreement for the quantum dot band gap energy dependence of the position of the first two conduction band states of the PbS quantum dots (Fig. 1) showing that the method can be used for this purpose. We will discuss the limitations of this method and future experiments using other semiconductors and adsorbed species.

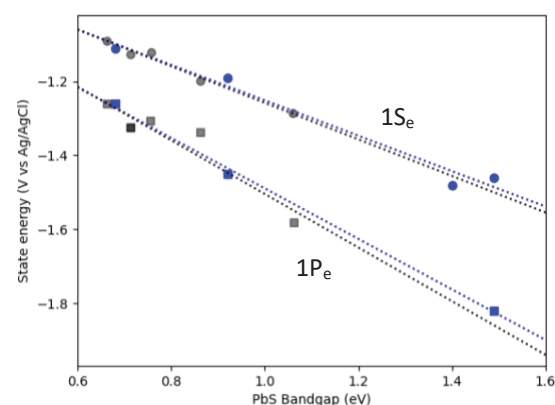


Fig. 1 Comparison of PbS quantum dot energy levels estimated using the electrochemical capacitance method (blue symbols) with literature results from STS measurements for PbS dots (Diaconescu et al Phys. Rev. Lett. **110**, 127406; grey symbols) obtained using scanning tunneling spectroscopy. The dashed lines are corresponding fits of the 1Se (circles) and 1Pe (squares) states as a function of the PbS bandgap for both methods. Since STS does not yield energy levels on an absolute scale, we offset the STS results to the electrochemical scale using a constant factor.

Silicon Nanocrystal-Molecular Catalyst Hybrid Photocatalysts

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Strong electronic coupling is achieved between the molecular catalyst cobaloxime ([Co]) and silicon nanocrystals (Si NCs) through an ethylenepyridine linker derived from vinylpyridine (vpy) to form a semiconductor-molecular catalyst hybrid (Si-vpy-[Co]). This ethylenepyridine tether produces striking changes in the physical behavior of the hybrid system that are absent in the analogous formylpyridine-based construct (Si-fpy-[Co]), indicating that coupling strength is highly dependent on linker chemistry. We will present data from steady-state photoluminescence (PL), UV-vis absorption, and transient absorption (TA) spectroscopies, cycling voltammetry (CV), spectroelectrochemistry (SEC), electron paramagnetic resonance (EPR) spectroscopy, and DFT calculations suggesting that new, hybridized states and strong electronic coupling emerges in Si-vpy-[Co]. The TAS shows an intense signal forming within 250 fs and persisting for at least 5 ns as shown in Figure 1a. These data are compared to those collected from SEC at three different electrochemical potentials, which assigns this TAS feature to a mixture of singly and doubly reduced [Co] species (Figure 1a), suggesting that these long-lived charges originate from high-energy hot electrons localized in [Co]-centered states.

This poster also will delve deeply into DFT calculations that indicate the observed hybridized states emerge not from the expected frontier orbitals, but instead from hybridization between deep Si NC band states and high-lying molecular orbitals of the ethylenepyridine tether and cobaloxime catalyst. Surprisingly, such high-energy hybridized states exist for both Si-vpy-[Co] and Si-fpy-[Co] systems, but strong electronic coupling is found in only Si-vpy-[Co]. The distinction comes via careful inspection of the DFT that shows strong electronic coupling exists in Si-vpy-[Co] due to σ -bonding character at the *Si-ethylenepyridine linker (where *Si denotes a surface Si atom, Figure 1b). These findings highlight how molecular linkers can modulate charge transfer pathways and redefine energy landscapes in systems designed for artificial photosynthesis and related photochemical applications.

Lastly, we will present preliminary photocatalysis data for a related hybrid semiconductor-catalyst system and show its benefits compared to a two-component homogenous sensitized system.

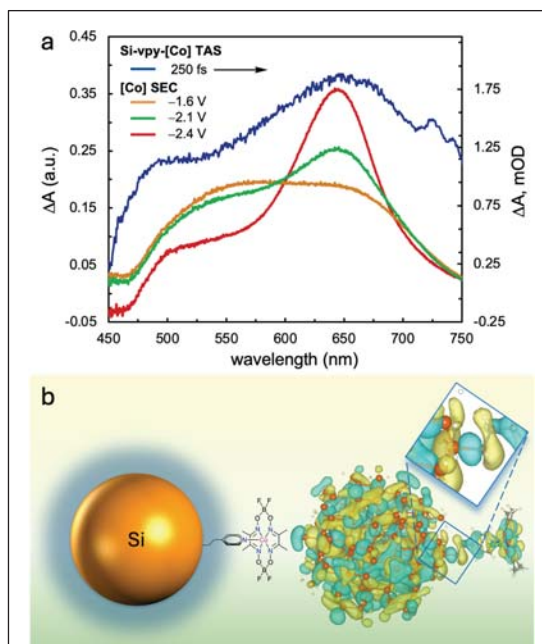


Figure 1. (a) Difference spectra of [Co] SEC absorption data overlaid with Si-vpy-[Co] TAS data at 250 fs. (b) Electron probability visualization from DFT data showing σ -bonding character at the *Si-ethylenepyridine linkage that results in strong electronic coupling in Si-vpy-[Co].

Quantifying Outer Sphere Coulombic Interactions in Water-Promoted Reductive Catalysis

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Efficient photo- and electrocatalytic reductive conversions of carbon oxygenates to value-added fuels and feedstocks using soluble molecular catalysts is rare in aqueous media due to the insolubility of reduced intermediates. Furthermore, water is typically insufficiently acidic to promote the necessary proton-coupled reactions. This poster discusses the ability of pendant cationic groups to address both challenges by enabling water solubility and fully aqueous electrocatalysis by Re and Mn-based catalysts and by the specific stabilization of transition states for the water-assisted rate-limiting protonolysis step.

Regarding aqueous catalysis, we have prepared Mn-bpy based catalysts with pendent tetra-alkylammonium cations related to previously published Re congeners.¹ The cations enable complete compatibility with aqueous buffered media, and the catalysts exhibit bi-modal reductive processes consistent with a low overpotential protonation-first pathway and a high overpotential reduction-first pathway. These differ by ~0.3 V in overpotential and approximately 10-fold in rate. The former operates with an attractive 0.3 mV overpotential at pH 6.8 and durably produces CO with complete selectivity in stark contrast to literature reports of immobilized Mn catalysts in water, which typically produce large amounts of H₂ competitively. Mechanistic details ascertained through electroanalytic methods and aqueous pulse-radiolysis will be presented. Comparison to water-soluble Re catalysts will be made, and projected kinetic improvements will be suggested.

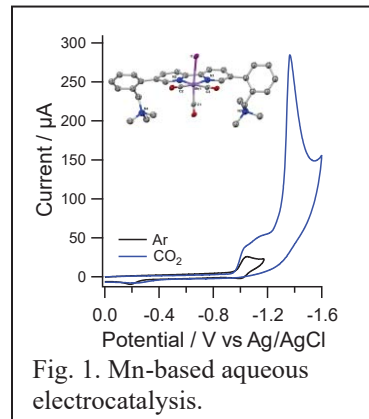


Fig. 1. Mn-based aqueous electrocatalysis.

Quantification of the coulombic interactions between cations and active sites can be made by changing the number and symmetry of the pendent groups. Here we compare Re catalysts bearing two cations on opposite sides of the ligand, two cations on the same side of the ligand, and one cation and discuss how each orientation controls rates and overpotentials for electrocatalysis with water or trifluoroethanol as weak acid sources in acetonitrile and compare the findings to a 5-phenyl-bipyridine neutral ligand model system. The cations promote bimodal catalysis with water as the acid, but we have found that the low overpotential mechanism is not “protonation-first” but is instead “CO₂-first” with CO₂ functioning as the oxide acceptor at mild overpotential. Comparison of these systems to published high-efficiency photochemical reactivity² will be presented.

(1) Rotundo, L., et al. Fast catalysis at low overpotential: Designing efficient dicationic Re(bpy²⁺)(CO)₃I electrocatalysts for CO₂ reduction. *J. Am. Chem. Soc.* **2024**, 146 (36), 24742–24747. (2) Wang, Z., et al. Efficient self-Sensitized photochemical CO₂ reduction using Re(bpy²⁺)(CO)₃(I)²⁺ and Re(bpy²⁺)(CO)₃(CH₃CN)³⁺ photocatalysts with pendent ammonium cations. *J. Am. Chem. Soc.* **2025**, 147 (22), 18796–18813.

The Impact of Electric Fields on Charge Transfer Excited States of Transition Metal Complexes

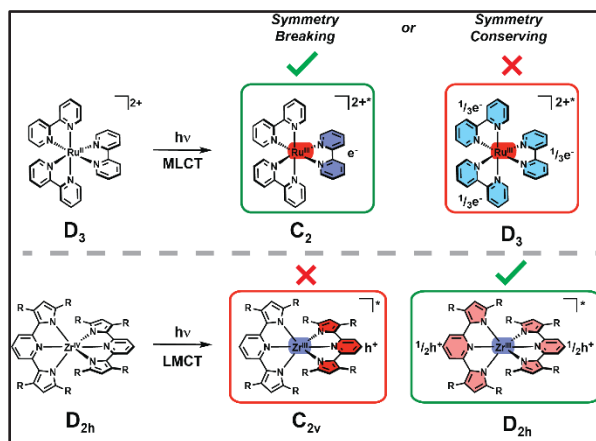
Matthew Goodwin, Hayden Mann, and Gerald J. Meyer

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This research focuses on the impact of an electric field on light driven interfacial electron transfer at metal oxide interfaces and on the absorption and photoluminescence spectra of transition metal complexes. This poster presentation will focus on the latter topic with particular emphasis placed on spin disallowed transitions and those that involve a change in the electronic symmetry [1,2]

Previous DOE-supported research revealed that the electroabsorption spectra of the metal-to-ligand charge-transfer (MLCT) $[M(\text{bpy})_3]^{2+}$ complexes, where bpy is 2,2'-bipyridine and $M = \text{Fe}, \text{Ru}, \text{Os}$, differed significantly in the longer $> 550 \text{ nm}$ wavelength region where singlet-to-triplet transitions are expected. More recent studies of a larger number of $\text{Ru}(\text{II})$ and $\text{Fe}(\text{II})$ diimine complexes revealed a surprising sensitivity to the identity of the diimine ligands without a strong dependence on the metal center [1]. The insensitivity to the central metal indicated that the field enhancements were not a result of spin orbit coupling that should scale as $(Z_{\text{eff}})^4$. Liptay analysis indicated large 8-12 D excited state dipoles and a measurable change in the polarizability. As expected, the triplet charge transfer distances were significantly smaller than the singlet, although the difference was small for the iron complexes. Ongoing work seeks to measure the diimine ligands and related organic compounds to test the applicability of El Sayed's rules.

The electroabsorption spectra of the ligand-to-metal charge transfer (LMCT) excited states of $\text{Zr}(\text{IV})$ complexes with two tridentate ligands revealed that light absorption initiates a large change in polarizability without a dipole moment change. This was unexpected as charge transfer transitions are generally assumed to be vectoral. Hence, as indicated in the accompanying figure the D_{2h} symmetry of the ground state is preserved in the excited state, behavior that is in sharp contrast to that observed for $[M(\text{bpy})_3]^{2+}$ complexes that undergo symmetry breaking charge transfer. A mixed-valent model is proposed to rationalize this very different behavior that is based on the ability of the d orbitals of the central metal to induce inter-ligand electronic coupling.



1. Impact of Diimine Ligand on Singlet-to-Triplet Charge-Transfer Electroabsorption in Iron and Ruthenium Complexes. Maurer, A.B.; Loague, Q.R.; Goodwin, M.J.; Meyer, G.J. *J. Phys. Chem. A* **2024**, 128, 3506-3515.
2. Quadrupolar Ligand-to-Metal Charge Transfer Excited States in Octahedral $\text{Zr}(\text{IV})$ Complexes. Goodwin, M. J.; Loague, Q. R.; Tordella, M. N.; Leary, D. C.; Vecchi, P.; Jackson, G. N.; Milsmann, C.; Meyer, G. J. *J Am Chem Soc* **2025**, 147, 36393-36406.

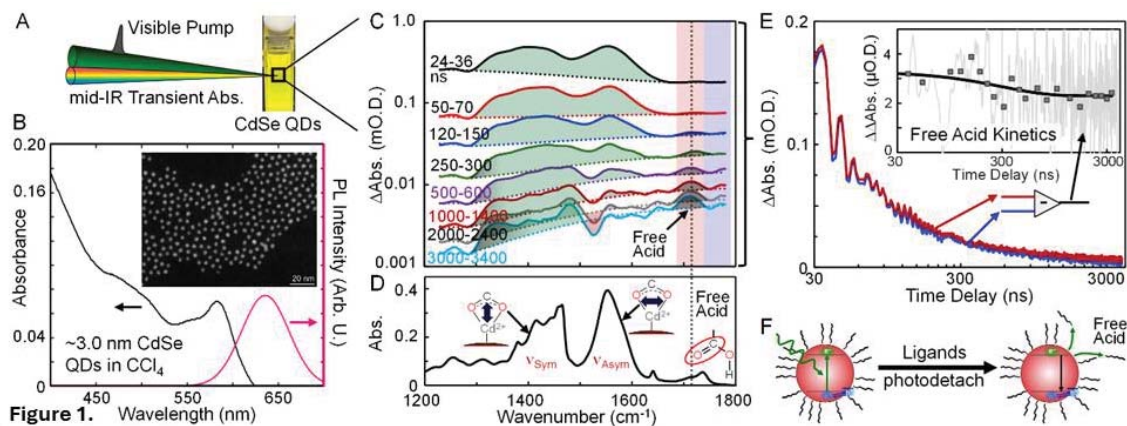
Dynamic Nanocrystal-Ligand Boundaries – Reversible Photoinduced Ligand Detachment

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University Park, PA 16802

The ligand-nanocrystal boundaries of colloidal quantum dots (QDs) mediate the primary energy and electron transfer processes involved in photocatalysis while also protecting nanocrystal surfaces from photochemical degradation and maintaining colloidal stability. In recent work, we demonstrated using time-resolved infrared (TRIR) spectroscopy that certain types of ligand-nanocrystal interactions exhibit marked reduction in surface bonding strength in the excited states of the nanocrystals. Ligands with other types of surface anchoring groups do not exhibit such changes in excited state surface bonding. These findings suggest that it may be possible to design nanocrystal-ligand interactions to control when ligands exhibit weaker bonding to nanocrystal surfaces to simultaneously enhance both their photocatalytic activity and their durability.

The first step toward achieving this goal is to demonstrate that ligands can in fact be detached from nanocrystal surfaces to create a more permeable ligand shell when the nanocrystals are promoted to their electronic excited states. The second step is to show that this detachment is reversible, allowing ligands to reattach to the nanocrystal surfaces after the excited states have relaxed to restore the ground states of the nanocrystals. We demonstrated both steps in CdSe QDs in solution and identified the underlying origins of the changes in excited state surface chemistry. We used TRIR spectroscopy to investigate charge and molecular dynamics at the surfaces of CdSe QDs passivated by oleate ligands in solution following optical excitation to their excitonic excited states (**Figure 1**). We observed Fano-type vibrational features indicating coupling of the ligands to the electronic states of the nanocrystals. We also observed the formation of free oleic acid ligands that



photodetached from the nanocrystal surfaces and diffused into the surrounding solvent environment. These freely diffusing ligands produced the free acid carboxylic vibrational features around 1700 cm⁻¹ in **Figure 1C**. Analysis revealed that photoinduced ligand detachment occurred with nearly unit quantum yields from the CdSe QD surfaces following single-photon absorption. Furthermore, we revealed that the photoinduced ligand detachment process was fully reversible in solution, as indicated by the complete restoration of the steady-state infrared absorption spectra of the QDs in solution after prolonged exposure to the excitation laser.

Photoinduced Charge Transfer Selectivity at Hybrid Molecular–Semiconductor Interfaces

Haoqing Su, Xiaohan Ma, and Shu Hu

Department of Chemical and Environmental Engineering

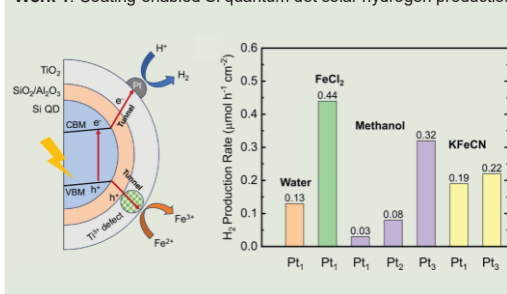
Yale University

New Haven, CT 06510

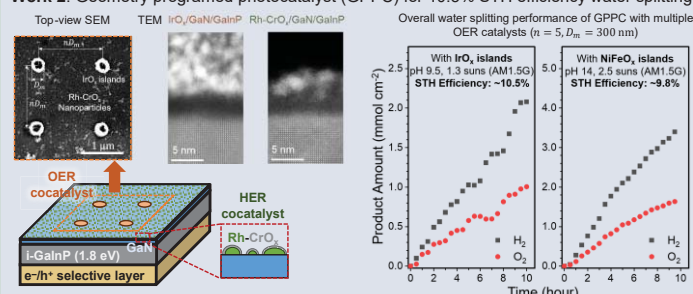
Photocatalysis features multiple, localized redox reactions operating intrinsically within nanoscale proximity at catalytic interfaces, yet the overall photochemical conversion efficiency is governed by the coupled interplay of light absorption, charge separation, interfacial charge transfer, catalysis, and mass transport across the full catalyst–reactor system. In nanoscale photocatalyst particles, or under sufficiently intense illumination, semiconductor band bending can become substantially diminished, approaching near-flat-band conditions and leaving only a limited asymmetric energetic driving force for charge separation. This limitation motivates the search for a new and broadly applicable pathway to photoinduced charge separation, one that remains effective even when the semiconductor operates with minimal energetics-induced driving force.

A particularly promising direction is therefore to harness hybrid molecular–semiconductor photocatalytic interfaces. Along this direction, we will report two discoveries. First, we show that efficient charge separation can be achieved in nanometer-sized Si quantum dots by coupling a porous Si QD film to the $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox manifold at semiconductor–liquid interfaces protected by conformal $\text{Al}_2\text{O}_3/\text{TiO}_2$ bilayer coatings. The coated Si quantum-dot films maintain activity for more than 72 h, establishing a durable, earth-abundant platform. Secondly, we identify a new charge-transfer regime in GaN-coated 1.84 eV GaInP that achieves 10.5% solar-to-hydrogen efficiency for unassisted overall water splitting. We attribute this behavior to a molecular-like photoinduced hole-transfer manifold involving hybrid $\text{Ir}-\text{O}^{2-}$ states, which confers selective hole transfer for water oxidation and thereby enables efficient charge separation with minimal recombination under near-flat-band conditions.

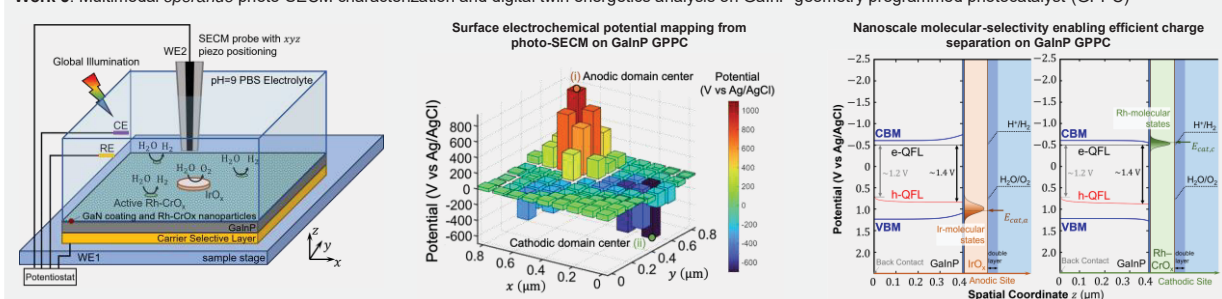
Work 1: Coating-enabled Si quantum dot solar hydrogen production



Work 2: Geometry programed photocatalyst (GPCC) for 10.5%-STH efficiency water splitting



Work 3: Multimodal *operando* photo-SECM characterization and digital twin energetics analysis on GaInP geometry programed photocatalyst (GPCC)



Two-dimensional Electronic Vibrational Spectroscopy: Analysis of a Minimal Pigment-Protein Complex, and a New Method to Reveal Coherence

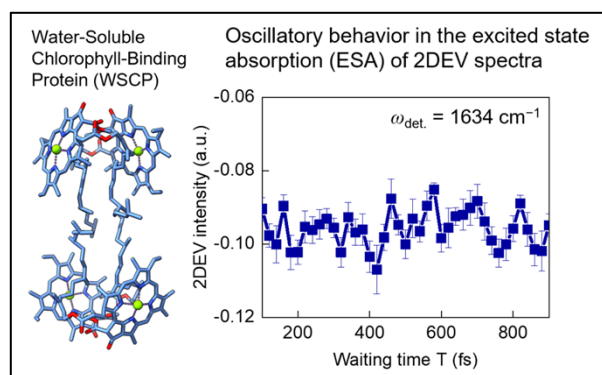
Graham R. Fleming^{1,2}, Mao-Rui Cai², Kunyan Zhang^{1,2}, Lam Lam^{1,2}

¹Molecular Biophysics and Integrated Bioimaging Division
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and

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The mixing of electronic and vibrational states is an ongoing area of exploration in areas ranging from exciton relaxation in photosynthesis to exciton fission. When considering the full Redfield tensor multiple possibilities emerge beyond population relaxation: population to coherence transfer, coherence to population transfer and coherence to coherence transfer.



In our 2DEV spectroscopic study of the water-soluble chlorophyll protein which binds only four chlorophyll molecules we identify distinct excited state features that exhibit ultrafast downhill energy transfer. We see clear oscillations in the excited state signals with a frequency of 284 cm^{-1} . The interpretation of these oscillations in 2DEV spectra is different from that in 2D electronic spectra because an infrared pulse is used as probe. The relatively narrow bandwidth of the IR pulse means many

vibrational wavepacket signals lie outside the bandwidth of the IR pulse centered at 1600 cm^{-1} . After exploring the possible signal origins via non-secular Redfield theory, we find that the likely origin of the oscillating signals is coherence to population transfer. Thus coherence-to-population transfer provides a mechanism by which vibronic coherence can become observable in 2DEV spectroscopy. Coherences generated by broadband electronic excitation influence population relaxation and remain detectable even when the direct detection of the coherence is limited by spectral location and bandwidth constraints.

We propose a new two-dimensional experiment tentatively called “Reversed 2DEV” spectroscopy. The pulse sequence is IR, vis, vis, i.e. the reverse of 2DEV with the initial infrared pulse also serving as the local oscillator for heterodyne detection of the emitted infrared signal. The two-dimensional signal has two IR axes, giving excellent spectral resolution. The 2D maps show both diagonal and off-diagonal peaks and through the use of phase cycling it is possible to separately observe 2D spectra from different Liouville pathways enabling selective observation of distinct vibronic contributions. In addition, the peaks in the 2D maps show differing oscillation frequencies that reflect the energy differences between coupled states.

Investigation of resonance energy transfer in nanoclusters and hybrid nanocluster-carbon nanotube architectures

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Irvine, CA, 92697

Metal nanoclusters (NCs) are atomically precise nanoparticles whose photochemical properties can be tuned with ultra-high precision. This research program's major goals are to test theoretical predictions about excited-state energy transfer processes between NCs and to develop broad-spectrum light harvesting systems (LHS) based on nanocluster chromophores. To achieve these goals, it is necessary to address the challenge of organizing NCs with nanometer-scale precision. This research overcomes this challenge using a bioinspired approach based on programmable DNA assembly and a uniquely tunable class of DNA-stabilized silver NCs (DNA-Ag_N).

We report investigation of resonance energy transfer (RET) efficiency for a series of donor-acceptor pairs of atomically precise NCs. Donor and acceptor DNA-Ag_N pairs are selected from libraries of DNA-Ag_N that have been designed using machine learning (example in Fig. 1A).¹ Then, using the novel DNA scaffold construct in Fig. 1B, the separation between donor and acceptor is varied systematically to experimentally determine RET efficiency for a range of inter-NC separations (Fig. 1C). A range of NC sizes and shapes is being investigated to determine if NC properties influence how RET scales with inter-NC separation. We also report the design and preliminary characterization of RET cascades for UV-to-NIR downconversion. Fluorescence lifetime imaging microscopy (FLIM) shows evidence of RET in a two-NC cascade assembled onto a DNA nanostructure “breadboard.” Finally, hybrid nanostructures composed of atomically precise DNA-Ag_N with controlled chiroptical properties and single-walled carbon nanotubes (SWCNTs), with chiralities selected by DNA sorting, have been assembled. These systems will be used to investigate the effects of chirality on RET efficiency and as platforms for photoinduced current generation.

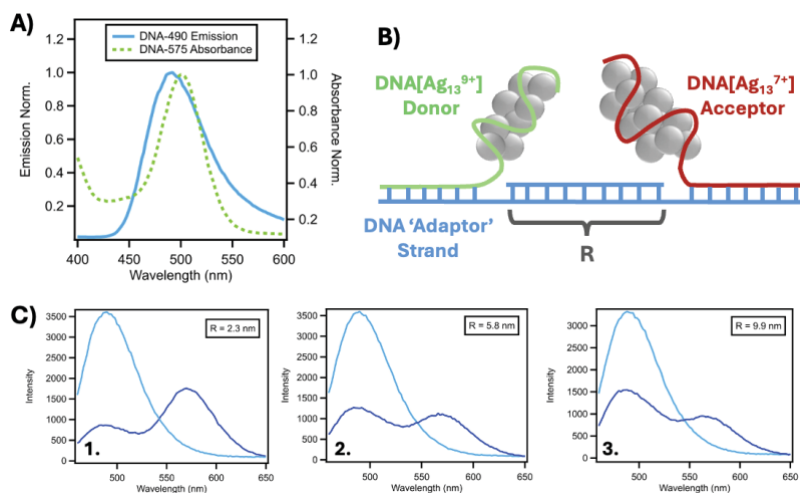


Fig. 1 A. Donor and acceptor NCs selected for spectral overlap. B) Schematic of DNA scaffold for nanoscale control of NC-NC spacing. C) Inter-NC spacing controls RET efficiency.

Acknowledgements: We thank Dr. Ming Zheng of NIST for training and guidance on DNA for chiral selection of SWCNT and Prof. Matthew Sheldon for use of his FT300 spectrometer.

¹ Sadeghi, Mastracco, González-Rosell, Copp, Bogdanov, *ACS Nano* 2024, **18**, 26997–27008.

Tuning Heterojunctions between Carbon Nitride and Single Atom Catalysts for Enhanced Solar CO₂ Reduction

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This project aims to understand how well-defined heterojunctions dictate charge separation in photocatalysis for efficient solar fuel production. We have synthesized heterojunctions between graphitic carbon nitride (C₃N₄) and single atom catalysts (SACs) for use in CO₂ reduction under visible-light irradiation (**Fig. 1**). The heterojunction between C₃N₄ to SACs has been tuned by varying the synthesis time (0 – 3 hours) and subsequently the size of the SAC.



Fig. 1. Tuning the structure of heterojunctions by varying the reaction time and subsequently the size of SACs. A covalent organic polymer is employed as the SAC for this project.

Infrared spectroscopy was employed to follow changes in the structures of the synthesized SACs. Pyrolysis at 220 °C for longer times led to the formation of SACs with extended polymeric network, as indicated by disappeared and broadened absorption features in the infrared spectra (**Fig. 2a**). Two SACs prepared after different times of pyrolysis, SAC-1 (40 minutes) and SAC-2 (3 hours), were chosen to form heterojunctions with C₃N₄ by reacting with urea at 600 °C. Interestingly, the heterojunction prepared from the light-colored SAC-1 shows stronger photoresponse in the visible region than that prepared from the dark-colored SAC-2 (**Fig. 2b**).

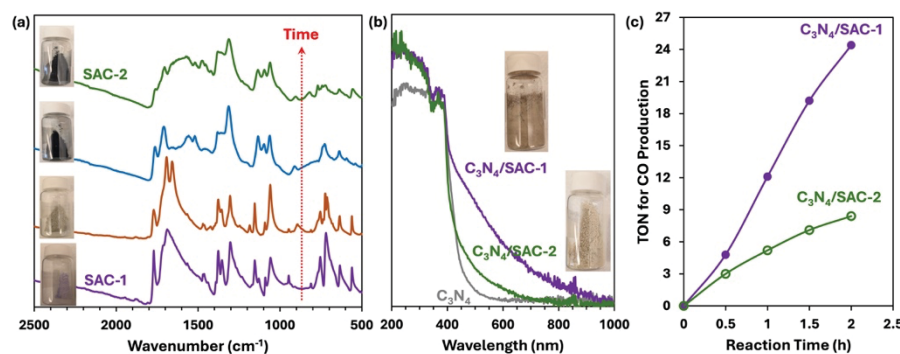


Fig. 2. (a) Infrared spectra of SACs; (b) Optical spectra of C₃N₄ and two C₃N₄/SAC heterojunctions; (c) TONs for CO production in solar CO₂ reduction (TEOA as the electron donor; Co loadings are 0.10 and 0.12 μmol/mg for C₃N₄/SAC-1 & C₃N₄/SAC-2, respectively).

In photocatalytic CO₂ reduction, C₃N₄/SAC-1 demonstrated significantly higher activity than C₃N₄/SAC-2 towards CO production (**Fig. 2c**). Likely, C₃N₄/SAC-1 contains more abundant heterojunctions and subsequently improved charge separation than C₃N₄/SAC-2. Further studies with time-resolved photoluminescence spectroscopy will be conducted to confirm the key role of heterojunctions in promoting photoinduced charge separation. We also plan to investigate the C₃N₄/SAC heterojunctions using X-ray transient absorption spectroscopy in collaboration with Dr. Lin X. Chen at Argonne National Laboratory.

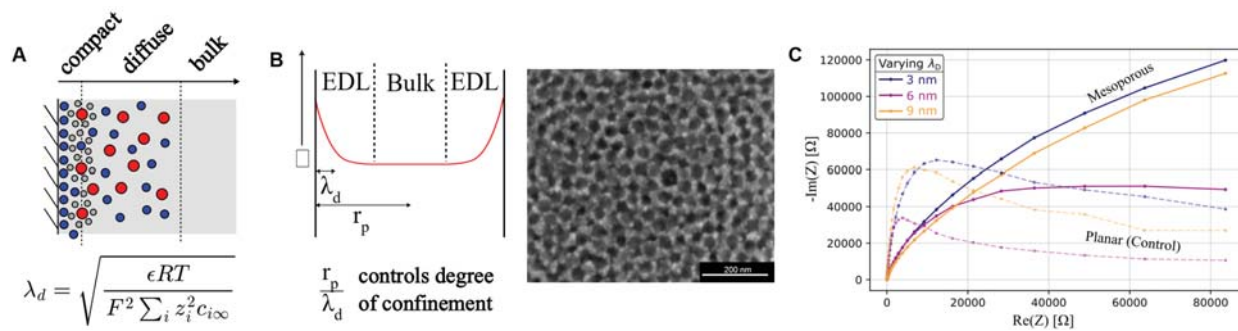
Confinement-Dependent Electrical Double Layer Dynamics in Porous Electrodes

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 Berkeley, CA 94720

The arrangement of ions at an electrode/electrolyte interface (electrical double layer, EDL) governs the distribution of electric potential and ionic charge, directly controlling reaction kinetics, charge transfer rates, and ion transport in (photo)electrochemical systems. While EDL behavior at planar, unconfined surfaces is reasonably well understood (Fig A), the physics of confined EDLs within porous electrodes remains poorly characterized experimentally. Here, EDLs from pore walls can overlap when the pore radius r_p approaches the screening length λ (Fig B): this confinement fundamentally alters the electric field distribution, ion mobility, and charge screening capacity within the pore space, with important consequences for energy storage, electrocatalysis, and photoelectrochemical systems. This has important implications for adaptive junction photoelectrochemical systems, where incomplete pore-space charge screening is predicted to modify band bending motivating the need for a systematic understanding of confined EDL physics.

To address this gap, we are developing a platform of model mesoporous metal electrodes (Au, Pt) with systematically tunable pore sizes, fabricated via block copolymer micelle-templated electrodeposition (Fig B) to tune the confinement ratio r_p/λ . While λ in dilute electrolytes is classically described by the Debye length λ_D , which decreases monotonically with increasing ion concentration c_∞ , our recent work has demonstrated that at higher electrolyte concentrations, λ becomes orders of magnitude larger than Debye theory predicts. By varying electrolyte concentration, we independently tune λ . Preliminary electrochemical impedance spectroscopy (Fig C) on mesoporous Au electrodes already reveals signatures of this transition: the fractional Warburg diffusion exponent decreases systematically with increasing confinement ratio, indicating a crossover from normal Fickian transport toward non-Fickian ion dynamics consistent with distributed tortuosity and emergent ion-ion correlations.

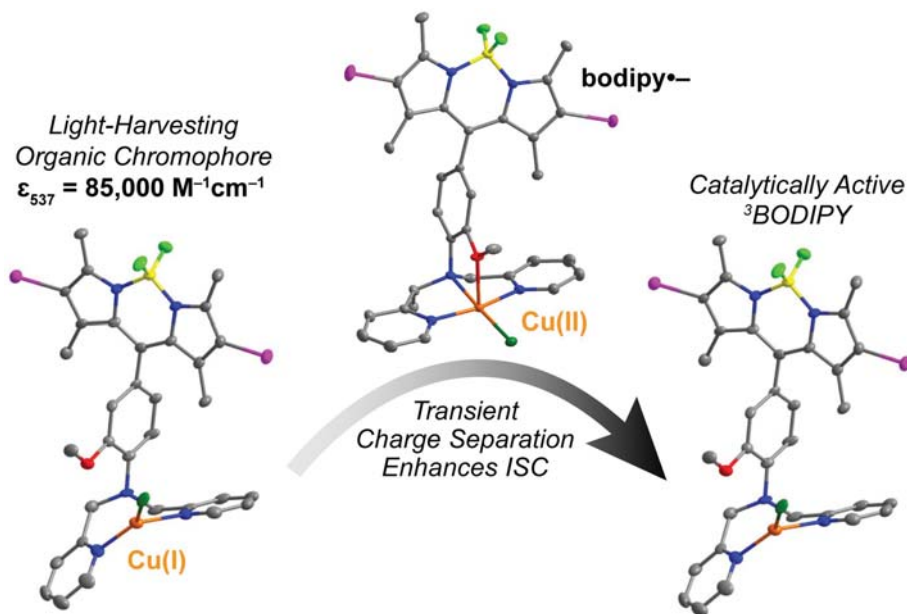
Building on these early results, we will employ a complementary suite of experimental probes to systematically characterize confined ion dynamics across multiple length and timescales, including synchrotron-based XPCS, EQCMD and EIS, and Stark-shift spectroscopy. Together, these measurements will establish quantitative scaling relationships between confinement ratio and ion transport timescales, identify the crossover from Fickian to collective glassy dynamics, and directly link nanoscale EDL structure to macroscopic (photo)electrochemical behavior.



Exploiting Ligand-Centered Transitions to Enhance Upconversion in First-Row Transitional Metal Photosensitizers

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We report the development and study of a series of conformationally switchable copper complexes. These complexes undergo oxidation state-dependent structural changes that mediate fast electron transfer. To define the factors governing the observed rapid redox chemistry in these complexes, we prepared and studied a homologous series of compounds in which the inherent fluxionality of the complexes are modulated through substituent effects. The results of these studies support that dynamicity facilitates rapid and reversible electron transfer in these first row transition metal complexes. We have also applied these switchable coordination complexes toward improving radiation energy conversion processes. By functionalizing them with organic chromophores exhibiting optimal light-harvesting capabilities, we have amplified the upconversion efficiency from 6 to 12%, placing them among the top performing photosensitizers constructed from earth-abundant metals. We further use transient absorption spectroscopy and a series of control compounds to show that this enhancement results, at least in part, from the transient formation of a charge separated intermediate that is uniquely stabilized by our switchable ligand scaffold. Through the complete characterization and application of these complexes in mediating triplet-triplet annihilation upconversion catalysis, we show that both the Cu(I) ion and the conformationally switchable ligand are required for the observed enhancements. These results reveal the power of our bioinspired approach, and lay the groundwork for future innovations therein.

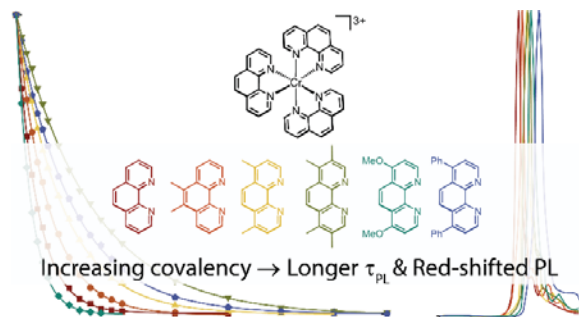
Tailoring Photophysics in Earth-Abundant Transition Metal Photosensitizers

Michael C. Rosko, Adrienne P. Faulkner, Alexandra T. Barth, Jonathan P. Wheeler, Irene Y. Dzaye, Ann Marie May, and Felix N. Castellano*

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Successful excited-state-enhancing substituent effect strategies applied in homoleptic Cu(I) metal-to-ligand charge transfer (MLCT) chromophores have been adapted to the heteroleptic phenanthroline (HETPHEN) platform, leveraging 2,9-mesityl-1,10-phenanthroline (mesPhen) in conjunction with a series of seven distinct 2,9- and 2,3,4,7,8,9-substituted phenanthrolines. The newly conceived CuHETPHEN complexes feature MLCT lifetimes ranging from 62 ns to 443 ns, all of which exhibit unprecedented room-temperature photoluminescence and demonstrate quantitative adherence to the energy gap law. TD-DFT calculations successfully modeled the systematic variation in electronic transition intensities, accounting for the experimentally observed UV-Vis absorption bands across the entire series of molecules while providing detailed structural explanations for the variations in spectral profiles. These heteroleptic Cu(I) diimine chromophores exhibit thermally activated delayed fluorescence (TADF), with delayed fluorescence occurring between closely spaced $^1\text{MLCT}$ and $^3\text{MLCT}$ excited manifolds, having energetic separations of $\Delta E = 698\text{--}1009\text{ cm}^{-1}$, as demonstrated here for the first time. Nanosecond and ultrafast transient absorption spectroscopy verified the MLCT nature of these excited states and extracted the time constants for the initial pseudo-Jahn-Teller distortion and intersystem crossing throughout the entire series of molecules.

The ambiguous design rules for controlling light absorption, photoluminescence, and excited-state decay in pseudo-octahedral Cr(III) chromophores pose key challenges for their implementation as photosensitizers in photocatalysis and optoelectronics applications. Tailored metal–ligand interactions ultimately controlling excited-state decay in these open-shell coordination complexes remain underdeveloped. The influence of 1,10-phenanthroline (phen) ligand substitution on the static and dynamic photophysical properties of six distinct homoleptic $[\text{Cr}(\text{phen})_3]^{3+}$ chromophores is evaluated. Installation of electron-donating methyl or methoxy groups enhances metal–ligand covalency, rigidifying the coordination environment and suppressing nonradiative decay channels. For example, $[\text{Cr}(\text{tmp})_3]^{3+}$ (tmp = 3,4,7,8-tetramethyl-1,10-phenanthroline) exhibits a ligand-field excited doublet state lifetime of 695 μs , which represents a threefold increase over $[\text{Cr}(\text{phen})_3]^{3+}$. The photoluminescence quantum yield (Φ_{PL}) is also enhanced fivefold in the former, increasing from 0.66% to 3.4%. These facile changes in ligand substituents markedly influence excited-state reduction potentials ranging from 1.01 to 1.45 V vs SCE across the series. Long-lived $^2\text{E}/^2\text{T}_1$ excited states drive efficient singlet oxygen sensitization ($\Phi_{\Delta} = 0.59$ to 0.98) that match and surpass the reactivity of $[\text{Ru}(\text{bpy})_3]^{2+}$ under identical conditions. These results suggest that diimine ligand functionalization represents a simple design strategy for manipulating the photophysical and photoredox properties of earth-abundant Cr(III) LF chromophores.



Metal-Organic Frameworks as a Tunable Platform for Photocatalysis

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The development of functional metal–organic frameworks (MOFs) for catalysis requires simultaneous control over active sites, charge transport, and dynamic structural response. Here, we present two complementary strategies to tune catalytic function in MOF-based systems: (1) electrocatalytic water oxidation using molecularly defined active sites and (2) photodynamic deligation to modulate reactivity in photoactive frameworks.

For electrocatalytic water oxidation, a ruthenium-based catalyst, $[\text{Ru}(\text{Mebimpy})(\text{dcbpy})\text{H}_2\text{O}]^{2+}$, is incorporated into UiO-67 thin films grown on conductive substrates. These films exhibit efficient oxygen evolution under near-neutral conditions (pH 6), operating at ~ 600 mV overpotential with a turnover frequency of ~ 0.3 s⁻¹ and $\sim 59\%$ Faradaic efficiency. The MOF architecture enables a >12 -fold increase in electroactive surface coverage relative to monolayer systems, with $\sim 43\%$ of Ru centers addressable. Charge transport proceeds via diffusion-limited redox hopping ($D \approx 5 \times 10^{-11}$ cm² s⁻¹), enabling catalytic activity throughout the film. Controlled electrolysis produces ~ 0.86 mmol O₂ over 1 h, a ~ 6 -fold enhancement over catalyst-free frameworks, while maintaining structural integrity and minimal leaching. We further demonstrate that secondary coordination sphere modifications provide a powerful handle to tune catalytic performance. Systematic variation in sulfonate ($-\text{SO}_3^-$) group number and distribution modulates both proton-coupled electron transfer (PCET) kinetics and charge transport. Increasing sulfonation enhances proton transport and facilitates redox hopping, leading to improved activity. Tetra-sulfonated MOFs outperform di- and non-sulfonated analogues, achieving higher oxygen production, Faradaic efficiency ($\sim 82\%$), and turnover numbers (~ 48 per Ru in 1 h), along with increased kinetic isotope effects consistent with enhanced PCET. These results highlight how MOF design can integrate catalytic and ion-transport functionalities in confined environments.

In parallel, we investigate the role of framework dynamics in multivariate MOFs, where controlled linker heterogeneity tunes structural flexibility. Using MIL-101(Fe) as a model system, we examine how linker substituents influence photocatalytic N₂-to-NH₃ conversion. In this system, μ_3 -oxo Fe clusters undergo redox cycling via photodynamically generated Fe²⁺ states that enable N₂ activation. Substituent-dependent tuning of linker electronics modulates ammonia production rates from ~ 100 to 700 $\mu\text{mol g}^{-1} \text{h}^{-1}$, with fluorinated frameworks showing the highest activity. These trends correlate directly with the lifetime of photodeligated states, as measured by time-resolved infrared spectroscopy. Transient ligand dissociation is evidenced by changes in carboxylate vibrational modes and the appearance of new C=O and C–O bands. Photodeligated state lifetimes span from ~ 12 μs to ~ 34 μs across the series, with longer-lived states corresponding to higher catalytic activity. Ongoing studies probe how framework flexibility governs ligand release and rebinding, revealing emerging relationships between deligation kinetics, transient coordination environments, and photocatalytic function.

Together, these results demonstrate that local chemical environment and dynamic structural behavior are interdependent parameters governing MOF-based catalysis. The combined approach establishes a foundation for designing adaptive materials with tunable reactivity for photochemical and energy-relevant transformations.

Selective Photochemical Reactions for the Discovery of Triplet Photosensitizers

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Triplet photosensitizers readily form triplet states upon irradiation, making them essential to applications including photocatalysis, triplet-triplet annihilation photon upconversion, and photodynamic therapy. While many common photosensitizers rely on transition metals, organic photosensitizers without heavy atoms can exhibit improved absorption coefficients and excited-state lifetimes. However, their discovery still largely relies on one-at-a-time synthesis and testing, creating a bottleneck in the elucidation of design rules.

I will present a discovery approach based on coupling desirable characteristics—strong absorption of light, high intersystem crossing yield, and long triplet lifetime—to reactivity. Reaction efficiency is used as a proxy for properties that are not compatible with high-throughput experimentation. Selective photoreactions are used to covalently “tag” triplet sensitizers from libraries of compounds. We perform photochemical reactions in a 96-well photoreactor, and isolate and analyze the products using matrix-assisted desorption/ionization mass spectrometry of self-assembled monolayers (SAMDI-MS).

To initially demonstrate this approach, we took advantage of a well-known Yang-type reaction, in which ketones with a low-lying $n\text{-}\pi^*$ transition engage in intermolecular C–H abstraction and recombination. We designed “tags” that undergo C–H abstraction and contain a handle for click chemistry (thioacetate). We installed a quaternary ammonium group on the “tag”, which enhanced ionization efficiencies of the photo-tagged products in SAMDI-MS, enabling semi-quantitative analysis. After validating this workflow with known ketones representing positive and negative controls, we employed cheminformatics/DFT-driven screening strategies to identify compounds predicted to undergo the Yang-type photoreaction. In parallel, we are testing the “hit” compounds for polymer upcycling to produce high-value feedstocks, using our screening approach to identify photosensitizers that tolerate common additives and contaminants.

In parallel, we are using Dexter Energy Transfer (EnT) reactions to identify novel photosensitizers beyond ketones, wherein the distance dependence of EnT can be harnessed to selectively tag photosensitizers in pooled experiments. EnT catalysis has enabled synthetic transformations, including the photosensitized N–O bond cleavage in oximes for substrate functionalization. We are particularly interested in using these compounds as “tags” because they have relatively low predicted triplet energies (ranging from 42–47 kcal/mol). We have validated this approach for known photosensitizers such as isopropylthioxanthone (ITX) and triazines. However, tagging is not selective due to the long-lived nature of radicals formed, and we are currently investigating alternative tag candidates that produce short-lived carbene intermediates.

The ultimate goal of this project is to develop an experimental platform for materials discovery with the potential to reveal non-intuitive structure-property relationships. This poster will summarize our efforts in library design, selective photoreaction development, data analysis, and characterization, and the application of the resulting photosensitizers to polymer upcycling.

Dissociative Electron Attachment as a Key Mechanism in Radiation Chemistry Enabling a Unified Framework

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Dissociative Electron Attachment (DEA) is a key elementary process governing low-energy electron–molecule interactions, with critical implications for radiation chemistry, material processing, radiation biology, and plasmas. In radiation chemistry in particular, the importance of DEA is amplified by the abundant production of low-energy secondary electrons (typically < 20 eV) generated along radiation tracks. These electrons efficiently attach to molecules, forming transient negative ions that initiate bond cleavage and drive chemical transformations in irradiated media. Despite decades of extensive experimental and theoretical studies, from simple diatomic systems to complex biomolecules, DEA research remains largely fragmented and case-specific. A systematic framework that identifies universal fragmentation pathways and links them to underlying molecular structure and electron dynamics is still lacking. Addressing this gap is essential for advancing predictive capabilities in electron-driven chemistry, especially in radiation-related environments.

This work presents our recent studies on a comparative approach to DEA, focusing on how transient negative ion formation and subsequent dissociation pathways are governed by recurring structural motifs. Case studies include model systems, including amides and carbohydrates. Our future work will expand these studies to identify common patterns and key factors that govern fragmentation in other classes of compounds such as sulfur-containing species. In addition, ongoing and recent projects relevant to radiation chemistry are highlighted, emphasizing systems where low-energy electrons play a dominant role in inducing molecular damage and transformation.

By analyzing trends in ion yields, in respect to their shapes and resonance energies, and site-selective fragmentation, this work aims to move beyond isolated observations toward identifying general principles of DEA. Establishing such correlations is a crucial step toward developing predictive models that can describe electron-induced processes in complex chemical systems exposed to ionizing radiation.

Effect of Film and Shell Thickness on the Performance of Solution-Processed WO₃-BiVO₄ Core-Shell Nanoporous Film Photoanodes

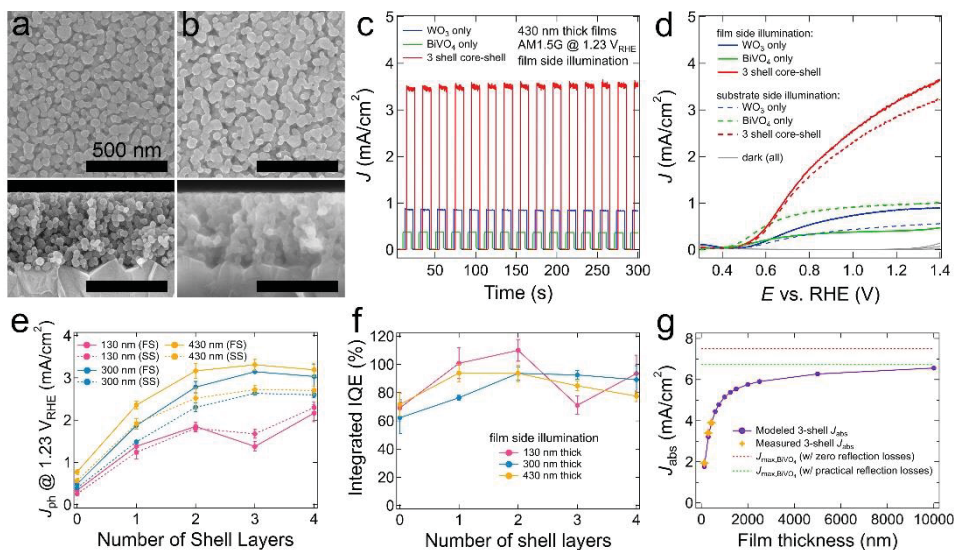
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The lack of efficient, stable, and low-cost materials for water oxidation is the major barrier to the development of practical photoelectrochemical (PEC) water splitting technologies. Detailed fundamental studies of prospective materials are needed to understand and control the factors that govern their water oxidation performance (efficiency and stability) and develop suitable photoanode architectures for practical PEC water splitting. This project combines studies of high-quality bulk single crystals and nanoporous films to understand the properties and photoelectrochemical behavior of three promising metal oxide semiconductors for light-driven water oxidation and to test new concepts and strategies to enhance light-to-hydrogen efficiency and durability.

This poster presents a detailed study of the performance of WO₃-BiVO₄ core-shell nanoporous film photoanodes as a model system to test the merits of our solution-processed nanostructured architecture for photoelectrochemical water splitting. The photoanodes showed integrated internal quantum efficiencies of 70-100% with short-term stable photocurrent densities for sulfite oxidation as high as 3.8 mA/cm² (50% of the theoretical limit for BiVO₄). The photocurrent of the WO₃-BiVO₄ core-shell films is a factor of 3-9 higher than that of single-component nanoporous BiVO₄ films (depending on incident light direction) and a factor of 4-5 higher than that of WO₃ core-only films, demonstrating that this core-shell architecture can overcome the charge transport limitations common to visible-bandgap photoanode materials such as BiVO₄. The performance of the WO₃-BiVO₄ photoanodes is limited by incomplete light absorption, which itself is determined by the thickest uncracked WO₃ films that have been made so far (~500 nm). Measurements as a function of incident light direction showed that the photocurrent is not limited by electron transport through the WO₃, so thicker films are expected to yield higher photocurrent and conversion efficiency.

Figure 1. (a) SEM images of a 430 nm thick WO₃ core film. (b) SEM images of a WO₃-BiVO₄ core-shell film made with three layers of BiVO₄. (c) Chopped light chronoamperometry. (d) Linear sweep voltammetry. (e) Photocurrent density. (f) Integrated IQE. (g) Absorption-limited photocurrent density. Purple line: optical model results.



Chiral Graphene Nanoribbons as Platforms for Photoinduced Spin-Polarized Charge Transfer and Transport

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Program Scope. This project investigates how molecular chirality in extended π -conjugated nanoribbons drives light-induced spin polarization and spin-selective charge transport at condensed-phase interfaces—a new frontier for solar photochemistry. We synthesize helical chiral graphene nanoribbons (chGNRs) and helicene-derived perylene diimides with exceptionally large chiroptical responses, and interface them with transition-metal dichalcogenides (TMDCs) such as WSe₂ so that circularly polarized photoexcitation generates spin-polarized excitons and carriers without magnetic fields. Helicity-resolved ultrafast transient reflectance, stroboscopic scattering microscopy, and conductive AFM track spin-polarized charges from ultrafast to microsecond, building a quantitative mechanistic framework for photoinduced chirality-induced spin selectivity (CISS).

Recent Progress. We have developed bottom-up routes to defect-free chGNRs tens of nm long with control over length, ends, and sidechains, producing the largest visible-range CD of any polymer (Bao, *Angew. Chem. Int. Ed.* 2025, e202508426). Exploiting spin–valley locking in monolayer TMDCs, our contact-free WSe₂/chGNR platform quantifies spin-selective interfacial electron transfer with >45% CISS polarization at room temperature, free of the ferromagnetic-contact artifacts that have clouded CISS quantification. Complementary conductive-AFM on thiol-capped chGNR dimers on Au/Ni shows near-complete spin transmission/rejection versus handedness (Jiang, *J. Am. Chem. Soc.* 2025, 147, 12982). PDI-helices provide record visible and NIR dissymmetry (*Adv. Opt. Mater.* 2025, 13, 2403061).

Future Plans. Three coordinated objectives establish a predictive structure–function description of photoinduced CISS: (1) boost dissymmetry (target $|g| > 0.1$) via controlled aggregation, length, and helical curvature, and align chGNR films by side-chain-directed adsorption; (2) benchmark CISS against g-factor, CD, orientation, order, and temperature to disentangle helical electrostatic potentials, spin–orbit coupling, and phonons in light-atom systems; (3) realize unusual transport in aligned films.

Modulation of Hole Transfer Through Bandgap Engineering of Halide Perovskite QDs

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The transfer of photogenerated electrons and holes from semiconductor nanocrystals to acceptor molecules is primarily dictated by the band energy level alignment and coupling between the donor-acceptor systems. While the latter has been explored in terms of ligand chemistry and acceptor binding groups to optimize charge transfer, the relationship between the driving force ($-\Delta G$) and charge transfer rate in the perovskite donor-acceptor system is rather limited. Halide perovskite nanocrystals (CsPbX_3 ($\text{X}=\text{Cl}, \text{Br}, \text{I}$)) provide a unique platform for controlling the bandgap energy via a facile halide ion exchange¹ or through size quantization effects² (Figures 1A and 1B). By tuning the valence band energy of perovskite nanocrystals, we now examine the dependency of rate constant of hole transfer on driving force ($-\Delta G$).

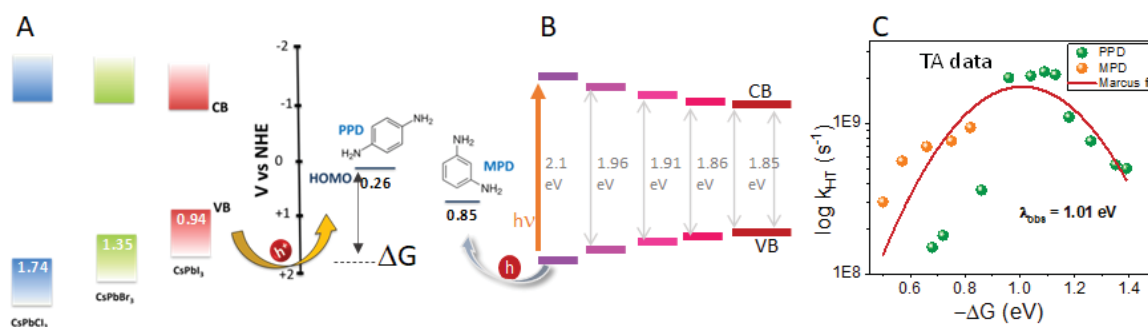


Figure 1. Varying ΔG with valence band energy of the perovskite nanocrystals through (A) Halide (Cl:Br:I) composition and (B) Size quantization effects. (C) Plot showing the dependence of hole transfer rate constant (k_{HT}) on the driving force ($-\Delta G$).

Aromatic amines such as p-phenylene diamine, are useful probes to monitor the transfer of photogenerated holes from perovskite nanocrystals of varying bandgap. The rate constants of hole transfer ($0.15\text{--}2.2 \times 10^9 \text{ s}^{-1}$) which is dependent on the thermodynamic driving force $-\Delta G$, follows Marcus electron transfer theory with a reorganization energy of $\sim 1 \text{ eV}$ (Figure 1C).¹ Since this observed reorganization energy is greater than the contribution from solvent reorganization around the nanocrystal, we consider the reorganization energy within the nanocrystal lattice to be a major contributing factor. The experimentally observed normal and inverted regions of charge transfer as expected from the Marcus theory, further affirm the importance of energy level modulation while designing nanocrystal-based donor-acceptor light harvesting systems.

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Excited-State Energy and Charge Transfer at Quantum Dot-Ligand Interfaces

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In hybrid organic/semiconductor nanoscale architectures, modulating the coupling between the chromophore and the energy/charge transfer partner systematically to achieve certain outcomes (e.g., efficient photon upconversion, downconversion, or photocatalysis) relies upon an understanding of how coupling mechanisms change with system design. We have investigated three ligand systems comprehensively after their exchange on PbS quantum dot (QD) surfaces: a tetracene-based dicarboxylic acid (Tc-DA),¹ a series of perylene-based dyes, and chiral dicarboxylic acids. Tc-DA exhibits perplexing behavior compared with conventional ligands, showing an extreme concentration dependence that leads to two distinct triplet types after energy transfer from the photoexcited ligand: a triplet exciton and a triplet excimer. We characterize the conditions that lead to this behavior as it relates to face- vs. edge-on geometries at the QD surface (Figure 1) and the associated excited-state dynamics.^{2,3} The triplet energy transfer rate is enhanced by several orders of magnitude over prior observations to show evidence of arrival on ps timescales after QD photoexcitation.

A more synthetically flexible and environmentally stable series of perylene dyes shows tunable switching between charge and energy transfer with substitution due to energy shifts with respect to the conduction and valence band of the QD. Further, the regio-isomers exhibit dramatically different excited-state behavior, which we assign to the nature of ligand binding and packing, determined through FTIR studies. The question of how these QD-ligand interface geometries affect triplet dynamics requires QDs with smaller band gaps than for those with Tc-DA ligands to enable resonance and open channels for energy transfer. We find that the details of ligand exchange change significantly with these smaller QDs, with less evidence of face-on ligands and a higher degree of colloidal solubility. Including an ethynyl group directly between the carboxylic acid and the perylene core supports efficient triplet energy transfer and subsequent upconversion with a rubrene emitter. How the evolution is directed toward ligand-centered triplets vs charge-separated states involves the subtle juxtaposition between energy and geometry at the interface.

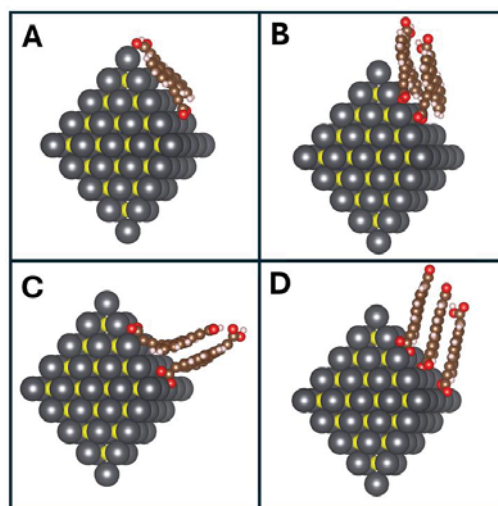


Figure 1. Calculated geometries of tetracene diacid ligands on a PbS QD surface.

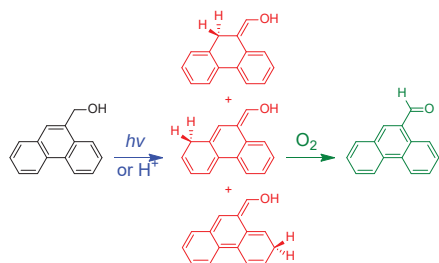
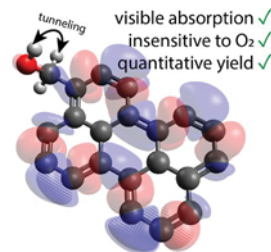
¹Pompetti, N. F.; Smyser, K. E.; Feingold, B.; Owens, R.; Lama, B.; Sharma, S.; Damrauer, N. H.; Johnson, J. C. *J. Am. Chem. Soc.* **2024**, *146* 16, 11473– 11485, ²Martinez, M. S.; Nolen, M. A.; Pompetti, N. F.; Richter, L. J.; Farberow, C. A.; Johnson, J. C.; Beard, M. C. *ACS Nano* **2023**, *17*, 15, 14916– 14929. ³Feingold, B.; Pompetti, N.; Martinez, M.; Blackburn, J.; Reid, O.G.; Beard, M.C.; Johnson, J.C. *ACS Nano* **2025**, *19*, 46, 40245–40257.

Photooxidation of Polycyclic Aromatic Alkyl Alcohols: Mechanisms and Scope

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We have discovered a novel photochemical reaction wherein organic dyes bearing hydroxymethyl groups oxidize to their corresponding aldehydes with concomitant elimination of H₂. Our efforts are focused on understanding the mechanism(s) of these photooxidations by combining steady-state physical organic chemistry techniques (isotope labeling, kinetic studies, and photophysical characterization) with optical transient absorption spectroscopy and computational chemistry. We aim to piece together a complete picture of the reaction from the initial photon absorption to the formation of products in the electronic ground state. Insights from this work will allow us to identify the requisite properties of such constructs for photochemical H₂ release and develop *in silico* screening methods to design improved materials for molecular hydrogen storage, which we will experimentally validate by synthesizing these new dyes and evaluating their performance.

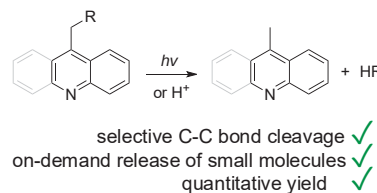
We previously focused our efforts on anthracenes and acridines, which are acutely sensitive to oxygenation in the triplet excited state and thus require rigorously anaerobic conditions. To overcome this problem, we screened several dyes that are more robust to O₂ and found that the photooxidation reaction proceeds for a broad range of polycyclic aromatic hydrocarbons and heterocycles. For example, 3-perylenemethanol exhibits nearly quantitative conversion under ambient atmosphere with visible (440 nm) light. We have measured a kinetic isotope effect consistent with proton tunneling, confirming the intramolecular nature of the reaction and revealing how the methylene and hydroxyl hydrogen atoms couple across more than 2 Å.



Although all other dyes we have investigated undergo photooxidation under air-free conditions, 9-phenanthrene-methanol unexpectedly exhibits a strict O₂ dependence while still evolving H₂ gas. We previously reported that the thermal oxidation of hydroxymethylated *N*-heteroarenes also requires O₂, suggesting that the photooxidation reaction may occur by a similar mechanism for dyes with less polarized transition dipoles. Notably, both the photochemical and thermal

oxidations of deuterated 9-phenanthrene-methanol result in aldehyde products bearing the same aromatic deuteration patterns consistent with an initial hydride transfer step.

Finally, we discovered that 4-ethylquinoline and 9-ethylacridine undergo quantitative conversion to their methylated analogs in the presence of carboxylic acids at elevated temperatures or under photochemical conditions. Such selective and facile aliphatic C-C bond activation is unprecedented, and we now aim to explore its scope and mechanism to determine how such reactivity may be achieved among a broader range of common substrates.



CdS/ZnSe Quantum Dot Co-gels: Bifunctional Type-II Heterojunction Photocatalysts for Visible Light Water Splitting Reactions

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The Solar Photochemistry Quantum-Dot (QD) Gel Team is focused on designing photocatalysts for water splitting reactions by (1) integrating quantum dot components into macroscopic type-II heterojunction porous assemblies (gels) capable of separating (and directing the flow) of photogenerated electrons and holes; and (2) selective decoration (or integration) of co-catalysts to exploit the photogenerated carriers for facile water oxidation/reduction. This endeavor comprises QD gel network synthesis, co-catalyst installation, and catalytic testing (Brock), informed by computational modeling of band structures, alignments, and optical properties of QD assemblies (Liu), and supported by static and time-resolved spectroscopies (Huang). In our prior work, we

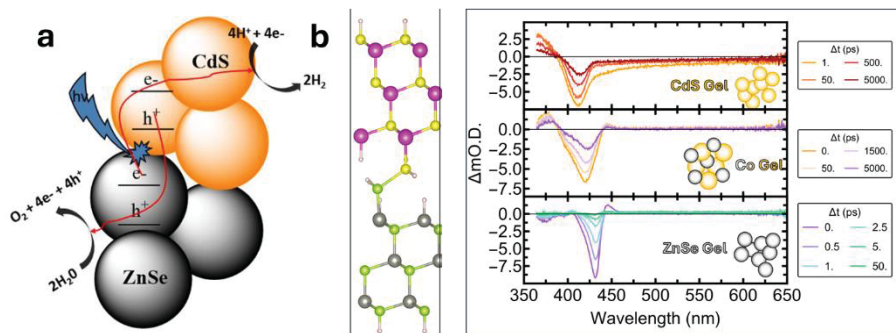


Figure 1. (a) Scheme of type-II CdS/ZnSe gel network for HER & OER; (b) Relaxed model of the CdS-ZnSe interface, and transient absorption spectra of CdS (top), ZnSe (bottom) and CdS/ZnSe co-gel (center).

demonstrated that CdS gels are 2.5-4 x more efficient for hydrogen evolution (HER, 3690 $\mu\text{mol H}_2 \text{ h}^{-1} \text{ g}^{-1}$) than discrete QDs, and the introduction of colloidal Pt leads to increased activity that is different when the Pt is incorporated into the QD gel during assembly (6810 $\mu\text{mol H}_2 \text{ h}^{-1} \text{ g}^{-1}$) vs. wet-loaded post

assembly (4565 $\mu\text{mol H}_2 \text{ h}^{-1} \text{ g}^{-1}$). This difference is reflected in exciton bleach dynamics and is consistent with the energy difference between the QD conduction band minimum and the Pt Fermi level computed for the two scenarios. We hypothesize that incorporating a second QD component with suitable electronic properties to create a type-II heterojunction will enhance carrier separation, thereby increasing HER activity and enabling bifunctionality (OER), as shown in **Figure 1a**.

In the present work, we demonstrate formation of CdS-ZnSe QD co-gels and show that they dramatically outperform single-component gels (CdS or ZnSe) for either HER or OER (**Table 1**). These data will be explained in the context of electronic structure calculations of the type-II QD heterostructure and spectroscopic measurements of exciton dynamics (**Figure 1b**). Future work on our efforts to combine the type-II heterostructured co-gel with co-catalysts will also be discussed.

Table 1. Activity of aerogel (AG) and co-gel (CG) for HER and OER: Xe lamp, 425 nm cutoff, 1.0 mg catalyst in 50 mL aqueous solution with $\text{Na}_2\text{SO}_3/\text{Na}_2\text{S}$ (HER) or $\text{Na}_2\text{S}_2\text{O}_8$ (OER) as sacrificial reagents.

Catalyst	H_2 rate ($\mu\text{mol h}^{-1} \text{ g}^{-1}$)	O_2 rate ($\mu\text{mol h}^{-1} \text{ g}^{-1}$)
CdS AG	3,700 $\pm$ 210	12,400 $\pm$ 670
ZnSe AG	1,024 $\pm$ 190	15,870 $\pm$ 530
CdS-ZnSe CG	14,530 $\pm$ 580	16,080 $\pm$ 750

Radiolysis of Uranyl Nitrate Compounds

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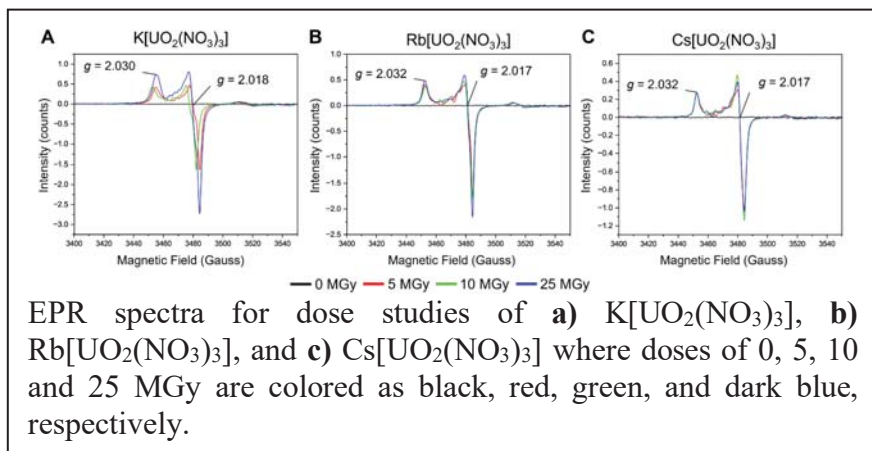
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All actinides are radioactive and emit ionizing gamma rays and alpha particles that can modify their local chemical environment. The ionizing radiation can lead to chemical decomposition of the medium giving products that can disrupt separation processes or waste management. Uranium nitride compounds are especially important as they are ubiquitous throughout nuclear waste separations. This project brings together radiochemistry knowledge of synthesizing and handling radioactive materials with radiation chemical techniques to examine their radiation stability and to gain insights on the mechanism of their radiolytic decay.

The radiolysis of the solid uranium trinitrate compounds $[\text{UO}_2(\text{NO}_3)_2] \cdot 3(\text{H}_2\text{O})$ and $\text{M}[\text{UO}_2(\text{NO}_3)_3]$ ($\text{M} = \text{K}^+, \text{Rb}^+, \text{Cs}^+$) was performed with gamma rays and 5 MeV He ions, the latter to mimic alpha particles radiolysis. The compounds were characterized before and after radiolysis by electron paramagnetic resonance (EPR), Raman and Infrared spectroscopy to probe radiation induced changes to the molecular structure.



Gamma radiolysis followed by EPR and DFT analysis found that the equatorial bidentate bound nitrate converts to a monodentate $\text{NO}_3^\bullet$ radical. This result is significant in that it shows that the main bond broken is the metal-ligand bond, which has many repercussions in separations. He ion radiolysis was used to extend the doses to 25 MGy. The EPR spectra for three of the compounds shown in the figure also exhibit the characteristic signature of the $\text{NO}_3^\bullet$ radical.

Further work will extend these studies to other anions such as chlorides, carbonates, and oxalates to better understand the uranium-ligand bond stability.

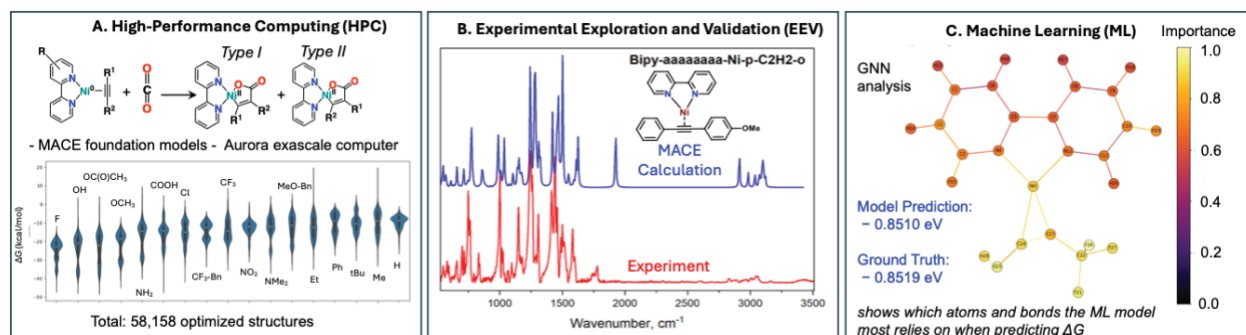
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Data-Driven Discovery of Structure–Reactivity Relationships in Oxidative Addition at Zerovalent Nickel Centers

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Nickel catalysts occupy a central role in solar-driven and electrochemical fuel-forming reactions due to their rich redox chemistry, spanning oxidation states from Ni(0) to Ni(III/IV). Oxidative addition at zerovalent nickel complexes is widely proposed as a key reactivity-enabling process. However, predictive structure–property relationships governing oxidative addition remain poorly understood due to the vast chemical space of ligand–substrate combinations and the limited accessibility of air-sensitive Ni(0) intermediates.



Here, we establish a closed-loop discovery framework that integrates high-performance computing (HPC), experimental exploration and validation (EEV), and machine learning (ML) to uncover the molecular determinants of oxidative addition in Ni(0)–alkyne complexes. Equivariant graph neural networks (EGNNs) are trained to learn structure–reactivity relationships from large datasets of Ni-containing reactants and products generated using HPC workflows that combine machine-learned interatomic potentials (MACE foundation models) with exascale resources on Argonne’s Aurora supercomputer (~1,200 nodes / 14,400 GPU tiles). To ensure chemical realism, selected Ni complexes were synthesized and experimentally characterized, providing direct comparison between predicted and observed structures and reactivity and revealing constraints on ligand stability and synthetic accessibility that inform model refinement.

We find the chemical descriptors that control both the Gibbs free energy landscape and regioselectivity of substrate insertion into the Ni–alkyne bond, leading to distinct metallacyclic (Type I vs. Type II) products. Alkyne ligands exert a dominant influence on reactivity, surpassing bipyridine ligands due to stronger π -backbonding with the Ni(0) center. Regioselectivity arises from a combination of steric accessibility at the metal center and electronic stabilization of the resulting metallacycle, highlighting the interplay between geometric and electronic effects. This work demonstrates how integration of interpretable machine learning and targeted experiments can accelerate discovery of mechanistic principles in transition metal catalysis.

Probing Charge Separation and Local Photocatalytic Activity by Photo-SECM

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This project is aimed at using nanoelectrochemical techniques for nanoscale characterization of activity and heterogeneity of photocatalysts. We employed photo-scanning electrochemical microscopy (photo-SECM) to directly visualize photoinduced charge separation in monolayer MoS₂–WS₂ in-plane heterojunctions produced in Fengtao Fan's lab at Dalian Institute of Chemical Physics.¹ Spatial separation of photogenerated carriers was observed, with electrons accumulating in MoS₂ and holes in WS₂, leading to strongly asymmetric interfacial kinetics revealed by photo-SECM (Fig. 1A) in agreement with the surface photovoltage microscopy (SPVM, Fig. 1B) data, while photoluminescence (PL; Fig. 1C) images showed that the interface acts as a recombination center that limits efficient carrier extraction.

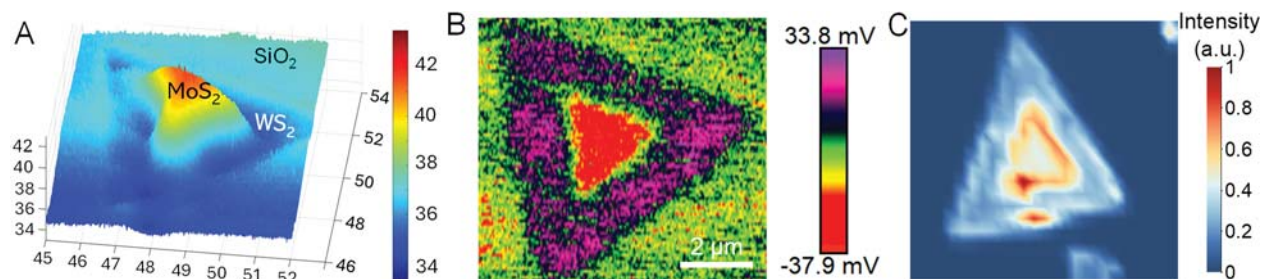


Fig. 1. Constant-height photo-SECM image (A), SPVM image (B), and PL image (C) of in-plane MoS₂–WS₂ heterojunctions. (A) Solution contained 1 mM ferrocenemethanol in 0.1 M phosphate buffer (pH 7), the tip potential was 0.4 V vs Ag/AgCl, and the tip radius 150 nm.

We introduced amperometric/potentiometric photo-SECM technique that enables nanoscale interrogation of photocatalytic processes under *operando* conditions.² This method employs a single SECM tip capable of both amperometric and potentiometric measurements. In collaboration with the Hu group (Yale University) we demonstrated its capability to simultaneously probe local product fluxes and surface potentials of Pt-Nb:TiO₂ photocatalysts. For overall water splitting, we resolved distinct nanoscale cathodic and anodic regions separated by only by ~150 nm, with surface potentials differing by ~1.2 V. This mapping revealed that charge separation in Nb:TiO₂ occurs on the scale of hundreds of nm, as verified by complementary characterization techniques. Our findings demonstrate how the asymmetric surface energetics captured by SECM directly correlate with local charge-transfer processes.

In the future, we will use amperometric and potentiometric tunneling modes of photo-SECM for correlating potential and flux maps and interpreting them through transport/kinetic modeling and extend this approach to practically important semiconductor/cocatalyst systems.

1. Huang, Q.; Wang, Z.; Liu, R.; Yao, H.; Ni, C.; Bo, T.; Wu, S.; Sun, F.; Fan, F.; Mirkin, M. V. In Situ Imaging Reveals Efficient Charge Separation in Monolayer MoS₂–WS₂ Type-II Heterojunctions. *J. Am. Chem. Soc.* **2026**, *148*, 8417–8422.
2. Bo, T.; Su, H.; Wang, Z.; Bae, J. H.; Askarova, G.; Hu, S.; Mirkin, M. V. Probing Charge-Transfer Processes in Pt/TiO₂ Photocatalyst by Amperometric/Potentiometric Photo-SECM. *Proc. Natl. Acad. Sci. USA*, DOI: 10.1073/pnas.2527861123.

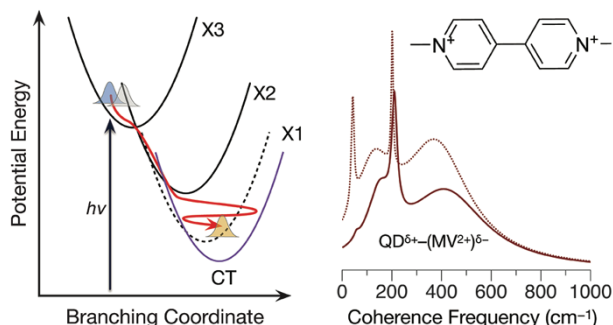
Vibronic Coherences and Conical Intersections Mediate Photoinduced Charge Transfer in CdSe Quantum Dots

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We will discuss recent findings using broadband multidimensional electronic spectroscopy with 7-fs mid-visible laser pulses that photoinduced charge transfer from CdSe quantum dots (QDs) to surface-bound methyl viologen (MV²⁺) acceptors is mediated by a vibronically coherent, nonadiabatic mechanism. An analysis of coherences shows that a mixed QD–MV charge-transfer (CT) state is populated on the <50 fs time scale after optical preparation of the X3 (1P_{3/2}–1P_e) state, well prior to the appearance of the one-electron photoreduced ground state (MV^{•+}). A partial redistribution of charge from the core of the QD to the acceptor is revealed by excited-state coherences of an out-of plane vibrational mode local to MV²⁺ and of a low-frequency mode mixing a MV²⁺ mode with the longitudinal optical (LO) phonon of the QD core. The ultrafast damping of these coherences indicates that excited-state wavepackets travel from the optically prepared, Franck–Condon structure through a conical intersection to reach the CT state. These results suggest that vibronically coherent processes generating CT intermediates can be exploited to improve the efficiency of QD-based solar cells and photocatalysts.



Hetherington, C. V.; Mohan T. M., N.; Shameem, S. A.; Beck, W. F.; Levine, B. G. Conical intersections shed light on hot carrier cooling in quantum dots. *J. Chem. Phys.* **2025**, *163*, 214703. DOI: 10.1063/5.0295696.

Mohan T. M., N.; Shameem, S. A.; Leslie, C. H.; Hetherington, C.; Cavey, K.; Zhang, M.; Van Patten, P. G.; Levine, B. G.; Beck, W. F. Excited-State Vibronic Coherences With Mixing of Core–Ligand Character Promote Hot-Carrier Cooling in Oleate-Capped CdSe Quantum Dots. *J. Chem. Phys.* **2026**, *164*, 064703. DOI: 10.1063/5.0305043.

Shameem, S. A.; Mohan T. M., N.; Tilluck, R. W.; Hetherington, C. V.; Levine, B. G.; Beck, W. F. Ligand control of ultrafast hot-carrier cooling in CdSe quantum dots by a coherent nonadiabatic mechanism. *J. Phys. Chem. Lett.* **2026**, *17*, 1055-1061. DOI: 10.1021/acs.jpclett.5c03429.

Mohan T. M., N.; Shameem, S. A.; Leslie, C. H.; Hetherington, C. V.; Levine, B. G.; Beck, W. F. Photoinduced charge transfer and vibronic coherence in CdSe quantum dots with methyl viologen acceptors. *J. Phys. Chem. C* **2026**, in press, DOI: 10.1021/acs.jpcc.6c2147.

Small Changes, Big Impact: Nuances of Earth-Abundant Photosensitizers

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The development of efficient, earth-abundant photosensitizers hinges on deepening our understanding of excited-state dynamics in earth abundant complexes. Herein, we report our progress in this field on several fronts: (1) Investigation of the photophysical and electrochemical properties of a series of Lewis acid (LA)-bound non-heme (nH) manganese(IV)-oxo complexes, $[(nH)Mn^{4+}O]^{z+}-(LA)_Y$, a potential new class of first-row transition metal photosensitizers, (2) Advancing the synthetic approach and preparation of $[(nH)Mn^{4+}O]^{z+}-(LA)_Y$'s, and (3) Visible-light absorbing core-shell nanoparticles based on earth abundant materials. Our team uses a multi-pronged approach to advance the way earth-abundant metal photosensitizer species are designed, synthesized, purified, characterized, and applied to real-world scenarios.

The goal of this project is to clarify nuances of photoinduced excited state dynamics in LA bound $[(nH)Mn^{4+}O]^{z+}$ complexes. This work corroborates literature reports of 6 - 7 μ s, counterion-dependent excited-state lifetimes (τ) in $[(nH)Mn^{4+}O]^{z+}-(Sc^{3+})_Y$, where nH = *N*-benzyl-*N,N',N'*-tris(2-pyridylmethyl)-1,2-diaminoethane (BnTPEN). Additionally, series' of $[(BnTPEN)Mn^{4+}O]^{z+}-(LA)_s$ are prepared to probe excited state dynamics, where LA = Sc^{3+} , Al^{3+} , Lu^{3+} , In^{3+} , and Ce^{3+} salts. Complexes are evaluated with ultraviolet-visible (UV-vis), electron paramagnetic resonance (EPR), transient photoluminescence (TRPL), and transient absorption (TA) spectroscopies. All complexes demonstrate a $S = 3/2$ (i.e., Mn(IV) quartet) ground state, characteristic LA- and LA-counterion dependent hypsochromic shifts upon LA binding in the UV-vis-NIR (1010 – 1020 nm to 500 – 700 nm), and long excited state lifetimes ($\tau = 800$ ns – 7 μ s). Importantly, degradation of $[(BnTPEN)Mn^{4+}O]^{z+}-(LA)_s$ is minimally discussed, uncharacterized, and omitted from excited state behavior interpretation in literature. Yet, oxidative generation of the $[(BnTPEN)Mn^{4+}O]^{z+}$ complex introduces several potential degradation pathways. This work also seeks to understand degradation sources by implementation of easily removed solid-supported oxidants.

Finally, this project examines catalytic conversion of hydrocarbon waste into value-added fuels in titanium nitride (core) - titanium oxide (shell) nanoparticles (nNP) decorated with trace Au-NP. A series of TiN@TiO₂ are prepared and analyzed with X-ray diffraction (XRD), mass-spectrometry, NIR spectroscopy, and transmission electron microscopy (TEM). The current systems (no Au-NP) demonstrate substantial water production upon white-light illumination, indicating promise for potential photocatalytic applications.

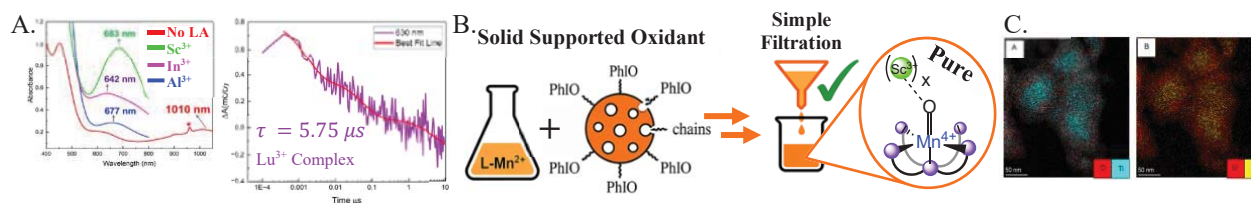


Figure 1. UV-vis and ns-TA of $[(BnTPEN))Mn^{4+}O]^{z+}-(LA)_s$ (A.), Solid-supported oxidant synthetic scheme (B.), and as-prepared nanoparticles of TiO₂ (left, C.) and TiN@TiO₂ (right, C.).

Si QD Sensitization of Organic Triplets as Revealed by Time-Resolved EPR

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The primary objective of our research is to elucidate the fundamental mechanisms of light-to-chemical energy conversion, encompassing the capture, transformation, and storage of light energy within high-energy molecular bonds. Within the Photochemistry program, we aim to emulate and draw inspiration from the principles of natural photosynthesis. A central focus is to identify the atomic and electronic structural factors that govern these energy conversion processes. To characterize both stable and transient states, we employ a range of advanced spectroscopic techniques, including Electron Paramagnetic Resonance (EPR) spectroscopy. EPR provides valuable insights into the electronic structure, kinetics, and spin dynamics of systems containing unpaired electrons. Our group specializes in time-resolved multifrequency EPR spectroscopy combined with in situ pulsed laser excitation, enabling the study of charge and energy transfer in both organic and inorganic systems. Long-lived triplet states in donor–acceptor systems are fundamental to various photophysical processes relevant to photocatalysis, singlet fission, photon upconversion, and quantum information science. Efficient generation and manipulation of triplet states require systems where exciton formation, transfer, and relaxation can be precisely controlled. Hybrid nanostructures composed of quantum dots (QDs) and organic dye molecules have emerged as versatile platforms, as the tunable electronic properties of QDs can interact with the defined excitonic characteristics of molecular dyes to form donor–acceptor pairs capable of producing and utilizing long-lived triplet excitons via Dexter-type energy transfer (TET) or charge-separation pathways. While prior studies on lead and cadmium chalcogenide QD-organic conjugates have demonstrated TET between nanocrystals and molecules, the silicon QDs explored here offer advantages such as low toxicity and covalent chemistry, enabling modulation of electronic coupling between QDs and dye molecules and thus influencing the efficiency of Dexter-type TET.

Here, we present the first time-resolved EPR investigation of TET in colloidal silicon QDs conjugated with various organic molecules. Triplet formation and spin dynamics are monitored using time-resolved continuous wave and pulsed EPR spectroscopy. Remarkably, the electron spin polarization of these conjugates exhibits fully emissive patterns—an unexpected result not accounted for by conventional spin-orbit or radical-pair mechanisms typically observed in purely organic donor–acceptor systems. The underlying mechanism of this novel TET is discussed.

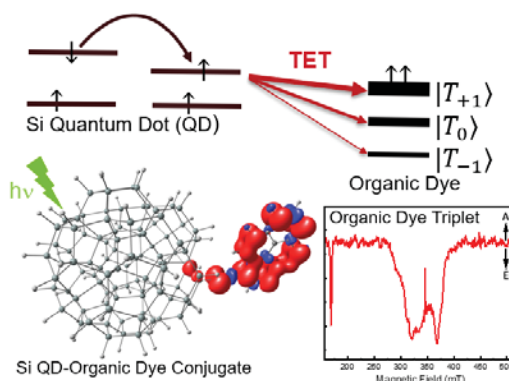


Figure. Light-induced Triplet Energy Transfer (TET) in hybrid silicon quantum dot (QD)-organic molecule conjugates results in selective population of triplet spin energy levels in the organic molecule acceptor.

The Impact of Integrated Redox Centers on Multiexciton Dynamics

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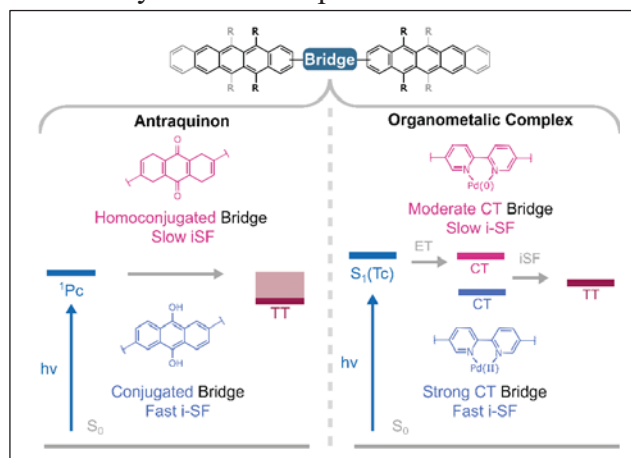
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Exerting precise control over processes driven by singlet and triplet excitons is of paramount importance in organic optoelectronics and photochemistry. The foundational principles underpinning energy and charge transfer have led to robust guidelines to molecularly engineer advanced excitonic materials. While singlet excitons (S_1) in visible light absorbing organic chromophores are short-lived, the strong delocalization of the wavefunction and coupling to the external radiation field permit energy transfer over long distances. In contrast, lower energy triplet excitons (T_1) feature predominantly localized wavefunctions and relatively short-range length scales for energy transfer. Nevertheless, transfer processes from triplets can be efficient due to their relatively long lifetimes, as transitions to the ground state tend to be spin-forbidden.

We recognize that singlet fission (SF) offers new opportunities to explore energy and charge transfer events that are mediated by the multiexciton state—a triplet-pair [T_1T_1]. Achieving the efficient conversion of triplet-pair multiexcitons for photochemical applications requires a deeper understanding of how covalently-linked, charge-accumulating functional groups modulate multiexciton dynamics. This necessitates a reexamination of fundamental principles related to energy, spin angular momentum conservation, and wavefunction engineering. In this program, we address several fundamental challenges that currently impair multiexciton harvesting from inter-/intra-molecular singlet fission (xSF and iSF, respectively) chromophores by either energy or charge transfer processes. This has allowed us to identify discernible photochemical reactions emanating directly from the [T_1T_1] state.

Here, we present a distinct approach to probe the redox states of multi-electron-active groups in intramolecular singlet fission (iSF) molecules. Since the iSF rate is highly sensitive to subtle changes in interchromophore electronic coupling, it serves as an intrinsic sensor of local electron density, independent of specific donor or acceptor groups. We demonstrate this concept in two novel systems: an anthraquinone-bridged pentacene dimer and a palladium-bipyridine-bridged tetracene dimer (see Figure), both of which maintain efficient iSF while incorporating strong redox moieties. These bridges alter chromophore coupling through several mechanisms: (a) tuning frontier orbital energetics via bridge resonance and quantum interference; (b) promoting specific geometrical arrangements that facilitate orbital overlap, commonly referred to as through-space chromophore interactions; and (c) modulating virtual or real charge-transfer (CT) state energies involved in the SF mechanism.



Using Ligand Design, Alternate Proton Donors, and Light Flux to Direct Multi-Electron, Multi-Proton Photochemical Reaction Pathways

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In this poster presentation, we report on our investigations into using extended electronic conjugation to create “good” chemical sites that drive multi-electron, multi-proton fuel-forming reactions at low overpotentials and with high catalytic turnover frequencies.¹⁻³ These constructs thus break the traditional trade-off between thermodynamic (effective overpotential) and kinetic (maximum turnover frequency) performance metrics. We also extend concepts and analytical techniques developed for benchmarking homogeneous electrocatalysts to the study of photoelectrosynthetic assemblies, which, in addition to electrons and chemical substrates, require photons as reagents.⁴ Our results show how ligand design, proton donor selection, and light flux can be used to control local pH at light-absorbing semiconductor interfaces and steer the quantum efficiency of the desired reaction pathways.³⁻⁵

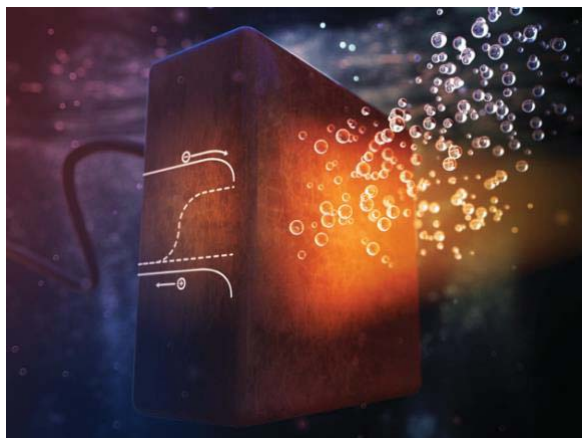


Figure 1. Artistic depiction of a light-absorbing semiconductor modified with molecular catalysts for effectively steering multi-electron, multi-proton reactions involving complex architectures and interfaces (image adapted from cover of reference 1)

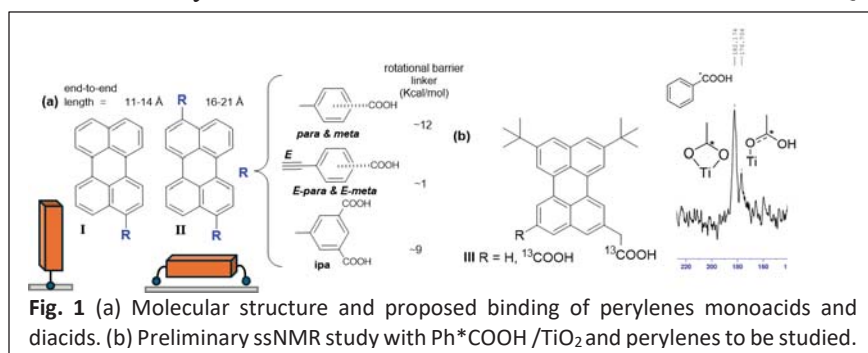
- (1) D. Nishiori, E. A. Reyes Cruz, L. K. Hensleigh, N. P. Nguyen and G. F. Moore, **Shedding light on overpotentials and underpotentials in (photo)electrochemical reactions**, *Chem. Soc. Rev.*, 2026, **55**, 3737–3765.
- (2) E. A. Reyes Cruz, D. Nishiori, B. L. Wadsworth, N. P. Nguyen, L. K. Hensleigh, D. Khusnutdinova, A. M. Beiler and G. F. Moore, **Molecular-Modified Photocathodes for Applications in Artificial Photosynthesis and Solar-to-Fuel Technologies**, *Chem. Rev.*, 2022, **122**, 16051–16109.
- (3) D. Nishiori, J. P. Menzel, N. Armada, E. A. Reyes Cruz, B. L. Nannenga, V. S. Batista and G. F. Moore, **Breaking a Molecular Scaling Relationship Using an Iron-Iron Fused Porphyrin Electrocatalyst for Oxygen Reduction**, *J. Am. Chem. Soc.*, 2024, **146**, 11622–11633.
- (4) D. Nishiori, L. K. Hensleigh, N. P. Nguyen, I. Peterson and G. F. Moore, **Wavelength-Resolving Catalytic Turnover Frequencies and Identifying Alternate Proton Donors in Solar-Fuel-Forming Reactions**, *ACS Catal.*, 2025, **15**, 6361–6371.
- (5) L. K. Hensleigh, D. Nishiori, I. D. Peterson and G. F. Moore, **Exploring Attached-Buffer Effects and Gibbs–Donnan Equilibria in Ionomeric Energy-Transduction Materials**, *Chem. Comm.*, 2026, **62**, 4744–4748.

Linker Design for Photoactive Molecules at Semiconductor Interfaces

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Molecular-level control of charge and energy transfer at hybrid molecule/inorganic interfaces is one of the prerequisites to enable innovative solar energy technologies. Our approach to achieve this is to use molecular design of linker groups to vary binding orientation, conformation, and binding modes of light harvesters bound to metal oxide semiconductors (MO_n) and, more recently, to PbS quantum dots (QD). The poster will present research progress in the following areas. (1) Orientation effects of perylenes/QD and MO_n . We synthesized two families of perylene derivatives, monoacids **I** and diacids **II** in Fig. 1, designed to bind upright or parallel, respectively, to inorganic surfaces due to the number (1 vs 2), position (*para* vs *meta*), and rotational barrier of the linker. They were studied on TiO_2 and ZrO_2 at RU, and on QDs at NLR. Both monoacid **I**-



meta and diacid **II**-**meta** exchanged the oleate ligand when bound to PbS (QD exciton ~1.6 eV) but exhibited very different emissive properties: a significant change of the QD exciton lifetime was observed only for **II** at higher ligand exchange (1

mM concentration of **II**), with spectra indicative of charge transfer. This suggests that linker design may be used to control QD/chromophore charge transfer. The combined effect of binding orientation, and presence of an ethynyl group **E** are under investigation and will be discussed. (2) NMR studies of aggregation and binding mode. Aggregation influences triplet excited state formation and other photoinduced processes, and the binding mode (mono- vs. bi-dentate) of a COOH group significantly influences electronic coupling. However, the ability to characterize both on surfaces remains very limited. At RU we are developing NMR methods to characterize (a) the stacking mode of polyaromatic hydrocarbons, and (b) the binding mode of COOH to MO_n . The study of **I-E-para** in Fig. 1 (a) in THF and DMSO through a combination of 1D and 2D NMR, NOESY, and DOSY methods allowed to characterize concentration- and solvent-dependence of molecular packing. Specifically, aggregation constants, aggregates size and distribution, estimates of chromophore-chromophore distance, stacking orientation in aggregates (slip-stacked, head to tail etc.), were obtained. This information complements spectroscopic methods. These solution studies are a first step to study packing on surfaces by solid state NMR (ssNMR). To characterize the COOH binding mode to TiO_2 and ZnO we are studying at UDel the ^{13}C ssNMR of perylenes **III** in Fig 1 with ^{13}C labeled COOH anchors. Both approaches (^{13}C labeling and 2D methods) will be combined in a coordinated effort.