Proceedings of the

# Forty-Sixth
# DOE Solar Photochemistry
# P.I. Meeting

Bethesda North Marriott Hotel
and Conference Center
Rockville, Maryland
June 2-4, 2025

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

# FOREWORD

The 46th Department of Energy Solar Photochemistry Principal Investigators' Meeting, sponsored by the Chemical Sciences, Geosciences, and Biosciences Division of the Office of Basic Energy Sciences (BES), is being held June 2-4, 2025 at the Bethesda North Marriott Hotel and Conference Center in Rockville, Maryland. These proceedings include the meeting agenda, abstracts of the formal presentations and posters, and a list of participants.

The Solar Photochemistry Program supports fundamental, molecular-level research on solar energy capture and conversion in the condensed phase and at interfaces. This conference is the annual meeting of the PIs who conduct research with support from this Program. The objective of the meeting is to foster the exchange of scientific ideas and collaboration among researchers.

The meeting this year also features five invited presentations to be given by PIs who also serve as directors of an Energy Frontier Research Center (EFRC) with relevance to the Solar Photochemistry portfolio. Those speakers are:

- Greg Scholes, Bioinspired Light-Escalated Chemistry (BioLEC) EFRC that has the mission "To combine light harvesting and solar photochemistry to enable more powerful editing, building, and transforming of abundant materials to produce energy-rich feedstock chemicals."
- Shane Ardo, Ensembles of Photosynthetic Nanoreactors (EPN) EFRC whose goal is to "Understand, predict, and control the activity, selectivity, and stability of solar water splitting nanoreactors in isolation and as ensembles."
- Erin Ratcliff and Neal Armstrong, Center for Soft PhotoElectroChemical Systems (SPECS) that endeavors to "understand the factors controlling charge and matter transport processes in inexpensive, scalable, and durable π-conjugated polymer (plastic) materials…."
- Jenny Yang, Center for Closing the Carbon Cycle (4C), which aims to "advance synergistic capture and conversion of carbon dioxide ($CO_2$) from dilute streams into useful products through the convergent study of sorbents and catalysts.
- Matt Beard, Center for Hybrid Organic Inorganic Semiconductors for Energy (CHOISE) that seeks "To enable unprecedented synthetic control over spin, charge, phonon and light properties through synthesis and characterization of crystalline Hybrid Organic Inorganic Systems, their interfaces and heterostructures."

Thank you to Teresa Crockett and 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 Science

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# 46th DOE SOLAR PHOTOCHEMISTRY-
# P.I. MEETING

**June 2-4, 2025**

**Bethesda North Marriott Hotel and Conference Center**
**Rockville, MD**

**Monday, June 2**

7:30 a.m. Breakfast

## SESSION 1
## Opening Session

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

9:00 a.m. Energy Capture and Conversion in Self-assembled Chlorophyll Analogues
**Jon Lindsey**, North Carolina State University
**Gabriella Schlau-Cohen**, Massachusetts Institute of Technology

9:30 a.m. Modular Nanoscale and Biomimetic Assemblies for Photocatalytic Hydrogen Generation
**Kara Bren**, **Todd Krauss**, and **Ellen Matson**, University of Rochester

10:00 a.m. The Photosystem II SuperComplex: Antenna Design and Dynamics
**Graham Fleming**, Lawrence Berkeley National Laboratory

10:30 a.m. Break

## SESSION 2
## Light-driven Molecular Catalysis

Claudia Turro, Chair

11:15 a.m. Mechanistic Insight into Metal Hydride Photochemistry Enables Catalytic $H_2$ Evolution and Hydrogen Transfer
**Alex Miller**, University of North Carolina, Chapel Hill

11:45 a.m. Improving the Efficiencies of Photo(electro)catalytic Processes using Molecular Catalysts
**Jerry Manbeck**, Brookhaven National Laboratory

12:15 p.m. Working Lunch (*discussion of the scientific presentations throughout the meeting*)

1:35 p.m. Informal Networking

## SESSION 3
## Light Harvesting Involving Nanoparticles

Matt Law, Chair

3:00 p.m. Photodriven Energy and Electron Transfer in Semiconductor-Molecular Hybrids
**Prashant Kamat**, Notre Dame Radiation Laboratories

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|---|---|
| 3:30 p.m. | Light Harvesting in Semiconductor Quantum Dots<br>**Warren Beck**, Michigan State University |
| 4:00 p.m. | Probing energy transfer in nanocluster architectures using DNA-directed assembly<br>**Stacy Copp**, University of California, Irvine |
| 4:15 p.m. | Ultrafast Spin-Exchange Interactions for Hot-Carrier Harvesting in Quantum Dots<br>**Victor Klimov**, Los Alamos National Laboratory |
| 4:45 p.m. | Break |

## SESSION 4
## Chromophores
Lisa Olshansky, Chair

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|---|---|
| 5:00 p.m. | Fundamental Mechanisms for Solar Energy Conversion in Artificial Photosynthetic Assemblies<br>**Karen Mulfort**, Argonne National Laboratory |
| 5:30 p.m. | Selective Photochemical Reactions for the Discovery of Triplet Photosensitizers<br>**Julia Kalow**, Northwestern University |
| 5:45 p.m. | Earth Abundant Photosensitizers Enabling Solar Photochemistry<br>**Phil Castellano**, North Carolina State University |
| 6:15 p.m. | Working Dinner |
| 7:00 p.m. | (*during dinner*)<br>Bio-Inspired Light-Escalated Chemistry: Amplifying chemical reactions with light<br>**Greg Scholes**, Princeton University |
| 7:30 p.m. | Posters (Even numbers) |

**Tuesday, June 3**

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|---|---|
| 7:30 a.m. | Breakfast |

## SESSION 5
## Spectroscopy
Dugan Hayes, Chair

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|---|---|
| 8:30 a.m. | Ultrafast Functional Structural Dynamics in Solar Energy Conversion<br>**Lin Chen**, Argonne National Laboratory |
| 9:00 a.m. | Distinct Reaction Mechanisms of Ir Blue Dimer Photocatalysts Unraveled by Time Resolved Spectroscopy<br>**Jier Huang**, Boston College |

9:15 a.m. Triplet-Pair Mediated Systems for Multiexciton-Driven Photochemistry
**Matthew Sfeir**, City University of New York
**Luis Campos**, Columbia University

9:45 a.m. Photoactive Ligand Design for Directing Excited-State Dynamics
**Justin Johnson**, National Renewable Energy Laboratory

10:15 a.m. Break

## SESSION 6
## Semiconductor/Molecular Interfaces
Mike Rose, Chair

11:00 a.m. Linker Design for Molecular-Level Control at Semiconductor Interfaces
**Elena Galoppini**, Rutgers University

11:30 a.m. Designing Silicon-Molecular Catalyst Hybrid Photocathodes
**Nate Neale**, National Renewable Energy Laboratory

12:00 p.m. Working Lunch (*discussion of the scientific presentations throughout the meeting*)

1:30 p.m. Informal Networking

## SESSION 7
## Architectural and Environmental Impacts on Water Splitting
Jing Gu, Chair

3:30 p.m. Characterization of structural, physical, and chemical characteristics of semiconductor/metal interfaces on functioning hybrid photocatalysts
**Suljo Linic**, University of Michigan

4:00 p.m. Harnessing resonant multiple scattering for solar photoelectrochemical energy conversion
**Rob Coridan**, University of Arkansas

4:30 p.m. Exploring the effect of thermal energy by the plasmonic photothermal catalyst in water splitting
**Iltai Kim**, Texas A&M University

4:45 p.m. Break

## SESSION 8
## $CO_2$ Reduction via CISS or Reactions Mediated by Ensembles
Annie Greenaway, Chair

5:00 p.m. Controlling Electrochemical $CO_2$ Reduction using Chirality Induced Spin Selectivity
**Jao van de Lagemaat**, National Renewable Energy Laboratory

5:30 p.m. Solar $CO_2$ Reduction using Single Atom Catalysts on $C_3N_4$ Modified with Dianhydrides
**Gonghu Li**, University of New Hampshire

5:45 p.m. Probing Local Potentials and Rates of Nanoscale Photocatalysts
**Shu Hu**, Yale University

6:15 p.m. Working Dinner

7:00 p.m. (*during dinner*)
Ensembles of Photosynthetic Nanoreactors (EPN) Energy Frontier Research Center
**Shane Ardo**, University of California, Irvine

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

**<u>Wednesday, June 4</u>**

7:30 a.m. Breakfast

## SESSION 9
## Photoinduced Charge Transfer / Transport
Alex Martinson, Chair

8:30 a.m. Pulse Radiolysis Probes Deep into Redox Catalysis and (Proton-Coupled) Electron Transfer
**Dmitry Polyanski (or other)**, Brookhaven National Laboratory

9:00 a.m. Molecular engineering control of photo-induced charge transfer and transport in donor-acceptor frameworks
**Jenny Lockard**, Rutgers University

9:15 a.m. Photoelectrochemical Formation of Strategic Fuels Using Soft (Molecular Semiconductor) Materials – The Center for Soft PhotoElectroChemical Systems (SPECS)
**Erin Ratcliff**, Georgia Institute of Technology
**Neal Armstrong**, University of Arizona

9:45 a.m. Break

## SESSION 10
## Carbon Capture Integration
Javier Concepcion, Chair

10:30 a.m. From Captured $CO_2$ to Value-added Chemicals: A Photochemical Approach
**Ksenija Glusac**, Argonne National Laboratory

11:00 a.m. Center for Closing the Carbon Cycle EFRC
**Jenny Yang**, University of California, Irvine

11:30 a.m. Working Lunch (*discussion of the scientific presentations throughout the meeting*)

## SESSION 11

## Coherent Effects

Libai Huang, Chair

| | |
|---|---|
| 12:45 p.m. | Ultrafast Electron and Energy Transfer: Some New Results<br>**Greg Scholes**, Princeton University |
| 1:15 p.m. | Light Harvesting and Charge Transfer Dynamics in Chromophore Single Crystals<br>**Michael Wasielewski**, Northwestern University |
| 1:45 p.m. | Unprecedented Control of Spin, Charge, and Light with Hybrid Organic Inorganic Semiconductors<br>**Matt Beard**, National Renewable Energy Laboratory |
| 2:15 p.m. | Closing Comments<br>**Chris Fecko and Jenny Roizen**, DOE Office of Basic Energy Sciences |
| 2:30 p.m. | Adjourn |

# Energy Capture and Conversion in Self-assembled Chlorophyll Analogues

Jonathan Lindsey,[1] Gabriela S. Schlau-Cohen,[2] Phuong Tran,[1] Arup Kundu,[2] Madelyn N. Scott[2]
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Tetrapyrroles are Nature's chromophores; most notably, they include the chlorophylls, bacteriochlorophylls, and porphyrins that capture and convert solar energy at a scale sufficient to power most life on Earth. While these molecules have been extensively studied as monomers and within proteins, their properties in synthetic, strongly coupled organizations remain largely unexplored. Our investigations focus on engineering and self-assembling novel tetrapyrrole macrocycles into materials that selectively and specifically engender energy transport or charge separation. Our integrative program encompasses molecular design, synthesis, spectroscopy, and theoretical simulations which, taken together, offer insights into the structural features that underpin patterns of molecular assembly and how the intermolecular interactions generated by such aggregate organizations drive each photophysical outcome (**Figure 1**). During this reporting period, we began preparation of two manuscripts. In addition, work is ongoing to develop and produce fully synthetic bacteriochlorin compounds for chlorosomal assemblies.

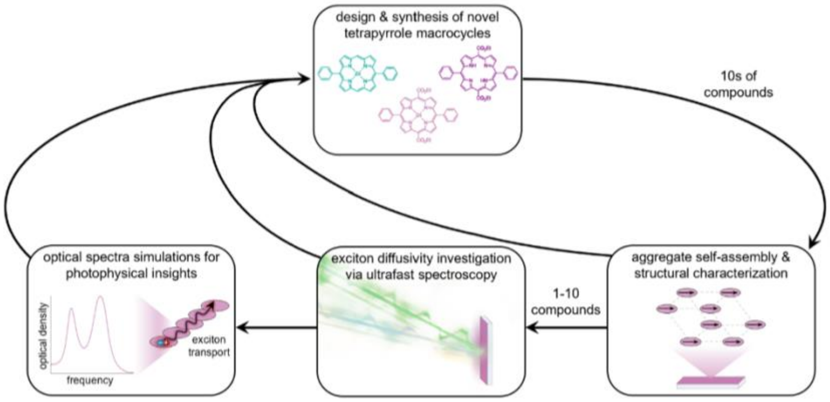

**Figure 1. Rational design, screening, and characterization of tetrapyrrole supramolecular aggregates for targeted photophysical functions**. More than 10 novel tetrapyrrole macrocycles were synthesized and screened for their ability to self-assemble into ordered aggregates. A subset of 1-10 promising molecular aggregates were measured by ultrafast optical spectroscopy to probe exciton diffusivity. Experimental data were interpreted in conjunction with simulations of the optical spectra to reveal structure-function relationships and guide iterative molecular design.

We applied the integrated workflow to an initial set of porphyrin compounds. The Lindsey group synthesized seven porphyrins and shipped them to the Schlau-Cohen lab for studies of self-assembly in thin films and exciton migration therein upon illumination. Porphyrins were characterized by single-crystal X-ray diffraction (SCXRD) and steady-state spectroscopy followed by an evaluation of their aggregation properties. This initial screen identified a promising candidate for aggregate formation, Por1-Zn (**Figure 2a**).

We introduced two different types of aggregates of Por1-Zn: a solution phase aggregate suspended in water, prepared by rapid injection method; and a solid spin coated film. Steady state absorption and fluorescence spectra (Figure 2.a, b) suggest clear formation of molecular aggregates. The structure of the aggregate in film was characterized with Grazing-Incidence Wide-Angle X-ray Scattering, which suggested long range ordered repeating units of ~5.7 nm along with short range orderedness. To estimate the singlet exciton diffusion in these aggregates, we employed femtosecond transient absorption (TA) spectroscopy to probe exciton-exciton annihilation (EEA). Our global analysis to the fluence dependent EEA (Figure 3.f, g) gave rise to a diffusion constant of 7.1 x $10^{-3}$ $cm^2s^{-1}$ and 5.5 x $10^{-3}$ $cm^2s^{-1}$ for the for the solution aggregate and film leading to 51 nm and 43 nm diffusion length (Figure 3.h) respectively. These results suggest a long-range singlet exciton transport in our designed aggregates of Por1-Zn macromolecule, having significant potential for optoelectronic applications.

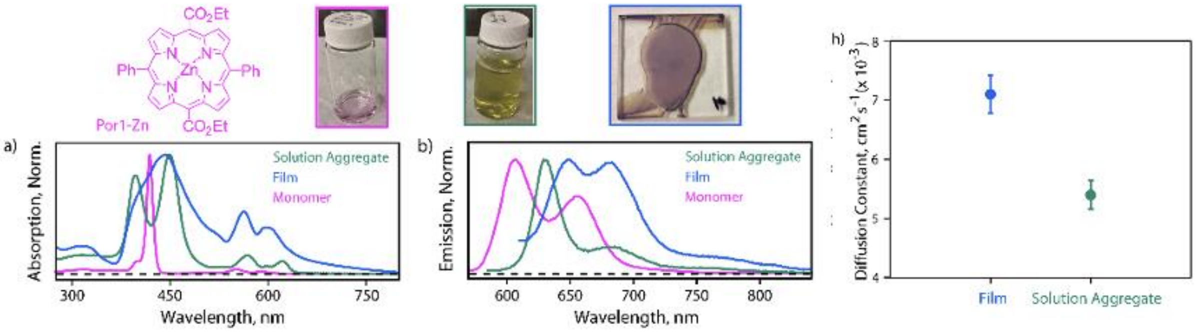

**Figure 2.** Molecular structure of the Por1-Zn tetrapyrrole macromolecule and the images of the monomer solution (in THF), solution aggregate and spin coated film of Por1-Zn (top of left two panels). Comparative (a) absorption, (b) fluorescence spectra and (c) fluorescence lifetime of the solution aggregate, film and monomer of Por1-Zn. (d) GI-WAXS profile of Por1-Zn film. Obtained distance parameters are labeled to the corresponding peaks. (e) Femtosecond transient absorption spectra collected at 1 ps for the Por1-Zn solution aggregate, film and monomer subsequent to photoexcitation at 400 nm. (f) and (g) Fluence dependent singlet exciton decay for the solution aggregate and film respectively. (h) Diffusion constant values for the solution aggregate and film estimated from the singlet-singlet exciton annihilation kinetics.

Two of the newly synthesized porphyrins, Por2-Zn and Por3-Zn, were prepared with use of a TBDMS-protected hydroxymethyldipyrromethane. These compounds show characteristic porphyrin-like absorption with a bathochromic shift both in the Soret and Q-bands due to the presence of extra two phenyl groups. Ongoing work is characterizing their excited-state manifold.

**Future plans:**

- Preparation of the Por1-Zn aggregate results for publication.
- Preparation of Por2-Zn and Por3-Zn characterization for publication.
- The synthesis of porphyrin, chlorin, and bacteriochlorin analogues of the chlorosomal bacteriochlorophylls is underway.
- The integrated workflow established during the first year of the award will be applied to chlorosomal analogues.

## DOE Solar Photochemistry Sponsored Publications for the reporting period 08/01/2024-04/15/2025

(1) "Synthesis of Porphyrin Triads Chelated with Thallium(III) for Studies of Ground-State Hole/Electron Transfer," Wang, J.; Taniguchi, M.; Bocian, D. F.; Lindsey, J. S. *J. Porphyrins Phthalocyanines* **2024**, *28*, 515-526. DOI: 10.1142/S1088424624500524

(2) "Synthesis of (Oxo)chlorin Dimers Chelated with Thallium(III)," Aravindu, K.; Taniguchi, M.; Bocian, D. F.; Lindsey, J. S. *J. Porphyrins Phthalocyanines* **2024**, *28*, 527-535. DOI: 10.1142/S1088424624500548

(3) "GOUTERMAN – A Module for Simulations of Tetrapyrrole Optical Spectra," Du, H.; Taniguchi, M.; Diers, J. R.; Kirmaier, C.; Bocian, D. F.; Lindsey, J. S.; Holten, D. *Photochem. Photobiol.* **2025**, *in press.* DOI: 10.1111/php.14057.

(4) "Database of Frontier Molecular Orbitals for Diverse Tetrapyrrole Macrocycles," Diers, J. R.; Taniguchi, M.; Du, H.; Kirmaier, C.; Lindsey, J. S.; Holten, D.; Bocian, D. F. *J. Porphyrins Phthalocyanines* **2025**, *in press.*

(5) "Noninvasive Cardiac Modulation via Triplet-Sensitized Photoswitching in the Phototherapeutic Window," Naimovičius, L.; Miroshnichenko, M.; Opar, E.; Bharmoria, P.; Hölzel, H.; Morikawa, M.-A.; Kimizuka, N.; Dapkevičius, M.; Lekavičius, J.; Radiunas, E.; Kazlauskas, K.; Cilleros-Mañe, V.; Riefolo, F.; Matera, C.; Harmandar, K.; Taniguchi, M.; Dumoulin, F.; Lindsey, J. S.; Gorostiza, P.; Moth-Poulsen, K. *Nat. Commun*. **2025**, *in press.*

(6) "Amino Acid Betaxanthins: Absorption, Fluorescence, and Stability," Esteves, L. C.; Pinheiro, A. C.; Machado, C. O.; Taniguchi, M.; Lindsey, J. S.; Bastos, E. L. *J. Nat. Prod. submitted 04/02/2025*.

(7) "Performance of Chatbots in Queries Concerning Fundamental Concepts in Photochemistry," Taniguchi, M.; Lindsey, J. S. *Photochem. Photobiol.* **2025**, *in press*. DOI: 10.1111/php.14037.

(8) "Acquisition of Absorption and Fluorescence Spectral Data Using Chatbots," Taniguchi, M.; Lindsey, J. S. *Digit. Discov.* **2025**, *4*, 21-34. DOI: 10.1039/D4DD00255E *Cover art for the issue.*

(9) "Chatbots Can Guide Measurement of Absorption Spectra with Improved Quality," Taniguchi, M.; Lindsey, J. S. *Proc. SPIE* **2025**, *13339*, 133390A. DOI:10.1117/12.3043918

(10) "Conformational Analysis of Swallowtail Motifs in Porphyrins," Cao, P.-L. D.; Chau Nguyen, K.; Nevzorov, A. A.; Jovanovic, M.; Nalaoh, P.; Lindsey, J. S. *J. Org. Chem.* **2025**, *90*, 146-157. DOI: 10.1021/acs.joc.4c02059.

(11) "Single-Crystal X-Ray Structure Analysis of a Synthetic Chlorin," Tran, V.-P.; Nalaoh, P.; Lindsey, J. S. *J. Porphyrins Phthalocyanines* **2025**, *29*, 262-269. DOI: 10.1142/S1088424625500221

# Modular Nanoscale and Biomimetic Assemblies for Photocatalytic Hydrogen Generation

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The overarching goal of this project is to develop, understand, and optimize photochemical systems for hydrogen ($H_2$) production from water. These systems center on nanocrystalline quantum dots (QDs), which absorb visible light, catalyze $H_2$ production, and/or transfer electrons to a bioinspired cocatalyst. To accelerate the slow hole transfer step from the QD, polyoxovanadates (POVs) are being explored. A key objective of this work is to develop structure-function relationships governing activity of these systems.

A limitation to the implementation of CdSe QDs in these systems is the efficient removal of photogenerated holes. Previously, our team has demonstrated that incorporation of oxygen vacancies in POV-alkoxides improves hole transfer kinetics by enabling *in situ* surface coordination of the metal oxide assembly to P=O moieties of tetradecaphosphinic acid (TDPA) capped QDs. To further generalize this approach, we have recently demonstrated the ability to tune the efficiency of hole transfer from CdSe QDs to POV-alkoxides as a function of surface ligand density. By partially stripping native ligands from the QD surface with a mild stripping agent (trimethyloxonium tetrafluoroborate; Meerwein's salt, MS), we have shown that the extent of hole transfer from QD to cluster increases as more of the QD surface becomes accessible to the sterically-hindered cluster (**Figure 1**). Further, we have quantified the extent of cluster coverage on the QD surface as the nanocrystal is treated with increasing amounts of stripping agent, establishing a proportional relationship between amount of ligand stripped and the fraction of QD surface area that as a result is made available for charge transfer. These results demonstrate the importance of obtaining precise control over the nanocrystal surface to achieve effective hole transfer between CdSe QD donors and molecular acceptors.

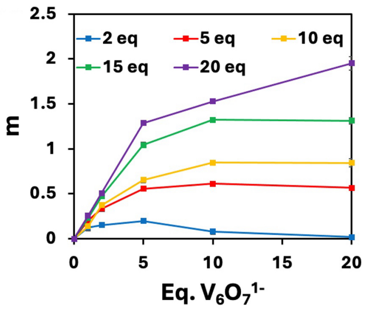


**Figure 1.** Number of equivalent hole acceptors *m* interacting with the QDs for different concentrations of MS related to the equivalents of $V_6O_7^{1-}$ cluster per QD.

We have continued to discover new bioinspired cocatalyst-QD photocatalytic systems. In one example, we investigated proton reduction catalysis using a thiomolybdate cluster (molecular formula $[Mo_3S_{13}]^{2-}$) and CdSe QDs capped with an amphiphilic phosphonate capping ligand, TEGPA (TEGPA = tetraethylene glycol monomethyl ether phosphonic acid). The use of TEGPA capping ligands allow for photocatalysis studies in mixtures of organic/aqueous solvents, while tuning the reaction medium to be consistent with the stability of the active catalyst. Enhanced $H_2$ production is observed in samples where TEGPA-capped CdSe QDs were combined with $[Mo_3S_{13}]^{2-}$ (catalyst) and

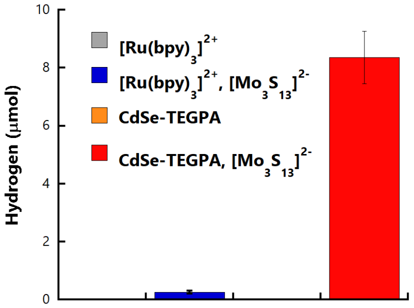


**Figure 2.** Photocatalytic $H_2$ production after 24 hours of irradiation in 9:1 DMF:$H_2O$. Appreciable $H_2$ is produced only when TEGPA-QDs, $[Mo_3S_{13}]^{2-}$, and ascorbic acid is present.

ascorbic acid (AA; sacrificial electron donor and $H^+$ source), in comparison to catalyst/$Ru(bpy)_3^{2+}$/AA mixtures or CdSe QD/AA alone (**Figure 2**). Quenching of TEGPA-capped CdSe QD photoluminescence by $[Mo_3S_{13}]^{2-}$ is observed, consistent with the transfer of charge between the photoexcited CdSe and the cocatalyst. Additional work in this objective has continued in the development of cobalt porphyrin-based catalysts for $H_2$ production in combination with QDs. Pairing cobalt(III)-tetrakis(4-sulfonatophenyl)porphyrin (CoTPPS) with mercaptopropoionic acid (MPA) capped CdSe QDs significantly enhances $H_2$ production with respect to the absence of cocatalyst. However, using the cobalt porphyrin peptide CoMP11-Ac as a cocatalyst more than doubles the amount of $H_2$ produced (**Figure 3**). Analysis of electrocatalytic $H_2$ production activity by these two catalysts suggests that CoMP11-Ac has higher $H_2$ evolution activity, in particular in the presence of AA, which is proposed to enhance proton transfer to these catalysts.

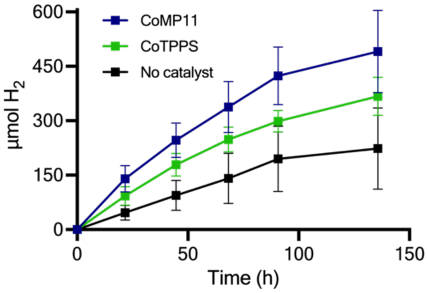
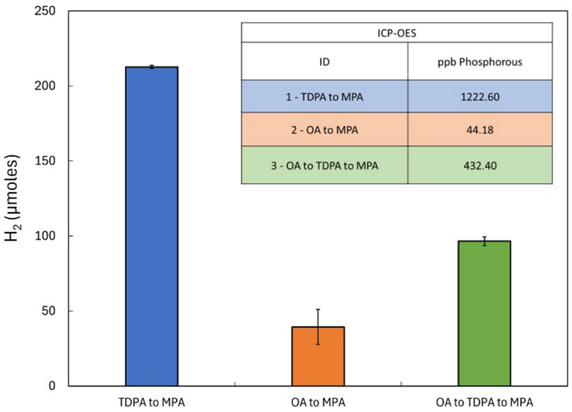


**Figure 3.** Hydrogen production over 130 h in 0.5 M ascorbic acid, pH 4.5, 530-nm irradiation, by CdSe-MPA (1 mM) alone (black) or in the presence of 1 mM CoTPPS (green) or CoMP11-Ac (blue).

We also explored whether the processing history of CdSe QDs had an appreciable effect on photocatalytic $H_2$ production. Specifically, CdSe QDs were synthesized using two different methods: QDs were capped with tetradecylphosphonic acid (TDPA) or with oleic acid (OA). Both sets of QDs had similar size, size-distribution, shape, and crystal structure, and were capped with MPA to afford solubility in water. Given their near identical properties, we hypothesized they would perform similarly for photocatalytic $H_2$ production. However, as seen in **Figure 4**, nanocrystals natively capped with TDPA were five times more active for photocatalytic proton reduction in comparison to the QDs with original OA ligands. Interestingly, exchanging the OA for TDPA before MPA-capping led to a three-fold increase in catalytic activity (**Figure 4**), suggesting that residual surface-bound TDPA may be contributing to the higher activity. Indeed, ICP-OES measurements of QDs capped with TDPA, OA, and with OA exchanged to TDPA that all subsequently had their surface capping ligands exchanged for MPA revealed that exposing QDs to TDPA led to some residual phosphorous being present (**Figure 4**, inset). Ongoing experiments have the goal of exploring different phosphorous-containing ligands in order to determine the chemical form of the catalytically active phosphorous species on the QD surface.



| ICP-OES | |
|---|---|
| ID | ppb Phosphorous |
| 1 - TDPA to MPA | 1222.60 |
| 2 - OA to MPA | 44.18 |
| 3 - OA to TDPA to MPA | 432.40 |

**Figure 4.** When TDPA is exchanged on OA-CdSe QDs before ligand exchange with MPA, there is a boost in photocatalytic activity, suggesting the phosphonate ligand contributes to this increase. ICP-OES confirms higher phosphorous presence contributes to higher activity (inset).

**DOE Solar Photochemistry Sponsored Publications 2022-2025**

1. Potential- and Buffer-Dependent Selectivity for the Conversion of $CO_2$ to CO by a Cobalt Porphyrin-Peptide Electrocatalyst in Water. J. L. Alvarez-Hernandez, A. A. Salamatian, J. W. Han, K. L. Bren, *ACS Catal.* **2022**, *12*, 14689-14697. DOI: 10.1021/acscatal.2c03297

2. A Cobalt Mimochrome for Photochemical Hydrogen Evolution from Neutral Water, E. M. Edwards, J. M. Le, A. A. Salamatian, N. L. Peluso, L. Leone, A. Lombardi, K. L. Bren, *J. Inorg. Biochem.*, **2022**, *230*, 11753. DOI: 10.1016/j.jinorgbio.2022.111753

3. Physicochemical Implications of Surface Alkylation of High-valent, Lindqvist-type Polyoxovanadate-alkoxide Clusters, A. A. Fertig, S. M. Gulam Rabbani, W. Brennessel., P. Miro, E. M. Matson, *Nanoscale* **2022**, *13*, 6162-6173. DOI: 10.1039/D0NR09201K

4. Charge-State Dependence of Proton Uptake in Polyoxovanadate-Alkoxide Clusters. E. Schreiber, W. W. Brennessel, E. M. Matson, *Inorg. Chem.* **2022**, *61*, 4789-4800. DOI: 10.1021/acs.inorgchem.1c02937

5. Bioinspired and Biomolecular Catalysts for Energy Conversion and Storage. A. A. Salamatian, K. L. Bren, *FEBS Lett.* **2023**, *597*, 174-190. DOI: 10.1002/1873-3468.14533

6. *Shewanella oneidensis* MR-1 Respires CdSe Quantum Dots for Photocatalytic Hydrogen Evolution. E. H. Edwards, J. Jelušić, R. M. Kosko, K. P. McClelland, S. S. Ngarnim, W. Chiang, S. Lampa-Pastirk, T. D. Krauss, K. L. Bren. *Proc. Natl. Acad. Sci. USA,* **2023**, *120*, e220697512, DOI: 10.1073/pnas.2206975120.

7. Hydrogen Evolution Catalysis by a Cobalt Porphyrin Peptide: A Proposed Role for Porphyrin Propionic Acid Groups, J. L. Alvarez-Herandez, A. A. Salamatian, A. E. Sopchak, K. L. Bren, *J. Inorg. Biochem.*, **2023**, *249*, 112390. DOI: 10.1016/j.jinorgbio.2023.112390

8. Efficient Hole Transfer from CdSe Quantum Dots Enabled by Oxygen-Deficient Polyoxovanadate Clusters, N. M. B. Cogan, K. P. McClelland, A. A. Fertig, T. M. Tumiel, W. W. Brennessel, T. D. Krauss, E. M. Matson, *Nano Lett.*, **2023**, *23*, 10221-10227. DOI: 10.1021/acs.nanolett.3c02749

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# The Photosystem II SuperComplex: Antenna Design and Dynamics

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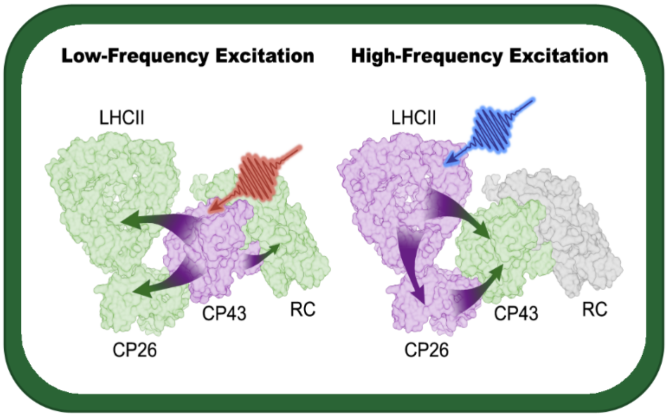

A combined experimental, theoretical and modeling approach was applied to the $C_2S_2M_2$ (312 chlorophylls (Chls)) and the $C_2S_2$ (208 Chls) super complexes of Photosystem II. The experiments used two-dimensional electronic-vibrational spectroscopy [15] and intensity cycling pump probe spectroscopy [17] both in the $C_2S_2$ SC. Calculations and modeling were made in both the $C_2S_2M_2$ and $C_2S_2$ SC's at the trajectory level [12] and the ensemble level [16]. We found that energy flow is bidirectional in the supercomplexes, with excitations initially close to the reaction center (RC), initially moving away from their reaction center [15, 12]. The distance, on average, that an exciton travels was evaluated both from experiment via the 5th order nonlinear response and from kinetic Monte Carlo simulations via the trajectory displacement method [17]. We found the diffusion length to be 7.4nm in $C_2S_2$ and 9.7nm in $C_2S_2M_2$ [17]. Turning to an ensemble view, the time dependent Shannon entropy and enthalpic contributions to $\Delta G$ were calculated for the $C_2S_2M_2$ SC [16]. Remarkably, up to 50% of the average fluorescence lifetime is taken up with entropy driven exploration of the landscape before more directed, enthalpic division, motion towards the reaction center takes over [16]. When one of the two reaction centers is closed, the entropy term dominates $\Delta G$ for longer, allowing the ensemble to explore the pathways that lead to the other open reaction center.

Questions about quantum coherence remain from our 2DES papers in 2007 and 2009. In particular, can you show experimentally that a system evolves quantum mechanically? This can be done by exploring photon statistics on a picosecond time scale. I will describe how this might be done and describe progress to date on measuring $G^{(2)}(\boldsymbol{\tau})$ on a longer timescale for single photons and thermal light sources.

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5. Closing lecture: Directing and Controlling Materials and Molecules. G. R. Fleming Faraday Discussions, 237, 419-427 (2022)
6. From Antenna to Reaction Center: Pathways of Ultrafast Energy and Charge Transfer in Photosystem II. S-J Yang, et al. Proc. Natl. Acad. Sci. 119, e2208033119 (2022)
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# Mechanistic Insight into Metal Hydride Photochemistry Enables Catalytic $H_2$ Evolution and Hydrogen Transfer

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The proposed research seeks to understand and advance *molecular photoelectrocatalysts*, transition metal complexes capable of mediating both electrochemical hydride generation and photochemical fuel formation. The research approach connects the photophysics and photochemical mechanisms of isolable metal hydride complexes with the development of photoelectrocatalytic $H_2$ evolution and hydrogen transfer reactions. The presentation will focus on recent progress understanding the photochemistry and photoelectrocatalysis of nickel hydrides.

Nickel hydride complexes of the type $[HNi(diphosphine)_2]^+$ generate $H_2$ upon visible light illumination, enabling molecular photoelectrocatalysis by a 3d transition metal catalyst (**Figure 1A**). The mechanism of $H_2$ evolution was studied through kinetic analysis of quantum yields, time-resolved spectroscopy, and computational methods, leading to a proposal that a short-lived excited state with Ni–H σ* antibonding character undergoes homolysis to release a solvated hydrogen atom that reacts with a ground-state hydride complex to generate $H_2$. The biggest current limitation of the nickel hydride system is the relatively low quantum yield ($\Phi_{H2} = 0.005$). Two hypotheses were investigated: the excited state lifetime could be sufficiently short that thermal relaxation occurs before homolysis, or the homolysis could be efficient but the released H• rapidly re-forms the Ni–H bond before productive chemistry occurs. Systematic structural variations have been made to distinguish between these pathways and improve photochemical $H_2$ evolution. **Figure 1B** summarizes initial studies of Ni hydrides with more rigid ligands, which uncovered more than five-fold increases in $\Phi_{H2}$. The improvements in quantum efficiency are promising for planned attempts to observe photochemical intermediates using time-resolved spectroscopy.

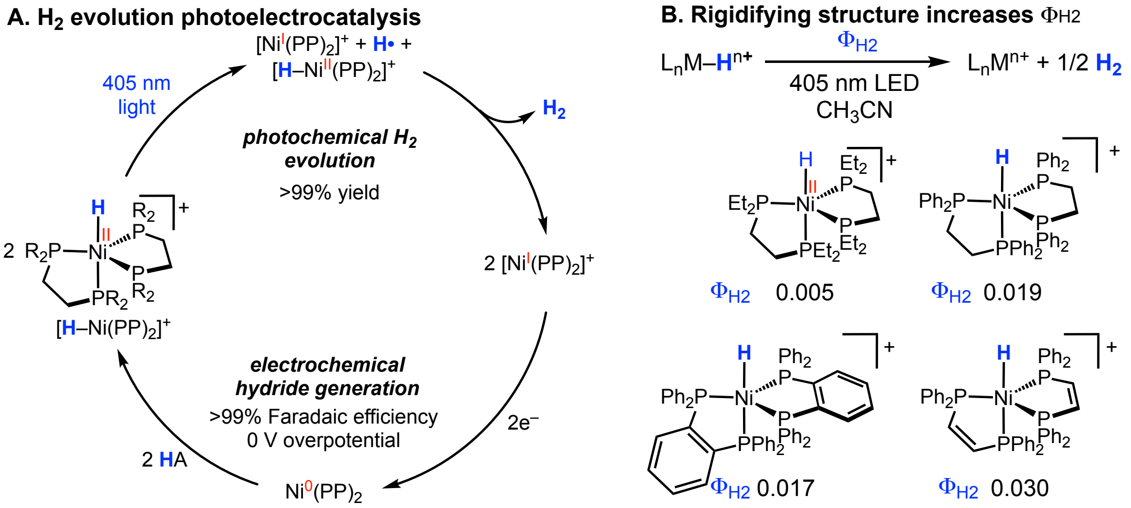
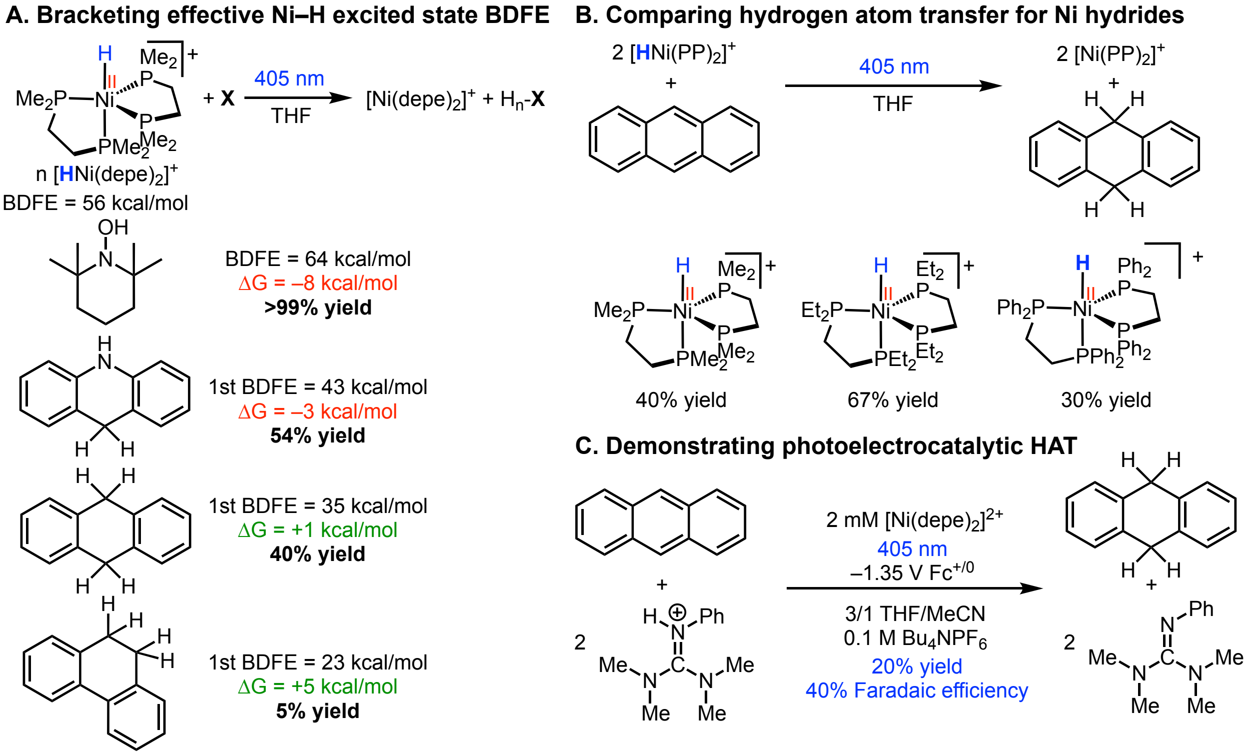


**Figure 1**. (A) Proposed mechanism of photoelectrocatalytic $H_2$ evolution via excited state homolysis. (B) Structure-function studies on rigidification for improved $H_2$ quantum yield ($\Phi_{H2}$).

If $H_2$ evolution proceeds via a mechanism with solvated hydrogen atoms as intermediates, hydrogen atom transfer (HAT) reactions should be possible. Indeed, photolysis of $[HNi(diphosphine)_2]^+$ complexes in the presence of TEMPO• generates TEMPO–H in high yield, with complete suppression of $H_2$ evolution in some cases. A comprehensive study varying the catalyst, solvent, and hydrogen atom acceptor was conducted. **Figure 2A** compares a range of hydrogen atom acceptors that bracket the effective BDFE of the photogenerated H atom source. The ability to reduce anthracene and phenanthrene is consistent with the Ni hydrides being extremely potent photochemical hydrogen atom donors, effective BDFE ca. 20 kcal/mol. The first hydrogen atom transfer would be ca. 30 kcal/mol uphill in the dark in some cases. The highest yields of dihydroanthracene were found for $[HNi(depe)_2]^+$, which forms a stable nickel(I) product after HAT (**Figure 2B**). Photoelectrocatalytic reduction of anthracene to dihydroanthracene was demonstrated, with activity under visible light at applied potentials that were more than 1 V less negative than the direct reduction of anthracene in the dark (**Figure 2C**).



**A. Bracketing effective Ni–H excited state BDFE**

**B. Comparing hydrogen atom transfer for Ni hydrides**

**C. Demonstrating photoelectrocatalytic HAT**

**Figure 2**. (A) Photochemical HAT to various organic acceptors correlates with the thermodynamic strength of the first bond dissociation free energy (BDFE). (B) Photochemical anthracene reduction as a function of Ni hydride structure. (C) Photoelectrocatalytic anthracene reduction.

Demonstrating both $H_2$ evolution and HAT with the same catalysts highlights the versatility of the nickel catalysts. A key finding is that excited state homolysis to generate reactive hydrogen atom donors is a mechanism that specifically enables the observed tuning between reaction pathways. This stands in contrast to prior work on 5d metal hydrides, which underwent excited state self-quenching that inherently generates a proximal pair of reactive species that with a strong kinetic bias towards $H_2$ evolution. Current research is focused on continued expansion of first-row transition metal hydride structures to improve the photochemical quantum yields, shift the light absorption profile to the red, and understand mechanisms of catalyst degradation.

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# Improving the Efficiencies of Photo(electro)catalytic Processes using Molecular Catalysts

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This talk addresses our recent efforts to improve photon-to-chemical conversion efficiencies using second-sphere ligand functionalization to enable new mechanisms of self-sensitized photocatalysis on the Re(bpy)$(CO)_3$Cl platform. When applied to Mn-based electrocatalysts, fast rates and low overpotentials for $CO_2$ reduction are obtained in purely aqueous media. Finally, radiation induced graft polymerization is presented as a new approach to photocatalytic assembly with self-sensitized photocatalysis demonstrated as a proof-of-concept.

Self-sensitized photocatalysts represent a unique class of molecules capable of the dual roles of light absorption and catalysis without the assistance of an external chromophore. Examples of this reactivity remain comparatively scarce and generally limited to structural derivatives of a few main classes of compounds due to several constraints including long-lived excited states, photostability of reduced species, and viable pathways to $CO_2$ binding reactivity, which usually requires a second reduction. Thus, these rare molecules are desirable for their operational simplicity and perplexing in their mechanistic details. Rhenium(I) tricarbonyl complexes *fac*-$[Re(bpy)(CO)_3(L)]^{n+}$ are the classic examples of self-sensitized photocatalysts, and while the majority of work in the field has focused on this class of molecules, the mechanisms, especially the nature of $CO_2$ binding, remain vigorously debated. Evidence for various pathways, e.g. i) binding of $CO_2$ to the one-electron reduced (OER) species, ii) solution electron transfer between two forms of the OER, one with a weak O-bound $CO_2$ ligand, and iii) binuclear binding of $CO_2$ with two OER species.

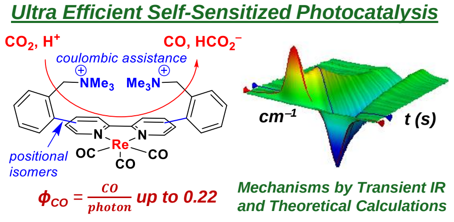

Figure 1. Efficient photocatalysis enabled by disproportionation.

Here we present a series of dicationic halido or tricationic solvento complexes *fac*-$[Re(bpy^{2+})(CO)_3X]^{n+}$ $(PF_6)_n$ (where X = $Cl^-$ or $I^-$ (n = 2), or $CH_3CN$ (n = 3) and $bpy^{2+}$ is bipyridine modified by two $-CH_2-(NMe_3)^+$ tetra-alkylammonium cations) that have been investigated as self-sensitized and sensitized $CO_2$ reduction photocatalysts. Four structural isomers differing in the position of the cations have been tested in *N*,*N′*-dimethylacetamide solvent (DMA) using 1,3-dimethyl-2-phenyl-2,3-dihydro-1*H*-benzimidazole (BIH) as the electron donor, and the position of the cationic pendants has a significant impact on the catalyst turnover number and quantum efficiency ($\phi$). Up to 315 self-sensitized turnovers of CO have been achieved, and an extremely efficient quantum yield ($\phi_{CO}$) of 22% has been measured. Time-resolved infrared spectroscopy and theoretical calculations were used to characterize the catalytic cycle including the ligand exchange between one-electron reduced halido and solvento species as well as the binding of $CO_2$ to the putative two-electron reduced (TER) species. The $CO_2$-reactive TER catalyst was formed by disproportionation or intramolecular electron transfer between two forms of the OER catalyst as indicated by the formation of the fully oxidized catalyst concurrent with $CO_2$ binding. This is the first direct observation of disproportionation in self-sensitized catalysis on the pathway to the TER species and it is enabled by the native properties of the charged catalysts, i.e. ligand lability of the OER species and positive redox potentials attributed to the pendent cations. When $[Ru(bpy)_3]^{2+}$ was used as a sensitizer, catalyst durability improved, and the selectivity toward formate increased as high as 3.3:1 over CO (total TON = 1570) due to acidification of the reaction, which promotes formation of the hydride intermediate, as BIH was consumed and deprotonated.

In an effort to improve the sustainability of this approach, Mn-based electrocatalysts have been synthesized. The cationic ligand platform is also compatible with *fac*-$[Mn(bpy^{2+})(CO)_3Br]^{2+}$, and four isomers have been prepared. Unlike Re-based catalysts, the Mn catalysts show poor reactivity in organic solvents and decompose as indicated by deposition on the electrode. On the other hand, the Mn congeners exhibit excellent electrocatalytic reactivity in water / $KHCO_3$ with so-called *protonation-first* (~200 $s^{-1}$) and *reduction-first* (~800 $s^{-1}$) mechanisms occurring at -1.10 and -1.40 V vs SCE, respectively. In previous literature, the reduction first pathway was obtained using moderately strong acids in organic solvents. We observed that the mechanisms and selectivity for CO vs $H_2$ production change with the nature of the isomer. For example, the 5,5-ortho isomer produces exclusively CO, while the 6,6-ortho isomer is active for proton reduction.

Finally, radiation induced graft polymerization (RIGP) will be discussed as a new technique for assembly and immobilization of catalysts and chromophores for photo(electro)catalytic reactions. RIGP is a versatile method for generating stable carbon radicals on a large choice of substrates. In a second step, thermal radical polymerization is used to grow a chosen material onto the initial support. Here we have grown (4-chloromethyl)-polystyrene on sheets of high-density polypropylene support and have installed $Re(bpy)(CO)_3Cl$-type catalysts and $Ru(bpy)_3^{2+}$ chromophores by post-synthetic covalent attachment. Initial data show that the immobilized Re catalysts function as self-sensitized photocatalysts despite the nonconductive nature of the support. Mechanistic implications and future directions will be presented.

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# Photodriven Energy and Electron Transfer in Semiconductor-Molecular Hybrids

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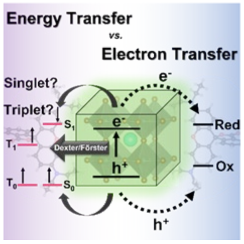
Semiconductor nanocrystals that absorb in the visible and near infrared, serve as building blocks to harvest photons and initiate energy or electron transfer to surface bound chromophores. The multifunctional properties of semiconductor nanocrystals make it challenging to steer the energy and or electron transfer pathway selectively (Scheme 1). Proper selection of the semiconductor nanocrystal donor requires consideration of the nanocrystal bandgap, along with the alignment of valence and conduction band energies relative to that of the acceptor, in order to achieve desired output of energy or electron transfer.



Scheme 1. Multifunctional characteristics of Semiconductor nanocrystals.

**Singlet vs. Triplet Energy Transfer.** By employing halide perovskite nanocrystals as a model donor, we have obtained mechanistic insights into singlet or triplet energy transfer processes. The singlet and triplet characteristics of the semiconductor nanoparticle enable tuning of energy transfer pathways through its bandgap engineering. The alignment of energy levels between the semiconductor donor and the singlet/triplet energy levels of the acceptor dye, plays integral role in directing energy transfer. For example, in a prototypical $CsPbBr_3$ nanocrystal - rhodamine dye assembly, singlet energy transfer is observed because of its high bandgap ($E_g$= 2.47 eV). However, when the donor is a low bandgap semiconductor, viz., $CsPbI_3$ ($E_g$=1.87 eV), one observes only triplet energy transfer. From the bleach recovery kinetics, we obtain rate constants of triplet energy transfer ($k_{triplet}$) between $0.25\times10^9$ $s^{-1}$ to $1 \times10^9$ $s^{-1}$ for the three rhodamine dyes. It is interesting to note that $k_{triplet}$ with $CsPbI_3$ is nearly two orders of magnitude smaller than the singlet energy transfer seen with $CsPbBr_3$ nanocrystals (Figure 1). Although both singlet and triplet energy transfer deactivation pathways are thermodynamically favorable with $CsPbBr_3$ donor, we observe only singlet energy transfer to rhodamine dyes ($E_{singlet}$ ~ 2.19 eV), as it kinetically outcompetes triplet energy transfer. The existence of fast and slow energy transfer steps is indicative of the fact that singlet exciton and triplet exciton (or trap site) states are involved in the transfer of

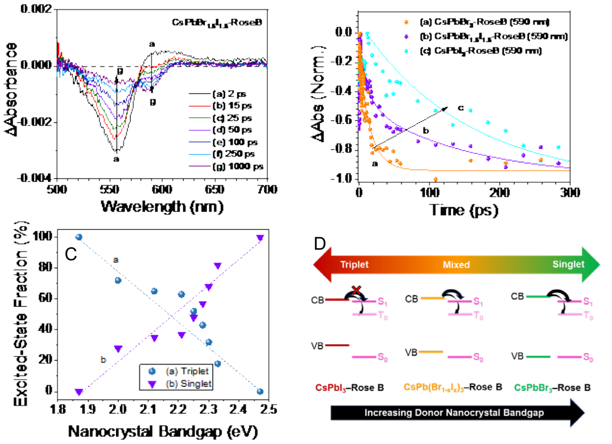


**Figure 1.** (A) Transient spectra recorded after 400 nm laser pulse excitation for $CsPbBr_{1.5}I_{1.5}$ interacting with RoseBengal(RoseB). (B) Normalized RoseB bleach growth profiles following 400 nm laser pulse excitation of (a) $CsPbBr_3$–RoseB, (b) $CsPbBr_{1.5}I_{1.5}$–RoseB, and (c) $CsPbI_3$–RoseB samples in deaerated toluene. (C) Quantum efficiency of energy transfer process as measured from the yields of (a) triplet and (b) singlet excited states following the excitation of $CsPb(Br_{1-x}I_x)_3$ -RoseB in toluene. (D) Scheme illustrating the energetics of the perovskite nanocrystal–RoseB system.

singlet and triplet energy respectively. In situations where both singlet and triplet energy transfer are possible, kinetic competition favors participation of singlet exciton state process in the energy transfer. In the case of $CsPbI_3$ as a donor singlet energy transfer from $CsPbI_3$ ($E_g$ = 1.87 eV) to rhodamine dye is not energetically feasible, and thus slower kinetic route to generate triplet rhodamine dye proceeds.

Bandgap tuning of the donor nanocrystals was carried out through compositional engineering (e.g., halide alloying in perovskites) to probe the energy transfer from mixed halide perovskite nanocrystals. Tuning of the donor bandgap with mixed halide perovskites (e.g., $CsPb(Br_xI_{1-x})_3$) allows for population of both singlet and triplet excited states of the acceptor dye. Other strategies, like doping the donor with photoactive states from $Mn^{2+}$ centers, or tuning functional groups on the acceptor to modifying donor/acceptor binding lend further control over excited-state interactions. We have further incorporated these semiconductor nanocrystal donors and one or more chromophore acceptors to induce singlet and triplet energy transfer phenomena and achieve Down-shift or Up-convert incident photons.

**Forward and Back Electron Transfer.** By employing methyl viologen as the electron acceptor, we have succeeded in mapping the electron transfer from excited $CsPbI_3$ nanocrystals to viologen as well as hole trapping process. The electron transfer to viologen is an ultrafast process ($k_{et}$ = $2\times10^{10}$ $s^{-1}$) and results in the formation of extended charge separation as electrons are trapped at surface bound viologen sites and holes at iodide sites. The $I_2^{-\bullet}$ formation, which is confirmed through the transient absorption at 750 nm, provides a convenient way to probe trapped holes and its participation in the back electron transfer process. By employing a series of mixed halide compositions, we were able to tune the band gap and valence band energy of the perovskite donor. The back electron transfer rate constant ($k_{bet}$= 1.3 –2.6 $\times10^{7}$ $s^{-1}$) is nearly three orders of magnitude smaller than that of forward electron transfer, thus extending the lifetime of charge separated state. The weak dependence of back electron transfer rate constant on the valence band energy suggests trapping of holes at halide (I or Br) sites are involved in the back electron transfer process (Figure 2). The ability to extend the lifetime of charge separated pair can offer new strategies to improve the redox properties semiconductor based photocatalytic systems.

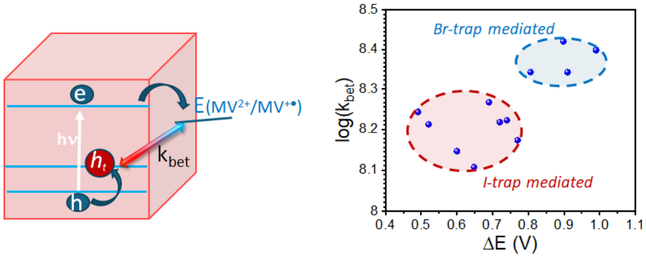


Figure 2. Dependence of back electron transfer on the energy difference (ΔE) between $MV^{2+}/MV^{+\bullet}$ redox potential and valence band energy of different perovskite nanocrystals with different halide compositions.

**Future Work:** Since it is possible to vary the conduction band and valence band energy of the donor perovskite nanocrystal through size quantization effects or by varying halide composition, we can systematically investigate the driving force (-ΔG) dependence of the kinetics of electron and hole transfer. By employing methyl viologen as electron acceptor and p-phenylene diamine (PPD) as hole acceptor, we plan to validate the relationship between hole transfer and electron transfer rate constant and –ΔG, using Marcus-electron transfer theory. Fundamental understanding of electron and hole transfer, and back electron transfer processes in semiconductor nanocrystals will allow us to maximize the efficiency of photocatalytic reduction/oxidation processes.

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# Light Harvesting in Semiconductor Quantum Dots

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This project is probing the light-harvesting dynamics of semiconductor quantum dots (QDs) using broadband multidimensional electronic spectroscopy (2DES/3DES) and electronic structure calculations. The results support a many-electron, molecular theory for the electronic structure of QDs, where the vibrations of organic surface-capping ligands serve as branching modes in a coherent nonadiabatic mechanism for nonradiative decay. This picture is being used to address the mechanisms of photoinduced charge transfer and triplet-triplet excitation energy transfer from CdSe QDs to surface-bound acceptors.

Previous work in the Van Patten/Zhang group established a methodology for QD surface chemistry characterization, discriminating between bound and unbound ligands via thermal desorption – direct analysis in real-time – mass spectrometry (TD-DART-MS). Current work has expanded on the technique, demonstrating the essential ability to quantify various common ligands, such as oleate, hexadecylamine, and trioctylphosphine oxide bound to CdSe QDs, with detection limits down to 500 ppb. This fast and sensitive approach could deepen understanding of QD surface interactions and inform the rational design of QDs with optimized stability and functionality.

In a recent publication, the Levine group discusses how the coupling between core electronic excitations and ligand vibrations occurs through two distinct mechanisms. Lower frequency ligand modes couple directly to core vibrations, which are driven by core electronic excitations. However, higher frequency vibrations tend to be local to the ligand and are driven directly by the delocalization of core electronic excitations on the ligands.

In current work, the Beck group has employed a combination of global modeling of the 2DES spectral amplitudes and an analysis of coherences in oleate-capped CdSe QDs to define the timescales for the electronic and vibrational processes that promote hot-carrier cooling. The results lead to an improved understanding of the mixing of the QD's core LO phonon mode with higher frequency vibrations that are local to single oleate ligands on the surface of the QD. Based on the hypothesis that cooling occurs via a cascade of conical intersections, theoretical calculations predict that energy flows into a set of vibrational modes that are consistent with the experimental observation of vibronic coherences. As in the case of amine-passivated QDs, delocalization of both vibrational modes and electronic excitations contributes to energy dissipation into the ligand vibrations.

This picture for the activation of surface-ligand vibrations is the foundation for determining how the photoinduced charge-transfer and triplet–triplet excitation energy transfer properties of QDs depend on the extent of mixing of the core electronic and ligand vibrational states. Recent 3DES results with methyl viologen dication acceptors adsorbed onto the surface of oleate-capped CdSe QDs show that an intermediary charge-transfer state is populated with retention of vibronic coherence following hot-carrier cooling on the <200-fs timescale. Two classes of rapidly damped coherent wavepacket motions are observed, involving mixed core lattice vibrations and out-of-plane deformations of the methyl viologen acceptors. Theory supports the assignment of these vibrations to the initial formation of a charge-separated character prior to the transfer of an electron to the methyl viologen acceptor on the ps timescale.

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# Probing energy transfer in nanocluster architectures using DNA-directed assembly

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Few-atom metal nanoclusters (NCs) are promising chromophores for artificial light-harvesting systems (LHS) that mimic natural photosynthetic LHS yet are also compatible with synthetic materials for charge carrier collection and for driving photochemical reactions. NCs combine the small sizes and intermolecular properties of molecular dyes with the large extinction coefficients, stabilities, and catalytic activity of nanoparticles. A growing body of theoretical work has supported the promise of NCs for increasing the efficiency of energy transfer for solar energy harvesting. However, the major challenge of organizing NCs into nanostructured LHS architectures has prohibited experimental investigation of energy transfer among NCs. Such studies are essential to develop NCs for solar energy harvesting platforms. Motivated by this need, the central goal of this research project is to experimentally investigate light harvesting, including processes such as resonance energy transfer (RET) and other near-field NC interactions, in atomically precise NC architectures. To achieve this goal, we are organizing multiple NCs with nanometer-scale precision using a bioinspired approach that is enabled by programmable DNA base pairing and a uniquely tunable class of DNA-stabilized silver NCs (DNA-$Ag_N$), as illustrated in **Figure 1**.

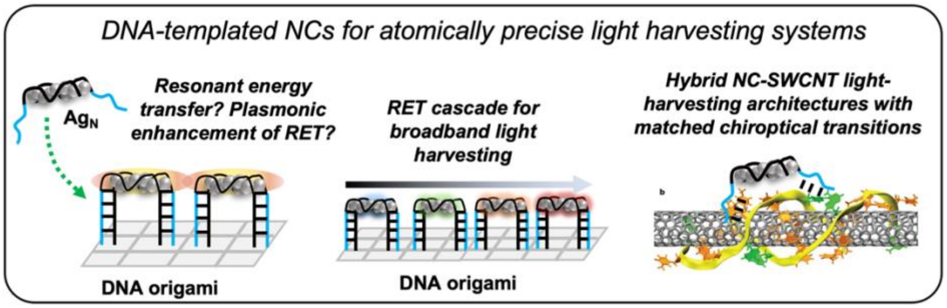

**Figure 1**: Schematic of DNA-directed self-assembly of NCs to enable experimental investigation of near-field effects in NC architectures.

Past research has shown that silver NC size and geometry can be precisely controlled by DNA sequence, enabling the preparation of atomically precise DNA-$Ag_N$ with sizes ranging from 10 to 30 atoms, NC shapes that vary from rod-like to spheroidal, and intense optical transitions ranging from ultraviolet to near-infrared. Moreover, the NC-templating DNA molecule can be extended for sequence-specific base pairing to other DNA strands. This strategy allows two atomically precise NCs to be linked together with nanometer-scale separation that is controlled by the DNA scaffold. DNA-organized NC pairs enable experimental investigation of the dependence of RET efficiency on NC separation as a function of NC size and geometry. We have developed a suite of NCs of various sizes and photophysical properties that have complementary single-stranded “tails” that leave the atom-precise NC core unchanged. Four example DNA-$Ag_N$ with functional DNA tails are shown in **Figure 2**. The high degree of similarity between fluorescence emission spectra of the original DNA-$Ag_N$ (dashed lines, **Figure 2**) and the DNA-$Ag_N$ with single-stranded tail (solid lines, **Figure 2**) strongly supports that the addition of the DNA tail does not appreciably alter the inorganic NC core and thus provides an inert molecular linker for pairing two atomically precise NC chromophores within nanoscale proximity. Using this approach, measurable RET has been achieved in a donor-acceptor NC pair, with an efficiency of ~20%. DNA linker length will be systematically varied to investigate the separation dependence of RET efficiency for this NC pair and for additional donor/acceptor pairs. We will thereby experimentally investigate whether the distance scaling of RET efficiency in NC pairs depends on NC size and geometry, which computational modeling has suggested to cause meaningful deviations from Förster theory.

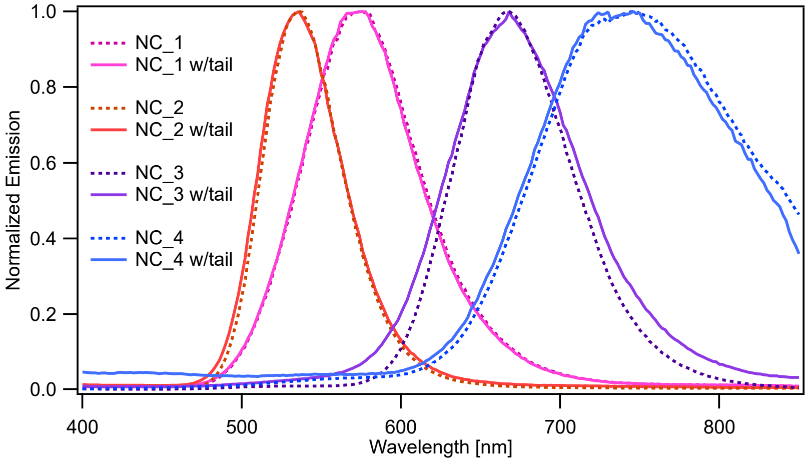

**Figure 2**: Four different DNA-$Ag_N$ engineered with single-stranded “tails” that do not perturb the NC structure and thus leave photoluminescence spectrum unchanged. Dashed lines: DNA-$Ag_N$ without DNA tail; Solid lines: DNA-$Ag_N$ with DNA tail. Each DNA-$Ag_N$ is stabilized by a different DNA oligomer template and has a unique NC size and structure.

Ongoing work also focuses on the design and assembly of RET cascades that are composed of multiple atom-precise NCs to mimic the energy gradients of natural LHS (**Figure 1**). With this materials system, we will experimentally characterize the upper limits of RET distance and energy down-conversion in NC arrays. Experimental findings will be compared to computational models for excited state processes in NC pairs and arrays. This work is expected to advance fundamental knowledge of the photochemistry of few-electron NC architectures and to guide development of NC-based materials for sunlight harvesting, for critical applications in electricity generation and solar fuels.

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# Ultrafast Spin-Exchange Interactions for Hot-Carrier Harvesting in Quantum Dots

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Hot, non-equilibrated electrons hold tremendous promise for advancing photoconversion and photochemistry. In addition to their superior reduction capabilities, hot electrons possess extended wavefunctions, high mobility, and the potential for long-range transport—provided they are stabilized before losing energy through phonon emission. Unfortunately, in conventional materials, ultrafast phonon-assisted cooling significantly limits their practical utility.

As part of this project, in 2019 we showed that hot electrons can be captured and utilized via ultrafast **spin-exchange (SE)** interactions in manganese (Mn)-doped quantum dots (QDs).[1] These interactions enable energy transfer at rates exceeding 10 eV ps$^{-1}$, effectively outpacing phonon losses and opening new avenues for hot-carrier-based applications.

Recently, we achieved a regime where regular and SE-Auger recombination, along with phonon-assisted carrier cooling, coexisted and could be resolved via femtosecond transient absorption (TA) measurements (Fig. 1).[2] Among these processes, SE-Auger recombination (~200 fs) was the fastest, occurring three orders of magnitude faster than ordinary Auger recombination (~230 ps)

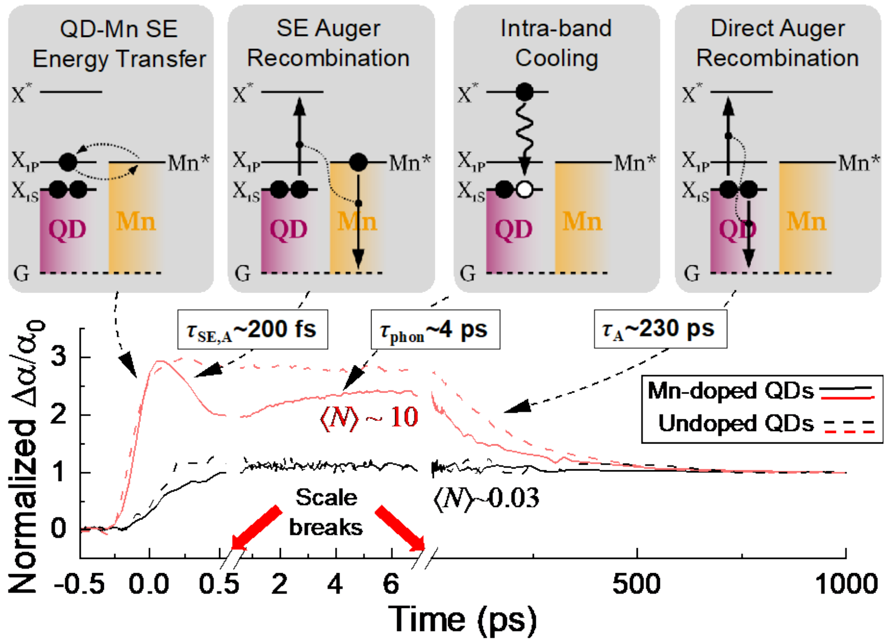

**Figure 1.** The coexistence of SE and regular Auger recombination was enabled by Mn-doped QDs, designed so that the band-edge (1S) transition energy ($E_{1S}$) < Mn spin-flip transition energy ($E_{Mn}$ = 2.1 eV) < excited-state 1P transition ($E_{1P}$). At low pump levels (⟨$N$⟩ < 2), decay is slow (~10 ns) and similar in Mn-doped (solid black) and undoped (dashed black) QDs, proceeding via non-SE processes. At higher pump levels (⟨$N$⟩ > 2), 1P excitons rapidly (<100 fs) transfer to Mn ions, triggering fast (~200 fs) SE-Auger recombination (solid red). The resulting hot carriers cool within ~4 ps, leading to 1S signal postgrowth, followed by regular Auger recombination (~230 ps). The undoped sample exhibits only standard Auger decay (dashed red).

and outpacing phonon-assisted cooling (~4 ps) by more than an order of magnitude (Fig. 1). This finding is particularly significant, as phonon-mediated energy dissipation is generally regarded as the fastest and most unavoidable process in semiconductors. The discovery of ultrafast SE-Auger recombination marks a paradigm shift, offering a powerful mechanism to harness hot-carrier kinetic energy that would otherwise be lost to phonons.

These findings were further validated through the demonstration of **SE-assisted photoemission (SE-PE)**, in which visible light induced a two-step Auger re-excitation that promoted a band-edge electron to the vacuum level.[2] This process enabled efficient generation of solvated electrons even under low-photon-energy (2.4 eV) excitation, achieving a yield of 3.5%—far exceeding those of other materials (even when excited by UV light), including the benchmark hydrogen-terminated diamond surface.

Additionally, we demonstrated that SE interactions enable **carrier multiplication (SE-CM)**—a process in which a single high-energy photon generates multiple excitons.[3] In Mn-doped PbSe/CdSe QDs, SE-CM was achieved via two successive spin-exchange steps, yielding multiexciton generation efficiencies of ~50% at just 0.3 eV above the CM threshold, defined by the Mn-ion spin-flip transition. These results represent more than a twofold improvement over undoped control samples.

To demonstrate the practical utility of SE-CM, we recently showed enhanced photocurrent in a real-world photoconductive device.[4] This was enabled by Mn-doped **inverted CdSe/HgSe QDs**,[4,5] where the low-bandgap HgSe shell facilitated charge extraction into the external circuit. Both transient absorption and photocurrent measurements confirmed SE-CM-driven carrier generation, as evidenced by a sharp increase in photocurrent just above the Mn spin-flip energy.

In our **future work** on this project, we aim to continue investigating **SE interactions** with an increased focus on phenomena relevant to advanced photochemistry. Specifically, we plan to develop novel approaches to enable high-efficiency **SE-PE under low-intensity continuous-wave excitation**, significantly enhancing the practical utility of this process. In addition, we intend to demonstrate the feasibility of **hot-electron regeneration via SE-Auger up-conversion** during dot-to-dot electron migration. Furthermore, we plan to showcase **hot-carrier-driven photoreduction** reactions facilitated by **SE-assisted electron transfer**.

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# Fundamental Mechanisms for Solar Energy Conversion in Artificial Photosynthetic Assemblies

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A central challenge in the realization of effective systems for artificial photosynthesis lies in the ability to transition from mechanisms that stabilize charge separation from initial transient excited states to those that enable the multi-electron, proton-coupled charge accumulation which is needed to drive water-splitting and couple it to fuels catalysis. Natural photosynthetic systems provide valuable design principles for efficient conversion of light energy to chemical fuels using molecular cofactors by implementing dynamic interactions between electron donors and acceptors and manipulating the cofactor microenvironment to stabilize multiple possible redox states, allowing precise control over electronic structure and spin state. Our team takes inspiration from natural photosynthetic systems in developing synthetic approaches for modular and hierarchical assemblies to test hypotheses related to the evolution of molecular, electronic, and spin structures during photoexcitation and charge transfer, as well as their responses to environmental changes. Targeted molecular, supramolecular, and hybrid assemblies are understood with high spatial and temporal resolution using advanced optical and EPR spectroscopies, as well as synchrotron X-ray techniques. This program has a particular focus on molecular microenvironment, molecular structure at interfaces, and spin effects on photochemistry and charge transfer (**Figure 1**); this combined effort contributes to a detailed understanding of the ground- and excited-state activity of molecular modules that is essential for creating assemblies that effectively promote solar to fuels conversion. This talk will highlight recent research progress from our group along the trajectory of artificial photosynthesis: from initial light-harvesting and directional charge transfer, to tracking charge separation and accumulation, to analysis of thin film catalysts and conductive substrates that will play a role in connecting oxidative and reductive chemistry.

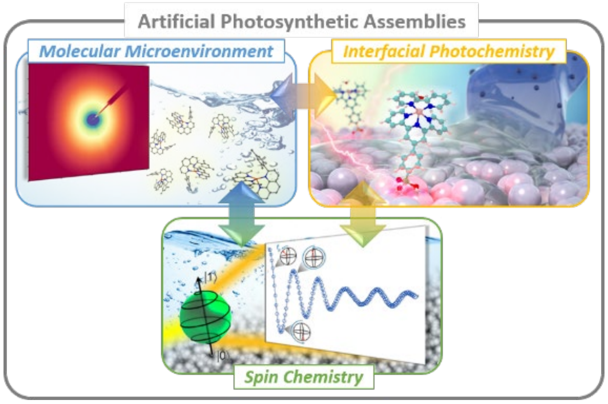

**Figure 1.** Program scope and connection between topic areas.

To investigate directional metal-to-ligand charge transfer (MLCT) and how MLCT localization impacts excited state kinetics, we have synthesized "push-pull" type molecular photosensitizers using the stable, asymmetric coordination environment of the heteroleptic Cu(I)bis(phenanthroline) (CuHETPHEN) platform. Previous work from our group demonstrated that the addition of electron-withdrawing groups at the 4,7-phenanthroline positions of the secondary CuHETPHEN ligand red-shifted the MLCT absorbance band up to 30 nm and resulted in a significant decrease in the excited state lifetime. However, contrary to these results, we observe that electron-withdrawing -$CF_3$ groups at the 2,9-phenanthroline positions of the blocking ligand results in a 5-10 nm blue shift of the MLCT band (**Figure 2**). The excited state lifetime decreases with the fluorinated blocking ligand as compared to the protonated parent module, only slightly for R = H (670 to 565 ps in $CH_3CN$), but substantially for R = $CH_3$ (13 to 1.4 ns in $CH_3CN$). CuHETPHEN complexes with R = $OCH_3$ and CN have been synthesized to investigate the combined effect of manipulating ligand electronic structure and immediate steric interaction with the copper center in its ground and excited state.

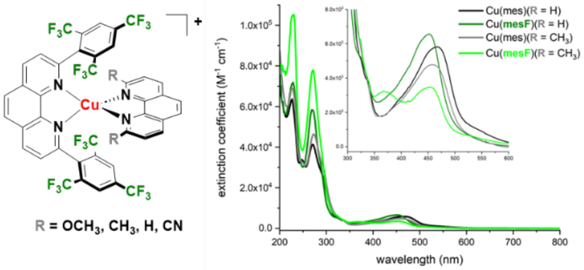

**Figure 2.** Top: molecular structure of push-pull CuHETPHEN complexes based on fluorinated blocking ligand. Bottom: optical absorbance spectra comparing effect of -$CF_3$ substitution and 2,9-phen sterics.

Advanced multifrequency EPR methods are used extensively in this program to track the kinetics of charge transfer, monitor photoinduced charge accumulation, and understand microenvironment effects on catalyst structure and activity. For example, using time-resolved EPR spectroscopy we observed formation of a spin-correlated radical pair following photoinduced charge transfer from organic dyes bound to ZnO quantum dots (QDs). In these systems we observe that the photoinduced kinetics and interaction between electron spins on the electron donating dye and ZnO electron acceptor are modulated by both dye molecular structure and QD diameter, establishing important design principles for integrating our group's Cu(I)-based photosensitizers into similar conjugate assemblies. Moving beyond single electron charge-separated states, we have recently demonstrated that a CuHETPHEN-anthraquinone dyad can reversibly and stably store two photo-generated electrons via a proton-stabilized intermediate. The singly reduced intermediate was analyzed by low temperature EPR spectroscopy and confirms that significant spin density resides on the quinone oxygen atoms. In HER catalysis, pulsed EPR methods, specifically ENDOR spectroscopy, were used to identify protonation sites in molecular Co(II) catalysts with available nitrogen sites in the inner and outer coordination sphere of the cobalt center and deduce the role of metal-ligand cooperativity and solvation effects on activity.

The talk will conclude by transitioning from work on molecular catalysts and assemblies to progress on photoinduced behavior of thin film catalysts and discovery of vapor-phase synthesis methods for new electrode substrates. Our group previously described a wavelength-dependent photoelectrochemical response of the thin film water oxidation catalyst CoPi, where 400 nm blue light hinders activity, but 630 nm red light enhances the OER activity of this catalyst. Subsequent X-ray transient absorption (XTA) studies conducted under different external potentials confirm that blue light induces a ligand-to-metal charge transfer (LMCT) transition from the oxygen atoms to cobalt within 100 ps of excitation, effectively reducing the concentration of key Co(IV) intermediates and producing soluble Co(II) centers, leading to film degradation. Finally, sequential infiltration synthesis methods were used to access transparent, conductive, and porous zinc-doped indium oxide thin films that will be utilized in high-energy X-ray scattering analysis of molecular structures at interfaces and during interfacial charge transfer. Future directions for this work include immobilization of molecular modules and assemblies onto porous conductive substrates to map effects of the electrode microenvironment on photoinduced and dark catalytic mechanisms.

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# Selective Photochemical Reactions for the Discovery of Triplet Photosensitizers

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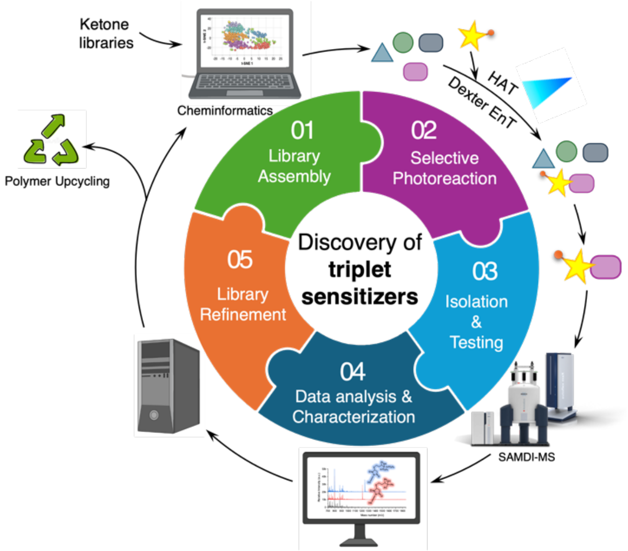

Triplet photosensitizers are compounds that readily form triplet states upon irradiation, making them essential to applications including photocatalysis, triplet-triplet annihilation photon upconversion, and photodynamic therapy. While many common photosensitizers rely on transition metals, organic photosensitizers 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 new approach to discovery triplet photosensitizers based on coupling desirable characteristics—strong absorption of light, high intersystem crossing (ISC) yield, and long triplet lifetime—to reactivity. Reaction efficiency, which is evaluated in high throughput, is used as a proxy for properties that are not compatible with high-throughput experimentation. In this approach, 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 the well-known Yang reaction, in which ketones with a low-lying n-$\pi^*$ transition engage in C–H abstraction and recombination to produce a tertiary alcohol. We designed “tags” that undergo C–H abstraction and contain a handle for click chemistry (thioacetate). The product and any unreacted tag are then deprotected and trapped on a SAM containing maleimides. Using an external standard, the conversion and yield may be rapidly approximated. After validating this workflow with known ketones representing positive and negative controls, we designed an initial library using cheminformatic analysis of commercially available ketones. This screen has already yielded a previously unknown triplet photosensitizer, which exhibited superior performance in polystyrene upcycling compared to the literature photosensitizer, benzophenone. In parallel, we also performed DFT calculations to develop a model to predict ketone performance. This model was used to select a broader range of commercially available ketones for high-throughput testing.

To expand the scope of this approach, we next tested the reactivity of known triplet sensitizers (BODIPY and ketocoumarin) with species known to generate reactive intermediates (carbene, nitrene, iminyl radical) upon energy transfer. We anticipate that such intermediates, if generated by Dexter energy transfer, could “tag” a wide variety of photosensitizers through C–H insertion or abstraction with the chromophore.

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 talk will summarize our efforts in library design, selective photoreaction development, data analysis, and characterization, and the application of the resulting photosensitizers to polymer upcycling.

# Earth Abundant Photosensitizers Enabling Solar Photochemistry

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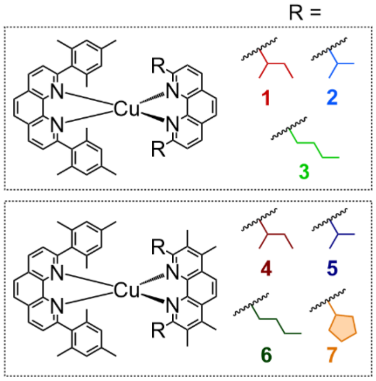

**Fig. 1.** Molecular structures of the heteroleptic Cu(I) photosensitizers.

Seven heteroleptic Cu(I) phenanthroline photosensitizers were synthesized and evaluated using steady-state and time-resolved absorption and photoluminescence (PL) measurements, electrochemistry, and electronic structure calculations. The structural limitations of 2,9-dimesityl-1,10-phenanthroline (mesPhen) restrict the coordination environment to heteroleptic architectures. Therefore, a second ligand based on 1,10-phenanthroline (phen, **1**–**3**) or 3,4,7,8-tetramethyl-1,10-phenanthroline (tmp, **4–7**) featuring various alkyl substituents at the 2,9-positions were prepared, **Fig. 1**. Chromophores **1**–**7** all feature metal-to-ligand charge transfer (MLCT)-based room temperature PL and long excited state lifetimes (τ = 62 – 443 ns in $CH_2Cl_2$). In contrast to the corresponding homoleptic species, the tmp-substituted **4**–**7** exhibit shorter excited state lifetimes than their non-methylated counterparts (**1**–**3**). Although exhibiting distinct photophysical trends, the Cu(I) heteroleptic series in **Fig. 1** follows a linear energy gap law correlation in $CH_2Cl_2$. Molecules **1**–**7** are shown to exhibit thermally-activated delayed fluorescence (TADF) between close-lying $^1$MLCT and $^3$MLCT states ($\Delta E = 713–1009\ cm^{-1}$) for the first time. Nanosecond transient absorption spectroscopy confirmed the MLCT assignments across the series, and the obtained excited state lifetimes were quantitatively similar to those obtained from transient PL experiments. Ultrafast transient absorption spectroscopy revealed the time constants for the pseudo-Jahn-Teller distortion (< 1 ps) and singlet-triplet intersystem crossing (7-10 ps) in these molecules, akin to that observed in homoleptic Cu(I) *bis*(phenanthroline) species.

Six Cr(III) *tris*(phen) photosensitizers (**8–13**) were evaluated to probe ligand substituent effects on their static and time-resolved spectroscopic properties, intended to model our corresponding visible light-harvesting structures. Substitution induces variation in the spin-flip phosphorescence lifetime, ranging from 199 μs (**8**) to 695 μs (**11**) at 298 K in $CH_3CN$, and red-shifts the $^2$E PL, spanning from 727 nm (**8**) to 740 nm (**13**) at 77 K in butyronitrile (**Fig. 2**). Ligand substitution appears to influence metal-ligand covalency, i.e., the nephelauxetic effect, lowering metal-centered PL transition energies across the series. Time-resolved spectroscopic studies established an inverse correlation between the ultrafast dynamics time constants and the observed time-resolved PL lifetimes.

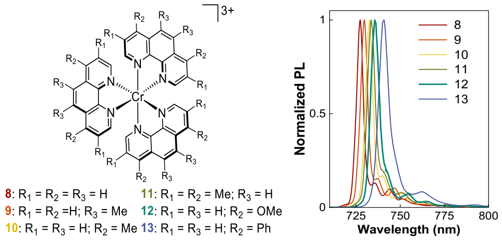

**Fig. 2.** Cr(III) *tris*-phenanthroline chromophores (left) and PL spectra displaying $^2$E emission at 77 K in butyronitrile (right).

Five Cr(III) *tris*(phen) photosensitizers (**14A–18A**) featuring arylethynyl groups appended at the 4,7-positions, produce impressive visible light-harvesting molecules (**Fig. 3A**, $\varepsilon_{420\ \mathrm{nm}}$ = 10,000 – 100,000 $M^{-1}cm^{-1}$). The femtosecond and nanosecond transient absorption profiles of the chromophores in **Fig. 3A** exhibit broad excited state absorption features atypical for metal-centered transitions. Chromophore **15A** is displayed in **Fig. 3C** and is intended to represent the series. The transient absorption difference profiles of **14A–18A** and their corresponding protonated free ligands reveal quantitatively comparable transient features; **Fig. 3D** displays the protonated ligand from **15A**. The combined transient data suggest a significant contribution of triplet ligand-centered character ($^3$IL) in these multiconfigurational excited states. Nanosecond transient absorption measurements in **14A-18A** have the same lifetimes observed in the corresponding $^2E/^2T_1$ spin-flip phosphorescence intensity decays. Preliminary work has expanded to examine the electronic structures and molecular photophysics of related Cr(III) complexes having synthetically accessible d$^0$ analogues, specifically, *tris*(quinolinolate) Cr(III) (**Fig. 3B**) and their corresponding Al(III) complexes, bearing π-conjugated quinolates.

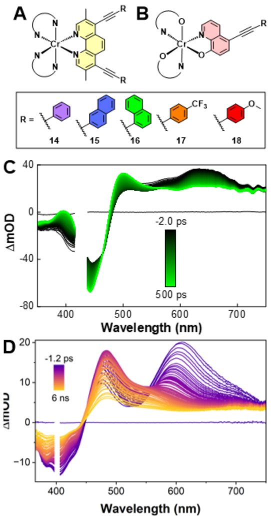

**Fig. 3.** (A) Cr(III) *tris*(phen) and (B) *tris*(quinolinolate) species. (C) Transient absorption profile of **15A** ($\lambda_{ex}$ = 420 nm). (D) Transient absorption profile of the H(dmpep) ligand ($\lambda_{ex}$ = 400 nm).

Another related series of homoleptic and heteroleptic Cr(III) complexes featuring tridentate ligand platforms. These exhibit strong blue light absorption ($\varepsilon_{400\ \mathrm{nm,\ max}}$ = 1.4 x $10^4$ $M^{-1}cm^{-1}$) and persistent excited state lifetimes (up to τ = 1.6 ms) in $CH_3CN$ at room temperature. Their excited state absorptions span the visible and near-infrared regions, suggesting their excited state configurations have significant ligand-centered character. In four of these molecules, femtosecond transient absorption experiments probing the near-infrared region revealed a sharp excited state absorption feature, characteristic of a discrete $^2T_1/^2E \rightarrow {}^2T_2$ ligand-field transition, $[Cr(ddpd)_2]^+$ is representative of this series, **Fig. 4A**. The development of this spectral feature (1388 nm) with time provided a direct spectroscopic signature for probing intersystem crossing dynamics ultimately leading to $^2T_1/^2E$ population. The kinetic traces for the formation of this ligand-field doublet transition at 1388 nm (τ = 2 ps) align with the broad excited state absorption recovery at 400 nm (τ = 3 ps) (**Fig. 4B**). A Jablonski diagram depicting the proposed excited state dynamics in $[Cr(ddpd)_2]^+$ is presented in **Fig. 4C**.

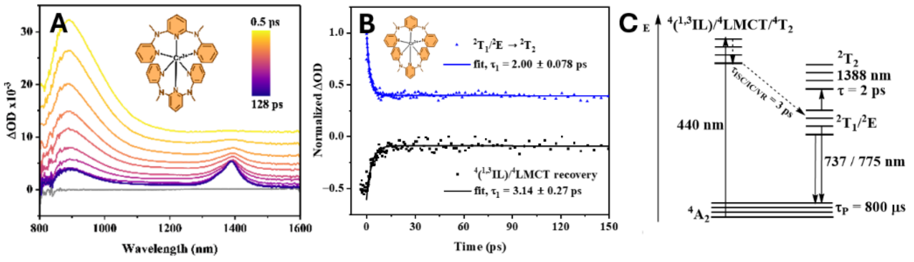

**Fig. 4.** (A) Near-infrared transient absorption profile of $[Cr(ddpd)_2]^+$ ($\lambda_{ex}$ = 400 nm). The feature at 1388 nm nm is assigned to the $^2T_1/^2E \rightarrow {}^2T_2$ transition. (B) Single-wavelength kinetics producing the $^2T_1/^2E \rightarrow {}^2T_2$ transition (blue trace) and the ground state bleach recovery at 400 nm (black trace, difference spectrum not shown). (C) Proposed Jablonski diagram for the excited state evolution process.

**DOE Solar Photochemistry Sponsored Publications 2022-2025**

1. *Long-lived Photoluminescence of Molecular Group 14 Compounds through Thermally Activated Delayed Fluorescence.* Gowda, A.S.; Lee, T.S.; Petersen, J.L.; Rosko, M.C.; Castellano, F.N.; Milsmann, C. *Inorg. Chem.* **2022**, *61*, 7338-7348. https://pubs.acs.org/doi/10.1021/acs.inorgchem.2c00182

2. *Real-Time and In Situ Viscosity Monitoring in Industrial Adhesives Using Luminescent Cu(I) Phenanthroline Molecular Sensors*. Dara, A.; Mast, D.M.; Razgoniaev, A.O.; Hauke, C.E.; Castellano, F.N.; Ostrowski, A.D. *ACS Appl. Mater. Interfaces* **2022**, *14*, 33976-33983. https://pubs.acs.org/doi/10.1021/acsami.2c06554

3. *$CsPbI_3$ Nanocrystals Go with the Flow: From Formation Mechanism to Continuous Nanomanufacturing.* Antami, K.; Bateni, F.; Ramezani, M.; Hauke, C.E.; Castellano, F.N.; Abolhasani, M. *Adv. Funct. Mater.* **2022**, *32*, 2108687. https://doi.org/10.1002/adfm.202108687

4. *Employing Long Range Inductive Effects to Modulate MLCT Photoluminescence in Homoleptic Cu(I) Complexes.* Rosko, M.C.; Espinoza, E.M.; Arteta, S.; Kromer, S.E.; Wheeler, J.P.; Castellano, F.N. *Inorg. Chem.* **2023**, *62*, 3248-3259. https://doi.org/10.1021/acs.inorgchem.2c04315

5. *Sterically Encumbered Heteroleptic Copper(I) β-Diketiminate Complexes with Extended Excited-State Lifetimes.* Kim, D.; Rosko, M.C.; Dang, V.; Castellano, F.N.; Teets, T. *Inorg. Chem.* **2023**, *62*, 16759-16769. https://doi.org/10.1021/acs.inorgchem.3c02042

6. *Enhanced Visible Light Absorption in Heteroleptic Cuprous Phenanthrolines.* Rosko, M.C.; Wheeler, J.P.; Alameh, R.; Faulkner, A.P.; Durand, N.; Castellano, F.N. *Inorg. Chem.* **2024**, *63*, 1692-1701. https://doi.org/10.1021/acs.inorgchem.3c04024

*7. Long Excited-State Lifetimes in Three-Coordinate Copper(I) Complexes via Triplet–Triplet Energy Transfer to Pyrene-Decorated Isocyanides.* Kim, D.; Rosko, M.C.; Castellano, F.N.; Gray, T.G.; Teets, T.S. *J. Am. Chem. Soc.* **2024**, *146*, 28, 19193–19204. *https://doi.org/10.1021/jacs.4c04288*

8. *Ligand Field Exciton Annihilation in Bulk $CrCl_3$.* Sridhar, S.; Khansari, A.; O'Donnell, S.; Danilov, E.O.; Castellano, F.N.; Maggard, P.M.; Dougherty, D.B. *J. Chem. Phys.* **2024**, *161*, 114706. https://doi.org/10.1063/5.0223772

9. *Steric and Electronic Influence of Excited-State Decay in Cu(I) Chromophores.* Castellano, F.N., Rosko, M.C. *Acc. Chem. Res.* **2024**, *57*, 2872-2886. https://doi.org/10.1021/acs.accounts.4c00476

10. *Structural Gating Enhances Long-Distance Light Driven Interfacial Electron Transfer.* Loague, Q.R.; Heidari, M.; Mann, H.J.; Danilov, E.O.; Castellano, F.N.; Galoppini, E.; Meyer, G.J. *ACS Cent. Sci.* **2024**, 10, 2132-2144. https://pubs.acs.org/doi/full/10.1021/acscentsci.4c01106

11. *Photophysical Characterization and Excited State Dynamics of Decamethylruthenocenium.* May, A.M.; Deegbey, M.; Fosu, E.; Danilov, E.O.; Jakubikova, E.; Castellano, F.N.; Dempsey, J.L. *J. Phys. Chem A.* **2025**, *129*, 1558−1565. https://pubs.acs.org/doi/full/10.1021/acs.jpca.4c06564

12. *Excited State Properties and Triplet State Photochemistry of Long-Lifetime Cu(I) Heteroleptic*

*Phenanthrolines.* Rosko, M.C.; Pyrch, A.; Faulkner, A.P.; Wheeler, J.P.; Kromer, S.; Bagemihl, B.; Castellano, F.N. *Inorg. Chem.* **2025**, submitted.

# Bio-Inspired Light-Escalated Chemistry: Amplifying chemical reactions with light

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Global demand for energy and goods derived from chemical synthesis is rising at an ever-increasing rate. Fossil fuels serve as our primary source of both energy and raw materials for these goods. A preeminent societal challenge is the replacement of fossil fuels with clean and renewable resources. In this arena, solar radiation represents a substantial and effectively inexhaustible source of energy. Significant progress is being made in the area of solar-to-electrical energy conversion and solar-fuel synthesis. Synthetic chemists have also begun to explore whether solar energy can fuel the synthesis of desirable goods. Led by efforts of PIs in the Bio-Inspired Light-Escalated Chemistry (BioLEC) Energy Frontiers Research Center (EFRC), researchers have demonstrated that it is possible to use visible light to drive new chemical reactions towards the production of feedstocks and fine chemicals. However, since most small molecules do not absorb visible light, it is necessary to introduce a photoredox catalyst to serve as an intermediary between visible light and the molecules undergoing reaction.

BioLEC is an EFRC focused on the development and use of photocatalysis for energy applications. Since launching in August 2018, the center has made significant advances in understanding what drives photoredox catalysis at a mechanistic level, worked to create new and more potent photocatalysts using biological systems and mechanistic insights as inspiration, and harnessed and amplified the power of photocatalysis for new energy-relevant applications. BioLEC researchers have also pioneered dual catalysis platforms in which a photoredox catalyst is combined with a distinct transition metal-based cross-coupling catalyst (metallaphotoredox) to enable the development of a wide array of challenging and unique C–C and C–heteroatom bond-forming reactions.

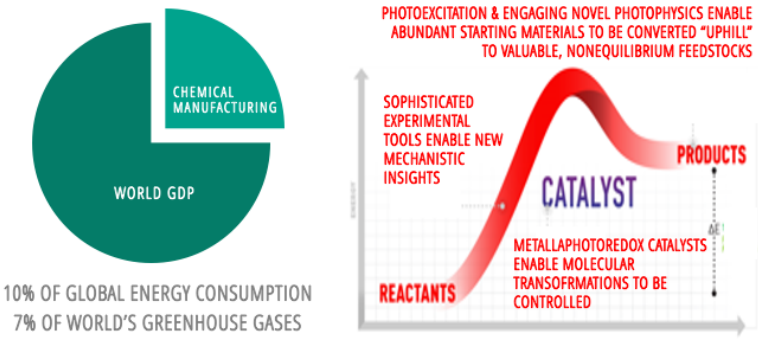
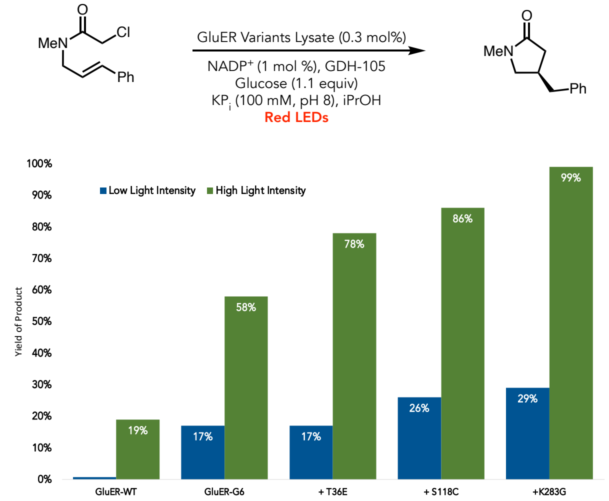


Figure 1. Left: the importance and impact of chemical manufacturing on GDP and energy consumption. Right: Diagrammatic overview of BioLEC's mission and aims.

Amongst other center efforts, BioLEC's unique approach to the detailed exploration of photocatalytic mechanisms uses a collaborative approach to decipher in detail how reactions proceed. Combining ultrafast and X-ray spectroscopies and computational approaches with more traditional spectroscopic analyses provides insights into how a variety of photocatalytic conversions operate at a molecular level. Moreover, to gain insights into how the molecular environment impacts the reaction, new spectroscopies have been developed within BioLEC, for instance to probe how catalyst counter ions can influence reactivity. By considering all aspects of the catalyst microenvironment, energetics and other factors, we can approach an understanding of the universal elements of photocatalytic mechanisms. This deeper understanding also enables finer tuning of photocatalysts and their reactions to improve yields, selectivity and scalability.

Beyond traditional photocatalysis with transition metal complex catalysts, BioLEC has also advanced work with photocatalysts borrowed from nature. Enzymes are generally attractive catalysts for chemical synthesis because they carry out transformations with unparalleled catalytic efficiencies and reaction selectivity. However, in enzyme-mediated organic synthesis, most reactions involve molecules operating from their ground states. Over the past 25 years, there has been increased interest in enzymatic processes that utilize electronically excited states accessed through photoexcitation. These photobiocatalytic processes involve a diverse array of reaction mechanisms that are complementary to one another.

As reactions using photoenzymes have reached greater utility, a need has arisen for spectral tuning of the enzyme's photoactivity to increase stability and scalability of the reactions. To this end, we engineered a flavin-dependent 'ene'-reductase (ERED) to change its photophysical properties. EREDs have been shown to catalyze radical cyclizations of alkyl halides when irradiated with visible light. The chromophore in these reactions is an enzyme-templated charge transfer (CT) complex involving the substrate and reduced flavin cofactor. In various enzymes, this complex absorbs in the blue/green region of the visible spectrum with a maximum absorbance at 490 nm. As the absorption of the complex should be strongly influenced by the structure of the protein-templating CT complex formation, we hypothesized that protein engineering under red-light irradiation would result in variants with red-shifted CT complexes. We expected that lower energy light would help to diminish enzyme degradation and increase the scalability of photoenzymatic processes. After five rounds of protein engineering, a variant was accessed that displays high reactivity with red (620 nm) and near IR (850 nm) LEDs (see Figure 2). Mechanistic experiments revealed that rather than red shifting the cyan absorption feature, the protein engineering campaign resulted in a new binding orientation that weakly absorbs in the red-light region. Computational modeling found that the cyan absorption is primarily a π to π* transition on the flavin cofactor. In contrast, the red absorption is calculated as π(FMN) to π*(substrate). These models indicate that the variants favor substrate binding orientations, allowing the π(FMN) to π*(substrate) transition. Transient absorption spectroscopy provided experimental evidence for a change in the binding orientation of the substrate when irradiated with red light. The results of this study demonstrate a photoenzymatic reaction that can reach a 10-gram scale while retaining high yield and enantioselectivity.



b. Modelling

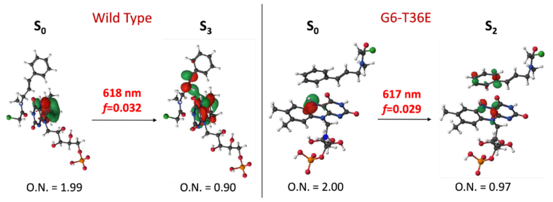


Figure 2. Protein engineering for red light activity.

**Up to Five DOE EFRC Sponsored Publications 2022-2025**

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2. John D. Sakizadeh, Rachel Weiss, Gregory D. Scholes, Bryan Kudisch, "Ultrafast Spectroscopy and Dynamics of Photoredox Catalysis", *Annu. Rev. Phys. Chem.* **2025**, *76*, 203.

3. Stephen DiLuzio, Lakshmy Kannadi Valloli, Max Kudisch, Daniel T. Chambers, Garry Rumbles, Obadiah G. Reid, Matthew J. Bird, Hannah J. Sayre, "Reconceptualizing the $Ir^{III}$ Role in Metallaphotoredox Catalysis: From Strong Photooxidant to Potent Energy Donor", *ACS Catal.* **2024**, *14*, 11378.

4. Jose M. Carceller, Bhumika Jayee, Claire G. Page, Daniel G. Oblinsky, Gustavo Mondragón-Solórzano, Nithin Chintala, Jingzhe Cao, Zayed Alassad, Zheyu Zhang, Nathaniel White, Danny J. Diaz, Andrew D. Ellington, Gregory D. Scholes, Sijia S. Dong, Todd K. Hyster, "Engineering a Photoenzyme to Use Red Light", *Chem* **2024***, 11,* 102318.

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# Ultrafast Functional Structural Dynamics in Solar Energy Conversion

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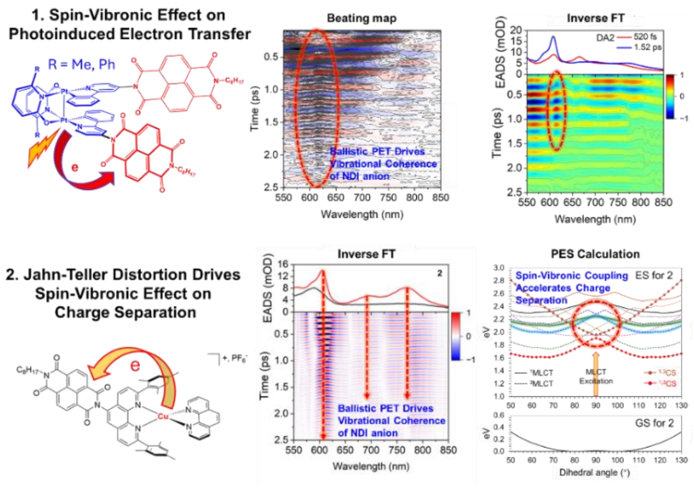
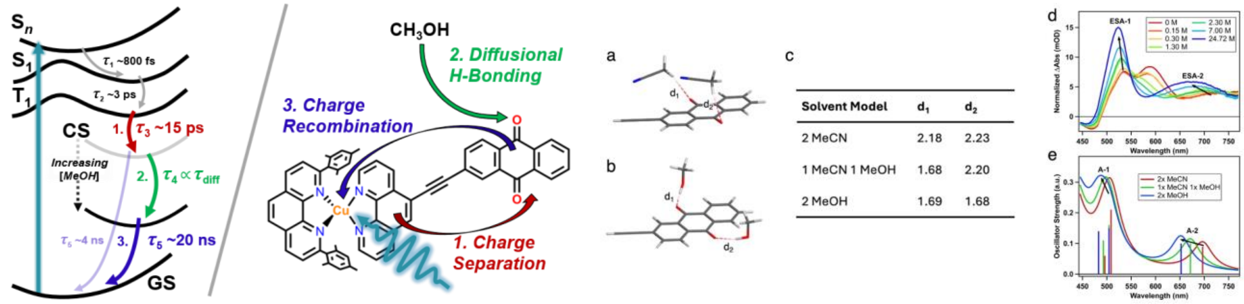
Our team's research aims to gain a critical understanding of fundamental light—matter interactions that influence photochemistry, photophysics, and photoredox processes in transition metal complexes (TMCs) across different molecular platforms. We explore ultrafast functional structural dynamics in photoexcited states with strongly coupled electronic and nuclear motions beyond the Born-Oppenheimer approximation in three tasks, A) identifying key excited-state reaction coordinates of transition metal complexes in photochemical reactions; B) steering photoinduced electron transfer processes towards charge accumulation and photocatalytic bond breaking reactions by chemical modifications and tailored light pulse sequences; and C) tracking functional structural and electronic dynamics along excited-state trajectories by ultrafast elemental specific inner shell spectroscopies and solution scattering at XFEL facilities. Specific examples are described below.

*1. Identifying key reaction coordinates of photoinduced electron transfer (PET) and intersystem crossing (ISC) processes* in transition metal complexes as light sensitizers and electron donors. The key reaction coordinates and environments for the supramolecular electron donor-acceptor systems consisted of transition metal complexes as electron donors or photosensitizers, which may control the outcome of the PET processes in terms of efficiencies and rates. We have utilized broadband transient absorption combined with computed excited state normal mode analysis to investigate ultrafast excited state trajectories of mainly two systems: 1) Pt(II)dimer-NDI and 2) Cu(I)-NDI. In particular, we focused on the spin-vibronic effect on PET in both systems. We found that ballistic PET initiated by the charge transfer excitation drives the donor-acceptors out of their thermal equilibrium structures, where the spin-vibronic effect in specific vibrational modes steers the PET trajectory, differentiating the coherent vibrational wavepacket dynamics along the PET reaction coordinates (Right Figure). Our findings open new possibilities for leveraging spin multiplicity-dependent potential energy surfaces to enhance the vibronic coupling, thereby improving charge separation efficiency. Meanwhile, the spin-vibronic effect on the ISC rates can now be computed with highly accurate electronic structure



methods that explicitly incorporate spin-orbit coupling, enabling predictive simulations of intersystem crossing dynamics.

*__2. Driving PET reactions via chemical and environmental modifications and tailored photoexcitation__*. Coupling multiple single-photon events with redox equivalence for photocatalysis is a challenge. This task aims to investigate correlations between PET reaction directionality and quantum yields with certain structural factors and the excitation sequences. We report the ground and excited-state characterization of CuEthyneAnQ by electrochemical and ultrafast optical transient absorption (OTA) spectroscopy measurements. We observed three effects: (1) after charge separation, a diffusion-limited hydrogen bond forms with the reduced $AnQ^{\bullet -}$; (2) the attenuation in charge recombination with protic solvent addition is due to hydrogen-bond stabilization following Marcus theory; and (3) a spectral shift occurs in the charge-separated state due to an increasing number of hydrogen-bond interactions. Complementary time-resolved IR focusing on the bridging -C≡C- enabled the PET processes to be followed in real time. Our results are supported by time-dependent density functional theory calculations with explicit solvent hydrogen-bonding interactions. Electronic structure calculations have been conducted to study how hydrogen-bonding interactions affect photoexcited charge transfer processes in a Cu-anthraquinone donor-acceptor dyad. TD-DFT calculations including explicit solvent molecules captured the blue shift and intensity increase of absorption bands with the addition of methanol as observed in the fsOTA spectra (figure below). Marcus parameter calculations show that adding methanol stabilizes the magnitude of the driving force for charge through H-bond stabilization, showing excellent agreement with experiments.



| Solvent Model | $d_1$ | $d_2$ |
|---|---|---|
| 2 MeCN | 2.18 | 2.23 |
| 1 MeCN 1 MeOH | 1.68 | 2.20 |
| 2 MeOH | 1.69 | 1.68 |

__3. Excited state electronic and nuclear dynamics in transition metal complexes and their super molecules probed by X-ray spectroscopy and scattering.__ The excited states of transition metal complexes and their counterparts of supramolecular D-A systems are examined by X-ray spectroscopy and scattering through their trajectories in terms of nuclear motions and electron density shifts. We follow electron density motions through transition metal complexes at different stages of charge separation via time-resolved N K-edge X-ray transient absorption (Poster by Cordones-Hahn). The nuclear motions in the excited state Pt dimer – NDI2 D-A systems were studied by ultrafast X-ray solution scattering, where the relative phases of Pt-Pt stretching nuclear motions in the excited and the ground state can be extracted (Poster by Mara) through careful analysis of the nuclear vibrational frequency as a function of time. These atomistic details achieved by these studies have enabled new insight into the fundamental interplays between electronic and atomic motions in the excited state. They will help to elucidate the mechanisms and dynamics of PET and to identify the critical vibrational motions coupled to the excited state reaction trajectories. Quadratic excited response theory and multiconfigurational methods have been developed to compute state X-ray absorption spectra.

**DOE Solar Photochemistry Sponsored Publications 2022-2025**

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# Distinct Reaction Mechanisms of Ir Blue Dimer Photocatalysts Unraveled by Time Resolved Spectroscopy

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Solar fuels catalysis, such as light-driven water oxidation coupled with the reduction of $CO_2$ or proton to fuels, involves multiple redox events that occur across broad time domains ranging from sub-picosecond to millisecond or even longer. A comprehensive understanding of these reactions is of critical importance as it underpins efforts to optimize them and establish fundamental frameworks for catalytic design. However, this goal has been exceedingly difficult as few techniques can reveal detailed information about the set of intermediate states along the reaction coordinate. This is largely due to that most existing tools use single pulse pump and can only be applied to study model reactions that feature well-defined single-charge redox events, failing to provide a complete picture of reaction mechanisms under realistic reaction environments. To fill this knowledge gap, we plan to develop a double laser pump capability and integrate it to the unique multiple X-ray probe transient absorption (XTA) data acquisition implemented at the Advanced Photon Source to understand water oxidation mechanisms. With this powerful new tool, we expect to offer unprecedented details of water oxidation mechanisms and exert significant impacts to the solar photochemistry community.

During the first year of the support, we aim to understand the catalytic mechanism of a well-behaved model water oxidation catalyst (WOC), the Ir blue dimer (inset of Figure 1a) with $Ru(bpy)_3^{2+}$ as photosensitizer (PS) using single laser pump-MXTA technique. While Ir blue dimer was designed to perform as a WOC and does so well under typical catalytic conditions in the presence of $Na_2S_2O_8$ sacrificial acceptor (EA), many conditions of its success are poorly understood. Through the use of numerous spectroscopic techniques including XTA, nanosecond optical transient absorption (OTA), and steady-state spectroelectrochemistry, we found two distinct reaction pathways of the Ir blue dimer catalyst, which was controlled by the relative concentrations of EA with respect to Ir blue dimer.

In the presence of excess EA, we observed the initial steps of the water oxidation reaction, where following rapid oxidation of the PS by EA, electron transfer (ET) from the Ir dimer to the oxidized PS results in the formation of the first redox equivalent. These results are directly supported by XTA collected at Ir L3 edge following the excitation of $Ru(bpy)_3^{2+}$ at 532 nm (Figure 1a) and OTA wherein the

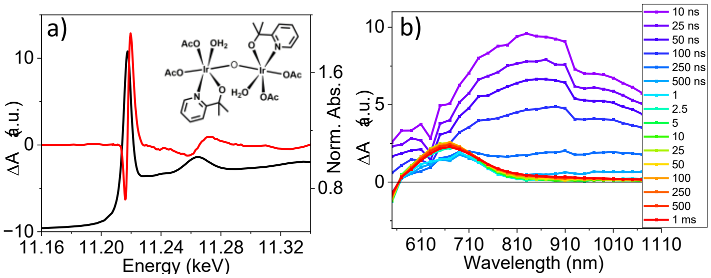

**Figure 1**. (a) Ground state Ir L3 XAS (black) and difference spectrum at a 20 μs time delay (red) following 532 nm excitation. The inset shows Ir blue dimer. (b) OTA spectra of Ir dimer in the presence of $Ru(bpy)_3^{2+}$ PS and EA following 532 nm excitation.

formation of the singly oxidized Ir dimer occurs at an observed rate of 1.0 x10$^{5}$ s$^{-1}$ with lifetime of 10 µs (Figure 1b). No additional changes are observed at the Ir L3 edge in XTA during the timeframe of 200 µs, suggesting that we only observed the first oxide state of Ir dimer. Indeed, investigations to several milliseconds within OTA displayed continued excited-state absorption features consistent with features observed in oxidative spectroelectrochemistry (not shown). While this reaction is still under investigation, initial insights into the formation, stability, and reactivity of the intermediates have been gathered and tests of catalytic behavior under alternative conditions have provided crucial data in the continuing efforts in understanding these complex catalytic mechanisms.

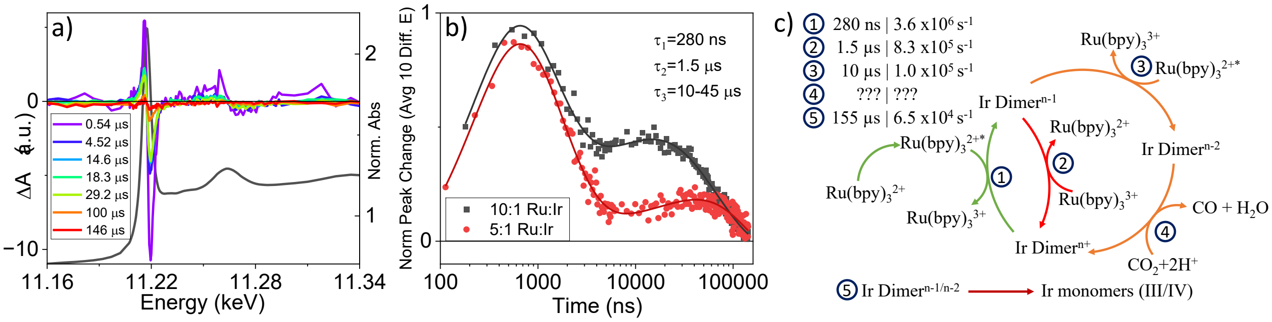

**Figure 2**. (a) Ground state Ir L3 XAS (black) and difference spectra at selected time points following 532 nm excitation; (b) Kinetic Traces from XTA following the major peaks at variable Ru(bpy)$_3^{2+}$ concentrations; (c) Proposed Reductive Catalytic cycle and observed rates.

In contrast, under lower concentrations of the EA, a reduction of the Ir blue dimer was observed due to ET from Ru(bpy)$_3^{2+*}$ to the ground state Ir blue dimer. This is again directly supported by XTA which shows the reduction of Ir metal center upon the excitation of Ru(bpy)$_3^{2+}$ (Figure 2a). Furthermore, it is found that a secondary reduction event can occur given a high enough concentration of the Ru(bpy)$_3^{2+*}$, driving the catalyst into an unstable doubly reduced state. This can be clearly observed from the presence of two bumps in the kinetic trace collected at 11.215 keV for Ru(bpy)$_3^{2+}$ to Ir blue dimer ratio = 5:1 or 10:1 in the absence of EA (Figure 2b). Figure 2c summarizes the ET rates and reaction pathways for these reduction reactions. Under conditions of 10:1 Ru(bpy)$_3^{2+}$:Ir blue dimer system, the ET rate from Ru(bpy)$_3^{2+*}$ to the Ir blue dimer is 3.6 x10$^{6}$ s$^{-1}$ in a highly competitive kinetic yield (~70%) against the emissive relaxation of Ru(bpy)$_3^{2+*}$ measured in water to be ~650 ns, or 1.54 x10$^{6}$ s$^{-1}$. The back ET from the reduced Iridium to the oxidized Ruthenium has an observed rate of 8.3 x10$^{5}$ s$^{-1}$, and the secondary reduction of the Ir blue dimer occurring at an observed rate of 1.0 x10$^{5}$ s$^{-1}$. While this secondary step is a low yield due to the backreaction, it is substantial enough that under a $CO_2$ atmosphere in the presence of a sacrificial donor, 111 nmol g$^{-1}$ h$^{-1}$ generation of CO can be seen through $CO_2$ reduction. While some backreaction continues to occur from this double reduced Iridium to reset the system, degradation of the dimer can be observed in the absence of $CO_2$, providing one possible explanation of catalytic instability over long reactions. Interestingly, negligible $H_2$ generation is observed even in slightly acidic conditions of pH=5.2. These results not only provide important insight on the potential major degradation pathway of Ir blue dimer during water oxidation reaction but also led to the discovery of a selective reductive molecular catalyst for $CO_2$ reduction. The unusual results have provided in depth details on the functionality of the Ir blue dimer, and begun to crack some of the complexities involved in this model water oxidation catalyst configuration.

# Triplet-Pair Mediated Systems for Multiexciton-Driven Photochemistry

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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. In this vein, 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 $[T_1T_1]$. In systems that meet the energetic criteria for SF, photon absorption produces a singlet exciton, which can rapidly decay into a correlated triplet-pair in a spin-allowed process. Harvesting the two free triplets ($2 \times T_1$) that are produced from dephasing of the triplet-pair has been the main focus of SF-based optoelectronic devices (**Figure**). However, we are shifting focus to harness the potential of the $[T_1T_1]$ state. Perceiving $[T_1T_1]$ as a distinct excited state with prolonged lifetimes, its own characteristic multi-reference wavefunction, total energy, and spin angular momentum,[10–12] presents a paradigm shift toward unprecedented multiexciton-driven photochemical processes. Therefore, it is imperative to develop a fundamental understanding of the impact of molecular architecture on controlling the fate of the triplet-pair to achieve uncharted spin conversion processes from SF.

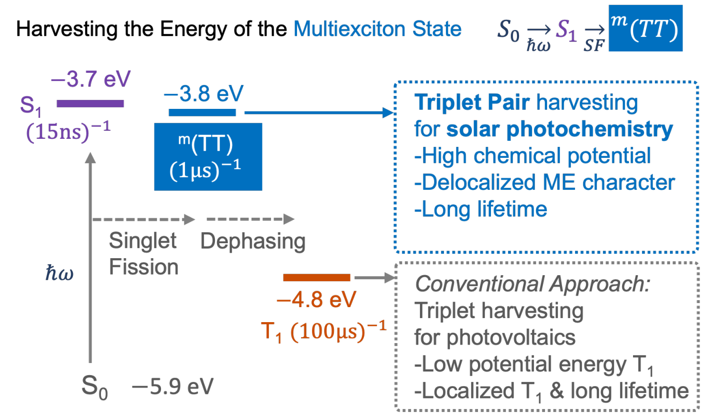

**Figure**. Highlight of the program goals.

Achieving the efficient conversion of triplet-pair multiexcitons to drive photochemical processes requires a reexamination of fundamental principles related to energy, spin angular momentum conservation, and the electronic factors governing the dynamics. The triplet pair presents new opportunities in photochemistry because of its distinct multiexcitonic nature that inherits key characteristics from both the singlet and triplet excitons (**Figure**). For example, the energy of the $[T_1T_1]$ state generated by intramolecular SF (iSF) is approximately twice that of an individual triplet. Although this places the triplet pair energy near the $S_1$ state in many common chromophores, it can exhibit much longer lifetimes since its recombination can be spin-forbidden, like the triplet exciton. The spin angular momentum of $[T_1T_1]$ can include net-singlet, triplet, and quintet configurations, with potential to enable photochemical and energy transfer processes inherent to individual $S_1$ and $T_1$ excitons. Still, it remains an elusive goal to control the photochemical conversion of $[T_1T_1]$ to a distinct product, including modifying the quantum electron and spin correlations of the triplet pair wavefunction to obtain the desired intermediates. Understanding and controlling this conversion process would gainfully impact SF light harvesting systems to drive interfacial charge transfer processes for multiexciton photochemistry.

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. Thus, in our work we introduce second-generation [G2] iSF chromophores with integrated photoredox active building blocks that are designed to achieve and control the triplet pair conversion to spatial separation of electron-hole pairs. While conventional studies of solution-phase systems can offer insights into the excited state dynamical processes, the [G2] iSF chromophores we are developing overcome fundamental challenges from intermolecular interfacial processes (e.g. weak excited state mixing and parasitic recombination process). For example, we recently reported that it is possible to sensitize molecules to their $T_1$ state directly from $[T_1T_1]$ by collisional energy transfer. While multiexciton sensitization is an important proof-of-concept study, individual triplet excitons are formed naturally during the evolution of the excited state. In this presentation, we will discuss conceptual design principles to develop [G2] iSF chromophores for unconventional processes.

In this presentation, we will discuss the unique features of the triplet pair wavefunction that enable new intramolecular photochemical processes, including quantum interference phenomena that affect both triplet pair formation and recombination processes. Our results imply that small changes to the structure of first-generation iSF chromophores can have outsize effects on the multiexciton wavefunction. We use this information to design functional multicomponent [G2] chromophores that exhibit a previously unknown triplet pair reaction, namely, a direct multiexciton charge separation ($S_1 \rightarrow [T_1T_1] \rightarrow \mathrm{CS}$). We elucidate the design rules that permit such a process to occur. This concept is further extended using integrated organometallic building blocks, where we observe a variety of photochemical conversion processes in which the charge density is rapidly transported between the different components. Importantly, the final products and key intermediates depend strongly on the identity of the metal and the strength of the bound ligands. Overall, this work is enabling the development of an extensive chemical toolbox capable of altering the chemistry of SF chromophores, building a foundation of multiexciton dynamics optimized for unconventional applications in photochemistry.

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# Photoactive Ligand Design for Directing Excited-State Dynamics

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Prior investigations in our group have been aimed at uncovering the influence of specific design features of molecular chromophores on singlet fission and excited-state charge transfer. Continued work in this area has elucidated a role for phonons in pentacene solids[3] and intermolecular coupling between anthradithiophene on the surface of mesoporous $TiO_2$.[5] Similar concepts are applied to molecules at 2D interfaces.[6,9] The goal of transducing triplet energy (or producing and maintaining its spin polarization[10]) at a semiconductor interface impels much of our current research, and in many cases, the behavior of the individual components cannot be taken at face value in the assembly. Modulating the coupling between the chromophore and the energy/charge transfer partner systematically remains a significant challenge that involves detailed fundamental spectroscopic studies and guidance from theory.

A unique molecular system we have studied comprehensively is a tetracene-based dicarboxylic acid (**Tc-DA**, Fig 1).[8] Its deposition into semiconductor surfaces from solution is affected by the intermolecular interactions that are more common at high concentrations typically used in sensitization. Solvent also plays a pivotal role through its participation in hydrogen-bonding. The aggregates that result have distinct photophysical pathways commonly observed in both dimers and solid-state singlet fission chromophores, including triplet pair and excimer formation. Control of the types of aggregates through solvent and concentration promises to direct the excited-state dynamics toward a particular function, whether it be triplet-pair formation, triplet-triplet annihilation based upconversion or long-lived charge separation.

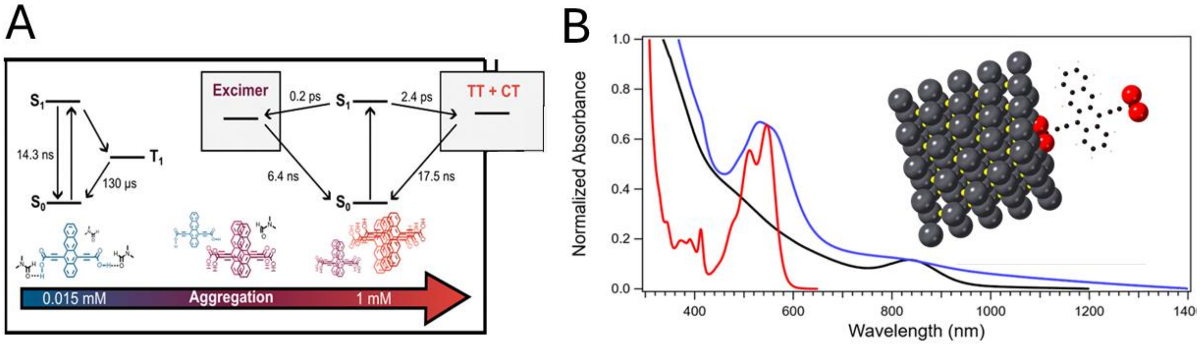

**Figure 1**. A, Schematic of excited-state behavior vs concentration for Tc-DA. B, Tc-DA absorption (red), PbS QD absorption (black) and ligand-exchanged absorption (blue), showing broadened features. Inset shows Tc-DA bound to the PbS nanocrystal.

Building on our understanding of intermolecular interactions in **Tc-DA**, we have performed ligand exchange on PbS quantum dots (QDs) of various sizes. Our prior work had demonstrated relatively slow (~100 ns) triplet formation after excitation of QDs with different diameters exchanged with a tetracene monoacid with the carboxylic acid in the pro-cata position. Exchange with **Tc-DA** with a peri-substituted geometry for the binding group results in insoluble QDs, severely broadened ligand absorption, and split electronic resonances (Figure 1b). These resonances imply strong electronic coupling that is confirmed through ultrafast transient absorption spectra of ligand-to-QD energy transfer. Specific regimes defined by ligand concentrations exhibit this behavior, which we attribute to a prostrate geometry for the tetracene core on the Pb-terminated QD surface, leading to orbital overlap and state mixing.

The question of how these QD-ligand interface geometries affect triplet dynamics requires QDs with smaller band gaps, 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 prostrate ligands and some degree of colloidal solubility. 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. The final state is distinct from the localized ligand triplet, exhibiting some evidence of an admixture with QD surface states. How this evolution proceeds toward ligand-centered triplets, and the further consequences of such behavior on subsequent dynamics are the subjects of ongoing studies.

Chirality induced spin-selectivity (CISS) has been shown by many groups (including at NREL) to direct chemical reactions toward certain products. A corollary that we term spin-selective photoinduced charge transfer (SSPCT) has the potential to be an equally influential route to photo(electro)catalytic transformations. Our initial work in this area involves the design, synthesis, and characterization of a chiral bridge to insert into a donor-bridge-acceptor system that includes a semiconductor acceptor. The bifunctional structure possesses axial chirality through a bonded diether bridge that connects two phenyl groups (Figure 2a). This bridge has been synthesized with high enantiomeric excess based on a simple procedure with a high degree of versatility toward auxiliary chiral features and electronic structure. Preliminary work toward understanding its circular dichroism (Figure 2b) and other optical properties will be presented. Additional studies involving its behavior attached to mesoporous oxides are ongoing, including magneto-conductance experiments and the analysis of chiral induction through the binding of an achiral donor dye, with the participation of a metal cation to provide spin-orbit coupling for eventual SSPCT. We anticipate these fundamental studies will lead toward developing photocatalytic selectivity in a variety of high potential barrier reactions.

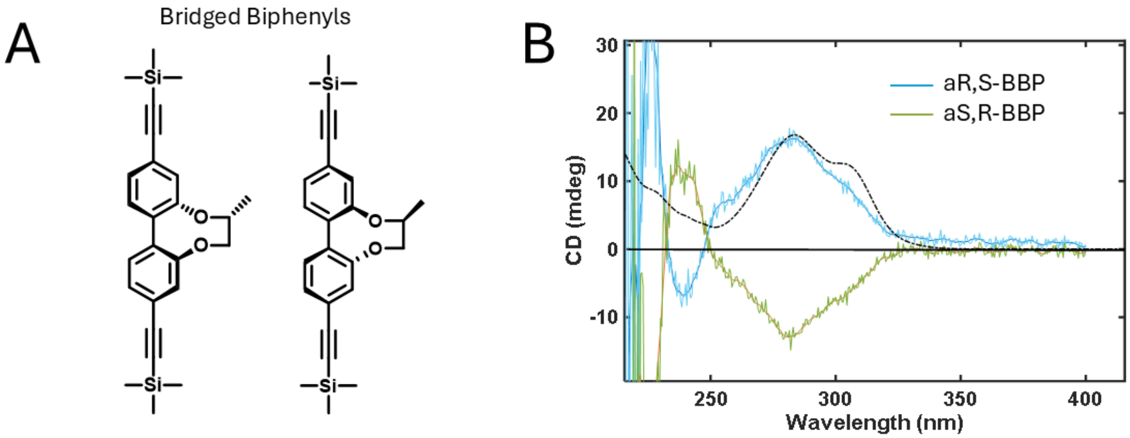

**Figure 2**. A, Bridged biphenyl derivatives. B, Circular dichroism spectra for the two enantiomers.

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# Linker Design for Molecular-Level Control at Semiconductor Interfaces

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Hybrid molecule-inorganic materials are essential components of solar energy technologies that produce electricity and fuels. They consist of a light-harvesting molecule or a photocatalyst interfaced with an electron-accepting inorganic material such as metal oxides, semiconductors, quantum dots, inorganic conductive oxides or perovskites. Our objective is to tune the hybrid properties through molecular design of the linkers, *i.e.* the components responsible for the surface attachment of the light harvester on the material where charge transfer occurs, **Fig.1**. As the inorganic material we typically work with semiconductors ($MO_n$: M = Ti, Zn, Al, Zr), transparent conductive oxide electrodes with the Meyer group (TCO), and more recently quantum dots (PbS) with the Johnson and Beard groups at NREL. As molecules we study polyaromatic hydrocarbon chromophores, such as perylenes. The talk will describe current and planned work in research directions that include: control and understand heterogenous charge transfer processes by providing functionality to the linker, for instance through conformational effects and synthetic modifications that strategically direct or influence binding; control long-range packing order of the bound molecules; development of NMR techniques to probe stacking in solution and surface bound, and binding mode. This molecular-level knowledge of the interface is valuable for fundamental studies of energy transfer and solar energy conversion.

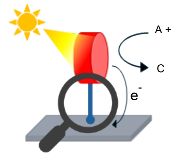


**Fig. 1** Spotlight on the linker

*Stacking control of perylenes on the surfaces (with J. Johnson, NREL)*. Molecular packing modes of PAHs, in solution, in the solid state or at interfaces, influence charge and energy transfer processes, such as sensitization and singlet fission. *We are developing ways to control π-π stacking, orientation, and slip-stacking on surfaces by two types of linker design (**1** and **2** in **Fig.2**).* We are studying molecular packing on metal oxide surfaces with single and mixed layers of **1** (n = 0, 1, 2). To date we have studied individual films and soon will start studying mixed layers. With **2** (a-c) we are studying the effect of planar binding mode to PbS QDs of 2 and 5 nm diameter, **Fig.2c**. We have preliminary data with **2a** indicating that binding is heavily influenced by the QD size. Finally, through a combination of 1D and 2D NMR, NOESY, and DOSY methods we characterized in detail concentration- and solvent-dependent molecular packing for **1** (n = 1): briefly, in THF a broad distribution of face-to-face π-stacked large pentamers is formed, and in DMSO a narrow distribution of slip-stacked dimers is observed. This information can be of interest for binding and for solution experiments aiming at singlet fission.

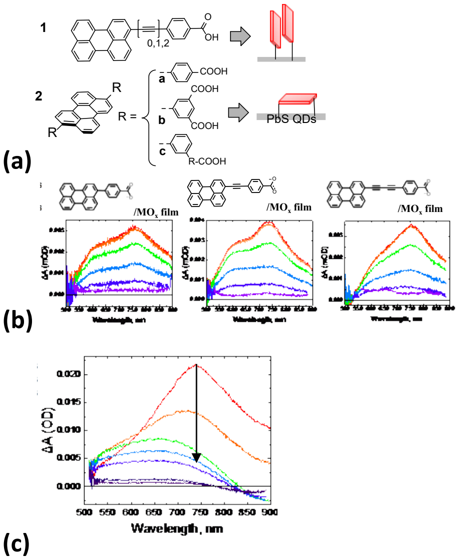
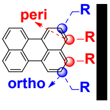


**Fig. 2 (a)** the compounds and concept. **(b)** TA of **1**/$Al_2O_3$. (red = 1 ps → purple = 6 ns) **(c)** TA of **2**/PbS 2 nm∅ (red = 0.1 ps → purple = 6 ns) and control. λex = 400 nm

Solution experiments are only a first step to characterize packing, and eventually we want to develop solid-state SS-NMR methods.

*Conformational and binding mode effects in perylenes with dual linkers (with Lars Gundlach, U Delaware).* We reported the synthesis and interfacial electron transfer (ET) studies of mono- and dual-linker perylenes probing the influence of the linker (i) attachment point (ortho/peri) and number (mono/bis); (ii) conjugation (alkene/alkane); (iii) binding modes (monodentate/bidentate) (**Table 1**). We concluded that in addition to predictable attachment point/conjugation effects (slower ET dynamics and weaker electronic coupling for ortho substitution and saturated linkers), conformational effects significantly influence ET rates. For the conjugated linkers ET from bis-peri was significantly slower than that from mono-peri. Theory attributes this behavior to conformational changes caused by steric interactions that enhance delocalization of the excited electron over the second non-binding linker and reduces electronic coupling, resulting in slower ET. For the saturated linkers two significantly different ET rates were assigned to two binding modes of the COOH group: bidentate (fast rate) and monodentate (slow rate), again consistent with theory work. These results again point towards the need to control binding mode and conformational effects as confirmed in a separate collaborative study with G.J. Meyer (UNC), where visible light absorption by a transition metal complex results in planarization of the *p*-phenylene ethynylene bridge units in the linker, and electron injection restores rotation, preventing recombination. We are currently separating surface binding from other linker effects by synthesizing perylenes with dual linkers with *different functions:* Linker 1 would provide strong binding while Linker 2 will be tested for microenvironment-responsive charge transfer (**Fig.3**).

**Table 1. Electron Injection rates (fs) of mono- & dual linker perylenes /$TiO_2$**

| Linker R | | -CH=CH-COOH conjug. | | $-CH_2-CH_2-COOH$ saturated | | |
|---|---|---|---|---|---|---|
| Compound | | Experimental | Calc. | $\tau_1$ fast | $\tau_2$ slow | $A_1:A_2$ |
|  | Mono-Ortho | 35.7 ± 3.5 | 28 | 329 | 2686 | 2.4 |
| | Bis-ortho | 17.7 ± 5.2 | 20 | 227 | 2517 | 5.1 |
| | Mono-Peri | 35.9 ± 6.0 | 13 | 180 | 1387 | 1.8 |
| | Bis-peri | 57 | 25 | 197 | 1231 | 1.3 |

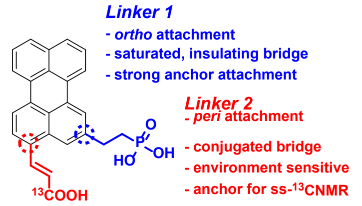


**Fig. 3** Dual linker design

## DOE Solar Photochemistry Sponsored Publications 2022-2025

Submission June 2025 *Aggregation studies of a perylene benzoic acid derivative: solvent and concentration effects probed by NMR and spectroscopy* Katherine Lloyd, Pavel Kucheryavy, Justin Johnson, Melissa Gish and Elena Galoppini (planned journal: J. Phys. Chem.)

1. *Structural Gating Enhances Long-Distance Light-Driven Interfacial Electron Transfer.* Quentin R. Loague, Marzieh Heidari, Hayden J. Mann, Evgeny O. Danilov, Felix N. Castellano, Elena Galoppini, and Gerald J. Meyer *ACS Central Science* **2024**, *10*, 2132-2144. DOI: 10.1021/acscentsci.4c01106.

2. **Special Collection: The Physical Chemistry of Solar Fuels Catalysis (Invited).** *Interfacial electron transfer of perylenes: Influence of the anchor binding mode.* Han Yan, Ryan Harmer, Binish Zafar, Elena Galoppini, Lars Gundlach; *J. Chem. Phys.* **2024**, *160*, 034706. DOI: 10.1063/5.0185342.

3. *Reorganization Energies for Interfacial Electron Transfer across Phenylene Ethynylene Rigid-Rod Bridges.* Marzieh Heidari; Quentin Loague; Rachel E. Bangle; Elena Galoppini; Gerald J.

Meyer *ACS Applied Materials & Interfaces* **2022**, *14*, 35205–35214. DOI: 10.1021/acsami.2c07151.

4. **Special issue on Functional Molecular Structures on Complex Oxide Surfaces (Invited).** *Energy alignment manipulation at the C60/TiO$_2$(110) interface using a blanket molecular dipole approach* Robert A. Bartynski, Sylvie Rangan, Jonathan Viereck, Katherine Lloyd and Elena Galoppini. *Surface Science* **2022** *723 122116 https://doi.org/10.1016/j.susc.2022.122117*

*Manuscripts in progress*

*Isophthalic acid Derivatives as Novel Anchor Groups The Influence of a Third Coordination Point* Marzieh Heidari, Quentin Loague, Lola Frey, Jenny Gavazi, Gerald J. Meyer, Elena Galoppini (planned journal: ACS Applied Materials and Interfaces)

*Properties of o-Carborane Triads: Non-covalent σ··π Interactions and Intermolecular Charge Transfer* Yang Zhang, Roger Lalancette, Kyle Cooper-Juchnewich and Elena Galoppini (planned journal: Journal of Photochemistry and Photobiology)

# Designing Silicon-Molecular Catalyst Hybrid Photocathodes

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Recent work from several groups have explored semiconductor-molecular catalyst hybrids to independently tune light harvesting and catalysis in artificial photosynthetic schemes, such as the significant contributions of the CHASE Fuels from Sunlight Energy Innovation Hub that has provided new insights on electron transfer and other processes for a range of molecular carbon dioxide reduction reaction ($CO_2RR$) catalyst-semiconductor systems including Si photocathodes.

Our lab recently introduced intrinsic silicon nanocrystal–molecular Re complex hybrid assemblies (Si-[Re] NCs) as model systems for understanding the energetic alignment of Si with prototypical $CO_2RR$ molecular electrocatalysts.[3] This work concluded that the conduction band edge energy of 3.9 nm diameter Si NCs is likely misaligned with the lowest unoccupied molecular orbital (LUMO) of the tethered [Re] complexes and prevents productive energy cascade of light-driven Si conduction band electrons to [Re] LUMO orbitals that is essential for driving $CO_2RR$. Consequently, we found photocatalytic $CO_2RR$ is dominated by direct light absorption from the surface bound [Re] complexes. The results of our prior work begged the question: What are potential design strategies to achieve optimal energetic alignment in a hybrid silicon-$CO_2RR$ electrocatalyst artificial photosynthetic system?

In this presentation, we will communicate our work exploring strategies for enhancing electronic interaction between Si NCs and surface tethered molecular Re electrocatalysts as models for $CO_2$-reducing hybrid photocathodes. Using density functional theory (DFT) combined with electrochemical, spectroscopic, and photocatalytic measurements, we determined that the intrinsic Si ($^{i}$Si) NC conduction band energy in $^{i}$Si-[Re] assemblies is below the [Re] LUMO and singly occupied molecular orbital (SOMO) energies even for strongly quantum-confined 3.0–3.9 nm diameter H-terminated and methyl-terminated $^{i}$Si NCs, respectively (Figure 1). We computationally analyzed design strategies to align the semiconductor conduction band edge and the electrocatalyst frontier molecular orbitals by varying the $^{i}$Si NC size, introducing boron as a dopant in the Si NC, and modifying the attachment chemistry to the [Re] complex aryl ligand framework. This DFT analysis identified a target hybrid structure featuring B-

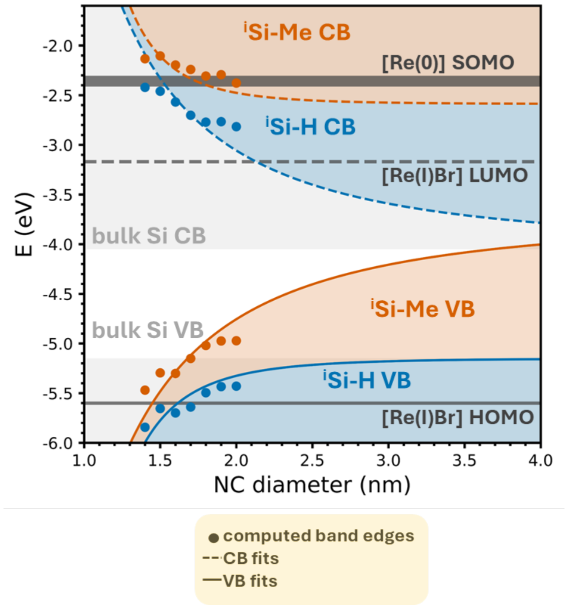

Figure 1. DFT predicted band edges (circles) as a function of NC model size compared to tethered [Re] frontier molecular orbitals (dark grey) and bulk silicon band edges (light grey). The red ($^{i}$Si-$C_{12}$) and blue ($^{i}$Si-H) shaded regions correspond to NC diameter dependent fits according to the DFT predicted band edges.

doped silicon (B:Si) NCs with a direct bond between a surface Si atom and an $sp^2$-hybridized C atom of the electrocatalyst bipyridine aryl ring ligand (B:Si-$C_{Ar}$[Re], Figure 2). We synthesized the B:Si-$C_{Ar}$[Re] NC assembly via reaction between B:Si NCs and $[Re(N_2bpy)-(CO)_3Cl]BF_4$ where $N_2$bpy = 2,2'-bipyridyl-4-diazonium provided by the Marinescu group. Evidence of direct hybridization between the B:Si NC and the surface [Re] electrocatalyst LUMO was provided by electrochemical measurements and transient absorption spectroscopy. However, this system did not provide any photocatalytic benefit owing to enhanced recombination.

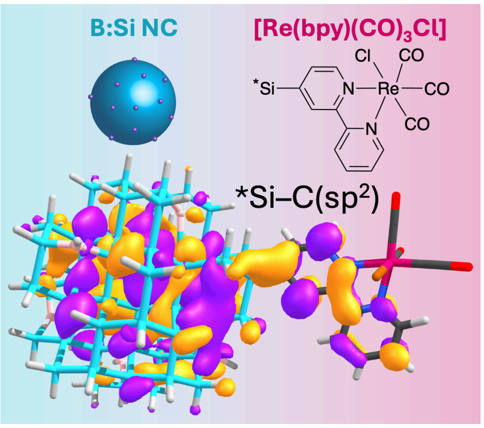

Figure 2. Computationally predicted orbital density plot for the empty 736α (Si LUMO) orbital of 1.5 nm B:Si-$C_{Ar}$[Re].

Ultimately, this work provides a guide for designing silicon semiconductor-molecular catalyst hybrid photoelectrochemical (PEC) systems. A hybrid PEC system may allow for dynamic control of the energetics of the semiconductor and catalyst frontier molecular orbitals, and the band bending present in a bulk PEC system may mitigate recombination that limited photocatalytic conversion in B:Si-$C_{Ar}$[Re] and would be expected for other electronically coupled hybrid systems. Since many $CO_2$RR molecular electrocatalysts feature high lying LUMOs and SOMOs, a key conclusion is that development of lower redox potential $CO_2$RR catalysts or the choice of a less energetically costly catalytic reaction (e.g., HER) may be required to produce a favorable match between the Si conduction band energy level and tethered catalyst vacant orbitals. Along these lines, we will present recent work on a system exhibiting strong electronic coupling between a molecular HER catalyst and $^i$Si NCs that is achieved from the significantly lower reduction potential of the HER catalyst cf. typical $CO_2$RR catalysts.

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2. "Intra- and Intermolecular Charge-Transfer Dynamics of Carbene−Metal−Amide Photosensitizers," M. S. Kellogg, A. R. Mencke, C. N. Muniz, T. A. Nattikallungal, F. Cardoso-Delgado, N. Baluyot-Reyes, M. Sewell, M. J. Bird, S. S. Saund, N. R. Neale, S. E. Bradforth, M. E. Thompson, *J. Phys. Chem. C,* **128**, 6621–6635 (2024). DOI: https://doi.org/10.1021/acs.jpcc.4c03368

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# Characterization of structural, physical, and chemical characteristics of semiconductor/metal interfaces on functioning hybrid photocatalysts

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Materials that are receiving the most attention in photo(electro)chemical water splitting couple semiconductor (SC) light absorbers to metal nanoparticle electrocatalysts (np-EC) to drive oxygen (OER) and hydrogen evolution (HER) half-reactions. In these systems, the SC provides a photovoltage that is used by the ECs to drive the electrochemical half-reactions. It has been recognized that such 'unburied' np-EC/SC interfaces behave very differently compared to their thin-film "buried" analogues, but the fundamental mechanisms governing interfacial charge transfer and photovoltage remain poorly understood. The challenge is that these np-EC/SC interfaces are highly dynamic under reaction conditions as well as very difficult to directly probe experimentally. To accurately capture the behavior of these systems, atomistic changes to the np-EC/SC interface under reaction conditions need to be understood and considered.

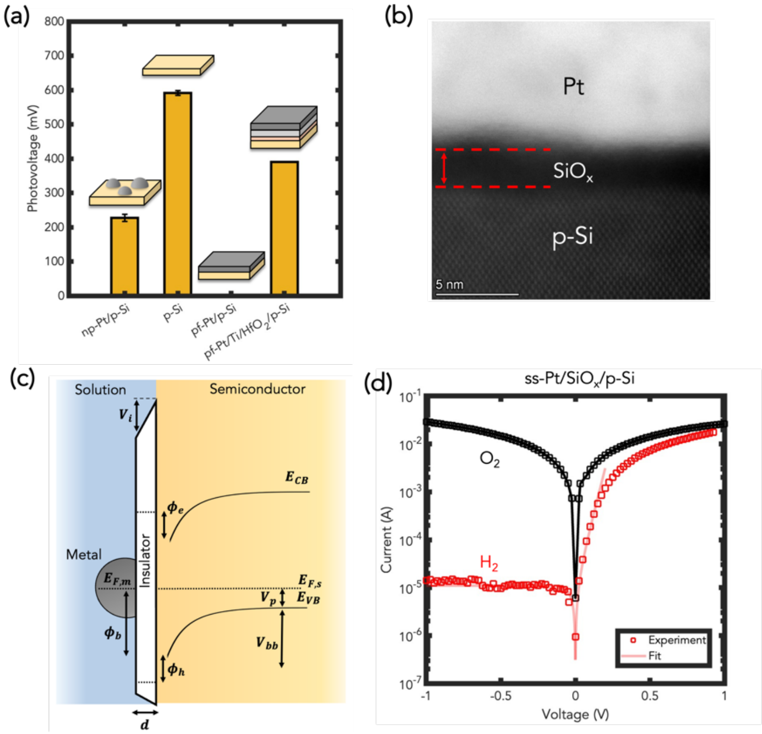

***Figure 1.*** *(a) Measured photovoltages of EC/SC model systems for light-driven HER. (b) Cross-sectional STEM image of the oxidized np-Pt/p-Si interface. (c) Illustrated energy band diagram of the oxidized np-EC/SC interface. (d) Dry solid-state current-voltage measurement of Pt/SiO$_x$ junctions in $H_2$ and $O_2$-saturated environments.*

Our work focuses on analyzing the physical mechanisms underlying the operation of functioning photo(electro)catalysts. The fundamental questions we seek to answer are:

(1) What are the origins of photovoltage for 'unburied' nanoscale EC/SC interfaces under operating conditions?

(2) How do dynamic reaction environments impact charge carrier selectivity and photovoltage through their interaction with the EC/SC interface?

To answer these questions, we deploy a range of analogous model systems, mainly focusing on different metal ECs on Si and $TiO_2$ SCs. The model systems include np-EC/SC, flat film EC/SC, buried junction flat film EC/SC, and buried-EC/SC models. These model systems allow us to shine light on similarities, differences and contradictions involved in the operations on these photoelectrocatalysts. By comparing the behavior of these model systems under diverse reaction conditions we can understand how reactive environments impact the behavior of unburied junctions relative to the buried analogs of these junctions.

Ultimately, we demonstrated that reactive environments play critical role in affecting the performance of EC/SC photoelectrocatalysts. We analyze and quantify a number of mechanisms by which this takes place, including: (i) the role of molecular adsorbates (such as $H_2$ and $O_2$) in governing interfacial dipoles on EC/SC interfaces and modulation of the Schottky barrier height and charge carrier selectivity, (ii) a spontaneously evolved thin oxide layers at the SC or EC facilitates tunneling-mediated charge transfer while suppressing recombination, providing an additional degree of control over interfacial energetics, and (iii) as well as the commonly cited pinch-off effect. We quantitatively described these findings through a comprehensive mathematical framework. These findings reveal that catalytic surface chemistry can serve as a powerful lever for tuning electronic structure and photovoltage in nanoscale photoelectrode architectures, opening new design strategies for high-efficiency solar fuel systems.

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# Harnessing resonant multiple scattering for solar photoelectrochemical energy conversion

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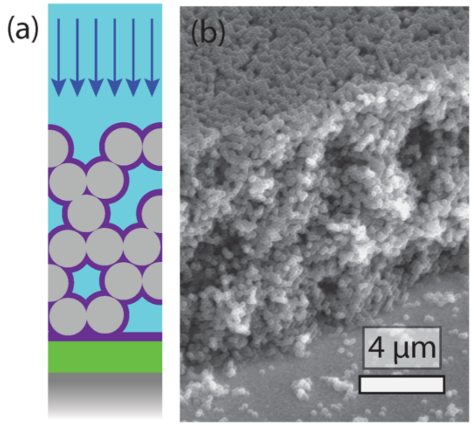

Figure 1 - (a) Schematic and (b) cross-section of an omission glass photoelectrode comprised of 200 nm $SiO_2$ nanospheres with pores formed by the removal of 200 nm polystyrene nanospheres. The omission glass is functionalized by a conformal 20 nm $TiO_2$ layer added by atomic layer deposition (ALD).

Semiconductors based on earth-abundant compounds often exhibit poor carrier collection yields due to short minority carrier diffusion lengths and excessive recombination. This can be alleviated by using ultra-thin film semiconductors to ensure that the photogeneration of carriers occurs near the semiconductor-liquid interface. However, thin films limit light absorption and necessitate light trapping strategies to increase the photogeneration rates. Photonic crystal templates can generate tailorable light trapping and "slow light" effects via periodic and precise nanostructure, though this is not a scalable strategy for photoelectrochemical (PEC) applications. It is therefore critical to identify alternative mechanisms for light trapping that tolerate disorder. Light trapping in disordered materials is generated by the diffusive transport caused by multiple scattering. In some cases, this multiple scattering can generate resonances and "slow light" effects that resemble those observed in photonic crystals. While resonant multiple scattering is a disorder tolerant light trapping mechanism, it is unclear if the effect is sufficiently adaptable, or even useful, for PEC applications.

In this talk, we will describe our recent work to control resonant multiple scattering for improving photoelectrochemical energy conversion rates in electrodes fabricated from nanosphere $SiO_2$/polymer colloidal composites. Our recent work involves the development of a tailorable nanostructure (referred to here as a *photonic omission glass*) that facilitates the modification of the characteristic porosity and dielectric contrast that tailors the mean free path of light through the electrode. We observed the emergence of multiple scattering resonances after coating the omission glass structure with a layer of $TiO_2$, which functions both as dielectric contrast and as a light-absorbing semiconductor. We show in finite-difference, time-domain (FDTD) simulations and spectroscopic characterization that the resonant multiple scattering effect improves light trapping for near band edge wavelengths near the interface between the structure and the bulk electrolyte. This effect, coupled with the increased internal active surface area, results in a hierarchically structured $TiO_2$ photoanode with orders of magnitude higher photocurrents compared to an equivalent planar photoanode for PEC reactions such as ferrocyanide oxidation and alkaline water oxidation.

Based on these results, we will describe our current and proposed work to extend the applicability of disordered photonics to visible-light photoelectrochemistry. One route is to integrate small-

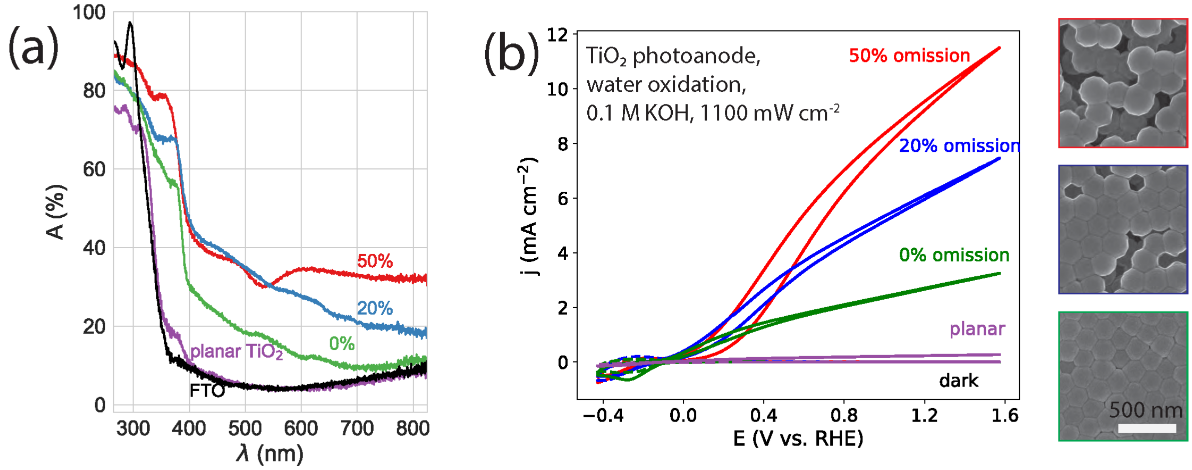

Figure 2 – Enhanced (a) absorption and (b) photoelectrochemical water oxidation yields in a 20 nm $TiO_2$-based omission glass photoelectrode with increasing degree of omission. "FTO" indicates the absorption spectra for the $F:SnO_2$-coated substrate used in these electrodes.

volume semiconductors into the $TiO_2$-based photonic glass photoelectrode by functionalizing the sacrificial polymer nanospheres during the synthesis. We will show results based on FDTD simulation and experimental work towards this photoelectrode design. The other route we will discuss is to convert the metal oxide layer covering the omission glass photoelectrode to visible light-absorbing oxynitride or nitride layers (e.g., ALD-derived $Ta_2O_5$ to TaON or $Ta_3N_5$) via ammonolysis. Both routes require us to develop new design approaches for photonic glass photoelectrodes to tailor the resonant transport to the absorption edge of the target semiconductor. In summary, we aim to show that controlling optical transport in disordered nanostructures can be advantageous for improving PEC energy conversion in scalable, composite photoelectrode designs.

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

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## Overview:

Hydrogen generation via water splitting can be achieved using photocatalysts that can directly convert solar irradiation into products. Recently, plasmonic nanoparticles (NPs) have been combined with these photocatalysts to improve catalytic performance. However, the plasmonic catalysis community is split regarding dominant plasmonic mechanisms. Some claim that plasmonic processes are solely a result of localized heating, while others also claim that very energetic carriers can be generated. One of the reasons for this debate is that the local heating effect has not been identified clearly. In this project, we will tackle this fundamental question of plasmonic heating vs. plasmonic hot carrier generation in an Au/$TiO_2$ material system for water splitting. Specifically, we will develop a hybrid temperature/evolved gas detection imaging technique based on high-sensitive surface plasmon resonance (SPR), which can detect simultaneously thermal energy and evolved gas (hydrogen and oxygen) at the nanoscale (or in submicron scale), based on the controlled plasmonic NPs array with electron-beam lithography technique, to help disentangle the two possible contributions in catalytic water splitting, especially providing new insight to the role of local heating of plasmonic NPs on hydrogen generation. The collective heating effect will also be examined. Furthermore, transient pump-probe transient absorption (TA) spectroscopy and near-field thermodynamics simulation, including quantum chemistry and multiphysics modeling to solve Maxwell and heat equations, will be done to explore the temporal kinetics of the plasmonic photocatalysts on the gas generation from femtoseconds to milliseconds, which can provide an important thermal property of the thermal diffusivity.

## Methodology:

The photoelectrochemical cell technique will be employed for water splitting. A hybrid temperature/evolved gas (hydrogen/oxygen) detection imaging technique will be developed based on high-sensitive surface plasmon resonance (SPR), which can simultaneously detect thermal energy and hydrogen/oxygen generation at the nanoscale, as in Fig. 1.

The evolved gas (hydrogen/oxygen) quantification by SPR imaging will be verified with the gas chromatography mass spectrometer (GC-MS) or gas analyzer in situ to provide an experimental correlation between the thermal energy and the generated gas in SPR hybrid thermometry/morphology imaging, enabling the local and collective heating effect on the catalytic reaction, which is not possible with the existing measurement techniques.

The various Au plasmonic NP (or nanodisk) arrays (Fig. 2-a) will be fabricated using the EBL fabrication recipe and cleanroom equipment at SNL. The various NP density and size will be prepared and coated with a traditional catalyst, such as $TiO_2$, to form a hybrid design of the antenna-reactor (A-R) complexes. The plasmonic NPs act as nanoantenna to enhance the light absorption, and thus promote the transfer of both hot carriers and heat to the active sites on the reactor.

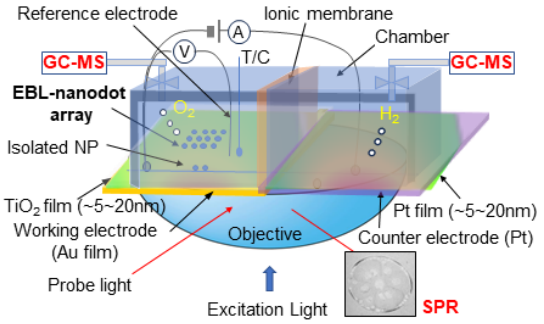

**Fig. 1 Schematic of a hybrid temperature / evolved gas detection imaging technique based on objective-based surface plasmon resonance (SPR) imaging.**

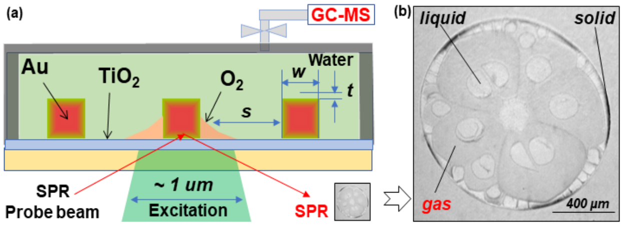

**Fig. 2 (a) A cross-sectional view of hybrid temperature/gas detection. (b) SPR image showing detection of liquid, gas, and solid phases simultaneously.**

Fig. 2-a presents a SPR thermometry from the bottom side and GC-MS measurement from the top side. Specifically, the SPR imaging will detect the morphology of generated gas (oxygen) near the plasmonic nanoparticles/photocatalyst, as in Fig. 2-b and will be correlated with the GC-MS analysis of gas components and the flow rate. Secondly, the morphology with the GC-MS measurement will be correlated with the SPR temperature measurement depending on various experimental conditions. Fig. 2-a provides a simultaneous detection of temperature and evolved gas generation for the individual photocatalyst particle. SPR detects the thermal energy variation and the evolved gas generation morphology by the change of refractive index of the test medium, water.

In addition, the nanoscale heating effect and the collective photothermal effect will be investigated by controlling the nanodot density and dimension, and by conducting transient absorption (TA) spectroscopy. Furthermore, the plasmonic thermodynamics simulation will be performed through modeling, heat equation solving using the experimental data from SPR thermometry and TA measurement.

## Expected Outcome:

It is expected to provide a breakthrough by measuring temperature and hydrogen/oxygen generation simultaneously from single and collective nanoparticles in photocatalysts, biomedical, energy conversion, and photothermal chemistry applications, providing a new diagnostic tool for the local and collective heating effect and the heat dissipation effect. In this project, we will establish a sustainable framework for basic research in collaboration with SNL. This project is a significant starting point for the PI to continue fundamental research, especially in basic energy science, by providing research capacity and expertise through the mutually beneficial relationship between TAMU-CC and SNL.

# Controlling Electrochemical $CO_2$ Reduction using Chirality Induced Spin Selectivity

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This paper reports on the effect of chirality-induced spin selectivity (CISS) in $CO_2$ reduction electrocatalysis on nanostructured plasmonic copper electrodes and its study using optical, electrochemical and ultrafast Kerr ellipticity spectroscopy. We elucidate the mechanism using (spectro)electrochemistry and ultrafast spectroscopy. The CISS effect leverages the lack of inversion symmetry of chiral molecules, chiral crystals, chiral semiconductors, and chiral shaped nanostructures to influence the orientation of the spin of charge carriers (electrons or holes) that pass through those chiral systems. The effect is thought to be caused by forcing the charge carriers to undergo a helical movement that either directs the carrier spin along the current direction through the spin current effects or by acting as a spin filter. Regardless of the mechanism of the effect, the resulting spin polarization potentially can suppress reactions at chiral catalytic surfaces that rely on the formation of singlet spin configurations in chemical bonds such as peroxide formation during the oxygen evolution reaction.

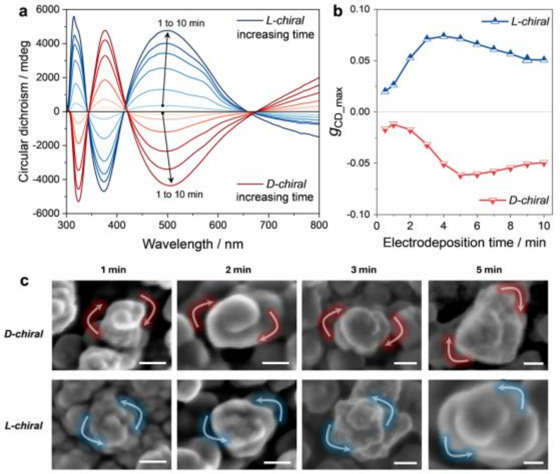

**Figure 1**. (a) Circular dichroism of *L-chiral* and *D-chiral* copper electrodes as a function of the electrodeposition duration from 1 – 10 min. (b) $g_{CD}$ values at each electrodeposition time shows the chiroptical response independent of the film thickness. (c) SEM images showing opposite direction of helical structures of the electrodeposited chiral Cu electrodes. Scale bar = 50 nm.

We prepared helical-structured copper (Cu) electrodes using chiral and achiral tartaric acid molecules as a structure-directing agent during electrodeposition on gold substrates. The chirality of the tartaric acid is shown to direct the helical direction of the copper nanostructures. Figure 1 a and b show the circular dichroism observed during the growth of the copper nanostructures as a function of deposition time. A clear opposite direction Cotton effect is observed with extraordinarily high amounts of dichroism. The plasmon resonance of the copper nanostructures is also visible at 570 nm in the dichroism spectra. Scanning electron microscopy (SEM) images (Fig

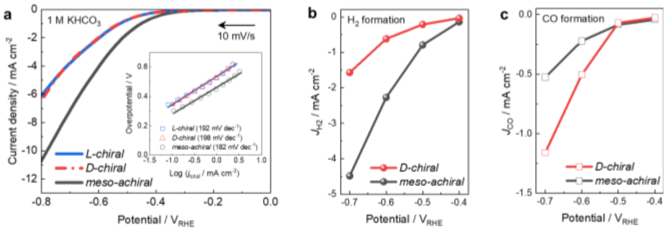

Fig. 2. Electrochemical characterization of chiral and achiral Cu electrodes in $CO_2$-saturated 1 M $KHCO_3$ (pH 7.8). (a) J-V curve measured by linear sweep voltammetry and corresponding Tafel slope (inset). Partial current densities of (b) $H_2$ evolution and (c) CO production on *D-chiral* and *meso-achiral* copper.

1c) show that the copper structures "curl" in opposite directions depending on the chirality of the tartaric acid used. The chiral Cu electrodes exhibit suppressed hydrogen evolution (Fig 2 a and b) but a lower onset potential for $CO_2RR$ compared to their achiral counterpart. We observe formate production only on the chiral electrodes and CO production is enhanced (Fig 2 b and c) on the chiral electrodes compared to achiral electrodes. We postulate that the chiral topology induces an electron spin accumulation at the electrode surface that reduces hydrogen formation since it prevents two hydrogen atoms with the same electron spin from combining to form hydrogen. However, the resulting higher density of surface-hydride atoms promotes $CO_2$ reduction to CO and induces the production of formate.

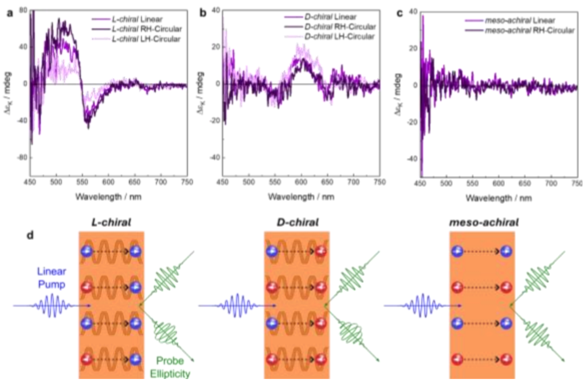

**Figure 3**: TRKE spectra measured at the front surface of a) *L-chiral*, b) *D-chiral*, and c) *meso-achiral* approximately 1 ps after photoexcitation of the back surface with a 400-nm pump pulse (2 mJ cm$^{-2}$). Purple lines: linearly polarized pump, dark and light purple lines: right- and left-hand (RH- and LH-) circularly polarized pumps, respectively. (d) Schematic of the experimental configuration using linearly polarized pump to excite electrons from the back side and probe ellipticity at the surface of Cu electrodes.

We studied the mechanism of the observed enhancements using time-resolved Kerr ellipticity (TRKE – figure 3) by generating carriers on one side and detecting the induced Kerr ellipticity on the opposite side. We found that carriers traveling through the helical structure become spin polarized as evidenced by the opposite sign of the TRKE signals depending on the pump polarization and the chirality sign of the nanostructures. These findings provide insights into the potential of chiral catalysts for controlling selectivity during $CO_2RR$ as well as other valuable reduction reactions involving nitrogen or CO where hydrogen evolution also is an undesired side reaction.

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# Solar $CO_2$ Reduction using Single Atom Catalysts on $C_3N_4$ Modified with Dianhydrides

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The overarching goal of this project is to advance the fundamental understanding of underexplored mechanisms regarding how well-defined heterojunctions dictate charge separation in photocatalysis for efficient solar fuel production. We propose to construct heterojunctions between graphitic carbon nitride ($C_3N_4$) and single atom catalysts (SACs). In such photosynthetic assemblies, water oxidation occurs on photoactivated $C_3N_4$, while the SACs mediate $CO_2$ reduction upon accepting photogenerated electrons from $C_3N_4$ (**Fig. 1**). We hypothesize that extended π conjugation at heterojunctions will serve to promote electron transfer from photoactivated $C_3N_4$ to SACs. The key role of heterojunctions in promoting photoinduced charge separation will be investigated using X-ray transient absorption spectroscopy in collaboration with Dr. Lin X. Chen at Argonne National Laboratory. Further studies with *in situ* spectroscopies will generate important information on reaction pathways on the SACs. The science drivers for this project are fundamental questions regarding the tunability of heterojunction structures at the molecular level, and effects of extended π conjugation on the properties of SACs and photoinduced charge separation across the heterojunctions.

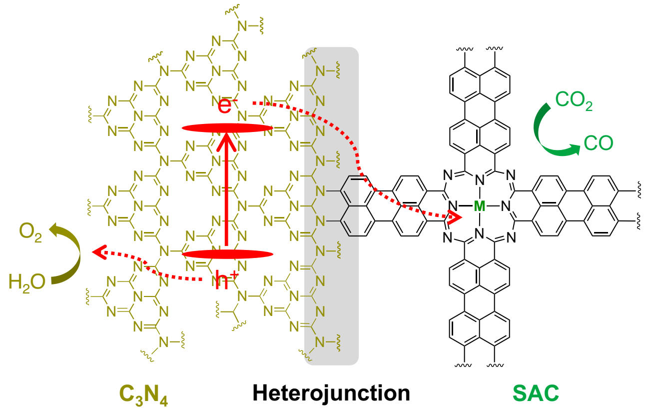

**Fig. 1**. An example of the proposed photocatalysts containing a $C_3N_4$/SAC heterojunction. M = Co or Fe.

We build on our prior achievements to synthesize photocatalysts containing $C_3N_4$/SAC heterojunctions. In particular, modified $C_3N_4$ materials have been prepared via pyrolysis of urea in the presence of different dopants, including 1,2,4,5-benzenetetracarboxylic dianhydride (denoted "DA"), 1,4,5,8-naphthalenetetracarboxylic dianhydride (denoted "NA") and 3,4,9,10-perylenetetracarboxylic dianhydride (denoted "PA", structures shown in **Fig. 2a**). Incorporation of such extended π-aromatic systems in $C_3N_4$ leads to interesting absorption features in the visible region (**Fig. 2**, **b** and **c**). Pristine $C_3N_4$ synthesized in the absence of any dopants exhibits a sharp absorption onset at < 450 nm corresponding to a $\pi-\pi^*$ direct bandgap transition of 2.7 eV for this *n*-type semiconductor. The less intense lower energy tail of this absorption band to ca. 560 nm is characteristic of lower absorption coefficient $n-\pi^*$ transitions. Increased visible absorption is evident for the dianhydride-doped materials (**Fig. 2c**). Characterization using solid-state photoluminescence (PL) spectroscopy indicates improved charge separation in the dianhydride-modified $C_3N_4$ materials. In particular, $C_3N_4$ materials doped with DA, NA and PA exhibit PL peak integrals of 68%, 41% and 27% respectively, relative to pristine $C_3N_4$ (**Fig. 2d**).

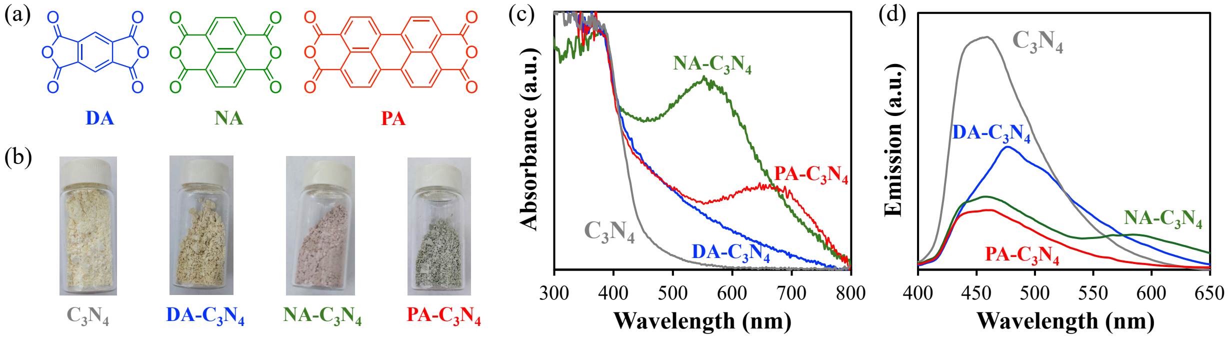

**Fig. 2**. (a) Molecular structures of DA, NA and PA; (b) photos of pristine $C_3N_4$ and $C_3N_4$ materials modified with DA, NA and PA; (c) UV-vis spectra and (d) photoluminescence spectra of these samples.

Following our established methods, Co SACs are prepared on the $C_3N_4$ materials and characterized with X-ray absorption spectroscopy (**Fig. 3a**). In photocatalytic $CO_2$ reduction studies, the Co SAC on NA-doped $C_3N_4$ exhibits the highest activity and selectivity towards CO production, whilst the PA-doped $C_3N_4$ exhibits relatively lower photocatalytic activity due to the presence of deep trap states. Notably, the photocatalytic activity of reported Co-based SACs exhibits a linear correlation with trends in photoinduced charge separation until the dopant LUMO( $\pi^*$) responsible for the dopant engineered conduction band trap states becomes too low in energy to efficiently drive charge transfer to the catalytic sites (**Fig. 3b**).

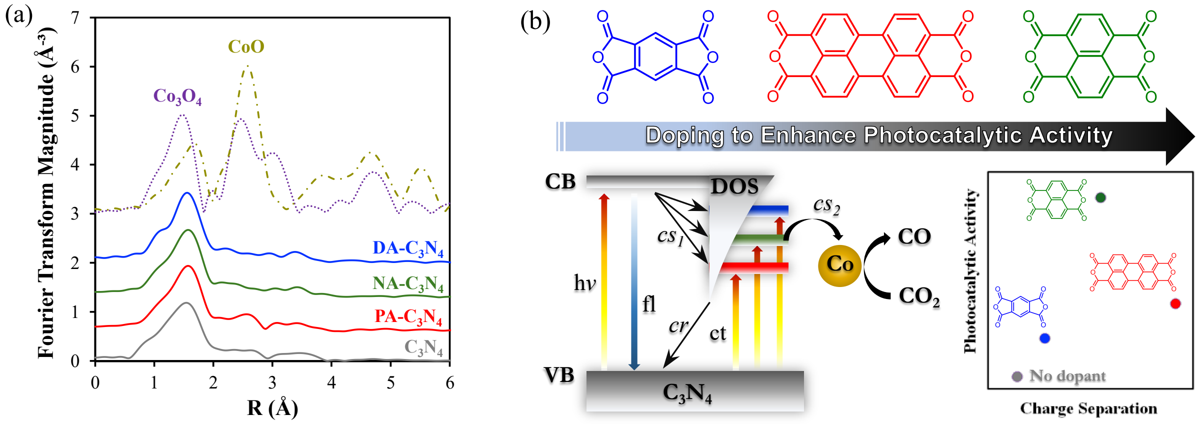

**Fig. 3**. (a) EXAFS spectra of Co SACs on pristine $C_3N_4$ and $C_3N_4$ materials modified with DA, NA and PA; (b) observed correlation between charge separation and photocatalytic activity.

Future plans include additional structural characterization of heterojunctions in the dianhydride-doped $C_3N_4$ materials and investigation of charge separation across the heterojunctions using *in situ* spectroscopic studies. In March 2025, Dr. Lin Chen gave an invited seminar at the PI's home department. Studies of the heterojunctions with X-ray transient absorption spectroscopy is currently being discussed for samples exhibiting the highest activity in photocatalysis.

## DOE Solar Photochemistry Sponsored Publications

St. John, A.; Flayhart, H.; Xiang, S.; Qian, Q.; Deskins, N.; Frenkel, A.; Rochford, J.; Li, G. "Dianhydride–modified Graphitic Carbon Nitride as a Support for Cobalt Single Atom Photocatalysts", *ACS Appl. Opt. Mater.* **2025**, 3 (4), 881–888.

# Probing Local Potentials and Rates of Nanoscale Photocatalysts

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Particulate photocatalysts, usually in a powder suspension or immobilized on a panel, host multiple concurring redox processes such as $H_2$ evolution or $CO_2$ reduction. Photocatalysts promise light-to-chemical conversion at scale, with efficiency limits comparable to photoelectrochemical cells. The basic research needs are pertinent to bridging the time and length scales of light excitation and chemical transformations and understanding the performance degradation mechanism. First, photocatalytic processes proceed sequentially — involving photon absorption, charge transport and separation, charge transfer, surface reactions, and mass transport — across multiple timescales. Thus, separating charges efficiently to drive reductive and oxidative half-reactions in nanoscale proximity becomes extremely difficult. Instead of trial-and-error, we develop tools to probe the photocatalyst/liquid interfaces. We developed a high-performance photocatalytic system by synthesizing thin-film model photocatalysts by topographical transformation of nanoparticulate semiconductors into planar thin films.

Secondly, to address stability and durability issues, we discovered coatings to modify the surfaces of photocatalysts and stabilize them. They operate in a fluid flow to achieve control over the co-catalyst microenvironment. Collaborating with Prof. Mirkin, we employ scanning electrochemical microscopy (SECM) with nanoscale resolution and optical illumination to probe the front and back potentials of thin-film model photocatalysts, such as GaInP crystalline semiconductors. GaInP/GaN/patterned-$IrO_x$/Rh-$CrO_x$ photocatalysts were designed to achieve high-efficiency solar-driven overall water splitting. The SECM tunnelling mode was used for the operando probing of front potentials of the photocatalysts under illumination in the 0.1 M pH 9.5 buffer solution. These potentials, together with the production rate under specific illumination conditions, enable us to build the AI-informed digital twin models for operating photocatalysts. This probing method can also be applied to other photocatalyst systems, such as $SrTiO_3$/Rh-$CrO_x$/$CoO_x$ systems. Future works include augmenting multi-physics modeling with physics-informed neural networks to elucidate the real-time variation of charge-transfer rate, probing tethered molecular Ir co-catalysts, as well as probing cascade $CO_2$ reduction photocatalysis utilizing dissolved carbonates for integrated carbon capture and conversion.

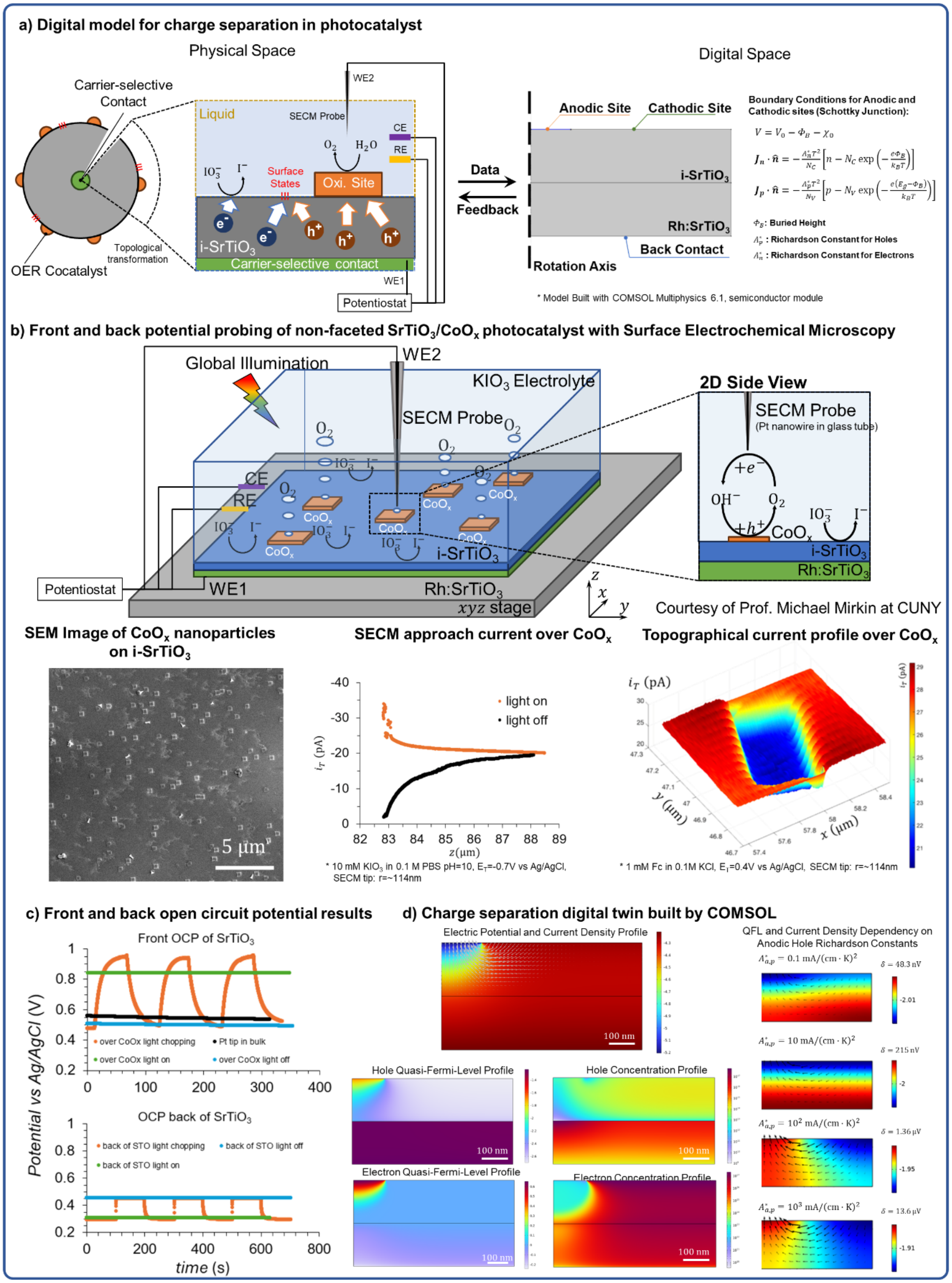

Figure: Combined characterization-modeling approach for probing parameters at semiconductor photocatalyst/liquid interfaces

**DOE Solar Photochemistry Sponsored Publications 2022-2025**

1. R.Yanagi, T.Zhao, D.Solanki, Z.Pan, and S.Hu, "Charge Separation in Photocatalysts: Mechanisms, Physical Parameters,and Design Principles", ***ACS Energy Letters***, 7, 432–452(2022). doi: 10.1021/acsenergylett.1c02516
2. X. Shen, T. Zhao, H. Su, M. Yang, J. Chen, Y. Liu, J. Li, R. Yanagi, D. Solanki, and S. Hu, "Tuning intermediate bands of protective coatings to reach the bulk-recombination limit of stable water-oxidation GaP photoanodes", ***Advanced Energy Materials***, 12, 220314 (2022). doi: 10.1002/aenm.202201314
3. R. Yanagi, T. Zhao, M. Cheng, B. Liu, H. Su, C. He, J. Heinlein, S. Mukhopadhyay, H. Tan, D. Solanki, and S. Hu, "Photocatalytic CO2 Reduction with Dissolved Carbonates and Near-Zero $CO_2$(aq) by Employing Long-Range Proton Transport", ***Journal of the American Chemical Society***, 145, 28, 15381-15392 (2023). DOI: 10.1021/jacs.3c03281
4. X. Zheng, R. Yanagi, Z. Pan, C. Zhou, T. Liu, B. Chen, K. Katayamai, S. Hu*, C. Chu*, "Photosynthesis of hydrogen peroxide from water and oxygen from a scaled-up 1-m2 reactor", ***Chem Catalysis***, 5, 1012238 (2025). (*co-corresponding authors) DOI: 10.1016/j.checat.2024.101238
5. B. Liu, Q. Zheng, S. Xiang, H. Su, Y. Zheng, C. He, R. Yanagi, W. Zhang, A. Kludze, S. Hu, "Photoelectrochemical Conversion of Dissolved Carbon in Seawater to Fuels under $CO_2$(aq) Molecular Flux", ***Nature Communications***, 16, 1558 (2025). DOI: 10.1038/s41467-025-56106-3

# Ensembles of Photosynthetic Nanoreactors (EPN) Energy Frontier Research Center

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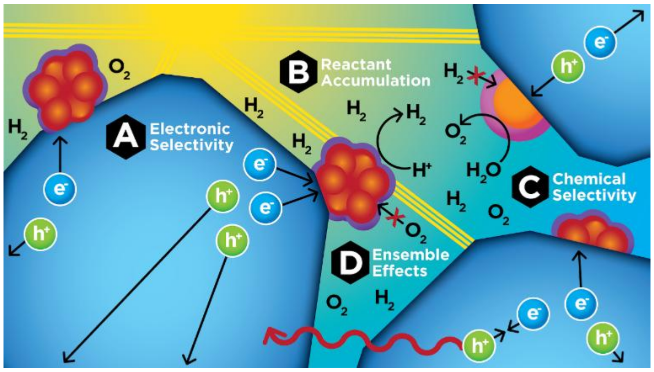
EPN EFRC aims to understand, predict, and control the activity, selectivity, and stability of photocatalytic nanoreactors in isolation and as ensembles. Concerted research efforts are organized as four thrusts with overlapping aims focused on **Electronic Selectivity** (A), **Reactant Accumulation** (B), **Chemical Selectivity** (C), and **Ensemble Effects** (D). Fundamental knowledge gained for the exemplary reaction of solar water splitting is being used to identify the physicochemical properties that in aggregate are responsible for ensemble behaviors. Discovery of general design rules may lead to new pathways for using light to store energy in chemical bonds.



Toward **Electronic Selectivity**, Thrust A aims to (i) use *operando* correlative multimodal microscopies to reveal charge separation mechanisms, and (ii) determine the influence of discrete photoinduced events on steady-state water splitting reactivity. Toward this, a combination of optical, PEC, electron, and scanning-probe microscopies were used to interrogate single nanoreactors, including $BiVO_4$, Rh-doped $SrTiO_3$, and ZnO particles, II-VI nanocrystals, InP nanowires, and metal–semiconductor heterostructures. This effort led to the advancement of electron energy loss spectroscopy (EELS) methods to deconvolute photoinduced thermal *versus* electronic ultrafast dynamics by Cushing, *operando* mid-infrared scattering-type scanning near-field optical microscopy (SNOM) to map water adsorption effects by Ge, and scanning PEC microscopy microfluidics to correlate structure with activity by Sambur. Electron microscopy measurements by Pan and Patterson uncovered dopant site occupation at the single atom-level in $SrTiO_3$ nanoreactors and mapped charge transfer at metal–semiconductor interfaces with 4D-STEM. Talin correlated optical and PEC properties with temperature effects and surface modifications. Together, these efforts represent advances in our ability to resolve charge transport and charge separation in individual nanoreactors, which we plan to expand through the development of additional low-light-excitation capabilities to assess reactivity *in situ*.

Toward **Reactant Accumulation**, Thrust B aims to (i) extend photogenerated charge-carrier lifetimes, and (ii) control species accumulation at atomically precise reaction centers during infrequent photon absorption. Toward this, a new viologen derivative synthesized by Miller was bound to II-VI semiconductor nanocrystals synthesized by Dukovic who measured associated binding thermodynamics and forward and backward electron-transfer rate constants. Ligand-like binding was observed to significantly slow interfacial electron transfer yet increase charge-separated-state lifetime. Additionally, a >200-fold enhancement in charge-separated-state lifetime was achieved using CdS nanocrystals functionalized with a custom phenothiazine derivative. Yang synthesized a new $Ni(P_2N)_2$ $H_2$ evolution electrocatalyst that was coupled to CdSe nanocrystals to deduce interfacial electron-transfer kinetics, including a strong pH dependence to the $H_2$ evolution yield. Via cross-cutting efforts, Sambur utilized single-molecule fluorescence microscopy coupled with high-resolution electron microscopy by Pan and Patterson and kinetic Monte Carlo data analysis by Dukovic to analyze energy transfer between ZnO nanocrystals and surface-anchored dye molecules, identifying that 20% of dye–nanocrystal pairs were inactive, which impacts overall energy transfer efficiency. Together, these results comprise a toolbox for extending photogenerated charge-separated-state lifetimes using molecular reaction centers, which we plan to utilize to demonstrate sequential charge-separation events from individual nanoreactors.

Toward **Chemical Selectivity**, Thrust C aims to (i) understand in atomistic detail the function of encapsulated molecular reaction centers, and (ii) codesign spatially distinct interphases for species-specific permeabilities and stabilities at low flux. Toward this, atomic layer deposition (ALD) was used to coat electrocatalysts in ultrathin nanoporous oxide coatings that were electrochemically characterized and computationally modeled to gain atomistic insights into function. Hurst, in collaboration with Esposito, made a major advancement in controlled area-selective ALD of $TiO_2$ layers on catalytic sites and established area-selective ALD process parameters leading to a desired balance between protection and selective redox reactivity. This was shown to be suitable for immobilization of Co(TCPP) molecular catalysts, protecting them without compromising $H_2$ evolution activity. In parallel, Shon developed a scalable sol-gel-based $TiO_2$ coating method and synthesized $TiO_2$-Au core–shell nanoreactors for the study of plasmon-initiated charge separation. Ogitsu developed machine-learning molecular dynamics simulations of ion transport through nanopores of $TiO_2$ and $SiO_2$, providing mechanistic insight into confinement effects, surface charge, and pH on proton and water transport. This work was complemented by experimental surface zeta potential measurements performed by Bala Chandran and Salako on $TiO_2$ nanoparticles. Together, this information is advancing our ability to design, deposit, and test ultrathin oxide coatings and geometries that enable highly selective redox reactions, which we plan to use to evaluate mechanisms of molecular catalysts within these complex interphases.

Toward **Ensemble Effects**, Thrust D aims to (i) experimentally validate interparticle interactions mediated by light and matter, and (ii) guided by simulations bridging microenvironments, program desired physicochemical properties. Toward this, Ardo, Bala Chandran, Hu, and Sambur revealed several factors that critically influence observed ensemble behavior, including photon recycling between nanoreactors via emission and reabsorption of light and the influence of photogenerated species at nearby nanoreactors, thus requiring highly selective redox reactions. Significant experimental and computational efforts have been directed toward developing a quantitative understanding of these particle–particle interactions, where the development and use of well-defined model platforms were crucial. Together, this information is revealing the mutual effect that neighboring nanoreactors have on observed activity, which we plan to continue to evaluate using techniques that allow for precise positioning and evaluation of individual nanoreactors.

EPN is leveraging our platform discoveries to design and construct photosynthetic nanoreactors from the bottom up, with the aim of controlling ensemble energy conversion efficiencies.

**Select DOE EFRC Sponsored Publications 2022-25** (#undergraduate student, *corresponding)

**1.** “Revealing the Role of Redox Reaction Selectivity and Mass Transfer in Current–Voltage Predictions for Ensembles of Photocatalysts,” Luisa Barrera, Bradley W. Layne, Zejie Chen, Kenta Watanabe, Akihiko Kudo, Daniel V. Esposito, Shane Ardo, and Rohini Bala Chandran,* *Energy & Environmental Science*, **2024**, *17(21)*, 8254–8273, DOI: 10.1039/D4EE02005G.

**2.** “Towards Spatial Control of Reaction Selectivity on Model Photocatalysts using Area Selective Atomic Layer Deposition on a Model Dual Site Electrocatalyst Platform,” W. Wilson McNeary, William D. H. Stinson, Moaz Waqar, Wenjie Zang, Xiaoqing Pan, Daniel V. Esposito,* and Katherine E. Hurst,* *ACS Nano*, **2024**, *18(51)*, 34708–34719, DOI: 10.1021/acsnano.4c10387.

**3.** “Unequal {110} Facets: The Critical Role of Surface Termination in Determining Photoelectrochemical Activity of Single $BiVO_4$ Particles,” Avishek Banik, Hiroaki Maekawa, Javier Fajardo, Brian Zutter, Francis M. Alcorn, Suhas Kumar, Kenta Watanabe, Akihiko Kudo, Nien-Hui Ge,* A. Alec Talin,* and Justin B. Sambur,* *ACS Nano*, **2025**, *19(6)*, 6250–6262, DOI: 10.1021/acsnano.4c15460.

**4.** “Revealing the Influence of Binding Motifs on Electron Transfer and Recombination Kinetics for CdSe Quantum Dots Functionalized with a Modified Viologen,” Olivia F. Bird, Kenneth M. Drbohlav,# Evan K. Gowdy,# Faith A. Flinkingshelt, Lauren M. Pellows, Benjamin F. Hammel, Bradley W. Layne, Shane Ardo, Jenny Y. Yang, Kenneth A. Miller, and Gordana Dukovic,* *The Journal of Physical Chemistry C*, **2025**, *129(11)*, 5556–5570, DOI: 10.1021/acs.jpcc.5c00740.

**5.** “Models and Measurements Quantify Photon Recycling, Charge-Carrier Diffusion, and Photon Scattering Contributions to Photoluminescence in InP Nanowire Arrays,” Danielle R. Lustig, Fangqi Chen, Wentao Zhang, Olivia F. Bird, Javier Fajardo Jr., Shane Ardo, Shu Hu, Gordana Dukovic, A. Alec Talin, Rohini Bala Chandran,* and Justin B. Sambur,* *The Journal of Physical Chemistry C*, **2025**, *ASAP*, DOI: 10.1021/acs.jpcc.5c01618.

# Pulse Radiolysis Probes Deep into Redox Catalysis and (Proton-Coupled) Electron Transfer

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Artificial photosynthesis (AP) exploits a variety of photochemical transformations with an ultimate goal of efficient storage of photon energy in a chemical form. Our research program focuses on mechanistic studies of reactions relevant to AP, including catalytic $CO_2$ and proton reduction or water oxidation, as well as charge transfer processes. In particular, we are interested in understanding the properties of highly reactive transient species which can be formed during AP processes. Our group employes pulse radiolysis (PR), a radiation chemistry transient technique which allows rapid generation of highly reactive redox intermediates and their characterization using transient spectroscopy.

In this presentation we will show unique advantages of PR for interrogating the properties of strongly oxidizing radicals in organic media. For example, while conventional electrochemical techniques can only estimate the reduction potentials of highly oxidizing radicals due to irreversibility of electron transfer, the PR-based equilibrium ladder approach provides accurate values of potential with only a few millivolt uncertainties, even for couples as positive as 1.45 V vs. $Fc^{+/0}$. The advantage of our approach as compared to similar measurements reported in the literature is that all reported potentials can be traced back to $Fc^{+/0}$ by using reference compounds with fully reversible voltammograms. These reference systems show an excellent match between potential values obtained from electrochemistry and those measured by PR equilibrium (Figure 1).

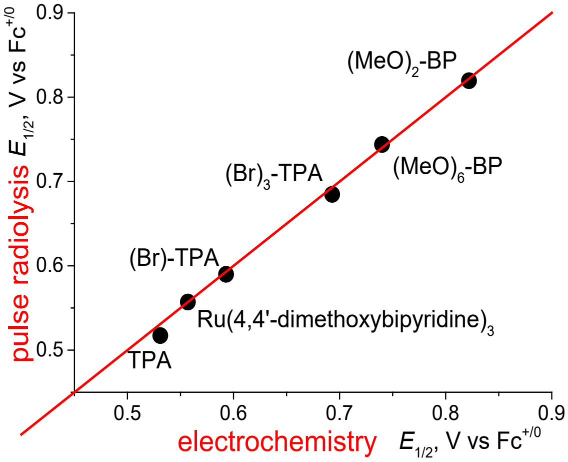

Figure 1. Formal reduction potentials $E^{o\prime}$ (vs. $Fc^{+/0}$) of radical cations determined by PR equilibria measurements as compared to potentials determined from reversible CV waves ($E^{o\prime} = E_{1/2}$).

We then utilized the PR equilibrium method to measure potentials of two homologous series of substituted biphenyl derivatives in 1,2-dichloroethane (DCE). In particular, the $E^{o\prime} - \Sigma\sigma_p^+$ correlation was explored by systematically varying the substituents in the same position in order to separate electronic and steric effects on redox properties. Interestingly, the $E^{o\prime} - \Sigma\sigma_p^+$ plot for *para*-substituted biphenyls is not linear and exhibits saturation at more positive potentials (Figure 2). We have interpreted the observed non-linear relationship by the existence of a strong stabilization of positive charge in the organic radical by radiolytically generated chloride anion

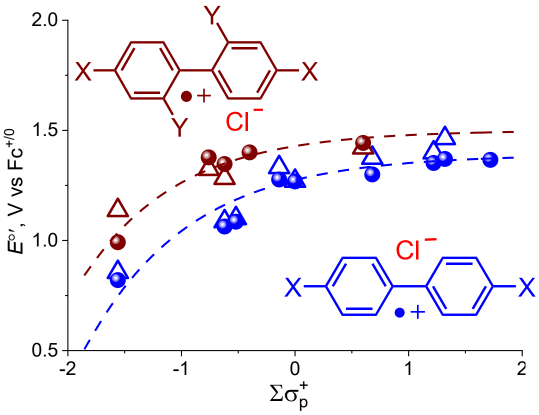

Figure 2. Reduction potentials of 4,4′–$X_2$ (blue spheres) and 2,2′–$Y_2$–4,4′–$X_2$ (wine spheres) biphenyl cations determined by PR as compared to potentials predicted by theory for corresponding [$BP^{\bullet+}$… $Cl^-$] pairs (triangles) plotted as a function of $\sum\sigma_p^+$.

($Cl^-$) as shown in Figure 2. Theoretical calculations of reduction potentials of these radical-ion pairs match experimentally observed trends. The origin of this stabilization arises from two types of interactions, namely electrostatic interaction between ions in the low dielectric medium and hemicolligation. The combined effect of both interactions results in overall lowering of the free energy of organic radical cations by the value $\Delta G_{\text{stab}}$ which includes contributions of ion pairing (IP) and hemicolligation (HC): $\Delta G_{\text{stab}} = \Delta G_{\text{IP}} + \Delta G_{\text{HC}}$, and the resulting effect on potential can be described as: $E_{\text{obs}} = E^\circ - 0.059 \log (1+ K_{\text{HC}}K_{\text{IP}}[Cl^-])$. The substitution of biphenyls in the 2,2′ positions hinders radical cations from adopting a planar geometry, resulting in an ca. 200 mV positive shift of observed potentials.[1,5]

Despite interactions with chloride anion, biphenyl radical cations remain potent oxidants and can be used to initiate oxidative electron transfer. We have measured the rates of proton-coupled electron transfer (PCET) between a benzimidazole phenol (BIP) PCET donor and a series of biphenyl radicals (Figure 3). The ability of PR to provide accurate driving forces (<15 mV precision) and rates of PCET allowed for precise analysis of the Marcus-type free energy relationship as shown in Figure 3. Independent measurements of diffusion coefficients and reorganization energy from temperature dependency of reaction rates afforded highly accurate experimental values of Marcus parameters for the PCET process. We have used these experimental values for refining existing theoretical PCET models and the development of new theoretical approaches for a more accurate PCET description.

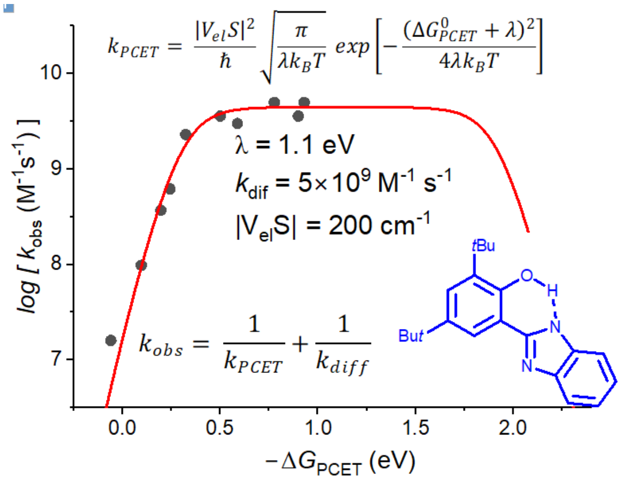

Figure 3. Free energy relationship of the observed rate of PCET oxidation of BIP molecule probed by PR.

Our current work is focused on the development of strategies for PR generation of organic radical cations in non-halogenated organic solvents. The lack of hemicolligation and ion pairing in these solvents is expected to produce oxidants with more positive reduction potentials, opening opportunities for studying a wider range of charge transfer reactions.

## DOE Solar Photochemistry Sponsored Publications 2022-2025

1. Polyansky, D. E., Transient methods for understanding the properties of strongly oxidizing radicals. *Chem. Commun.* **2025,** *61*, 3461-3471.

2. Desai, S. P.; Zhang, L.; Cappuccino, C.; Müller, A. V.; Grills, D. C.; Polyansky, D. E.; Sampaio, R. N.; Concepcion, J. J., Sustained, Selective, and Efficient Photochemical $CO_2$ Reduction to Formate by Electron-Deficient Ruthenium Polypyridyl Complexes. *J. Am. Chem. Soc.* **2025,** *147*, 4972-4983.

3. Zhang, L.; Müller, A. V.; Desai, S. P.; Grills, D. C.; Polyansky, D. E.; Sampaio, R. N.; Concepcion, J. J., Controlling Product Selectivity in Photochemical $CO_2$ Reduction with the Redox Potential of the Photosensitizer. *ACS Catal.* **2024,** *14*, 18477-18487.

4. Lee, K. Y. C.; Polyansky, D. E.; Grills, D. C.; Fettinger, J. C.; Aceves, M.; Berben, L. A., Catalyst Protonation Changes the Mechanism of Electrochemical Hydride Transfer to $CO_2$. *ACS Organic & Inorganic Au* **2024**.

5. 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.

6. Henke, Wade C.; Peng, Y.; Meier, Alex A.; Fujita, E.; Grills, David C.; Polyansky, Dmitry E.; Blakemore, James D., Mechanistic roles of metal- and ligand-protonated species in hydrogen evolution with [Cp*Rh] complexes. *Proc. Natl. Acad. Sci. U. S. A.* **2023,** *120*, e2217189120.

7. Polyansky, D. E.; Grills, D. C.; Ertem, M. Z.; Ngo, K. T.; Fujita, E., Role of Bimetallic Interactions in the Enhancement of Catalytic $CO_2$ Reduction by a Macrocyclic Cobalt Catalyst. *ACS Catal.* **2022,** *12*, 1706-1717.

8. Fujita, E.; Grills, D. C.; Manbeck, G. F.; Polyansky, D. E., Understanding the Role of Inter- and Intramolecular Promoters in Electro- and Photochemical $CO_2$ Reduction Using Mn, Re, and Ru Catalysts. *Acc. Chem. Res.* **2022,** *55*, 616-628.

# Molecular engineering control of photo-induced charge transfer and transport in donor-acceptor frameworks

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This collaborative research project aims to explore molecular engineering strategies for designing new materials and discovering new mechanisms for photo(electro)catalysis, particularly for solar fuels generation. The ideal material for optimal performance in this application area would exhibit strong visible light absorption and long-lived charge separated excited states, with the capacity for charge transport, while also affording a high density of accessible catalytic sites — a combination of properties that can be challenging to implement in traditional homo- or heterogeneous catalytic systems. As emerging alternatives, self-assembled, porous, polymeric materials composed of photoactive molecular building blocks offer tunability through both framework design and post-synthetic modification (PSM) for meeting these design targets. Our research in this area focuses on metal organic frameworks (MOFs), a class of porous solid-state materials, containing of metal ions or clusters connected through organic/organometallic linkers. MOFs offer unique host-guest reaction environments with high densities of potentially accessible catalytic sites that are not feasible with traditional homo or heterogeneous catalysts. Incorporating photoactive framework and/or guest components with electron donor-acceptor properties can lead to long-lived charge-separated excited states with the capacity for charge transport that are required for efficient photocatalysis. MOF structures offer tunability through both framework design and post-synthetic modification for facilitating photocatalytic pathways.

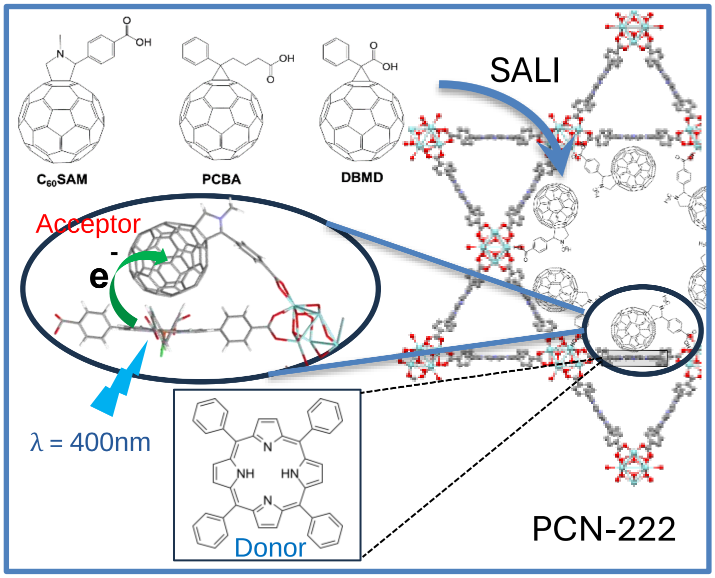

*Figure 1. Porphyrin donor-based MOF following solvent-assisted ligand insertion (SALI) of fullerene derivatives. Magnified region shows resulting cofacial interaction and photoinduced electron transfer.*

The project is geared toward understanding the photophysical implications of these material modifications and how these modifications can be implemented as molecular engineering controls for promoting long-lived photo-induced charge separation and long-range transport. The research plan is divided across three closely related subtasks aligned with these objectives. Thrust 1 involves building fundamental understanding of the electronic structure and photodynamic trends across a series of framework materials exhibiting donor-acceptor behavior in which electron acceptor guest species and their mode of introduction are systematically modified. Thrust 2 targets these photophysics as a function of electron donor framework composition and pore environment.

Thrust 3 explores these types of modifications as molecular engineering strategies for designing framework host-guest systems tailored to promote specific desired properties/functions (e.g. long-lived charge separation and transport for efficient photocatalysis). Using a set of frameworks containing photosensitizer/electron donor porphyrin linkers as the platform for these studies (Figure 1), we systematically adjust their composition and post-synthetic modification using established self-assembly procedures and solvent-assisted guest-insertion/ligand exchange strategies to tailor the donor-acceptor arrangements and therefore the charge transfer pathway and dynamics. As model electron acceptor species amenable to functionalization, fullerene derivatives are introduced as guest species and varied to modulate both the nature of the charge-transfer (CT) state and the driving force for its formation, preservation, and evolution that includes long-range charge mobility. Ultimately, as we focus on framework modification to promote photocatalytic behavior, design strategies will 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.

Optical transient absorption (TA) spectroscopy techniques, as a set of laser-based pump-probe methods used to gain information on excited state electronic structure and dynamics, serve as the primary tools for monitoring the photophysics and photoconductivity of these MOF systems. Characterization of photocatalytic performance will involve benchmark reactions, such as $CO_2$ reduction. NREL's longstanding expertise in applying these tools to problems involving photoinduced electron transfer and subsequent catalytic processes is intended to close the important feedback loops with efforts at Rutgers-Newark on the materials-driven aspects of the project. Through this fundamental study we expect to establish the nature of photoinduced CT excited states in specific MOF environments, including their formation, decay mechanisms and kinetics, as well as molecular engineering strategies that can be tailored for specific photocatalytic reactions.

This talk will focus on introducing the project and presenting some initial results, primarily along Thrust 1. Specifically, post synthetic introduction of fullerene acceptor guest species via solvent-assisted ligand insertion is used to control pore location and promote cofacial interaction with the metal free or Zn porphyrin linkers of the PCN-222 MOF, depicted in Figure 1. UV-vis titration experiments, DRIFTS and nitrogen adsorption isotherm analyses reveal porphyrin-fullerene binding strengths and confirm preferential pore locations. Furthermore, optical femtosecond TA spectroscopy results (Figure 2) reveal solvent-dependent photoinduced charge transfer and decay pathways. The implications of these results (Figure 2) as well as the future directions of this project will be discussed.

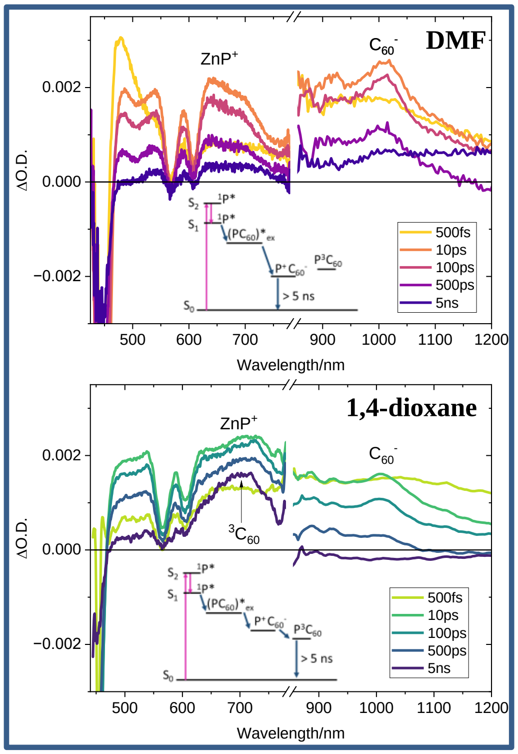

*Figure 2. Optical fs TA results for fullerene-loaded PCN-222(Zn) in DMF(top) and 1,4-dioxane (bottom) solvent environment*

# Photoelectrochemical Formation of Strategic Fuels Using Soft (Molecular Semiconductor) Materials – The Center for Soft PhotoElectroChemical Systems (SPECS)

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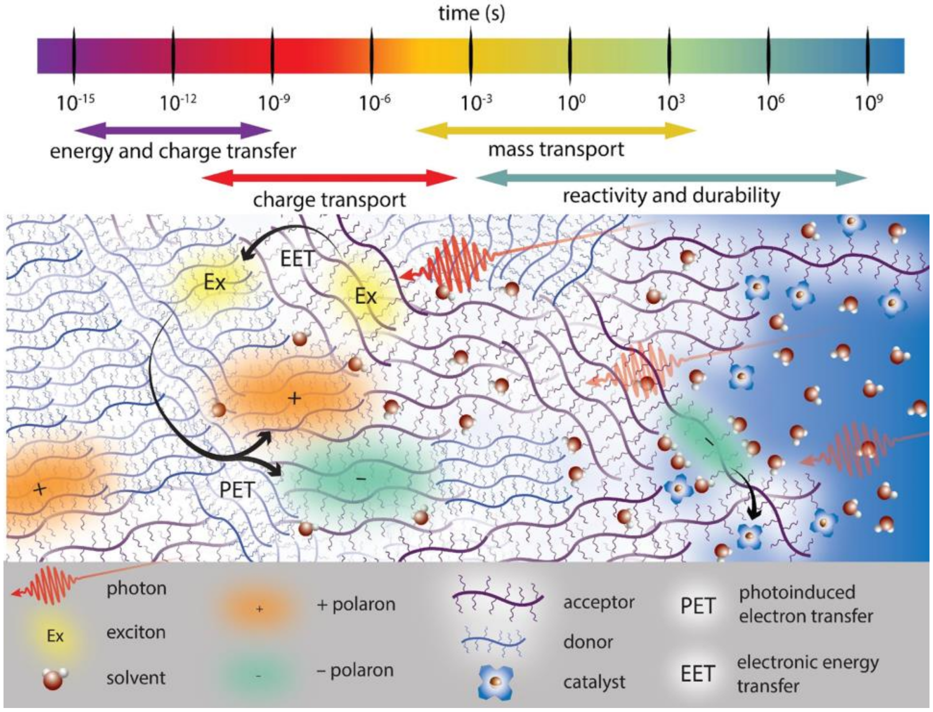
The Center for Soft Photoelectrochemical Systems (SPECS) is focusing on understanding the fundamental factors controlling charge and matter transport processes that underpin energy conversion and storage technologies across spatiotemporal scales in scalable, durable, π-conjugated polymer materials. SPECS is providing significant advances in understanding the nature of polarons in semiconducting polymers as a function of the varying chemical environment of the polymer–electrolyte interphase, a longer length scale description than discrete interfaces due to mixed electronic-ionic conduction. The interphase can store charge with long lifetimes due to Coulombic interactions between polarons and supporting intercalated counterions and solvent, where physicochemical variables such as the dielectric field, chain (chromophore) structure, interactions of polarons with counterions of varying hardness and valency, and polymer



SPECS' mission is to understand factors controlling charge and matter transport processes that underpin emerging energy conversion (i.e. photoelectrochemical catalysis) and energy storage technologies across spatiotemporal scales in scalable, durable π-conjugated polymer materials. The above schematic illustration shows relevant time scales of the polymer-electrolyte interphase, a term specifically chosen to describe the longer length scale phenomena that occurs with polymer-electrolyte interaction. Illustration shows processes occurring in a two-component polymer blends (donor and acceptor) and polymer-electrolyte system that can generate solar fuels, including light absorption to form an exciton, excitation energy transfer (EET) and exciton diffusion, photoinduced electron transfer (PET), and diffusion of charges to the edge of the polymer.

microstructure each can impact the nature and transport of polarons.

SPECS is also creating a nanometer-scale understanding of the compositional, structural, energetic and kinetic parameters that control photoelectrochemical formation of fuels on prototypical, durable bulk-heterojunction (BHJ) platforms. Early results demonstrate increased photo-generated carrier lifetimes and mobility in aqueous electrolytes over solid-state analog platforms, resulting in near 100% Faradaic efficiency for the generation of fuel from sunlight. Ongoing work is now focusing on understanding and improving the durability of the soft photocathode systems, which requires developing strategies for selectivity and suppression of parasitic redox reactions. SPECS is developing new materials that allow for co-design of transport pathways within the film, modification of polymer films to control hydrophobicity and bubble effects, catalytic site attachment, and preventing transport of electrolyte through polymer films. Spectroelectrochemical techniques, including UV/visible, Raman, and IR spectroscopy, reveal the impact of electrical doping, with demonstrations that the metal (i.e., catalyst) Fermi level shifts only upon polaron formation, suggesting charge transfer is indeed polaron mediated.

The new knowledge from SPECS has inspired the development of junctions with photovoltages that exceed 0.8 volts while retaining high applied bias photon-to-current efficiencies and molecular fuel evolution rates, with reasonable stability – an encouraging sign for an inexpensive, easily scaled materials technology. Significant challenges remain, however, to provide the appropriate understanding of the factors that control that efficiency, so as to provide design guidelines for future energy conversion platforms, and pathways to manipulate soft matter that might be integrated into other photoelectrochemical platforms.

**Five DOE EFRC Sponsored Publications 2022-2025**

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# From Captured $CO_2$ to Value-added Chemicals: A Photochemical Approach

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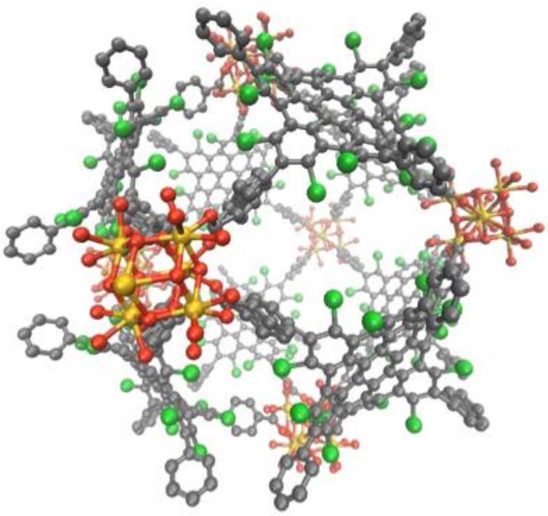
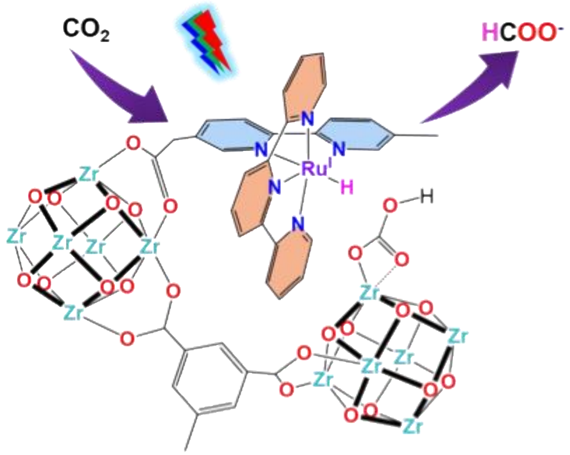
We investigate photoreductive $CO_2$ capture, an approach that integrates direct air capture of $CO_2$ with its conversion into value-added products, such as formate, using visible light as the energy source. While use-inspired, our work focuses on fundamental studies of molecular architectures that enable efficient light harvesting (light-responsive nanographene-based MOFs), $CO_2$ capture at low concentrations (O-capture via MOF-node hydroxyl groups), and catalytic conversion (mediated by redox-active transition metal complexes).

**A. Light-responsive nanographene-MOFs**



**B. Integrated Capture & Conversion**



Our work with light-responsive MOFs has led to the discovery of a series of MOF structures incorporating nanographene ligands. To enable the successful synthesis of these nanographene-MOFs, we developed a synthetic strategy that overcomes the solubility challenges caused by π-stacking of nanographene-based ligands, facilitating their integration into robust MOF architectures. The resulting materials exhibit broad UV/Vis absorption profiles, extending from the ultraviolet to the near-infrared, highlighting the richness of their light-harvesting properties. Crystallographic analysis reveals the diversity of their three-dimensional architectures. Moreover, these nanographene-MOFs display efficient symmetry-breaking charge transfer upon visible-light irradiation, enabling the accumulation of long-lived charge carriers and driving solar photochemistry using water as a terminal electron donor. Together, these findings underscore the potential of MOF-based chromophore assemblies to emulate nature's light-harvesting strategies for sustainable energy conversion.

The Zr nodes of MOFs have proven to be excellent platforms for integrated $CO_2$ capture and conversion. Specifically, we discovered that $CO_2$ efficiently inserts into the Zr–OH bonds of the nodes, forming Zr-bicarbonate species that undergo effective photochemical reduction to produce formate ions. The large Zr-cluster nodes feature numerous Zr–OH groups, enabling the incorporation of additional transition metal catalysts in close proximity to the captured Zr-bicarbonate sites. The post-synthetic modification was achieved using solvent-assisted incorporation of bipyridine-carboxylate ligands onto the nodes of the MOF, followed by the coordination of the Ru(II)-terpyridine moiety. A thorough characterization including $^1$H-NMR, diffuse reflectance UV/Vis spectroscopy, X-ray absorption spectroscopy and gas adsorption studies, combined with DFT calculations, provides strong support for efficient incorporation of the molecular Ru-complex at the loading of one Ru center per node. Compared to the homogeneous model catalyst $Ru(tpy)(bpy)^{2+}$, the Ru@MOF-808 system exhibited significantly higher formate yields. We propose that the mechanism involves hydride transfer from a photogenerated Ru-based hydride donor to the $CO_2$ acceptor in the form of the Zr-bicarbonate species, a hypothesis supported by DFT calculations. Overall, our results highlight the potential of Zr-based MOFs as integrated platforms for $CO_2$ capture and photochemical conversion into value-added products.

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# Center for Closing the Carbon Cycle EFRC

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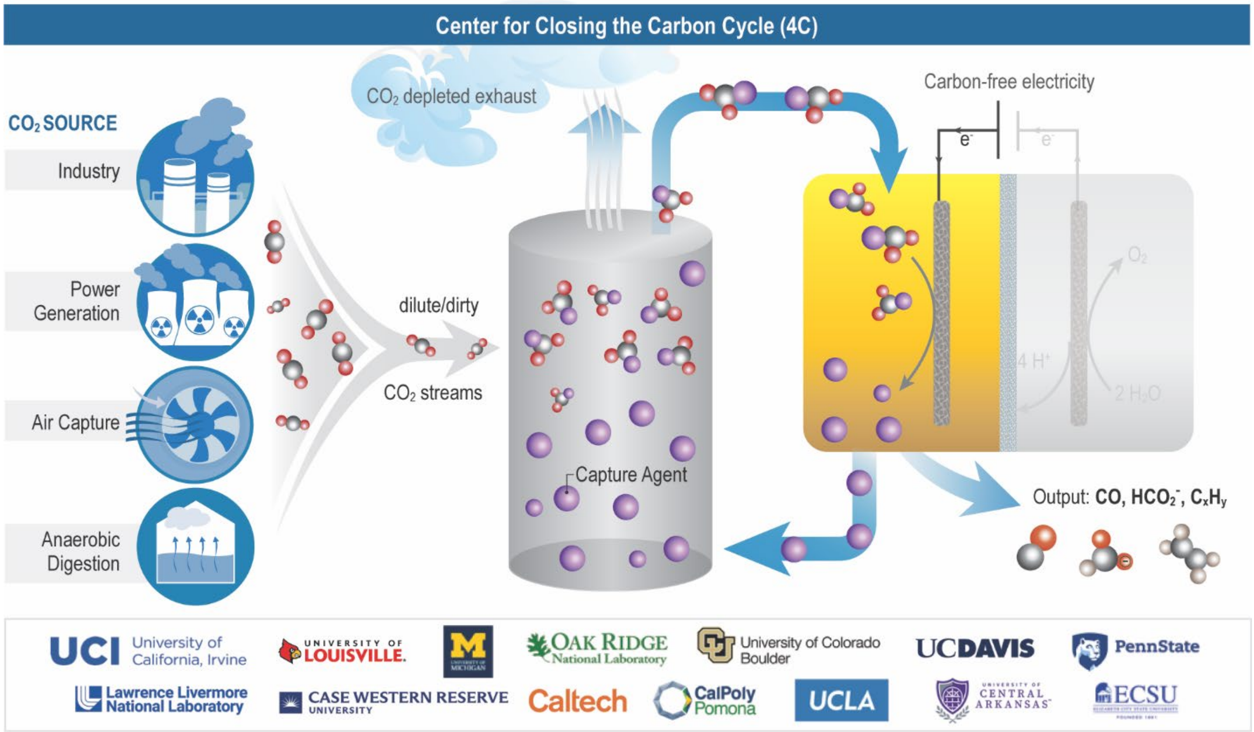
The Center for Closing the Carbon Cycle (4C) aims to advance the foundational science and define integration parameters for synergistic $CO_2$ capture and conversion, or reactive capture of $CO_2$ (RCC). While there has been significant independent research in either $CO_2$ sorption from dilute streams or pure $CO_2$ conversion, what is known is not necessarily translatable for combined capture and utilization. By linking the study of $CO_2$ sorbent properties with catalysts for functionalization, we have worked to develop integrated $CO_2$ capture and conversion systems that work synergistically to achieve higher product selectivity and overall efficiencies. The Scheme below outlines the scope of research. We have focused on the development of liquid phase sorbents that include molecular compounds and ionic liquids, which are then used directly for reduction by homogeneous and heterogeneous electrocatalysts to carbon-based products.



Research in 4C is focused on 4 goals: *1*. Define the chemical space for RCC sorbents and determine property descriptors for capture and subsequent valorization, *2*. Advance catalyst design by determining translatable knowledge from our understanding of direct $CO_2$ reduction ($CO_2R$), and identify unique catalyst considerations for using captured $CO_2$ as a feedstock, *3*. Understand and control speciation of the $CO_2$ sorbent on the electrocatalytic timescale, and *4*. Design catalyst microenvironments to work cooperatively with tailored sorbents to directly reduce sorbed-$CO_2$ from currently available dilute sources.

Research highlights and conclusions from 4C will be discussed in detail, including:

- Homogeneous and heterogeneous catalysts with single-atom site motifs addressed the intrinsic chemical speciation challenges of ammonium formation with amine sorbents by suppressing the hydrogen evolution reaction (HER). Corrosion was identified as an emergent phenomenon by some amines with metallic electrodes. Theoretical studies indicated amines that would reduce corrosion, which was corroborated by experiment. Two systems with improved activity and selectivity with amines compared to traditional $CO_2R$ were discovered.
- Carbenes were explored as a class of sorbents for electrochemical RCC. We found they convert chemisorbed $CO_2$ into different products than typical from physisorbed $CO_2$, demonstrating that reactive capture can enable different mechanistic pathways than conventional $CO_2R$. Thus, sorbents can serve a dual purpose for capture and directing product formation.
- The identity of cations in the electrolyte and hydrogen-bonding interactions from co-solvents play a major role in the electrochemical interface in ionic liquids (ILs), leading to a significant impact on RCC activity. Furthermore, $CO_2$ can be both chemisorbed or physisorbed in ILs, and its speciation is an activity descriptor for RCC. Favorable speciation can be achieved using non-covalent interactions, highlighting the need to co-design sorbents and catalysts
- Highly active materials were identified for the generation of $CO_2$ radicals for electrocarboxylation reactions. These maintain high activity in the reduction of dilute $CO_2$ streams to metal oxalates or for carboxylation of electron-rich substrates to form new C-C bonds.

New instrumentation and techniques were also developed, including a high-throughput Carbon Capture Screening Instrument (CCSI) for rapid evaluation of potential sorbents and Direct Air Capture (DAC) Raman-spectroscopy Flow-Cell to determine speciation during electrolysis.

**Up to Five DOE EFRC Sponsored Publications 2022-2025**

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# Ultrafast Electron and Energy Transfer: Some New Results

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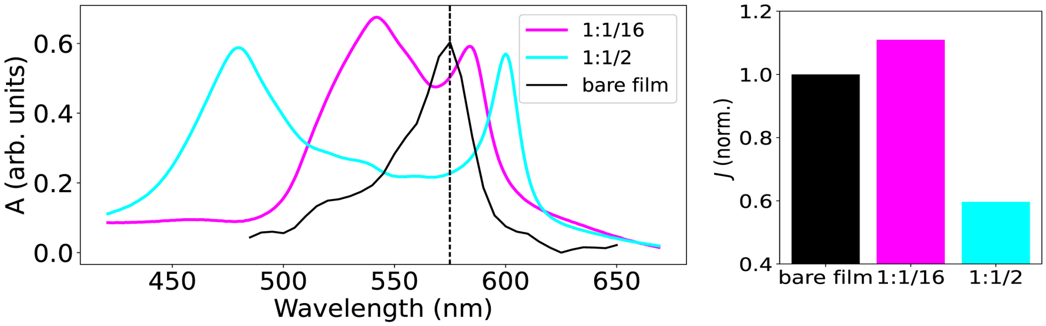
In the first topic of the talk, I will describe theoretical results that solve a question I have been puzzled by for several years, concerning how vibrational wavepackets are affected by an electron transfer reaction. Broadband pump–probe spectroscopy has been widely used to measure vibrational decoherence associated with the reaction coordinate in photoinduced ultrafast vibration-coupled electron transfer (VCET) reactions. We (and others) have used such experiments to provide insight into the interplay of intramolecular coordinates along the reaction coordinate. However, a general theoretical foundation for analyzing, and even for explaining rigorously, these data is lacking. In particular, a folklore conjecture informs us that vibrational wavepackets comprising modes associated with the reaction coordinate lose coherence on the time scale of the electron transfer reaction. But, while experimental results concur, it is difficult to explain why this should happen.

In recent work led by a postdoc, Yuanheng Wang, we studied vibrational decoherence in a model VCET reaction using the nearly exact time-dependent density matrix renormalization group simulation method. Our results suggest that electron transfer, in the nonadiabatic model, changes the vibrational equilibrium position abruptly—an example of a "quantum quench" event. This explains the concomitant vibrational decoherence. Finally, we have an explanation. However, this result also informs us that the folklore conjecture does not apply universally; there can be other set-ups of conditions at the molecular scale where wavepackets can may not lose coherence with ultrafast electron transfer.

In the second part of the talk, I will present an unpublished study of electronic energy transfer in a Fabry-Perot cavity, led by postdoc Kai Li. Molecular quantum electrodynamics (QED) has been widely explored in recent studies to explain phenomena arising from collective states known as polaritons. These phenomena include modifications in chemical reaction rates, tuning of photoinduced reactions, and perturbations in photophysics that govern electron and energy transfer processes. The idea is to confine a high concentration of light-absorbing molecules between two mirrors, spaced at integer multiples of half the wavelength corresponding to the molecular absorption band. This arrangement creates a cavity mode—a standing wave of the radiation vacuum—that hybridizes with the molecular absorption transition, giving rise to a modified spectrum characterized by distinct polariton bands. Coupling with $N$ molecules also generates $N-1$ 'dark' states, which retain the original molecular transition energy but possess vanishing transition dipole moments.

Electronic energy transfer (EET) is a well-studied process in which electronic excitation transfers non-radiatively from a donor molecule to an acceptor molecule — the donor returns to its ground state while the acceptor is simultaneously photoexcited. This process plays a fundamental role in photosynthetic light harvesting, sensitization of heterojunctions in organic photovoltaics, and color tuning in organic light emitting diodes, among other applications. The EET rate is governed by the celebrated Förster equation and its extensions, so that the rate is a product of an electronic coupling factor and a spectral overlap between donor emission and acceptor absorption densities of states. Either of these factors could be affected by the cavity. The electronic coupling is changed when donor or acceptor states are delocalized and the spectral overlap is affected by perturbations to the spectra.



Consider, for instance, the data plotted above. We show absorption spectra of samples for films of an energy donor CzIPN intermixed with an energy acceptor (SubPc). We compare high (donor:acceptor 1:1/2) and low (1:1/16) SubPc concentrations in the Fabry-Perot cavity and a bare film spectrum. Polaritonic peak splitting is more pronounced at higher acceptor concentrations. In the right panel we plot the relative spectral overlaps, which predict the ratios we expect to find for energy transfer rates. That is, for strong light-matter coupling conditions (the blue data), the EET rate should be almost half that of the EET rate recorded for the bare film.

To test this expectation, we used femtosecond transient absorption spectroscopy, to directly track the acceptor population growth due to EET following donor excitation. We explored multiple light-matter coupling strengths and two distinct donor-acceptor systems. Surprisingly, our results reveal systems where the EET rate remains unchanged despite cavity QED effects. We interpret these findings within the near-field versus far-field framework of EET, originally developed to explain counterintuitive observations in photosynthetic light harvesting (Scholes and Fleming 2000). The result is also consistent with our "entropy dominates" conjecture (Scholes et al. 2020).

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# Light Harvesting and Charge Transfer Dynamics in Chromophore Single Crystals

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**Scope of the Project.** Our research focuses on three related directions fundamental to understanding how to design and prepare systems that integrate light capture and charge generation for efficient solar energy conversion by investigating 1) new approaches to enhance light harvesting using singlet exciton fission (SF) in single crystals and polycrystalline films of molecular chromophores; 2) the structural and energetic requirements for efficient symmetry-breaking charge separation (SB-CS) in single crystals and polycrystalline solids to evaluate how the electronic and vibrational/vibronic properties of the individual chromophores influence neighboring molecules leading to SB-CS; and 3) the structural, electronic, and energetic requirements for photogenerating charge transfer (CT) excitons in donor-acceptor single cocrystals that produce free charge carriers for use in photovoltaics and driving energy-demanding reactions.

**Recent Results.** SF, SB-CS, and CT exciton formation in molecular assemblies are all part of a spectrum of related photophysical phenomena that can be exploited to enhance solar energy conversion efficiency. While we and others have shown that numerous molecules undergo these processes in systems ranging from covalent molecular dimers to polycrystalline solid films, there are far fewer studies in molecular single crystals. Terrylene-3,4-dicarboximide (**TMI**) (Figure 1) is particularly interesting because its electronic asymmetry results in significant intramolecular charge transfer character. We have now characterized the photophysics of **TMI** in solution, single crystals, and polycrystalline films. The absorption and emission spectra of **TMI** are strongly solvent dependent, indicating that the dipole moment change between the ground and excited state is 9.8 D. SF in **TMI** single crystals and polycrystalline films proceeds from an excited state having significant CT character in $\tau = 12.8$ and 16.3 ps, respectively, in near quantitative yield. This work shows that intramolecular CT states between chromophores may play a role in promoting SF.

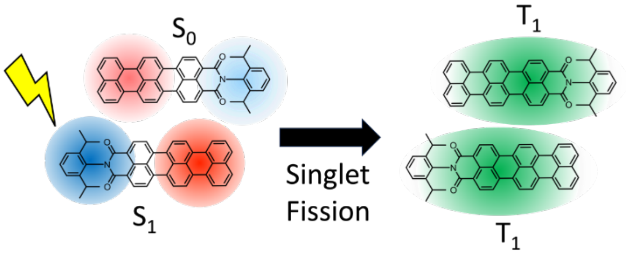

**Figure 1.** Illustration of SF in **TMI** single crystals.

SF and SB-CS can occur competitively between two organic chromophores. We have tuned the photophysics of a 9,9'-bianthracene (**BA)** single crystal between SF and SB-CS using solvent intercalation to change the electric field within the crystal. Crystals of **BA** were grown in *o*-xylene, chlorobenzene, *o*-dichlorobenzene, and benzonitrile, as well as solvent-free from a melt (Figure 2). The crystals were studied by X-ray diffraction, steady-state optical spectroscopy, and transient absorption microscopy to elucidate the role of the

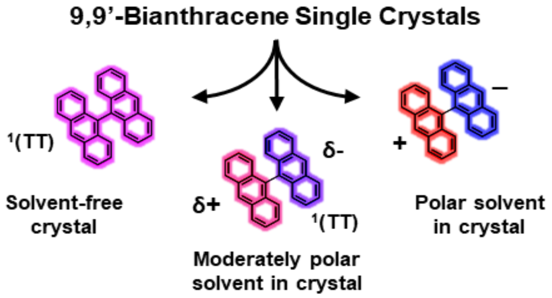

**Figure 2.** Competitive SF and SB-CS in **BA** single crystals.

intercalated solvent molecules. The crystals with no solvent in the structure underwent fast SF (< 2 ps), while the crystals with intercalated moderately polar solvents *o*-xylene, chlorobenzene, and *o*-dichlorobenzene showed evidence of charge-transfer-mediated SF. Finally, the crystals containing highly polar benzonitrile underwent SB-CS instead of SF. These results demonstrate that controlling solvation of **BA** within the crystal structure can tune its photophysics between SF and SB-CS.

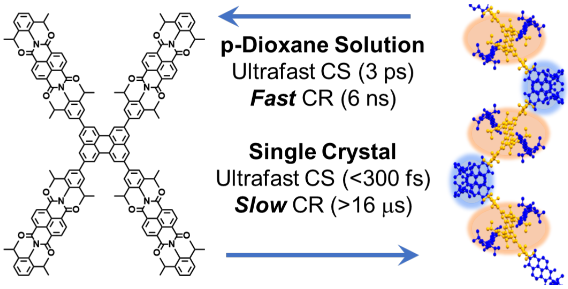

**Figure 3.** Chemical structure of **PerPh$_4$-NDI$_4$**.and its XRD crystal structure viewed along the *b*-axis with PerPh$_4$ highlighted in orange and NDI highlighted in blue.

Covalent D-A systems that pre-organize specific donor-acceptor structures can assist in engineering crystal morphologies that promote long-lived charge separation. We have investigated CT exciton formation in a single crystal of a 2,5,8,11-tetraphenylperylene (PerPh$_4$) donor to which four identical naphthalene-(1,4:5,8)-bis(dicarboximide) (NDI) electron acceptors are covalently attached at the *para* positions of the PerPh$_4$ phenyl groups to yield **PerPh$_4$-NDI$_4$**. X-ray crystallography shows that the four NDIs pack pairwise into two distinct motifs. Two NDI acceptors of one **PerPh$_4$-NDI$_4$** are positioned over the PerPh$_4$ donors of adjacent **PerPh$_4$-NDI$_4$** molecules with the donor and acceptor π-systems having a large dihedral angle between them, while the other two NDIs of **PerPh$_4$-NDI$_4$** form xylene-NDI van der Waals π-stacks with the corresponding NDIs in adjacent **PerPh$_4$-NDI$_4$** molecules. Upon selective photoexcitation of PerPh$_4$ in the single crystal, CT exciton formation occurs in < 300 fs yielding electron-hole pairs that live for more than ~16 µs. This demonstrates the effectiveness of covalently linked D-A systems for engineering single crystal structures that promote long-lived charge separation.

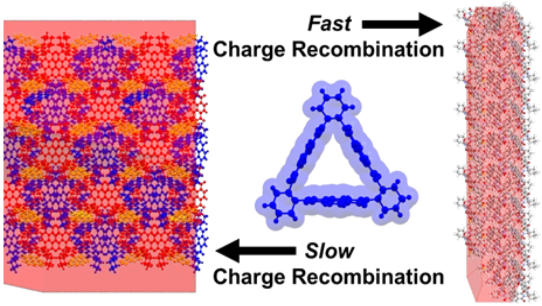

**Figure 4.** Structural motifs of 1D and 2D crystals of **(-)-NDI-Δ-PYR**.

We have also explored the photogenerated CT states of supramolecular tessellations formed by cocrystallizing a chiral tris(NDI) triangular prism **(-)-NDI-Δ** with pyrene, perylene, and *peri*-xanthenoxanthene electron donors (Figure 4). By manipulating crystallization conditions, one-dimensional (1D) and two-dimensional (2D) cocrystals with distinct structural motifs and morphologies are achieved. Femtosecond and nanosecond transient absorption microscopies and time-resolved electron paramagnetic resonance spectroscopy reveal that the CT state lifetimes are lengthened in the 2D cocrystals relative to the 1D cocrystals, which is attributable to the symmetry and molecular packing differences between them that modulate the CT interactions. This work shows how using pre-organized covalent multi-site charge carriers as donors or acceptors in cocrystals can be used to engineer molecular systems with tunable CT properties.

**Future Plans:** We will continue to investigate how the electronic and vibrational/vibronic properties of neighboring chromophores in ordered molecular solids influence whether these systems undergo SF, SB-CS, or create CT excitons that can produce free charge carriers for use in photovoltaics and driving energy-demanding reactions.

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# Unprecedented Control of Spin, Charge, and Light with Hybrid Organic Inorganic Semiconductors

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The Center for Hybrid Organic Inorganic Semiconductor for Energy (CHOISE) is an Energy Frontier Research Center (EFRC) with 17 PIs across 9 institutions. The goal of CHOISE is to demonstrate unprecedented control over spin, charge, phonon and light through the synthesis and characterization of organic-inorganic hybrid semiconductors their interfaces and heterostructures. In this presentation I will discuss one aspect of what CHOISE has learned over the past few years regarding a unique feature of these hybrid semiconductors that allows for control at room temperature of spin, charge and light without the use of magnetic fields or magnetic elements.

Hybrid semiconductors combine the unique capabilities and properties of the organic sub-components with properties of the inorganic component. The interaction of the inorganic and organic components can also lead to new functionality not found in either organic or inorganic systems. The most striking example of this is in the ability to introduce symmetry breaking within the inorganic metal-halide framework by introduction of the organic component. Tailoring of the interaction between the organic and inorganic components yields control over the degree and type of symmetry breaking and I will show a few examples. To ensure both local and global symmetry breaking we have explored the use of chiral organic molecules. The inorganic component borrows the homochirality of the organic component to yield a unique family of highly tunable chiral semiconductors.

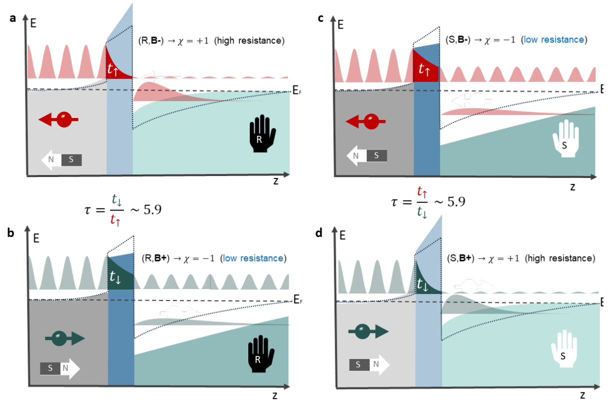

**Fig. 1. Modeling and CISS effect at the FM/c-HP interface. a-d**, Band alignment diagrams for the spin valves with tunnel barrier in the FM-dielectric-c-HP interface at zero bias voltage. Changes in the magneto-chiral local density of states affect the electrostatic screening at the interfaces and modulate the tunnel barrier.

Introducing chirality adds a new functional degree of freedom, enabling phenomena such as the circularly polarized galvanic effect, the chiral-phonon-activated Seebeck effect, and the chiral induced spin selectivity (CISS) effect. CISS phenomena describe a connection between structural chirality, electron spin orientation, and charge current that has implications for a variety of physical phenomena spanning chemistry, physics, biology, electrical engineering, etc. Utilizing

CISS we developed systems that can interconvert spin, charge and light at room temperature. We demonstrated that integration of c-HP with traditional semiconductors can transforms an existing commercially relevant III-V LEDs from a conventional LED semiconductor structure that controls the interconversion of light and charge to one that now also controls spin-to-light. Spin accumulation in the non-chiral III-V semiconductor leads to polarized light emission.

I will also discuss CHOISE studies of a room-temperature CISS-induced magnetoresistance (CISS-MR) response of >300% in a spin valve configuration consisting of a ferromagnet (FM), tunneling barrier, and c-HP. I will discuss how the CISS-MR is attributed to the formation of an interfacial spin-selective tunneling barrier (**Fig. 1**) induced by the chirality, which can produce current dissymmetry factors ($g_c$), that surpass the limit presented by the intrinsic spin polarization of the FM as generally assumed in the Jullière model. The CISS-MR exhibits a strong dependence upon the c-HP composition, revealing a structure-property relationship between CISS and structural chirality as quantified using the chirality continuous measurement. The large MR response differentiates from a subtle anisotropic MR that occurs in the FM and arises from the proximity effect at the FM/c-HP interface in the absence of a tunnel barrier.

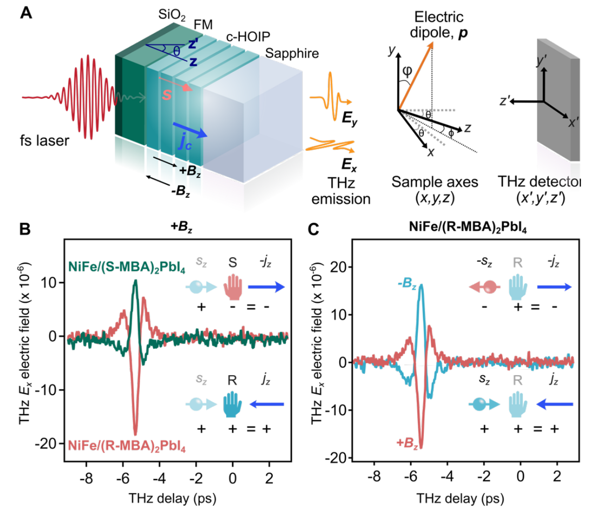

**Fig. 2.** THz emission spectroscopy (TES). A pure spin-current is injected into the chiral-HP and the spin-to-charge conversion vis ICISS is measured via the emitted THz radiation. The polarity and polarization of the emitted field is determined by the charge current direction.

We also investigated the inverse process, i.e. inverse CISS, that occurs via reciprocity and involves the conversion of an oriented spin to a charge current. We show that terahertz emission spectroscopy (TES) can directly measure the ultrafast charge current due to inverse CISS with picosecond time-resolution. Measurements of the THz polarity and polarization map the induced charge current direction in three-dimensions upon spin-injection. We find that ICISS produces a THz waveform for both up and down spins (**Fig. 2**) but the polarity of the charge current is 180° different when either the chirality or the spin polarization changes. We find ICISS response for both in and out-of-plane spin orientation, indicating that the global crystal chirality defines CISS.

These two results indicate that in chiral systems the spin and charge current are locked. We propose that in chiral systems there is an opposite spin accumulation at the opposing interfaces under equilibrium conditions, i.e., at the interfaces there is a splitting of the up and down spin fermi levels. Injection of either unpolarized charge (CISS) or spin (ICISS) drives the spin configuration out of equilibrium and movement of spin (CISS) or charge (ICISS) must compensate thus driving the spin-to-charge interconversion. These results will help guide the design of novel applications that utilize this locking of spin and charge in chiral systems. Adding chirality and control over spin through CISS provides new avenues for creative technological development.

I will also discuss future directions for CHOISE.

## Up to Five DOE EFRC Sponsored Publications 2022-2025

1. "Design of Two-Dimensional Hybrid Perovskites with Giant Spin Splitting and Persistent Spin Textures" Rayan Chakraborty**,** Peter C. Sercel**,** Xixi Qin, David B. Mitzi, Volker Blum**,** J. Am. Chem. Soc. 146, 34811−34821, **2024**

2. "Optical Activity of Chiral Excitons", P.C. Sercel, M.P. Hautzinger, R. Song, V. Blum, and M.C. Beard, *Advanced Materials,* **37**, 2415901, doi:https://doi.org/10.1002/adma.202415901 (2025).

3. "Remote chirality transfer in low-dimensional hybrid metal halide semiconductors", M.A. Haque, A. Grieder, S.P. Harvey, R. Brunecky, J.Y. Ye, B. Addison, J. Zhang, Y. Dong, Y. Xie, M.P. Hautzinger, H.H. Walpitage, K. Zhu, J.L. Blackburn, Z.V. Vardeny, D.B. Mitzi, J.J. Berry, S.R. Marder, Y. Ping, M.C. Beard, and J.M. Luther, *Nature Chemistry*, doi:10.1038/s41557-024-01662-2 (2024

4. "Room-temperature spin injection across a chiral perovskite/III–V interface", M.P. Hautzinger, X. Pan, S.C. Hayden, J.Y. Ye, Q. Jiang, M.J. Wilson, A.J. Phillips, Y. Dong, E.K. Raulerson, I.A. Leahy, C.-S. Jiang, J.L. Blackburn, J.M. Luther, Y. Lu, K. Jungjohann, Z.V. Vardeny, J.J. Berry, K. Alberi, and M.C. Beard, *Nature,* **631**, 307, doi:10.1038/s41586-024-07560-4 (2024).

5. "Ultrafast Inverse Chirality Induced Spin Selectivity via THz emission", Y. Dong, A. McConnell, M. P. Hautzinger, Md. A. Haque, A. H. Comstock, J.M. Luther, D. Sun, M.C. Beard, under review, **2025**

# Advanced characterization of bipolar membranes formed by diffusion–reaction doping

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Junctions formed at semiconductor interfaces generate space–charge regions. This can result in diode behavior, a prerequisite for efficient electronic charge separation and photoconversion. Space–charge regions also form at ion-exchange-membrane interfaces, which we are leveraging to demonstrate protonic charge separation from our new light-driven proton-pump platform.

Our recent discovery that some anion-exchange membranes can be doped via chemical conversion of their near-interface fixed cationic groups to fixed anionic groups has enabled several opportunities for spectroscopic and microscopic characterization (**Figure 1**), and analytical modeling. Most notably, we performed Kelvin Probe Force Microscopy (KPFM) on a suite of diffusion–reaction-doped junctions formed on planar thin-film membranes cast on glass slides. Data interpretation is ongoing to correlate built-in electric potential differences deduced from KPFM with those deduced from Mott–Schottky analysis of potential-dependent capacitance data, where we are actively working to overcome convoluting effects due to slow rates of $H_2$ oxidation.

We have also developed several analytical models to predict built-in potentials at membrane|liquid junctions and bipolar membrane junctions with ionically associated photoacid or photobase dye sensitizers. Notably, our experimental data are consistent with large liquid-junction-like potentials within the membranes due to diffusive crossover of salt from contacting aqueous electrolytes.

Collectively, we are using these new analytical approaches to complement data from more standard spectroscopies and microscopies to deduce additional fundamental information about our diffusion–reaction doping process.

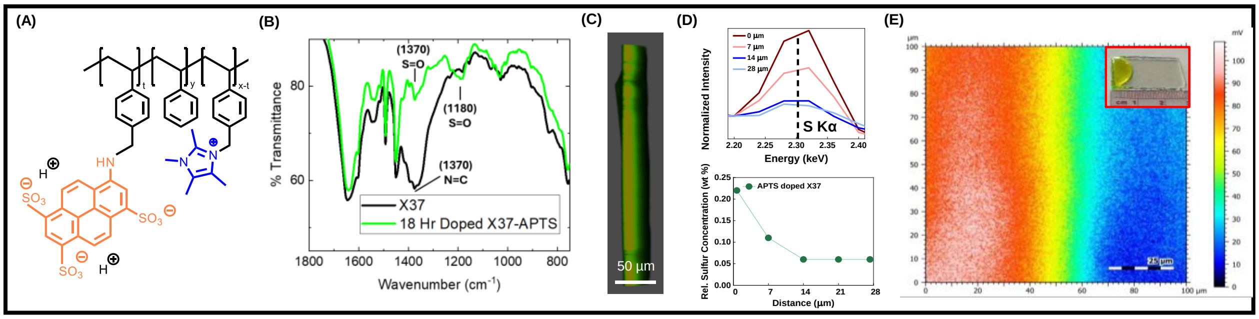

**Fig. 1 |** Structural, chemical, and electrostatic characterization of X37 and XA9 anion-exchange membranes diffusion–reaction doped with APTS$^{3-}$ to form monolithic bipolar membranes: **(A)** hypothesized chemical structure, **(B)** FTIR-ATR spectra before and after doping, showing spectral features consistent with covalent modification by APTS, **(C)** Cross-sectional confocal microscopy image showing photoluminescence from APTS, **(D)** Cross-sectional EDS point spectra as a function of distance showing the sulfur Kα peak due to APTS, and **(E)** KPFM surface potential map of an in-plane bipolar membrane formed by diffusion–reaction doping XA9 with APTS$^{3-}$, showing a distinct electric potential difference across the doping boundary. Inset: Digital camera image of the materials system.

# What Fano Resonances Tell Us About the Surfaces of Quantum Dots

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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 ligand-nanocrystal interactions to control when ligands exhibit weaker bonding to nanocrystal surfaces to simultaneously enhance both their photocatalytic activity and their durability.

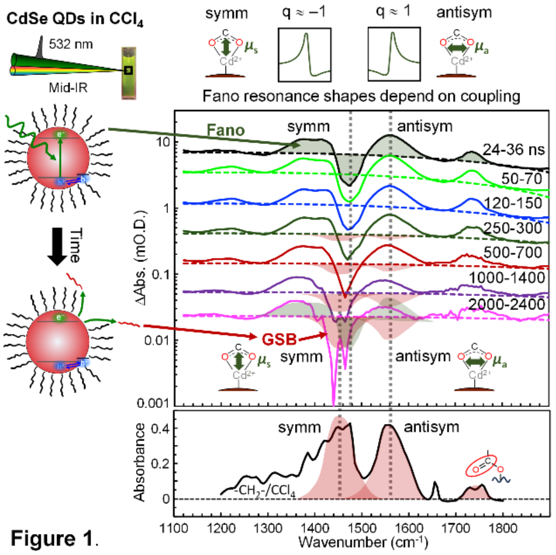

**Figure 1**.

An important step toward designing ligand-nanocrystal interactions for enhanced activity and durability of QD photocatalysts is to determine whether the overall quantum yield of charge transfer can be intentionally tuned by molecular and charge dynamics at this boundary in solution. **Figure 1** represents TRIR spectra measured of CdSe QDs passivated by stearate ligands in a CCl$_4$ solution following 532 nm excitation. As in our previous studies, transient vibrational features are superimposed onto broad absorptions corresponding to 1S-1P transitions of the QDs. The transient vibrational features are highlighted by green shading in the 24-36 ns TRIR spectrum and are characteristic of Fano-type resonances. Importantly, the vibrational peak pattern on longer time scales indicates that photoinduced ligand detachment indeed occurs in solution in analogy to our film studies. This can be observed through the approximately 20 cm$^{-1}$ red-shift of the negative-going vibrational feature toward the symmetric carboxylate stretch mode combined with the reduction in amplitude of the positive-going antisymmetric stretch feature around 1550 cm$^{-1}$ (see dotted lines in **Figure 1**). The appearance of ground state bleach features of both vibrational modes is the indication of ligand detachment from the QD surfaces because the vibrational frequencies of carboxylate groups are distinct when coordinated to metal ions.

Our findings reveal that Fano-type resonances are observed in ligands that couple to CdSe QD electronic states in CCl$_4$ solution, while absorptive vibrational features are observed in dry QD films. We believe this difference arises from the presence of solvent in the colloidal samples, which can **i**) displace carboxylate ligands from QD surfaces and **ii**) coordinate exposed QD surface sites that are uncovered by the ligand displacement. We hypothesize that these differences in the nanocrystal-ligand-solvent interactions change the coupling of the ligand vibrational modes to the electronic states of the QDs, leading to the shift from absorptive to Fano-type resonances.

# Directional Hole Transfer in Bioinspired Molecular Assemblies for Photocatalytic Water Oxidation

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Efficient charge separation remains a critical bottleneck in solar-driven water oxidation. This work presents a bioinspired approach to overcome this challenge by engineering directional **hole transport** within **carbon-based supramolecular assemblies**.

While carbon nanotubes (CNTs) are widely used for (photo)electrocatalytic reduction, their potential for oxidation reactions —particularly as hole transport media—remains largely underexplored. This project investigates the fundamental mechanisms of hole transport in CNTs functionalized with photosensitizers and water oxidation catalysts (WOCs), leveraging the complementary expertise of our collaborative team.

We designed a photocatalytic system composed of a BODIPY photosensitizer covalently linked to CNTs through a fluorene spacer, enabling **selective hole injection** into the CNT framework while **suppressing back electron transfer**. This design allows selective hole transfer into the CNT while simultaneously blocking unwanted electron migration from the photoexcited dye. Using a combination of **GFN-xTB nuclear dynamics** and **Extended Hückel quantum dynamics simulations**, we modeled the photoinduced charge transport process and confirmed efficient hole migration through the assembly. We demonstrated successful hole migration from the photoexcited BODIPY through the fluorene bridge into the CNT (Figure 1), while blocking electron transfer thanks to the fluorene's high-energy LUMO. To prevent detrimental self-oxidation from hole accumulation in CNTs, we incorporated a WOC as a terminal hole acceptor. We identified an Ir(III) precatalyst, [Cp*Ir(bpe)]Cl (bpe = 1,1-di(pyridine-2-yl)ethanoate), that upon activation with sodium periodate forms a distinctive blue Ir(IV) species. This WOC achieves **84% oxygen yield** under photocatalytic conditions and remains structurally intact, maintaining molecular integrity in a quiescent state for up to 10 days under ambient conditions. These results highlight a directional hole transfer mechanism enabled by rational molecular design and provide a foundation for developing robust, bioinspired systems for solar water splitting.

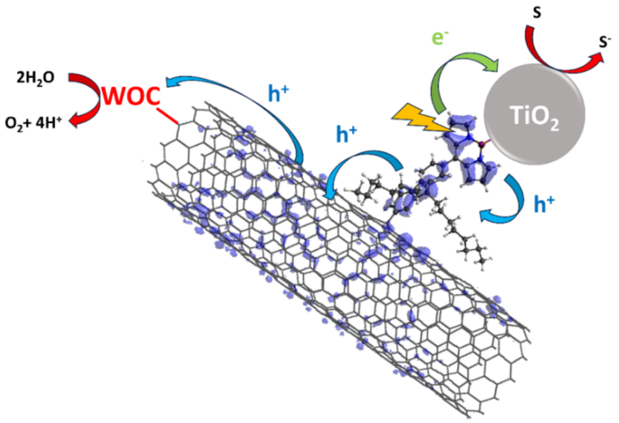

**Figure 1.** Charge transport dynamics in the photocatalytic system. The green arrow shows electron injection into TiO$_2$, blue arrows trace hole injection into the CNT, and red arrows represent chemical conversion processes. Blue isosurfaces visualize the hole distribution across the system at the end of the simulation. Abbreviations: h$^+$ = hole; e$^-$ = electron; S = sacrificial electron acceptor.

# Transient Ellipticity Measurements of Spin Dynamics in Nanocrystals and Chiral Electrodes

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We utilize time-resolved transient Kerr and/or Faraday ellipticity measurements to study the spin-dynamics in novel photochemical and catalytic systems. Our measurement technique also records the transient reflectivity or transient absorption simultaneously allowing for characterization of correlated charge and spin dynamics with picosecond time resolution. We applied these methods to three systems of interest to our solar photochemistry program. (1) Using time-resolved Faraday Ellipticity (see Fig.) or Transient circular dichroism (TRCD) we studied the correlated spin and carrier dynamics in quantum shells consisting of CdS/CdSe/CdS spherical nanocrystals where the quantum shell consists of ~1-2 nm thick CdSe sandwiched between CdS as both the core and 2nd shell.[1] The resulting electronic structure is similar to that of CdSe nanoplatelets but their form factor is a spherical nanocrystal rather than a nanoflake. In these structures the hole is isolate within the quantum shell while the electron is delocalized over the nanocrystal. The reduced electron/hole interaction results in long biexciton lifetimes (~ 10-20 ns) and surprisingly long hole spin lifetimes (~20 ns). We also observe an electron thermalization within the conduction band to ~ 100 ps and that also corresponds to the electron spin lifetime. (2) We used a unique transient Kerr ellipticity measurement to mirror dark electrocatalysis within chiral copper electrodes. A 100 ps 400 nm pump pulse impinges on the back side of the electrode inducing a transient Seebeck effect that results in a photoinduced current of ~ 1 mA traveling from the back to the front of the electrode (characterized through THz emission spectroscopy). A broadband white light probe is reflected off the front side and records the induced ellipticity. The phase of the induced ellipticity changes sign for the different handedness of the chiral electrode. Spins are polarized as they transverse from the front to the back of the chiral electrode through the CISS effect. (3) Transient Kerr ellipticity is used to integrate the spin dynamics at GaAs photoelectrode chiral interfaces. The experiment consists of photoexciting the GaAs/Pt interface and probing the spin-dependent electron transfer from the GaAs to the Pt catalyst. Linear excitation creates both up and down spins within the GaAs. When a chiral layer is placed between the GaAs and the Pt catalyst spins matched to the chirality transfer to the Pt leaving behind electrons with unmatched orientation.

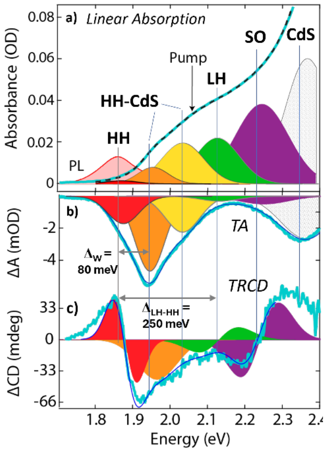

Fig. Simultaneous TA and TRCD of CdSe Quantum shells

[1] JACS, 2023, 145, 13326

# Dexter Energy Transfer: Pathways, Mechanisms, and Kinetics

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**Scope.** Our aim is to understand the mechanisms of Dexter energy transport in molecular and molecule-nanoparticle assemblies. Studies focus on: (1) extending the range of Dexter trans- port by engaging coherent coupling mechanisms, (2) leveraging Förster coupling "borrowing" to accelerate Dexter transport, (3) understanding how multi-acceptor assemblies may enhance transport through pathway coherence effects, (4) developing strategies to simulate quantum dynamics of energy transport using advanced quantum computing hardware and software, (5) bringing theoretical studies into contact with experiment through intensive collaboration.

**Förster borrowing.** We developed a model that describes Dexter transport mediated by borrowed Förster coupling, enabled by spin-orbit coupling interactions. We are exploring these effects in organometallic structures in ongoing studies.

**Dexter transport enhanced by long-range delocalization.** We developed strategies to accelerate Dexter transport, using bridge resonant interactions. Ongoing studies are exploring cyclophanes as building blocks in this context.

**Condensed phase dynamics.** We developed methods to describe condensed phase vibronic dynamics using density matrix renormalization group and matrix product state methods. We also built a strategy to describe how structures with multiple acceptors can enhance energy transfer by exploiting quantum interferences among vibronic pathways.

**Toward applications of quantum computing in energy and electron transfer.** In ongoing collaboration with the Brown and Kim groups in Duke's Quantum Center, we demonstrated the use of trapped-ion platforms as programmable analog quantum simulators to model condensed-phase chemical dynamics and open quantum systems. These studies point to regimes where quantum advantages may emerge, providing a foundation for simulating transport in complex chemical assemblies that are beyond reach using classical computers.

**Shell Thickness and Heterogeneity Dependence of Dexter transport in core-shell quantum dots with adsorbed molecules.** The reported Dexter transfer distance dependence on shell thickness in CdSe/CdS core/shell quantum dots is anomalously soft. This observation challenges the conventional understanding of the Dexter transport mechanisms. We found that the anomalous Dexter coupling decay arises from shell thickness dispersion effects.

**Transport dynamics faster than thermalization enables "uphill" charge transfer.** In ongoing collaboration with the Therien and Fleming groups, we have found that thermodynamics constraints of Boltzmann statistics can be overcome in hybrid energy-electron transport structures when the transport dynamics is faster than excited-state vibrational state thermalization. This research opens the door to capturing the energy of vibronically "hot" electronic excited states in solar energy conversion schemes.

# C-H Bond Formation with $CO_2$: Toward Carbon Neutral Fuel Production

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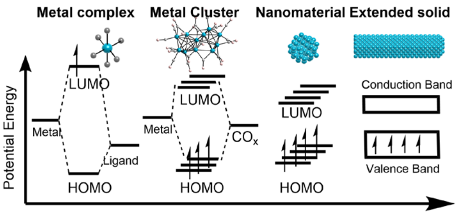
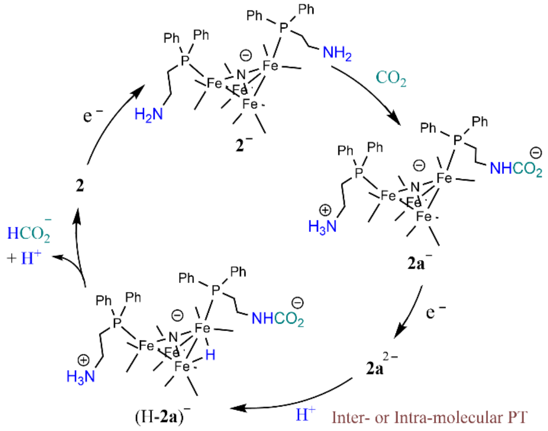
This project uses nanoscale metal clusters which have delocalized bonding, to model nanoparticle and heterogeneous (electro/photo)catalysis. Progress during the most recent grant period has deduced changes to reaction mechanisms and product outcomes that arise when the microenvironment around the catalyst is altered by strategic changes to the catalyst structure.



*Amine Groups Alter Product Selectivity and Rate of Catalytic Hydride Transfer Reactions.* Primary amines are common functional groups in the reaction environment surrounding an (electro)catalyst, and this includes catalysts ranging from metalloenzymes surrounded by amino acids, to electrocatalysts operating in amine industrial sorbents for $CO_2$ capture and conversion. Here the behavior of amine functional groups at the surface of an electrocatalyst was explored. Two different clusters were synthesized: $Fe_4N(CO)_{11}(Ph_2PCH_2CH_2NH_2)]^-$ has one amine, and $[Fe_4N(CO)_{10}(Ph_2PCH_2CH_2NH_2)_2]^-$ has two amine functional groups. Infra-red spectroscopic studies showed a reaction of each cluster with $CO_2$ to afford a secondary coordination sphere (SCS) carbamate group, and cyclic voltammetry (CV) investigations revealed a variety of roles for the amine SCS groups in the mechanism of catalyst hydride formation and hydride transfer (HT) to $CO_2$. The most prominent effect of the amine SCS group is stabilization of the intermediate hydride to lower formate yield.



*Catalyst Protonation Changes the Mechanism of Electrochemical Hydride Transfer to $CO_2$.* It is well-known that addition of a cationic functional group to a molecule lowers the necessary applied potential for an electron transfer (ET) event and this study explored the effect of a proton on the surface of a small metal cluster. This study included collaborative work with using Pulse Radiolysis at Brookhaven National Laboratory (BNL). Clusters which have phosphine ligands commonly undergo fluxional processes where the phosphine ligands move around on the surface of the cluster, and this fluxionality can be enhanced when ET processes occur. One result of this fluxional behavior is that determination of the redox couple for $[H\text{-}Fe_4N(PEt_3)_4(CO)_8]$ was not possible using CV. This is because the reduction event observed in CV was not electrochemically reversible because of fast fluxional processes. The results obtained at BNL allowed determination of the half-wave potential for the $[H\text{-}Fe_4N(PEt_3)_4(CO)_8]^{0/-}$ couple, and this half-wave potential value was used in studies of reaction kinetics for formate formation by $[H\text{-}Fe_4N(PEt_3)_4(CO)_8]$.

# Insights from pulse radiolysis into the photogeneration of charges and charge transport in the high-performance conjugated polymer IDTBT

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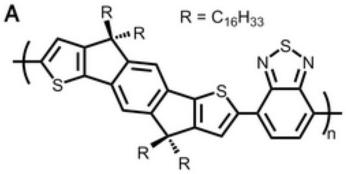
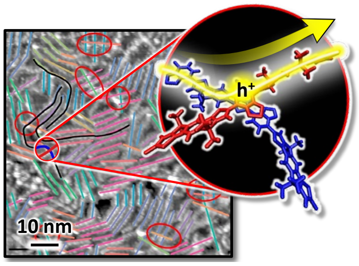
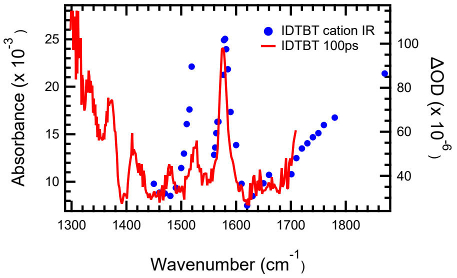




The high-performance donor-acceptor conjugated polymer indacenodithiophene-co-benzothiadiazole (IDTBT, see right) has unusual properties including a remarkably high charge mobility in films (up to 3.6 $cm^2V^{-1}s^{-1}$), despite having a near-amorphous microstructure, and an apparent ability to generate charge pairs upon photoexcitation of isolated chains in solution. We have used pulse radiolysis to study this polymer in two separate projects, looking at both aspects.

To investigate the intrachain charge mobility of isolated chains, pulse radiolysis was coupled with time-resolved microwave conductivity (PR-TRMC). The obtained mobility was the largest we have observed to date for a conjugated polymer and suggests that the bulk film mobility is close to that of single chains. Supporting computational studies (DFT, molecular dynamics, kinetic Monte Carlo) and scanning tunneling microscopy led to a conclusion that the high film mobility arises due to a highly interconnected network of perpendicular crossings at the benzothiadiazole unit (see fig.). These findings will lead to better design rules for high mobility conjugated polymer films that could have benefits for organic electronic applications such as photovoltaics or thermoelectrics, particularly where mechanical flexibility could be an advantage.

In a second study, we used pulse radiolysis with time-resolved infrared spectroscopy (PR-TRIR) to help to interpret the spectral signatures observed in ultrafast time-resolved infrared spectroscopy. While ultrafast TRIR is less common, it can potentially give richer information compared to traditional optical transient absorption spectroscopy (OTA) which may give overlapping broad electronic absorption features. By comparing with IDTBT polaron spectra from PR-TRIR (blue dots, left), it was confirmed that by 10 ps after photoexcitation, a radical charge pair is formed with a high yield of 60 ± 20 % (red trace, left), existing in rapid equilibrium with the exciton which decays with a 4 ns time constant. These surprising results suggest that charge generation in rigid push-pull polymers can be an efficient process, even in the absence of a separate electron acceptor.



1. J.F. Coker, S. Moro, A.S. Gertsen, X. Shi, D. Pearce, M.P. van der Schelling, Y. Xu, W. Zhang, J.W. Andreasen, C.R. Snyder, L.J. Richter, M.J. Bird, I. McCulloch, G. Costantini, J.M. Frost, & J. Nelson, *PNAS* 121 (37) e2403879121 (2024).

# Sensitizers for Solar Fuels Production: Group 11 and 12 Metal Complexes

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In our poster we will discuss our work toward developing sensitizers for photo-electrocatalytic reactions with two-coordinate carbene-metal-amide (cMa, M = Cu(I) and Au(I)) complexes[1, 2] and Zn[3] complexes with chelating donor-acceptor ligands. The complexes studied here absorb visible photons ($\varepsilon_{vis} > 10^3$ $M^{-1}cm^{-1}$), have long excited state lifetimes in solution ($\tau \sim 0.5$-$250$ μs) and have high excited state reducing potential, capable of reducing water via an electrocatalyst.[4]

Our poster will focus on three topics. The first topic involves our efforts to shift the absorption profile of the cMa complexes to cover the visible part of the solar spectrum and increase the lifetime in solution into the μs regime. Shifting from an interligand charge transfer (ICT) excited state to one that has mixed ICT and ligand excited (LE) character markedly enhances the lifetimes of these materials, pushing them as long as 250 μs in polar solvents. Increasing the excited state lifetime into the 100's of μs regime may allow us to carryout photoelectrocatalytic reactions with an electrode to regenerate the sensitizer, rather than a sacrificial reductant. We will discuss the physical and photophysical properties of these ultralong lived sensitizers.

The second topic will cover exploration of chelating donor-acceptor (D-A) ligands, as mononuclear complexes of $Zn^{(II)}$ and binuclear complexes of $Cu^{(I)}$, $Ag^{(I)}$ and $Au^{(I)}$. The Zn complexes absorb in the blue and violet part of the spectrum and the binuclear complexes absorb into the green. The excited states of the Zn complexes are ICT, while those of the binuclear analogs are mixed ICT/MLCT. The excited state lifetimes of both the Zn and binuclear materials are in the microsecond regime, with $\Phi_{PL}$ up to 0.6. Emission in these materials is via TADF. Our measurements for Zn-based compounds show that the complexes have very small energy gaps between their $S_1$ and $T_1$ states (*i.e.* < 25 meV). The long lifetimes are due to low oscillator strengths for their $S_1$ states. Methyl substitution was found to enhance both the photophysical properties and hydrolytic stability. We are in the process of evaluating the binuclear complexes, but based on absorption and emission characteristics, we suspect the $\Delta E_{ST}$ values and $S_1$ decay rates will be markedly higher than observed for the Zn-based compounds.

The third topic explores the role of spin–orbit coupling (SOC) in facilitating intersystem crossing (ISC) in cMa complexes. Prior studies have shown that singlet-to-triplet ISC rates in these systems span a wide range ($\sim 3$ to $120 \times 10^9$ $s^{-1}$), depending on the metal ion and ligand choices.[1] However, the precise contribution of SOC to ISC, and its interplay with TADF, is not well understood. Using a combination of transient absorption spectroscopy, time correlated single photon counting, and theoretical modeling, we investigate how structural modifications in cMa influences spin–orbit coupling constants (SOCCs). Through Arrhenius and Marcus–Hush theories, we experimentally determined that substituting Cu with Au increases the SOCC from ~1 $cm^{-1}$ to ~3 $cm^{-1}$, in agreement with the enhanced ISC rates. Further modifications to the carbene or carbazole units also lead to notable changes in SOCC values. Ongoing work focuses on evaluating how ligand rotation impacts these SOCCs.

1. Michael S. Kellogg, et al., *J. Phys. Chem. C*, (2024). *128*, 6621–6635. 2. T. Y. Li, et al., *Chem Rev*, (2024). *124*, 4332–4392. 3. D. A. Shariaty, et al., *Inorg Chem*, (2025). *64*, 1228–1240. 4. Collin N. Muniz, et al., *J. Am. Chem. Soc.*, (2023). *145*, 13846–13857.

# Distance Dependence of Free Carrier Generation in Low Dielectric Semiconductors

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Free carrier generation mechanisms in low-dielectric media, as found in organic solar cells (OSCs), are heavily debated. Low-dielectric organic semiconductors feature strong electrostatic interactions that can bind electrons and holes in coulombically-bound charge-transfer (CT) states. While large free carrier yields have driven OSC power conversion efficiencies above 20%, a unified mechanistic picture has yet to emerge for how the photo-chemical driving force for charge transfer dictates carrier yields and OSC efficiencies. This poster describes fundamental studies on two model donor-acceptor systems that allow us to develop and test models of charge separation in low-dielectric constant environments with great precision, with particular focus on how distance-dependent charge transfer impacts the balance between separated charges and CT states.

We use ground-state charge-transfer from molecular dopants to single-walled carbon nanotubes (SWCNTs) in low-dielectric solvent to probe how the *size* of dopants (and thus charge-transfer *distance*) influences free charge generation (Fig. 1a). Dark microwave conductivity tracks conductivity as a function of carrier concentration, and we find that doping efficiency is dictated by the ratio of long-range free charge states to short-range CT states. Quantitatively explaining the results requires revising the traditional calculation of *entropy* for free charge generation by employing the canonical partition function, which considers the distance-dependent density of micro-states available at fixed *temperature.* This is distinct from prior calculations employing the microcanonical ensemble, which counts states within the system at fixed *energy*.

Studies on dilute molecular donor/acceptor blends (Fig. 1b) reveal the connection between the photoinduced electron transfer driving force ($\Delta G_{CT}$) and the probability of forming free charges versus CT states. $\Delta G_{CT}$ controls the average charge transfer *distance*, skipping short-range CT states in the optimal case. We use photoinduced absorption detected magnetic resonance to measure charge separation distance distributions as a function of $\Delta G_{CT}$ and compare these with free charge yields measured by time-resolved microwave conductivity. Counter-intuitively, the *largest* driving force produces the *shortest* charge separation distance, explaining the Marcus-like "inverted regime" we observe for free carrier generation. These findings show how $\Delta G_{CT}$ controls the initial electron/hole pair delocalization, the critical step to photocurrent generation.

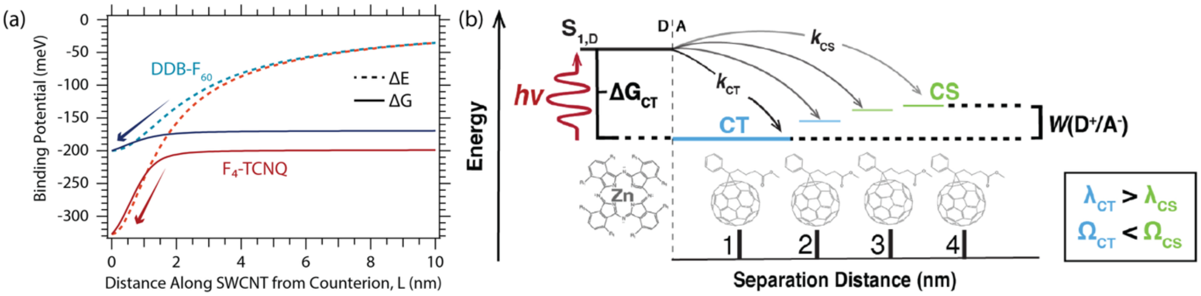

**Figure 1.** Distance-dependent charge transfer in (a) SWCNT/molecule and (b) small molecule donor/acceptor systems.

# Tuning Photocatalytic Functionality in CdS Quantum Dot Gels Via Component Integration and Surface Modification

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The Solar Photochemistry Quantum-Dot (QD) Gel Team is focused on designing water splitting photocatalysts by integration of QDs with co-catalysts to produce macro-scale through-wired porous assemblies (gels), combined with surface modification strategies to eliminate deep traps responsible for non-productive recombination. These efforts incorporate QD gel network-cocatalyst synthesis, modification, and catalytic testing (Brock), photophysics and time resolved spectroscopies (Huang), and computational modeling of band structures, alignments, and optical properties of QDs and QD assemblies (Liu). In our prior work, we demonstrated that CdS gels are 2.5-4 x more efficient for hydrogen evolution (HER) than discrete QDs, in the absence of a co-catalyst. Moreover, there is a strong structural component, with the cubic zinc blende polymorph being nearly 2x as active as hexagonal wurtzite. The activity towards HER increases as surface ligands are removed through annealing, but at the same time, the exciton lifetime decreases dramatically due to trap state formation upon ligand loss. Augmenting performance can be achieved by separating the light-harvesting/carrier transport processes from the catalytic evolution of $H_2$, motivating the integration of a co-catalyst that is "wired" to the photon-harvesting gel system (**Figure 1a**), and the use of surface modification strategies to reduce recombination at the semiconductor quantum-dot gel surface.

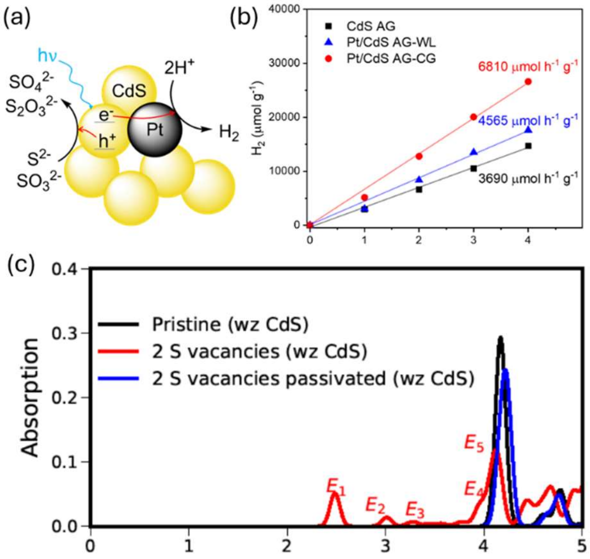

**Figure 1.** (a) Scheme of Pt co-catalyst CdS gel network for HER; (b) $H_2$ evolution as a function of time (hours) for CdS and Pt/CdS composites; (c) calculation of optical absorption for 2 S vacancies and effect of passivation on wurtzite CdS.

In the present work, the introduction of discrete ~3 nm Pt nanoparticles into the CdS gel structure will be described via two approaches (1) wet-loading (WL) of Pt onto preformed CdS gels and (2) co-gelation (CG) of CdS QDs and Pt to form composite gels. The effect of the approach on dispersion and location of Pt within the gel will be discussed in the context of exciton lifetimes, and photocatalytic HER performance (**Figure 1b**). In addition, the role of Cd and S vacancies on computed optoelectronic properties will be described along with the effect of passivation via heteroions ($Pb^{2+}$, $Cl^-$) (**Figure 1c**). These data will be compared to preliminary experimental efforts on passivation strategies assessed by photoluminescence and exciton lifetime measurements. Future work on our efforts to engineer complementary oxygen-evolution catalysts will also be described.

# Spontaneous Enthalpy-Uphill Charge Separation in Non-fullerene Acceptor Materials

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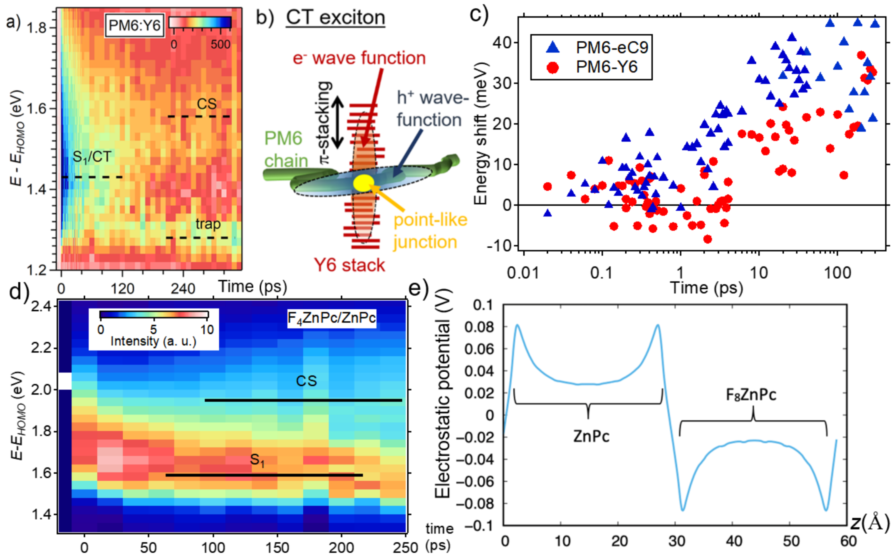
We used time-resolved photoelectron spectroscopy and multi-scale modeling to investigate the charge separation (CS) mechanism in organic donor/acceptor (D/A) interfaces. A major goal is to understand why bulk heterojunctions (BHJs) made with recent non-fullerene acceptors (NFAs) can enable efficient CS despite of a very small energy level offset at the 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 converts spontaneously (in 10 – 100 ps) into separated carriers (Fig. a) despite the CT exciton has a considerable binding energy of 0.15 eV. Spectrally, we found that the average electron energy *increases* 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 point-like junction (Fig. b). (Adv. Mater. 36, 2400578 (2024)) Very recently, we found that this enthalpy increase can occur at nearly an order of magnitude faster rate in the PM6:eC9 blend (in 1- 10 ps) (Fig. c). The eC9 is an improved version of the Y6, and PM6:eC9 OPV has an efficiency close to 20%. This result demonstrates that this spontaneous increase in the exciton energy is related to better OPV efficiency.

To understand molecular-scale features that would result in this enthalpy-uphill CS, we turn to a model D/A interface consisting of ZnPc molecules with different degrees of fluorination. For $F_4ZnPc/ZnPc$, we found that despite the energy offset at the D/A interface is less than 0.1 eV, enthalpy-uphill CS can still occur (Fig. d). Hence, one can separate excitons *without* an abrupt energy loss at the D/A interface, which against the conventional wisdom that an interfacial energy offset is necessary for efficient CS. Density functional theory (DFT) calculation shows that electrostatic field (Fig. e) from molecules can introduce band bending near the interface. This band bending can 'compensate' the binding energy of the CT exciton, which equalizes energies of localized and delocalized CT excitons. This can further strengthen the entropic driving force for CS.

Currently, we aim to further understand how the combined effect from geometry and electrostatic can make the entropy-driven CS become more efficient in certain NFAs.



a) TR-TPPE spectrum of PM6:Y6; b) CT exciton in PM6:Y6; c) Enthalpy upshift dynamics for two NFA BHJs d) Normalized TR-TPPE spectrum of $F_4ZnPc$ /ZnPc; e) Electrostatic potential vs distance calculated by DFT.

# p-Type $BiVO_4$ for Solar $O_2$ Reduction to $H_2O_2$

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The overall objective of our project is to understand and control 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) increase 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 most effectively and stably utilize surface-reaching charge carriers for desired redox reactions. In this presentation, we will discuss the synthesis and property of p-type $BiVO_4$, which can serve as a photocathode in a photoelectrochemical cell for solar $O_2$ reduction to $H_2O_2$. The conventional anthraquinone-based synthesis of $H_2O_2$ consumes $H_2$.

Among the various photoelectrodes, oxide-based photoelectrodes have the advantage of being more robust in aqueous media. Also, they are easy to fabricate, and their compositions can be tuned easily to enhance desired properties. Most oxide-based semiconductors are n-type due to oxygen vacancies serving as their intrinsic donor-type defects. As a result, most oxide-based photoelectrodes studied to date are photoanodes, and the realization of oxide-based photocathodes has been very limited. In this presentation, we report the synthesis, characterization, and application of p-type $BiVO_4$ with a monoclinic scheelite (*ms*) structure. Prior to our study, *ms*-$BiVO_4$ has been investigated only as a photoanode. p-type *ms*-$BiVO_4$ can be prepared via atomic doping of $Ca^{2+}$ at the $Bi^{3+}$ site. However, we show that $Ca^{2+}$ doping alone does not produce p-type *ms*-$BiVO_4$, and we discuss critical synthesis conditions required for the formation of p-type *ms*-$BiVO_4$. We then demonstrate that the Ca-doped *ms*-$BiVO_4$ photocathode can be used for solar $O_2$ reduction to $H_2O_2$ when coupled with appropriate catalysts (**Fig. 1**). We will also present computational results obtained by our theory collaborators (Prof. Giulia Galli, University of Chicago), which reveal that holes are stable as polarons in *ms*-$BiVO_4$ and have a low self-trapping energy. We will also discuss the formation energy and thermal ionization energy of a Ca dopant in $BiVO_4$ to better understand the p-type conductivity of Ca-doped $BiVO_4$.

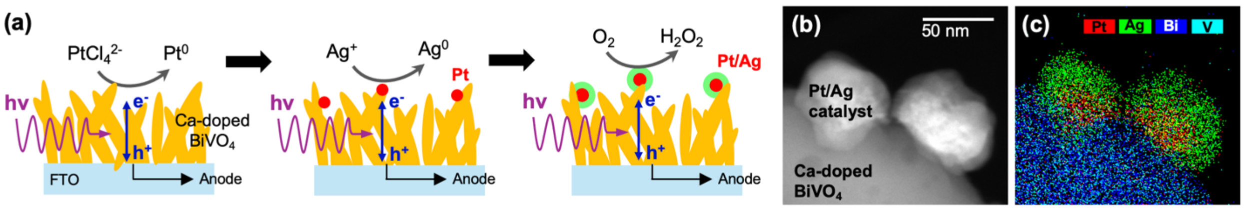

**Fig. 1.** (a) Schematic illustration of the photoelectrodeposition of Pt/Ag particle catalysts on Ca-doped $BiVO_4$ photocathodes and photoelectrochemical $H_2O_2$ production and (b-c) the elemental mappings of the STEM image focusing on Pt/Ag catalysts on Ca-doped $BiVO_4$.

# Ligand-Based Oxidative and Reductive Catalysis for Water Oxidation and Fuels Generation from $CO_2$

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Small molecule activation is at the heart of many important challenges for humanity in the 21st century. These include water oxidation to dioxygen and hydrogen peroxide, $CO_2$ reduction to fuels and dinitrogen reduction to ammonia and other commodity chemicals. In this presentation, the use of ligand-based catalysis for small molecule activation as a strategy that enables the transition to earth-abundant, first-row transition metals will be discussed. The photochemical reduction of $CO_2$ to formate with high selectivity using metal formyl and dihydroquinoxalinide intermediates as hydride donors will be demonstrated. The development of synthetic procedures, as well as the initial mechanistic studies using ruthenium complexes have been key to understanding the behavior of these systems before transitioning to the first-row analogues.

These complexes are highly active and 100% selective in the photochemical $CO_2$ reduction to formate. The formyl and dihydroquinoxalinide intermediates, generated by an ET-PCET mechanism, are the culprits in the hydride transfer to $CO_2$. The fact that the coordination environment remains saturated during the catalytic cycle (ligand-based) is very encouraging in transitioning to first-row transition metals.

A ligand-based approach to water oxidation catalysis based on $[M(bpy)_2(bi\text{-}bimH_2)]^{n+}$ will also be presented. This platform includes self-healing capabilities and because it is ligand-based, is amenable to first-row transition metals, a feature that we have demonstrated with cobalt- and iron-based catalysts.

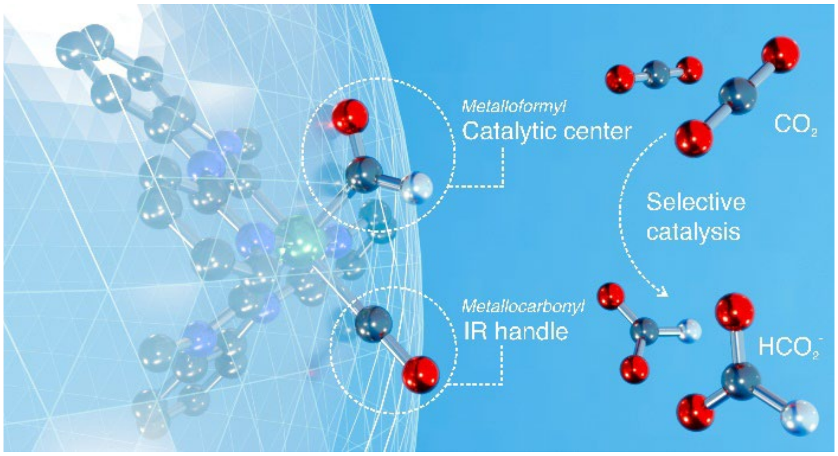

**Figure 1**. Ligand-Based $CO_2$ Reduction to Formate.

# Directional Excited State Charge Transfer for Solar Energy Conversion Tracked with Element Specificity

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Solar energy conversion to fuels and electricity requires multi-step photo-redox and photo-chemical processes. Following light absorption, the direction of electron density migration and nuclear motions resulting from photon energy dissipation are governed by the interplay between electrons and nuclei in excited states. Thus, a detailed understanding of the light-driven electronic and nuclear response of energy conversion materials is needed to optimize photochemical reaction outcomes, minimize energy losses, and increase light energy conversion efficiency. The continued development of novel ultrafast x-ray methods provides unprecedented opportunities for tracking electronic/nuclear motions in real time along excited state trajectories.

We are investigating the mechanistic role of bridging ligand motifs in transporting and/or accumulating redox units in photocatalytic chromophore-catalyst molecular dyads. We take advantage of the elemental specificity inherent to time-resolved x-ray absorption spectroscopy (XAS) to map the distribution of photoexcited charge density in real-time at distinct chromophore, bridge, and catalyst atomic sites. With an initial focus on tetrapyridophenazine (tpphz) bridged dyads, we have explored the hypothesis that the bridge may play an active role in catalysis by accumulating electrons, opposed to its intended role to facilitate longer-range metal-to-metal charge transfer. To do so, we developed N K-edge XAS as a probe of the electronic structure of the larger ligand and bridge framework. We demonstrated astonishing sensitivity to local electronic structure at the chemically distinct N sites, enabling real-time tracking of excited state charge distributions on the central phenazine motif of the bridge. By extending this spectroscopy to the ultrafast time domain for a model system containing common chromophore-bridge motifs we showed that the dominant pathway for electron localization on the bridge occurs with sub-100 fs kinetics, much faster than previously thought. Additional probes of the chromophore and catalyst metal sites in the dyads indicate that tpphz plays an active role in accumulating redox equivalents during photocatalytic reactions.

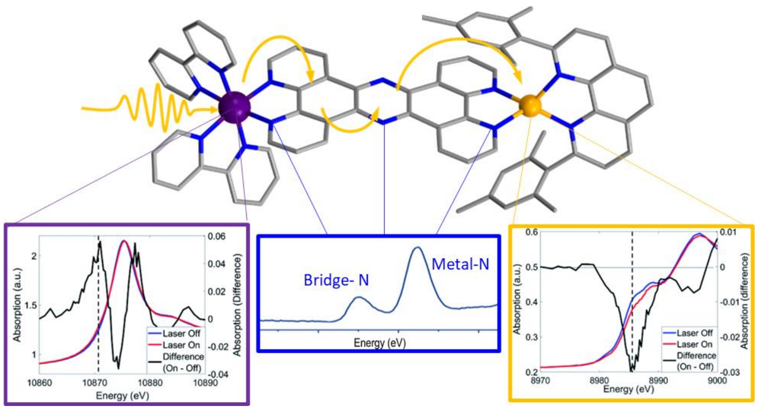

**Figure 1.** The combination of metal and ligand atom XAS provides an unprecedented view of excited state electron transfer processes in donor-acceptor dyads.

# Investigating Surface p$K_a$ and pH Using SERS Spectroscopy with 4-Mercaptobenzoic Acid in Deionized Water and Sodium Bicarbonate Electrolytes

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Our research presents spectroscopic measurements of the surface p$K_a$ at electrode/electrolyte interfaces using surface enhanced Raman Scattering (SERS) spectroscopy of 4-mercaptobenzoic acid (4-MBA). As the electrochemical potential is varied from negative to positive, the Raman intensity of the -COOH functional group (at 1700 cm$^{-1}$) decreases while the -COO$^-$ Raman intensity (at 1410 cm$^{-1}$) increases. The protonation/deprotonation of this surface-bound molecule reflects an electrochemically induced shift to more acidic conditions at negative potentials and more basic at positive potentials. By fitting the data to a normalized sigmoid function, we obtain the percentage of surface protonation/deprotonation, which can be related to the local p$K_a$ of the system. The percentage of surface protonation, which gives a proxy of the 2-dimensional surface p$K_a$, follows the Fermi-Dirac distribution as a function of applied potential. The electrolyte-electrode pH-neutral conditions at the interface are extracted by the linear-fitted intercepts of -log(COO$^-$/COOH) as a function of applied potential based on the Nernst equation, which are 0.25 V, 0.07 V, 0.08 V, and -0.46 V for DI water and 0.5 M sodium bicarbonate solutions with and without $CO_2$ purging, respectively. The shift of surface neutral conditions toward more positive voltages in the electrolytes with $CO_2$ purging indicates that the $CO_2$-dissolved bulk solutions become more acidic. The 25% reduction of protonation at negative applied potentials in $CO_2$-purged DI water suggests that the direct reduction of hydronium ions and/or carbonic acid increases the surface p$K_a$ in the microenvironment. Adding alkali cations (Na$^+$) attracts more proton donors toward the working electrode, resulting in the protonation capacity near the electrode surface, approximately -1.9 V$^{-1}$, double that of DI water, which is around -1 V$^{-1}$. Hydrogen evolution reaction (HER) pathways are not detected in neutral or basic conditions due to the low concentration of hydronium ions (< $10^{-6}$ M). The independence of the carbonic acid concentration with applied negative potentials, as measured by the surface p$K_a$ in the Helmholtz plane, indicates that changes in the local pH/surface p$K_a$ under neutral or basic bulk conditions are governed by the acid-base equilibrium of water, carbonic acid, bicarbonate, and carbonate ions.

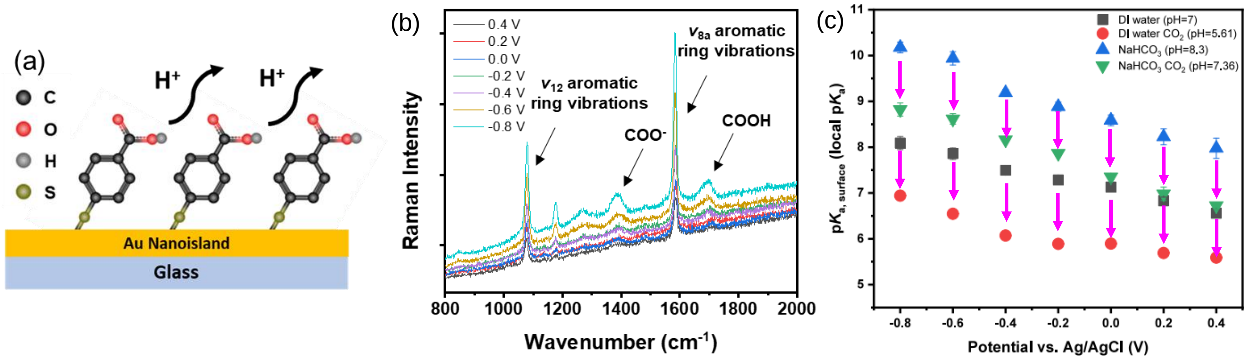

**Figure 1**. (a) Illustration of SERS-active 4-mercaptobenzoic acid (4-MBA) functionalized gold nanoisland electrode. (b) *in situ* Raman spectra of 4-MBA functionalized gold nanoislands under the conditions of 0.5 M $NaHCO_3$ with $CO_2$. (c) Sigmoid-normalized of protonated/deprotonated species on 4-MBA functionalized gold nanoislands, where the values of COO$^-$ percentage are marked as solid symbols and the values of COOH percentage are marked as hollow symbols.

1. **ACS Applied Materials & Interfaces**, DOI:10.1021/acsami.3c14116, v16, p9355–9361 (2024).
2. **ACS Applied Materials & Interfaces** DOI:10.1021/acsami.4c21030, v17, p17521–17529 (2025).

# Kinetics of Metal Hydride Formation at Electrode Interfaces

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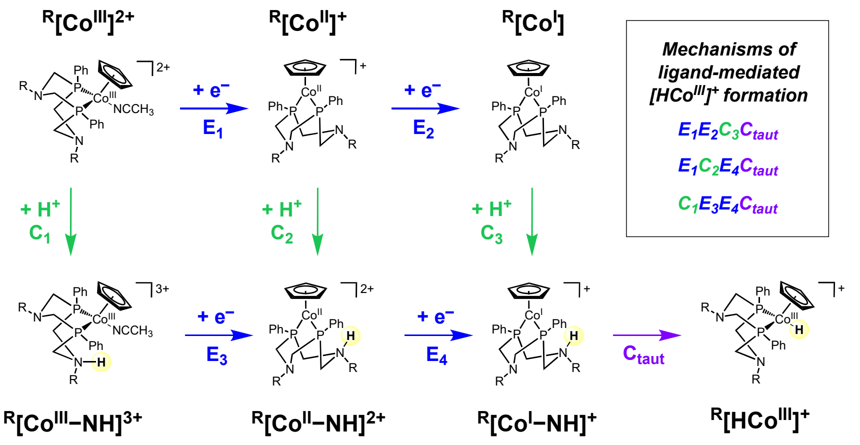

**Figure 1.** Mechanisms observed for the two-electron, one-proton transformation of $[Co^{III}Cp(P^{Ph}{}_2N^{R}{}_2)(CH_3CN)]^{2+}$ (**$^R[Co^{III}]^{2+}$**) to $[HCo^{III}Cp(P^{Ph}{}_2N^{R}{}_2)]^+$ (**$^R[HCo^{III}]^+$**). We have shown that depending on acid strength, acid concentration, and timescale between electron transfer steps, reactivity proceeds through $E_1E_2C_3C_{taut}$, $E_1C_2E_4C_{taut}$, $C_1E_3E_4C_{taut}$, or some combination of the three mechanisms.

In the proton-coupled electron transfer (PCET) reaction of $[Co^{III}Cp(P^{Ph}{}_2N^{R}{}_2)(CH_3CN)]^{2+}$ (Cp = cyclopentadienyl; $P^{Ph}{}_2N^{R}{}_2$ = 1,5-di-R-3,7-diphenyl-1,5-diaza-3,7-diphosphacyclooctane, R = Bn, $C_6H_4OCH_3$, or Ph), the two electron reduction of $Co^{III}$ is coupled to protonation of the $P^{Ph}{}_2N^{R}{}_2$ ligand, followed by tautomerization to form the $Co^{III}$–H complex. The $P^{Ph}{}_2N^{R}{}_2$ ligand provides a kinetically accessible protonation sites en route to formation of $Co^{III}$-hydride species. Three different PCET mechanisms are accessible; protonation of the $P^{Ph}{}_2N^{R}{}_2$ ligand can occur while the complex is in the $Co^{III}$, $Co^{II}$, or $Co^{I}$ oxidation state. Cyclic voltammograms recorded with proton sources that span a wide range of p$K_a$ values reveal that the mechanism changes as a function of amine substituent (R), acid p$K_a$, acid concentration, and timescale between electrochemical steps. Peak shift analysis of these electrochemical measurements, combined with digital simulations, DFT calculations, and thermochemical studies, show that the electronic donation at the pendant amine influences the accessible PCET mechanism and proton transfer kinetics related to cobalt hydride formation under analogous reaction conditions. This work shows how to exploit kinetic basicity using ligand-cooperative design to facilitate PCET reactions involved in energy related transformations.

Separately, a derivative of $[Co^{III}Cp(P^{Ph}{}_2N^{R}{}_2)(CH_3CN)]^{2+}$ with a simple chelating phosphine ligand, $[Co(Cp)(dppe_{\equiv H})(Cl)]^+$ ($dppe_{\equiv H}$ = 1,2-bis-(4-ethynyl-phenyl)phosphinoethane), was immobilized onto a glassy carbon electrode using two attachment strategies: Cu(I) catalyzed azide-alkyne click chemistry and reductive electropolymerization. This complex reacts through a two-electron, one-proton PCET reaction to form the $Co^{III}$–H complex. When voltammograms are recorded in the presence of acid, the response conforms to that predicted for a PCET reaction of an immobilized analyte. Through peak shift analysis, the rate constant for the elementary proton transfer step was quantified and compared to that of the solution-based analogue. This is the first reported kinetic analysis of a PCET reaction of an electrode-immobilized complex.

# Correlating Thermodynamic and Kinetic Hydricities of Transition Metal Hydrides

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Transition metal hydrides are crucial intermediates in a plethora of catalytic reactions, including reactions relevant to energy storage applications. In many of these reactions, hydride transfer either from a transition metal hydride to a substrate or from a substrate to a transition metal to form a transition metal hydride is the turnover-limiting step. Therefore, an increased understanding of hydride transfer with transition metals as either the hydride donor or acceptor is critical for the design of efficient photocatalytic systems.

Two different approaches have been utilized to quantify the ability of a transition metal hydride to donate a hydride. *Thermodynamic hydricity* is the free energy required to release a hydride ion, $H^-$, from a species in solution ($\Delta G^{o}_{H-}$).Thermodynamic hydricity is valuable for understanding observed reactivity or selectivity, and for predicting if a hydride transfer reaction will be favorable, but it often cannot provide insight into catalytic activity. *Kinetic hydricity* is the elementary rate constant for a particular hydride transfer reaction and is related to the free energy of activation ($\Delta G^{\ddagger}_{H-}$). In this contribution, I will present our computational modeling studies on **(i)** the prediction of thermodynamic and kinetic hydricities of a series of transition metal hydrides, **(ii)** linear free energy relations (LFER) between thermodynamic and kinetic hydricities (Fig. 1a) and **(iii)** the solvent dependence of LFERs (Fig. 1b).

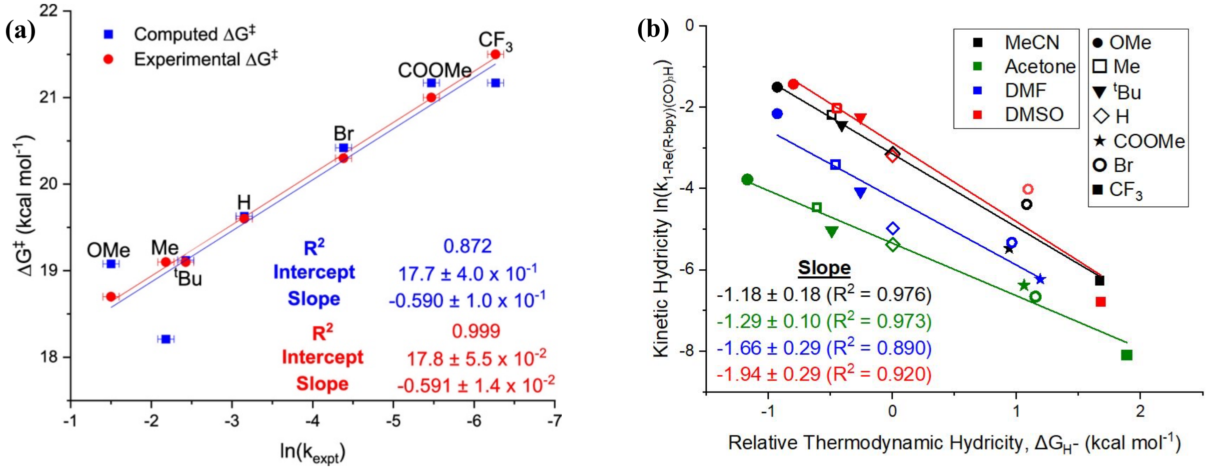

**Figure 1. (a)** Experimental activation free energies ($\Delta G^{\ddagger}_{expt}$, in red) and computed activation free energies ($\Delta G^{\ddagger}$, in blue) (kcal mol$^{-1}$) of Re($^{R}$bpy)(CO)$_3$H complexes versus the natural logarithm of relative experimental $CO_2$ insertion rates (ln($k_{expt}$)) **(b)** LFERs between relative thermodynamic hydricity and kinetic hydricity determined using the rate constants for $CO_2$ insertion for Re($^{R}$bpy)(CO)$_3$H in MeCN (black), acetone (green), DMF (blue), and DMSO (red).

**Acknowledgments:** We thank Prof. Nilay Hazari (Yale University) and Prof. Alexander J. M. Miller (University of North Carolina at Chapel Hill) for insightful discussions and for providing experimental results used in this study.

# Optical Gating of Spin-Based Quantum States for QIS

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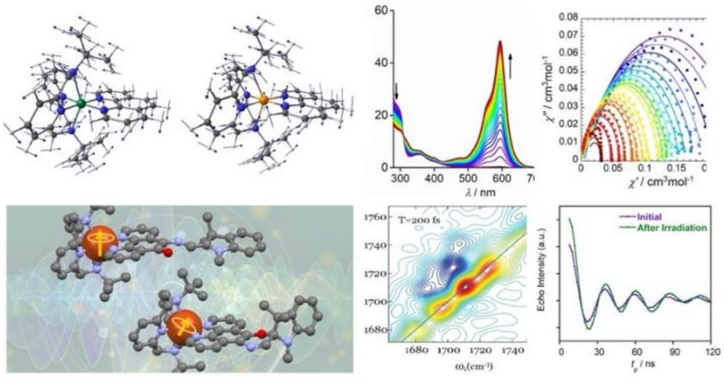
The optical manipulation of spin quantum states provides an essential strategy for quantum control with both temporal and spatial resolution for quantum computing, sensing, and communications. While significant progress has been made in the discovery of molecular spin-based qubits with long decoherence times, initialization and readout protocols for quantum information transfer require a fundamental understanding of the factors that control transitions between equilibrium and non-equilibrium states and the coupling of a quantum system to its environment. The larger the noise spectrum, the shorter the coherence time, and the more "quantum information" can be extracted from the environment. Optical processes have been utilized for initialization and readout in photoexcited spin states, in which transient spin states are often short-lived (us). Here, we report a series of optically bistable spin qubits in which the relative stability of the two states can be modulated by optical stimuli, leading to in-situ changes in coherence times and transition frequencies for initialization and readout. We investigate the structural factors that affect the modulation of spin sublevels through photoisomerization processes in metal-photochrome complexes, and demonstrate optically-gated modulation of zero-field splitting, hyperfine coupling, g-values, Rabi oscillation frequencies, and coherence times based on changes in delocalization of the ligand. Changes in the structure of the photochrome, the ancillary ligand, and the metal center (spin state) reveal the importance of electronic coupling between ligand and metal center within the quantum system. The changes in spin dynamics are attributed to contributions from first-order and second-order spin-orbit coupling, adiabatic and nonadiabatic contributions to spin-lattice relaxation, and the dielectric of the environment. The results provide a strategy for *in-situ* structural changes relevant to quantum sensors and quantum computing applications in quantum information science.



**References:** (1) Subrata Ghosh, Paul Oyala, Maksym Fizer, Vsevolod D. Dergachev, Sergey A. Varganov, and Natia L. Frank* "Quantum Coherence Enhancement Through Control of Metal-Ligand Covalency: Modulating Spin-Orbit coupling in Isostructural Complexes" *Submitted*. (2) Harini Wimalasekera, Anitha Alanthadka, Khetpakorn Chakarawe, Elvin V. Salerno, R. David Britt, Stephen Hill, and Natia L. Frank* "Optically-Gated g-Engineering in a Molecular Spin Qubit for Quantum Information Science" *Submitted*.

# Identification of Nuclear Coordinates Driving Solar Energy Conversion Processes using Ultrafast Raman Techniques

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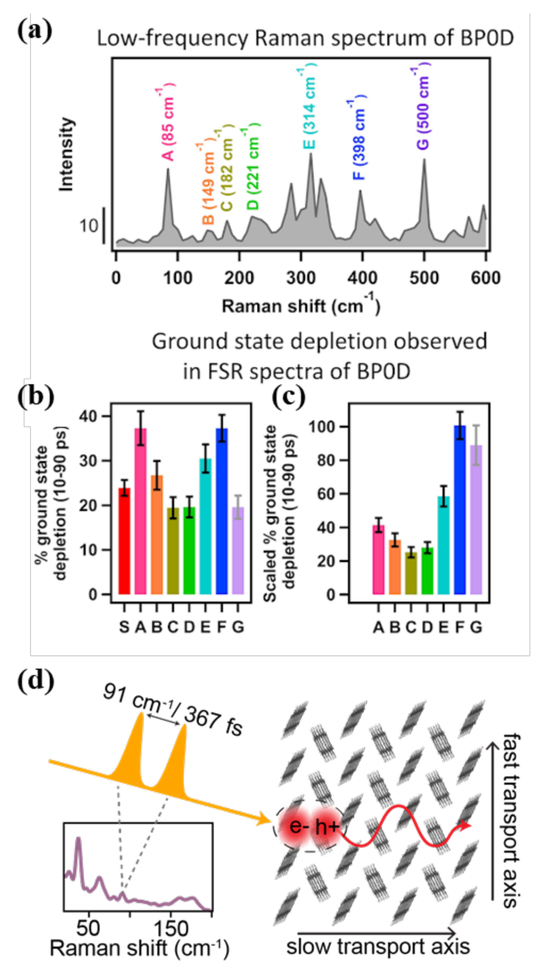
The goal of our DOE-sponsored research is to use advanced Raman spectroscopies to provide synthetic insight on molecular-based solar energy conversion systems. Specifically, we identify certain nuclear coordinates and vibrational coherences which can be rationally modified in order to improve function. We use femtosecond stimulated Raman spectroscopy (FSRS), which monitors ultrafast multidimensional structural changes, as well as resonance Raman intensity analysis, which provides information on dynamics immediately following photoexcitation. We have developed mode-selective FSRS, which is capable of quantifying the impact that a specific nuclear coordinate has on a chemical reaction.[1-2] This enables clear assignment of driving modes (those which promote the photochemistry), spectator modes (those which have no impact on the photochemistry), and killer modes (those which suppress the desired outcome). We have applied these approaches to a range of organic and inorganic systems,[1-3] and more recently have identified specific modes which promote or hinder exciton transport.[4] Additionally, we have quantified mode-selective activation in excitonic polaritons, finding that specific strong coupling conditions can effectively steer the reaction coordinate.[5] Overall our work showcases the ability of advanced Raman techniques to specifically identify the key contributors to multidimensional reaction coordinates.



Mode-selective FSRS of deuterated pentacene dimer including low-frequency Raman modes of interest (a) and effects on product yield (b, c). (d) Identification of low frequency modes promoting exciton transport.

1. Rich, Frontiera, J. Phys. Chem. Lett., 2020, http://dx.doi.org/10.1021/acs.jpclett.0c01834. 2. Lynch, Das, Alam, Rich, Frontiera, J. Phys. Chem. Au, 2023, https://doi.org/10.1021/acsphyschemau.3c00031. 3. Clapham, Das, Douglas, Frontiera, J. Am. Chem. Soc., 2024, https://doi.org/10.1021/jacs.4c03249. 4. Lynch, Mihm, Baugh, Sharifzadeh, Frontiera, in review, https://doi.org/10.26434/chemrxiv-2025-nvv8h. 5. Alam, Liu, Holmes, Frontiera, in review, https://arxiv.org/abs/2501.06364.

# Directing Reactivity and Charge Transfer at Photoelectrochemical Interfaces

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Research in my group focuses on directing photoelectrochemical (PEC) reactivity and charge transfer at the semiconductor|electrolyte interface. We are currently studying these factors through the lens of the oxygen evolution reaction (OER) and carbon dioxide reduction reaction ($CO_2RR$). Absent interface-sensitive methods, PEC performance of semiconductor photocatalysts (intrinsically tied to *surface* properties) can be misinterpreted in the context of *near-surface* or *bulk* properties. We have probed the mechanism by which the OER activity of mechanically strained $TiO_2$ thin films, grown on a NiTi superlastic alloy, increases as a function of strain. We determine that Ni from the substrate is incorporated into the $TiO_2$ layer and that strain exposes additional Ni sites, with the OER overpotentials and Tafel slopes of the $TiO_2$ decreasing as Ni site density increases (Fig. 1). This work highlights the challenges of correlating kinetic performance of PEC systems with intrinsic *surface* properties in the presence of heterogeneous *near-surface* composition.

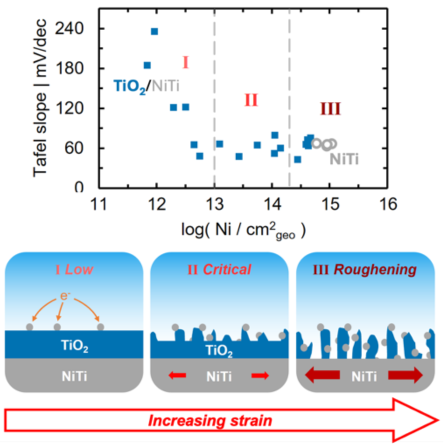

**Figure 1:** Role of electrochemically available Ni site density on Tafel slope (top) where vertical grey dashed lines delineate approximate distinctions between (I) low ($<10^{13}$ Ni/cm$^2_{geo}$, pink), (II) critical ($\sim10^{13}$ to $2\times10^{14}$ Ni/cm$^2_{geo}$, red), and (III) roughening regimes ($>2\times10^{14}$ Ni/cm$^2_{geo}$, dark red) on the $TiO_2$ surface (bottom) with increasing strain.

OER is the default oxidative half-reaction for fuel-forming cathodic reactions in aqueous environments, but it is rate limited by the kinetics of four electron transfer steps, leading to competition with more facile $H_2O_2$ production. Chiral-induced spin selectivity (CISS) has recently been shown to direct selectivity in electrochemical reactions, including in OER by supporting the formation of triplet $O_2$. We are building a coupled molecule-semiconductor platform, leveraging dye-sensitized photoelectrochemical cell architectures, to investigate the role of chiral bridge molecules in controlling the spin-selectivity of photoinduced charge transfer. We have designed and synthesized an axially chiral bridge molecule and are currently studying the optical properties of this bridge as well as its attachment to mesoporous oxides. This study will provide a systematic basis from which to develop guiding principles to describe spin-selectivity in PEC systems.

To generate products beyond CO, $CO_2RR$ requires a $H^+$ source. This has led to substantial study of $CO_2RR$ in in aqueous PEC environments, where reaction rates are limited by $CO_2$ solubility and competition with hydrogen evolution. We are currently certifying a high-pressure electrochemical reactor which will enable investigation of $CO_2RR$ in non-aqueous environments up to supercritical pressures. This pilot reactor will be used to establish electrochemical baselines for $CO_2RR$ on metallic surfaces with controlled $H^+$ concentrations, with future work focused on investigating elemental reaction steps under illumination.

# Using Pulse Radiolysis to Investigate Fundamental Processes in Solar Energy Conversion

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We use pulse radiolysis (PR) as a tool to investigate reaction mechanisms due to the powerful ability of PR to rapidly generate one-electron reduced or oxidized forms of solutes. Here, we present two applications of PR related to reactivity associated with solar energy conversion.

Tertiary amines such as triethylamine (TEA) and triethanolamine (TEOA) are commonly used to reductively quench excited states in photocatalytic systems. Following their one-electron oxidation, the resulting TEA$^{\bullet+}$ and TEOA$^{\bullet+}$ cations undergo proton transfer, resulting in the formation of a secondary reductant with an α-carbon-centered radical (TEA$^{\bullet}$ or TEOA$^{\bullet}$). However, the redox properties of these radicals remain poorly understood. We used a combination of laser flash photolysis and PR to determine their relative reducing powers, discovering that, in contrast to a commonly held belief, TEA$^{\bullet}$ is in fact a superior reductant than TEOA$^{\bullet}$, by ~0.2 V [1]. More recently, we have employed a family of ligand-substituted Re complexes, [ReCl($R_1R_2$-bpy)$(CO)_3$], as electron acceptors, and used PR to measure electron transfer rate constants to them from TEA$^{\bullet}$ across a 1.43 V range in driving force. The redox potential of TEA$^{\bullet}$ was benchmarked to within ±80 mV in $CH_3CN$ by using an empirical rate *vs*. free-energy correlation, electron transfer theory, and density functional theory calculations. The equilibrium potentials for TEA$^{\bullet}$ and TEOA$^{\bullet}$ were thus determined to be –1.98 V and –1.76 V, respectively vs. Fc$^{+/0}$. These transient radicals can therefore be broadly considered as strong homogeneous chemical reductants within the wider context of photoredox potentials.

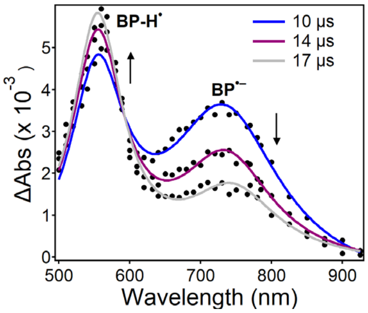

**Figure 1.** Pulse radiolysis of 12 mM benzophenone (BP) in $N_2$-saturated $CH_3CN$ containing 205 mM $HCO_2H$ & 250 mM [TBA][$HCO_2$].

Using PR coupled with time-resolved infrared spectroscopy (PR-TRIR) in $CH_3CN$, we have probed key intermediates in the catalytic cycles of a variety of $CO_2$ reduction catalysts. However, it has proved challenging to investigate critical proton-coupled electron transfer (PCET) steps, which involve the protonation of a reduced catalytic intermediate, since the solvated electrons are rapidly scavenged by most Brønsted acids that are added to the solution, thus preventing the initial reduction of the catalyst. Here, we describe recently developed strategies for overcoming this challenge, involving: (1) leveraging acid/base homoconjugation; (2) using dissolved $CO_2$ as an efficient scavenger of electrons in the presence of an acid; and (3) radiolytically producing a Brønsted acid. These strategies are demonstrated with the efficient production of the protonated benzophenone ketyl racidal, BP-H$^{\bullet}$ (see Figure 1). This new development opens many new opportunities to probe PCET reactivity in $CH_3CN$ by PR, which will allow catalytic mechanisms to be fully deciphered.

1. Carr, C. R.; Vrionides, M. A.; Grills, D. C. Reactivity of radiolytically and photochemically generated tertiary amine radicals towards a $CO_2$ reduction catalyst *J. Chem. Phys.* **2023**, *159*, 244503.

# Spin-polarized Oxygen Evolution Reaction Enabled by Chiral Molecule Coupled with Ferromagnetic Electrocatalysts

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The discovery of chiral-induced spin selectivity (CISS) revolutionized our understanding of the capabilities of chiral molecules in functioning as spin filters, aligning the spin orientation of electrons when electrons transmit through them. Recently, CISS has been exploited to direct solar energy conversion, especially the oxygen evolution reaction. However, even with the remarkable progress made, the impact of CISS when paired with electrocatalysts possessing varying magnetic properties remains unclear. To determine whether the spin polarization will be preserved on catalysts with different magnetic properties, ferromagnetic (FM) $CoFe_2O_4$ and paramagnetic (PM) $Co_3O_4$ were synthesized. It reveals that the spin-polarized charge carrier generated via CISS will maintain its spin alignment when L-(or D-) methionine are coupled with FM $CoFe_2O_4$ (L-(or D) $CoFe_2O_4$), similar to that observed under a magnetic field. The Tafel analysis and kinetic isotope studies suggest that without the CISS effect the first electron transfer step is the rate-determining step (RDS). However, with CISS, the RDS shifts to a combination of the first and second electron transfer steps. This conclusion was further supported by the in-situ infrared spectroscopy, which shows L-$CoFe_2O_4$ promotes the formation of OOH* intermediates. In the near future, we aim to build photoelectrochemical systems and employ spin-selective ultrafast spectroscopy to gain insights into the effects of CISS on light generation, charge separation, and charge transfer.

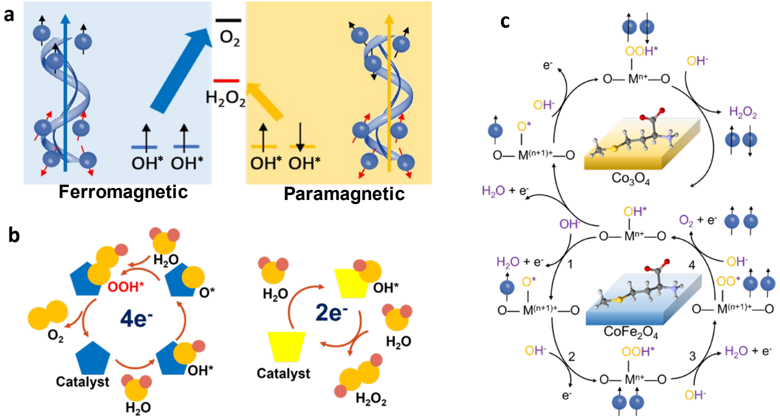

**Fig. 1: Chiral induced spin selectivity effect on FM and PM catalysts**. (a) The schematic of polarized OH* on catalysts with different magnetic properties under a constant magnetic field. (b) Schematics of four- and two-electron reaction pathways (c) Reaction pathways on FM $CoFe_2O_4$ and PM $Co_3O_4$ catalysts for OER

# Charge Separation and Ligand Exchange Reactions with Copper Complexes

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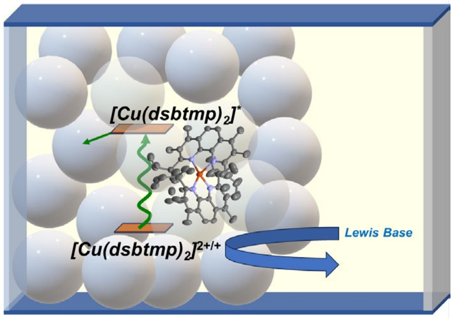
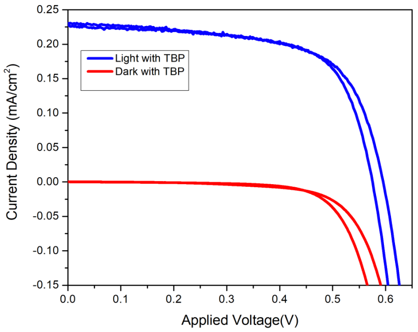
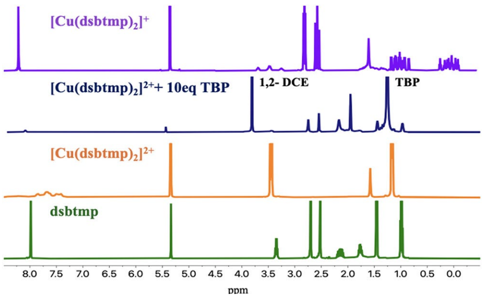
Solar photochemical systems that convert sunlight into electricity or chemical fuels rely on a series of electron-transfer steps following light absorption to generate a charge-separated state. In dye-sensitized solar cells, this charge separation typically occurs via two sequential processes: electron 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.

This study focuses on copper coordination complexes, particularly [Cu(dsbtmp)$_2$]$^+$ (dsbtmp = bis(2,9-di(sec-butyl)-3,4,7,8-tetramethyl-1,10-phenanthroline)), due to their long-lived excited states (exceeding 1 μs in various solvents), which are necessary to enable diffusion to the TiO$_2$ surface and subsequent electron injection. We demonstrate that solar-to-electricity energy conversion is achievable with this simplified, single-component system; however, the photocurrent remains sub-optimal.



Notably, the presence of an exogenous base, such as 4-tert-butylpyridine (TBP), is critical to device operation. We present data elucidating the multifaceted role of TBP in modulating performance. Although [Cu(dsbtmp)$_2$]$^+$ is found to be stable in the presence of bases, quantitative NMR spectroscopy reveals that TBP substitutes one of the dsbtmp ligands in the oxidized form [Cu(dsbtmp)$_2$]$^{2+}$. The effects of other bases—including 4-methylpyridine (4-MP), N-methylimidazole (NMI), and N-methylbenzimidazole (NMBI)—were also examined. Surprisingly, NMI was found to displace both dsbtmp ligands, yielding a putative [Cu(NMI)$_6$]$^{2+}$ complex. Preliminary results on how these bases influence the conduction band energy and suppress interfacial electron transfer will also be presented. Finally, we outline potential strategies to enhance both the efficiency and stability of this unique, single-component solar energy conversion system.





# Photooxidation of Polycyclic Aromatic Alkyl Alcohols and Amines: Mechanisms and Scope

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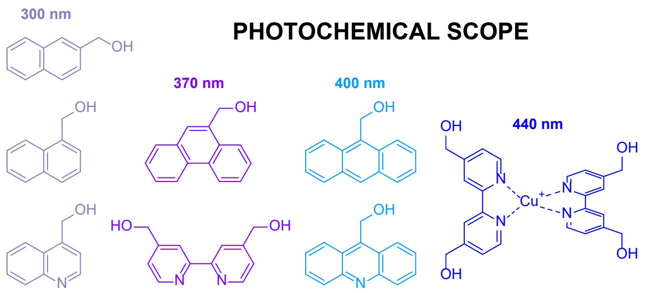
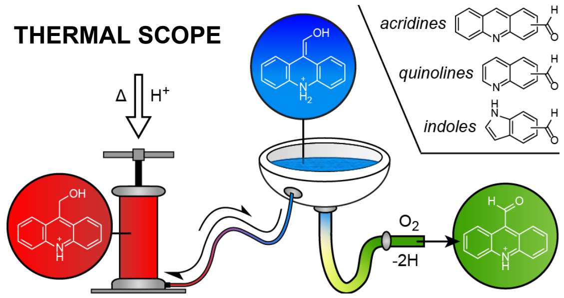
We have discovered a novel photochemical reaction wherein polycyclic organic dyes bearing hydroxmethyl groups oxidize to their corresponding aldehydes with concomitant elimination of $H_2$ as a byproduct. Our efforts are now focused on understanding the mechanism(s) of these photooxidations by combining steady-state physical organic chemistry techniques (isotope labeling, kinetic studies, and photophysical characterization) with optical transient absorption spectroscopy and time-dependent density functional theory. With this approach, we aim to piece together a complete picture of the reaction from the initial photon absorption event 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 $H_2$ release and develop computational screening methods to design improved materials for molecular hydrogen storage, which we will experimentally validate by synthesizing these new dyes and evaluating their performance.

In previous reporting periods, we focused our efforts on studying hydroxymethylated anthracenes and acridines. However, these systems are acutely sensitivity to oxygenation in the triplet excited state and thus require rigorously anaerobic conditions. To overcome this problem, we have screened several dyes that are more robust to $O_2$ and found that the photooxidation reaction proceeds for a remarkably broad range of polycyclic aromatic hydrocarbons and heterocycles and even transition metal complexes. In fact, **every dye we have screened to date undergoes this reaction, demonstrating that we have uncovered a fundamental photochemical process**.

While performing photochemical control experiments in the dark, we serendipitously discovered that 9-acridinemethanol also undergoes non-photochemical oxidation to its aldehyde in dilute aqueous acid. We have found that this reaction is also remarkably general and occurs not only for hydroxymethylated but also amino- and bromomethylated acridines, quinolines, and indoles and even many polycyclic aromatic hydrocarbons. Based on comprehensive regioselectivity screens, internal kinetic isotope competition, and density functional theory calculations, we propose a mechanism wherein migration of a methylene hydrogen by acid-catalyzed dearomative tautomerization yields an unstable enol/enamine intermediate that then irreversibly loses two hydrogen atoms to atmospheric oxygen. Among the reactants screened to date, the photo- and thermochemical reactions exhibit identical regioselectivities, and thus we expect the two pathways to share key mechanistic steps, a hypothesis we are now exploring through triplet sensitization.





# Solar-energy-driven interfacial multi-electron-transfer catalytic systems for fuels

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This ongoing collaborative photochemistry program is based on validation of key hypotheses on the roles of catalyst active site microenvironment on the stability and performance of polyoxometalate (POM) water oxidation catalysts (WOCs) and photoanodes composed of semiconductor (SC) electrodes and POM WOCs. To date, we have progress in the following areas:

**Microenvironment effects on POM-WOCs.** Recently, we have prepared mixed 3d-metal **M–[$Co_2TM_2X_2$]** systems (where M is counter cation, and TM are 3d-metals, such as Fe and Ni). We used multiple experimental and computational techniques to: (a) quantify both the location and percent occupancy of Co and TM in $Co_2TM_2P_2$, and (b) identify factors impacting structures and stabilities of these complexes. We show that electron-rich solvent donors greatly perturb POM electronic structure and properties via donor-acceptor interactions.

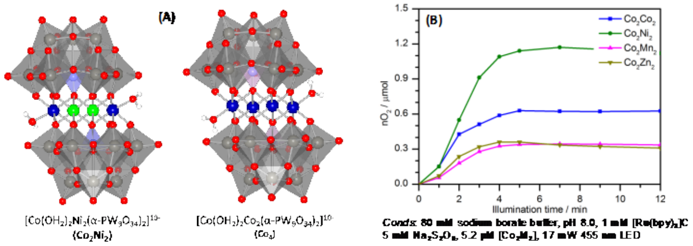

**Figure 1.** Structures of POM-WOCs, **$Co_4P_2$** (left) and **$Co_2Ni_2P_2$** (right) Co: blue; Ni: green; $WO_6$, gray octahedra.

**[Co-POM]-$TiO_2$ photoanode for WO in acid.** We have constructed a photoanode comprising the homogeneous WOC, $Na_8K_8[Co_9(H_2O)_6(OH)_3(HPO_4)_2(PW_9O_{34})_3]$ (**$Co_9$POM**) and nanoporous *n*-type $TiO_2$ photoelectrodes (henceforth "$TiO_2$-**$Co_9$POM**"). We used multi-component spectroscopic studies to demonstrate that the surface-bound **$Co_9$POM** retains its structural integrity. We extended and used our newly developed electric-field-induced second harmonic generation (EFISH) to identify charge transfer at the electrode/electrolyte interface.

In near future, we plan to extend our findings and elucidate (a) differences and similarities of *microenvironment factors* in solution, electrochemical, and photoelectrochemical conditions, and (b) roles of electronic and stereo-electronic properties of *catalyst microenvironments* in interfacial structure and charge separation and recombination kinetics of hybrid photoanodes (SC)/[POM-WOC], and (c) further validate applicability of the EFISH technique.

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2. Zhao, F.; Xu, Z.; Suo, S.; Lin, L.; Hill, C. L.; Musaev, D. G.; Lian, T. "A contactless *in situ* EFISH method for measuring electrostatic potential profile of semiconductor/electrolyte junctions", *J. Chem. Phys.* **2024**, *161 (9)*, 094703. https://doi.org/10.1063/5.0226128
3. Zhao, F.; Xu, Z.; Suo, S.; Yang, W.; Hill, C. L.; Musaev, D. G.; Lian, T.,Operando Contactless EFISH Study of the Rate-limiting Step of Light-driven Water Oxidation on $TiO_2$ Photoanodes." *in revision*.

# Molecular Engineering of Catalytic Sites in COFs to Accelerate Photocatalytic Water Oxidation

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Sustainable solar fuel production through $H_2O$ oxidation coupled with $CO_2$ or proton reduction requires the rational design of integrated photocatalytic architectures. While numerous configurations have been proposed, most reported systems focus on individual half reactions and rely on sacrificial agents. To ultimately achieve sustainable $CO_2$-to-fuel conversion, it is essential to avoid sacrificial agents and operate the reactions with $H_2O$ oxidation as the counter half-reaction. A key limiting factor in developing such systems has been a lack of methods to enable effective integration of light-harvesting unit, oxidation and reduction catalysts into photocatalytic architecture. Building on our recent success in utilizing covalent organic frameworks (COFs) as effective platforms for $CO_2$ reduction catalysts and their fundamental potential as $H_2O$ oxidation catalysts (WOC), we have been exploring the feasibility of COFs as *bifunctional* photocatalysts capable of simultaneously driving $CO_2$ reduction and $H_2O$ oxidation reactions. In this poster, we will present our recent progress in developing COFs as light driven WOC.

In our prior studies, we found that imine linkage in imine-based COFs play a prominent role in charge transfer (CT) direction, determining whether COFs can act as reduction or oxidation catalysts. As a natural extension of our prior work, herein we designed a structurally analogous COF by replacing BPY (left panel, Fig. 1a) with PDA (right panel, Fig. 1a) to form PDA-COF. With this design, we expect to 1) shorten the CT pathway to promote more efficient charge separation and 2) enhance the catalytic site density through anchoring of $CoCl_2$ WOC via coordination to N atoms in both imine linkage and PDA (Fig. 1a and 1b). We observed significantly enhanced $O_2$ evolution activity in Co-PDA-COF compared to Co-BPY-COF (Fig. 1c), suggesting that modulation of CT pathways and catalytic site density can effectively improve water oxidation efficiency. Inspired by these findings, our next step is to incorporate both WOC and $CO_2$ reduction catalysts to explore the potential of COFs as *bifunctional* photocatalysts.

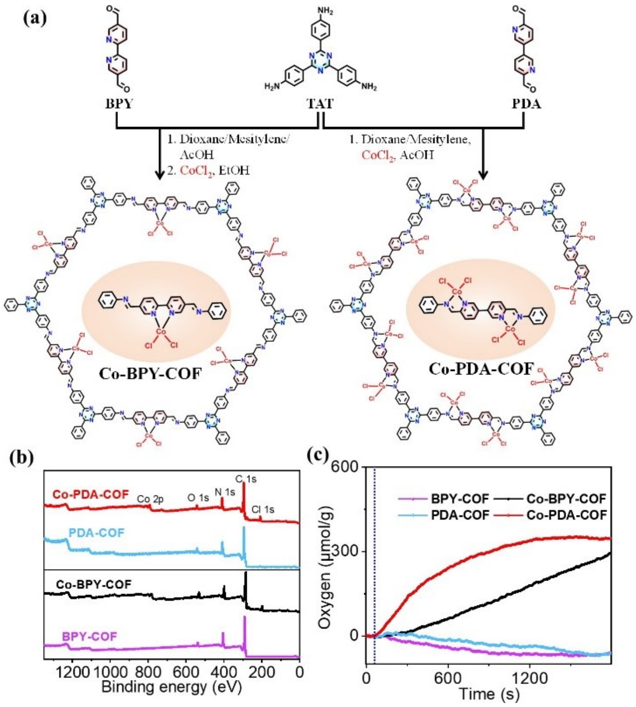

**Figure 1.** (a) Synthetic routes for Co-BPY-COF (left panel) and Co-PDA-COF (right panel). (b) The full range survey XPS spectra of Co-COFs to support the incorporation of Co sites. (c) The time-dependent photocatalytic $O_2$ evolution of Co-COFs.

# Manipulating the Emission and Charge Separation of the Triplet Pairs at Two-Dimensional Interfaces

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*Scope of the Project* In this project, we focus on investigating exciton transfer, transport, and dissociation at organic-inorganic Interfaces, which can play a critical role in converting light into electricity and fuels. Here, we demonstrate the integration of singlet fission molecules with two-dimensional (2D) transition metal dichalcogenides (TMDCs). Strong interfacial coupling facilitates both energy transfer and charge separation of the triplet pair state (**Fig. 1a**).

*Recent Results Brightening of ¹TT.* We strategically design the band alignment and spin interactions between TMDCs and the triplet pair state to enhance radiative recombination from ¹TT. Notably, photoluminescence (PL) from the ¹TT state of a pentacene derivative, 2,3-Dicyano-6,13-bis-(tricyclopentylsilylethynyl) pentacene (DiCN-TCPS-Pc) is amplified by over three orders of magnitude when coupled to monolayer $WS_2$ (**Fig. 1b**). Temperature- and magnetic field-dependent transient absorption and PL measurements reveal that dark excitons in $WS_2$ can efficiently transfer energy to the ¹TT state via a Dexter-like exchange mechanism. These results highlight a pathway to control triplet pair emission at hybrid 2D interfaces.

*Direct Charge Separation of ¹TT.* In DiCN-TCPS-Pc, singlet fission occurs rapidly (~1 ps), generating long-lived ¹TT states. We probe charge separation from ¹TT at the interfaces with $WS_2$ by monitoring the dynamics of the ¹TT excited-state absorption (ESA) band (~550 nm), along with the A exciton bleach and trion signatures of $WS_2$. Selective excitation of DiCN-TCPS-Pc at 690 nm in the $WS_2$ heterostructure produces an additional ~10 ps decay in the ¹TT ESA band, indicative of electron transfer directly from ¹TT state (**Fig. 1c-d**). In contrast, no decay of the ¹TT signal is observed in heterostructures with $WSe_2$, indicating a lack of electron transfer. This is attributed to the higher conduction band minimum (CBM) of $WSe_2$, precluding charge separation.

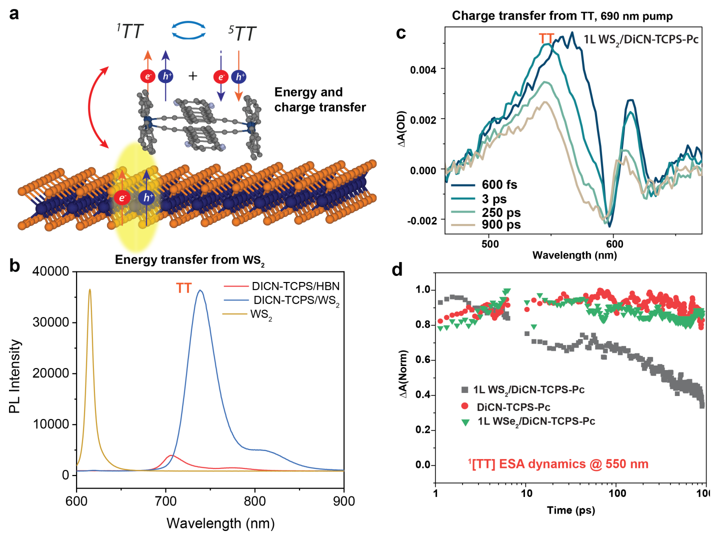

**Figure 1**. (a) Schematic illustration of triplet pair energy and charge transfer at the interface with $WS_2$. DiCN-TCPS-Pc molecules form dimers to prevent dissociation of ¹TT. (b) Emission from ¹TT is amplified by over three orders of magnitude when coupled to monolayer $WS_2$. (c) TA spectra (selective excitation of DiCN-TCPS-Pc at 690 nm) showing the ¹TT excited-state absorption (ESA) band (~550 nm), along with the A exciton bleach and trion signatures of $WS_2$. (d) Coupling to $WS_2$ leads to an additional ~10 ps decay in the ¹TT ESA band, indicative of electron transfer from ¹TT state.

*Future Plans* We will control dynamic processes—including energy transfer, charge separation, and coherent emission—at nanoscale interfaces to harness triplet pair states for advancing solar energy conversion and quantum information technologies.

# Light Harvesting, Energy Transport, and Energy Conversion with Molecular Frameworks

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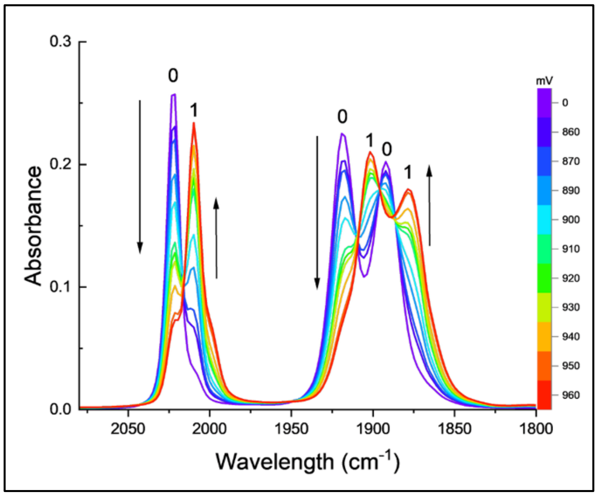
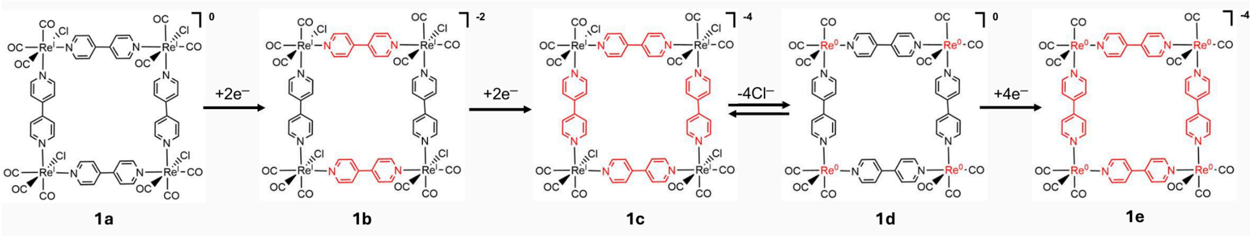
Arrays of molecular chromophores organized as porous crystalline frameworks – either metal-organic frameworks (MOFs) or hydrogen-bonded organic frameworks (HOFs) – can function as light-absorbing antennae for photochemically driving energy-relevant chemical reactions. As outlined below, this poster will touch on three ideas.

First, HOFs featuring 1D channels of ca. 20 Å width, can be photo-excited to create molecular excitons that are mobile enough to visit scores of chromophoric subunits during their brief excited-state lifetimes. When well-defined, catalytic, few-atom, molybdenum-sulfur clusters are installed in the channels, molecular hydrogen can be generated via photolysis of the HOF.

Second, automated layer-by-layer synthesis of chromophoric MOFs as thin films on transparent supports allows for fairly precise control over antenna layer thickness (i.e., ± one or two unit cells) and over catalyst density and siting. These studies reveal that with adequate chromophore-to-chromophore energy transfer, a remarkably small number of catalysts can carry antenna-powered photochemical reactions.

Third, polypyridyl complexes of tricarbonylchlororhenium(I) are known photocatalysts and electrocatalysts for the two-electron reduction of $CO_2$ to CO. With Prof. Lin Chen, we are exploring the potential of tetra-rhenium molecular squares to deliver as many as eight electrons and, when partially reduced, to function as red and near-infrared chromophores. Expanding the pool of electrons could lead to catalytic formation of more complex and useful reduction products. Shown in the accompanying figure are infrared spectroelectrochemical data in the carbonyl stretching region for a representative $Re_4$ square. Notably, squares can be stacked and aligned as porous crystalline solids.





# Advancing interfaces for the solar-driven production of hydrogen ($H_2$) and ammonia ($NH_3$)

K.M.K. Yap[1,2], S-W. Lee[1,2], Swathilakshmi[2], T. Lin[3], A.M. Aleman[1,2],
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J. Young[4], T.D. Deutsch[4], M. Steiner[4], J. Qiu[3], A.C. Nielander[2], T.F. Jaramillo[1,2]

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[3]Department of Chemistry and Biochemistry, San Francisco State University, San Francisco, CA
[4]National Renewable Energy Laboratory, Golden, CO

The development of solar fuels systems requires greater fundamental understanding of interfaces in order improve efficiency, selectivity, and durability. This poster will address efforts along these lines in two related areas, solar-driven hydrogen production and solar-driven ammonia production.

Our recent investigations into photo-electrochemical (PEC) hydrogen production have focused on understanding mechanisms of instability in order to design approaches for improved durability. We have developed several *in-situ* and *operando* methodologies based on inductively coupled plasma – mass spectrometry (ICP-MS), electrochemical mass spectrometry (EC-MS), as well as *in-situ* Raman Spectroscopy, which combined are capable of tracking material changes while quantifying interfacial corrosion with a great degree of sensitivity. We examine a model system consisting of Si/Mo/$MoS_2$, which drives the $H_2$ evolution reaction (Figure 1). We apply these techniques to gain insights into the diurnal durability of such systems, which informs approaches for improved durability.[1] Our research efforts on solar ammonia production have focused on designing interfaces capable of coupling high-performance III-V semiconductor absorbers with the non-aqueous Li-mediated nitrogen reduction (Li-$N_2$R) process.[2]

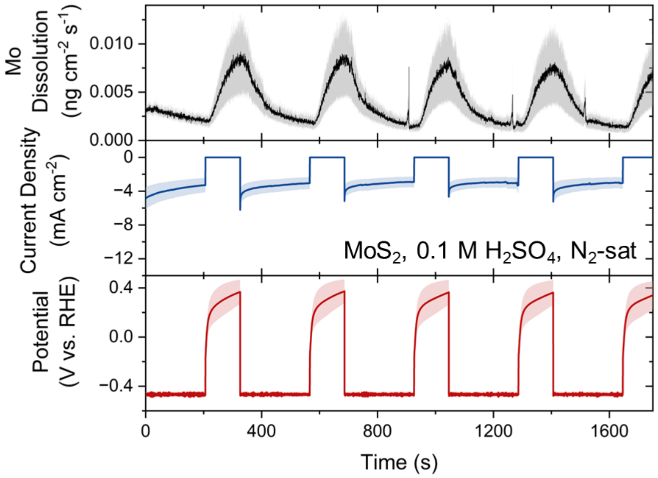

**Figure 1**. Quantitative online electrochemical ICP-MS analysis of a simulated diurnal drive cycle for Si/Mo/$MoS_2$ in $N_2$-saturated 0.1 M $H_2SO_4$ (aq.). $MoS_2$ corrosion is exacerbated during open-circuit conditions (simulating night-time), which informs strategies to improve diurnal durability.

[1] K.M.K. Yap, Swathilakshmi, T. Lin, A.M. Aleman, K. Yan, R.T. Hannagan, A. Mule, C.Y. Wang, S.-W. Lee, J. Zander, J. Qiu, T.F. Jaramillo, and A.C. Nielander, “$MoS_2$ degradation dynamics under simulated diurnal (photo)electrochemical $H_2$ evolution reaction conditions” (2025).

[2] S.Z. Andersen, V. Čolić, S. Yang, J. A. Schwalbe, A.C. Nielander, J. M. McEnaney, K. Enemark-Rasmussen, J. G. Baker, A.R. Singh, B.A. Rohr, M. J. Statt, S.J. Blair, S. Mezzavilla, J. Kibsgaard, P.C.K. Vesborg, M. Cargnello, S.F. Bent, T.F. Jaramillo, I.E.L. Stephens, J.K. Norskov, and I. Chorkendorff, “A rigorous electrochemical ammonia synthesis protocol with quantitative isotope measurements,” *Nature*, 570, 504-508 (2019).

# Mechanisms of Photochemical $N_2$ Reduction

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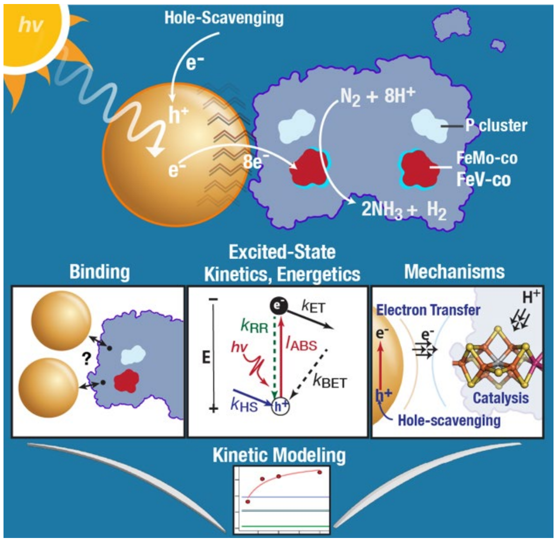

Performing the reduction of dinitrogen ($N_2$) to ammonia ($NH_3$) under ambient conditions is a formidable challenge to catalysis. Although the overall reaction is spontaneous, the high activation energy of the $N_2$ triple bond, 9.8 electron volts (eV), contributes to making $N_2$ reduction to $NH_3$ extremely difficult. Nitrogenases are metalloenzymes that are uniquely able to catalyze reduction of $N_2$ to $NH_3$, and thus are an ideal model for understanding how to activate and reduce $N_2$ without large inputs of energy. Nitrogenases are two-component enzymes comprising an iron (Fe) protein component that functions in electron delivery to the molybdenum-iron (MoFe) protein, which catalyzes $N_2$ reduction. Because the reaction is inherently electron-rich (8 electrons per-$N_2$ reduced), nitrogenase demands a constant high-flux of electrons to maintain turnover. Light-absorbing nanocrystal materials are ideally suited to meeting this demand, being able to capture and convert light to generate electrons of sufficient energy for $N_2$ reduction. We have advanced a system that replaces the Fe protein function of electron delivery with CdS nanocrystals (NC), combining photochemical electron delivery with the catalytic capacity of MoFe protein $N_2$ reduction. When NCs bind to the MoFe protein, the components form complexes that perform light-driven (excited-state) electron delivery and reduction of MoFe protein, resulting in the catalytic reduction of $N_2$ to $NH_3$.

The project objectives include developing knowledge of how the individual components and networks of interrelated reaction steps integrate into a functional light-driven $NH_3$ producing system (Figure). We have developed microscale thermophoresis and competitive binding techniques to understand the NC binding interaction in electron delivery to nitrogenase, revealing a NC size-dependence to binding strength. We developed methods to control and track light-driven electron transfer from NCs to MoFe protein, and the formation of reaction intermediates, using electron paramagnetic resonance (EPR) spectroscopy. Fits of the results to chemical master equations, and construction of kinetic models, have revealed that NCs not only function in electron transfer to MoFe protein, but also can photooxidize the enzyme. To better understand the oxidation process, we have begun to develop numerical modeling and experimental approaches to measure NC hole-scavenging using electrochemistry. Overall, the combination of these approaches is helping to provide a comprehensive understanding of how individual components contribute to the overall mechanism of $N_2$ reduction to ammonia.

# Multilayered Nanoporous Photoanodes of Mixed-Metal Oxides for Solar Water Splitting

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The lack of efficient, stable, and low-cost materials for water oxidation is a 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 solar-to-hydrogen efficiency and durability.

In this period of the project, large single crystals of two of the target oxides were successfully grown by the flux method and melt crystallization at temperatures of 800-1000 °C. Phase purity, elemental purity, and crystal quality were assessed by X-ray diffraction and elemental analysis. Variable-temperature Hall effect measurements are underway to determine carrier type, mobility, and concentration. Studies to establish the dielectric function, surface chemistry, and oxygen evolution reaction (OER) performance of these crystals are planned for the near future.

A general method has been developed to make high-quality nanoporous films of metal oxides by spin coating and calcining molecular inks that contain a porosity-generating sacrificial block copolymer. Phase-pure nanoporous films of $BiFeO_3$, $FeWO_4$, $WO_3$, $Fe_2O_3$, and $TiO_2$ were used to demonstrate the versatility of this approach. Film thickness, particle size, and film porosity are independently tunable by adjusting the ink composition and film processing conditions. The method was extended to produce core-shell nanoporous films featuring buried heterojunctions that can improve charge separation and boost OER efficiency. $WO_3$-$BiVO_4$ core-shell nanoporous film photoanodes show much larger photocurrents for sulfite oxidation compared to single-component nanoporous $BiVO_4$ film photoanodes of the same thickness (Figure 1), demonstrating that the core-shell architecture can overcome the charge transport limitations of visible-bandgap photoanode materials. The poster will summarize the results of extensive ongoing PEC experiments to understand the geometric, morphological, and compositional factors that govern the performance of these core-shell nanoporous film photoanodes in order to guide the fabrication of high-performance photoanodes that employ the one of the three novel shell oxides rather than $BiVO_4$.

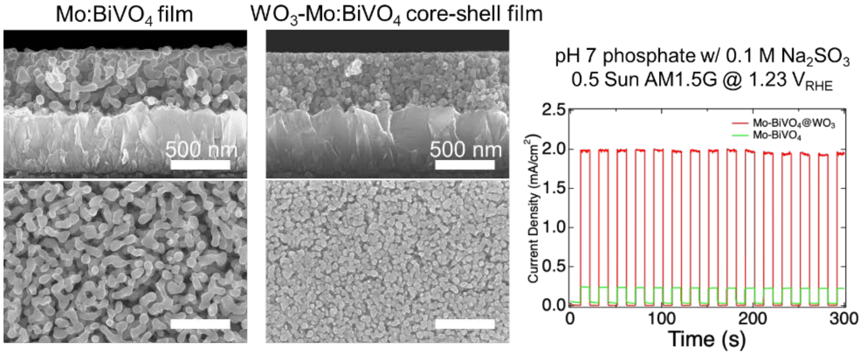

**Figure 1**. Comparative performance of nanoporous $WO_3$-$BiVO_4$ and $BiVO_4$-only photoanodes for sulfite oxidation.

# Investigating Spin-Dependent Photophysics in Mn(IV)-Oxo Photosensitizers: Tuning Photoactivity and Overcoming Barriers Through Intentional Design

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The development of efficient, earth-abundant photosensitizers for solar fuel production hinges on deepening our understanding of excited-state dynamics in first-row transition metal (FRTM) complexes. Herein, we report on our progress in the synthesis, electrochemical investigation, and photophysical characterization of a new class of Lewis acid (LA)-bound non-heme (nH) manganese(IV)-oxo complexes, $[(nH)Mn^{4+}O]^{z+}$-(LA). Literature demonstrates that LA binding and nH ligand architecture influence photoinduced intersystem crossing (ISC) between ligand field states, allowing manipulation of excited-state lifetimes ($\tau$) on the microsecond timescale. Employing steady-state UV-vis spectroscopy, electron paramagnetic resonance (EPR), transient absorption (TA) spectroscopy, and cyclic voltammetry (CV), we're investigating the impact of systematic variation in LA identity and nH ligand frameworks on the ISC rate ($k_{ISC}$) and $\tau$. Specifically, our work focuses on how modulation of the $Mn^{4+}=O$ bond distance, axial and equatorial nH ligand field strength, and dipolar properties impact $k_{ISC}$. Mechanistic insights into photoinduced spin-state selectivity in earth-abundant systems opens avenues for rational design of next-generation, FRTM photosensitizers capable of competing with rare-metal-based benchmarks.

In parallel, this project contributes to transforming the future energy sciences workforce through supporting the first cohort of students in an innovative postbaccalaureate bridge program developed at Metropolitan State University of Denver (MSU Denver). Through strategic partnership with the National Renewable Energy Laboratory (NREL) and local R1 and R2 institutions of higher education, this program combines tailored coursework, scaffolded mentoring structures, competitive compensation, and professional development opportunities with a 1.5-year immersive research experience. Undergraduates, post-baccalaureates, and postdoctoral fellows collaborate within research teams, building technical skills, scientific identity, and community. This model deliberately addresses barriers that limit STEM participation through a pioneering approach beyond that of traditional graduate school pipelines. Students are trained in sophisticated synthetic procedures and instrumentation while actively participating in our ongoing research efforts to synthesize and structurally characterize novel ligands and metal complexes as well as their photo-induced behavior. Ultimately, this integrated effort advances both scientific innovation in photosensitizer and workforce development in the energy sciences.

# Enhancing Durability and Efficiency of III-V Photoelectrodes for Solar Fuels Production

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Photoelectrochemical water-splitting using inorganic semiconductor (SC) photoelectrodes provides a method for generation of $H_2$ fuel from water and sunlight. III-V SC materials can provide high solar-to-fuels energy conversion efficiencies, but are not durable for extended time periods. To maximize the solar conversion efficiency, water-splitting devices generally use corrosive acidic or alkaline electrolytes, so strategies to enhance photoelectrode durability need to be applicable under these electrolyte and operating conditions.

We have shown that 100 nm thick metal oxide coatings deposited by atomic-layer deposition are optically transparent and protect against corrosion while allowing photogenerated carriers to efficiently oxidize water. However, extended durability is limited by defects in the coating. Consequently, we are developing insulating poly(ortho-phenylenediamine) (PoPDA) coatings to plug pinholes in protection layers. We are also studying $TiO_2$-coated microelectrodes to determine the failure mechanisms associated with intrinsic defects that lead to corrosion (Figure 1a).

We have also extended our protection layer studies to III-V photocathodes. First, we have elucidated the electronic band structure at the interface between p-InP and several candidate protection layers ($TiO_2$, $Nb_2O_5$, $HfO_2$, or $Ta_2O_5$). Photoexcited electrons readily pass through the InP/PL interface (Figure 1b) for systems with optimal alignment of the conduction band of the photoelectrode and the cathodic protection layer. As a case study we have also investigated in detail $Nb_2O_5$ as a protection layer for InP photocathodes in acidic electrolytes under hydrogen evolution conditions, to mitigate corrosion either by metal plating or electrode oxidation.

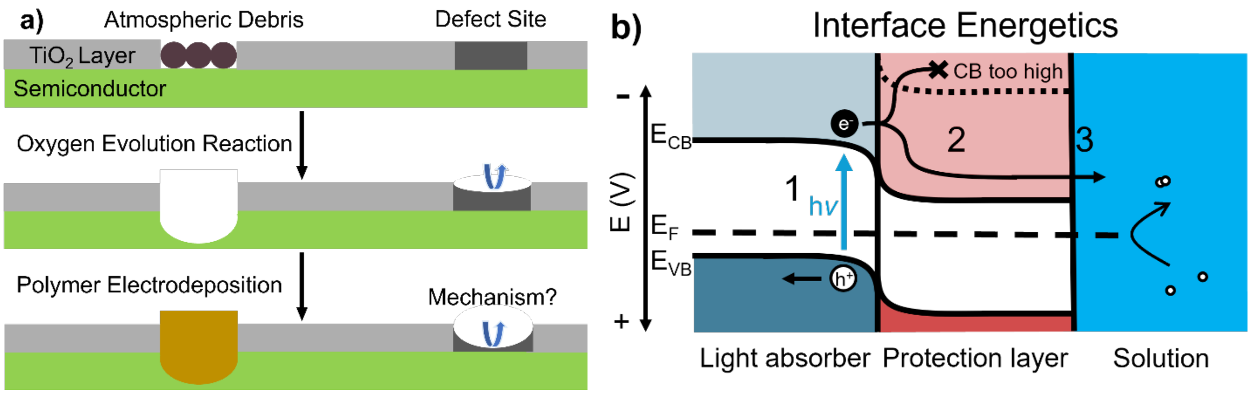

**Figure 1.** (a) Illustration of pinhole formation due to nonconformal deposition or *operando* corrosion at intrinsic defects. The remediation of extrinsic defects and the corrosion mechanism at intrinsic sites are being explored. (b) Energy diagram illustrating the needed conduction band alignment to enable electron flow from the photocathode to the solution. Misalignment can produce an energetic barrier at the interface that prevents conduction.

# Charge Transfer from Electrochemically Controlled Colloidal Semiconductor and Metal Nanoparticles

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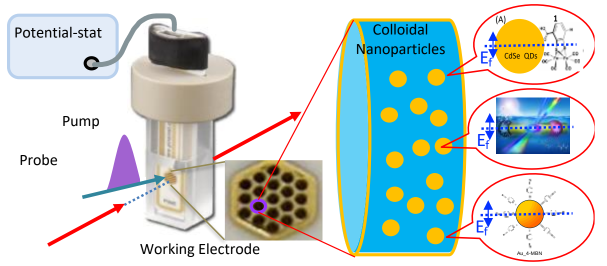

Figure 1. Schematic of in situ time-resolved spectroscopic study of charge separation in colloidal low dimensional semiconductor nano-heterostructures under electrochemical control (Ultrafast visible/IR SEC).

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 photocatalytic systems because elementary charge transfer and catalytic reaction processes 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. However, this comparison is often hindered by a major difference between them: "The Fermi level gap". In bulk electrodes, their Fermi level, one of the most important properties, is known and tuned by connecting them to an external potential-stat, while in NP systems, their Fermi level is set by ill-defined solution redox species and is often unknown and/or difficult to adjustable. 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 1).

In this talk, we will report our recent progress in ultrafast SEC of semiconductor quantum dots and plasmonic nanoparticles. We will first discuss the carrier and exciton dynamics of electrochemically charged NCs in solutions. The electrochemical charging effects in colloidal CdSe/CdS core/shell quantum dots (QDs) are systematically investigated using static SEC 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. At cathodic potentials, 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 due to the spin blockade effect and 316 ± 35 ps due to phonon bottleneck effect. Our study reveals rich effects of charging on QD excited state under nearly native conditions. We have also started preliminary study of plasmonic hot carrier induced adsorbate vibrational dynamics of colloidal 4-mercaptobenzonitril capped Au nanoparticles. We show that upon optical excitation of the Au plasmon band, the adsorbate molecules are excited, as probed by the CN stretching mode. About 50% of the adsorbate vibration excitation shows an instrument response limited rise, indicating hot electron transfer induced adsorbate vibration excitation. 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 selection vibrational mode excitation on plasmonic metals and their possible control by electrochemistry.

# Computational Modeling of Ultrafast Intersystem Crossing Dynamics

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Understanding the interplay between spin and non-adiabatic effects is essential for controlling photochemical processes, particularly in systems where multiple excited-state pathways compete. In this project, we analyze the reaction pathways and transitions among photochemically accessible singlet and triplet excited states in a representative bimetallic complex. Using a combination of time-dependent density functional theory (TDDFT) and multiconfigurational self-consistent field (MCSCF) methods, both incorporating spin–orbit coupling, we characterize the ultrafast dynamics following photoexcitation.

Our computational results indicate that intersystem crossing (ISC) constitutes the primary mechanism during the early stages of photochemical evolution, enabling efficient population transfer between singlet and triplet manifolds. Subsequently, internal conversion among triplet states becomes the dominant relaxation pathway as the system stabilizes into a higher-lying triplet state. Through detailed analysis of spin–vibronic interactions, we reveal how symmetry breaking and vibrational motions modulate spin–orbit coupling matrix elements, thereby activating otherwise forbidden ISC channels.

This work provides mechanistic insight into how tuning the relative strengths of spin–orbit and non-adiabatic couplings can modulate photochemical reactivity, offering design principles for controlling excited-state processes in bimetallic and related systems.

Building on this foundation, future efforts will focus on the development of quadratic and cubic response theories to simulate nonlinear spectroscopies, including pump–pump–probe experiments. These theoretical advancements will enable the direct simulation of complex ultrafast dynamics involving multiple excitation events, further deepening our understanding of excited-state processes at the intersection of spin, nuclear motion, and electronic structure.

# Decoding Semiconductor Voltammetry via a Convolutive Analytical Model and a Machine Learning Algorithm

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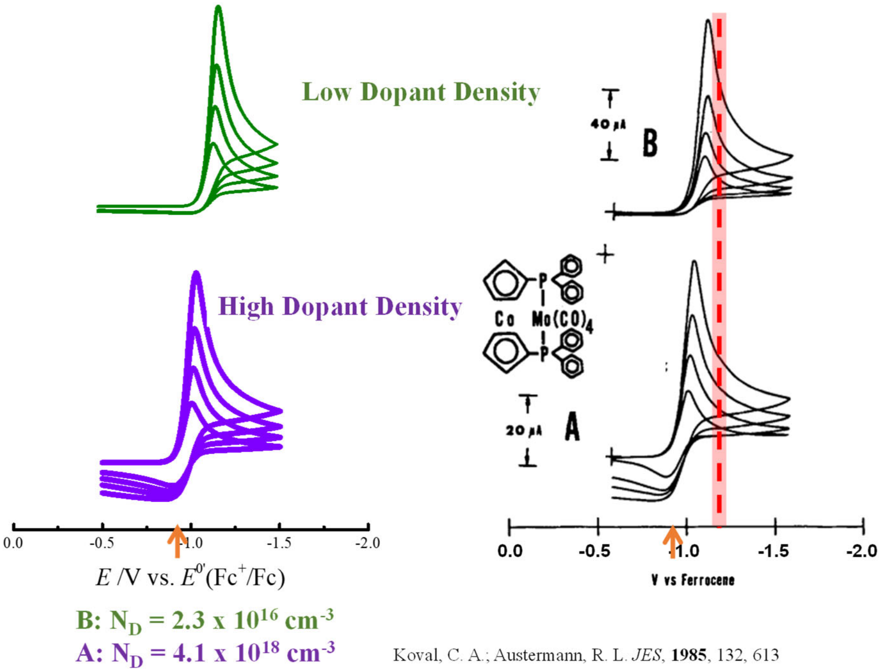

Koval, C. A.; Austermann, R. L. *JES*, **1985**, 132, 613

**Figure 1.** Comparison of (right) experimental voltammograms for n-InP and a cobalt-molybdenum metallocene reported by the Koval group in 1988 and (left) simulated voltammograms generated by the convolutive transform of semiconductor heterogeneous charge-transfer rate constants.

This presentation will describe the use of a convolutive transform to adapt the analytical expressions for the heterogeneous charge-transfer rate constants at semiconductor-liquid contacts developed in the prior project period. This extension of the model allows simulation of voltammograms for freely diffusing redox species to a planar semiconductor macroelectrode. Voltametric responses from this convolutive model will be presented as a function of system parameters of interest (e.g. band edge values, scan rate, standard potential of redox species, surface oxide thickness, dielectric constants of solvent, semiconductor, and surface layer(s)). The utility of this model to describe experimental data will be demonstrated on two different datasets. Voltammetric data with InP electrodes reported by the Koval group (**Figure 1**) and data with Si electrodes collected by our lab will be analyzed. A key finding is that it is possible to determine the semiconductor band edge values from sets of voltammograms with precisions comparable to or better than impedance measurements. The utility of this model to analyze sets of voltametric data with a machine learning algorithm will also be presented. Preliminary data will be presented on a methodology that allows the usage of the convolutive model without requiring a comprehensive understanding of the underlying mathematical framework.

# Dye-Sensitized Semiconductor Photoelectrodes and Z-Schemes for Solar Water Splitting

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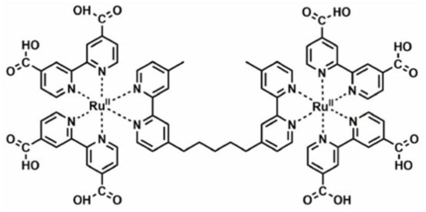
This project seeks to develop efficient colloidal Z-schemes for solar water splitting that exploit the favorable kinetics of light-induced charge separation at the dye-oxide semiconductor interface. In these systems the oxide semiconductor ($TiO_2$ or $SnO_2/TiO_2$) of the dye-sensitized solar cell is replaced by an internally platinized layered niobate that has a more cathodic band-edge potential, enabling a high quantum yield (typically 30-50%) for light-driven hydrogen evolution from EDTA solutions. In the Z-scheme, a reversible redox couple ($I^-/I_3^-$) replaces the sacrificial donor and couples the hydrogen-evolving system to a colloidal oxygen-evolving photocatalyst. Overall water splitting occurs, but new pathways for back electron transfer are introduced that severely compromise the quantum efficiency. In recent experiments we have shown how core-shell and polymer modification inhibit back electron transfer between the layered niobate and $I_3^-$, resulting in monochromatic quantum yields of ~4% for overall water splitting. Our current focus is on measuring the kinetics of each component of the Z-scheme to quantify the effects of microstructure and composition.



We have synthesized and studied new dimeric sensitizers that couple to oxide semiconductors through carboxylate or phosphonate anchoring groups. Interestingly, the carboxylate dimer shows more efficient charge injection and also better stability than the carboxylate-phosphonate heterodimer or the phosphonate dimer in aqueous buffer solutions.

Modification of the dye-sensitized niobate nanosheets with anionic polymers inhibits the adsorption of both $I^-$ and $I_3^-$ ions, and so the balance of forward and back reaction kinetics can be modulated by changing the $I^-/I_3^-$ concentration ratio. However, high concentrations of $I^-$ result in hole scavenging at the oxygen-evolving photocatalyst. For this reason we are modifying that photocatalyst with quaternary ammonium polymers such that selectively adsorb $I_3^-$. Our earlier Z-scheme experiments utilized platinized colloidal $WO_3$ as the photocatalyst for water oxidation. Flash photolysis experiments with colloidal $WO_3$ show inefficient electron scavenging by $I_3^-$, and the Pt co-catalyst is also problematic because it catalyzes the dark reaction between $H_2$ and $O_2$. We are now experimenting with monoclinic $BiVO_4$, which can be made in the form of micron-size colloidal particles or thin nanosheets and modified by a Co-POM co-catalyst for oxygen evolution. With 532 nm excitation, colloidal $BiVO_4$ shows rapid hole trapping and a conduction band electron absorbance that decays on the microsecond timescale. These photogenerated conduction band electrons are efficiently scavenged by $I_3^-$. The synthesis of $BiVO_4$ as thin nanosheets offers the interesting possibility of layering the hydrogen- and oxygen-evolving nanosheets by colloidal assembly to achieve vectorial electron transfer and a more efficient integrated Z-scheme.

# Characterizing Ultrafast Electron Transfer and Intersystem Crossing in Dimeric Pt(II) Complexes by Time-Resolved Wide-Angle X-ray Scattering

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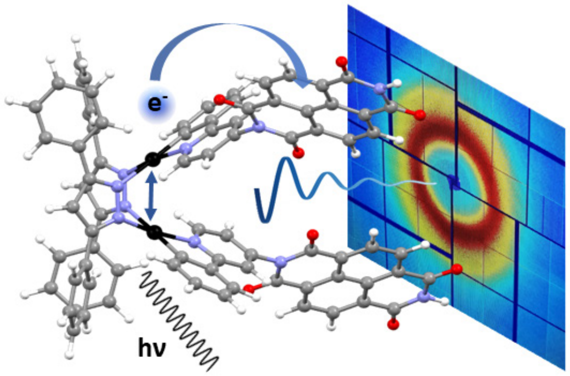
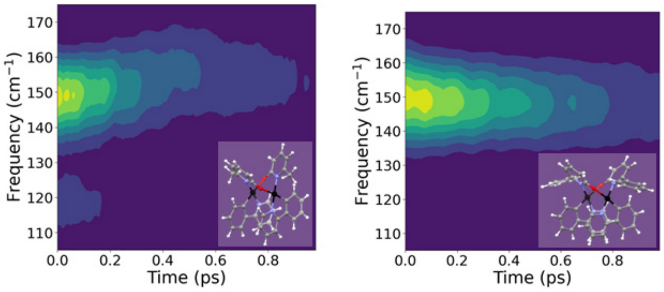
Charge transfer states in transition metal complexes are instrumental in the conversion of solar energy to charge or solar fuels in photosynthetic systems and are often accompanied by bond formation/breaking processes, affecting excited-state energies and ultrafast dynamics. Pt dimer complexes are useful 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 Pt-Pt distance has been identified as a key reaction coordinate in intersystem crossing (ISC) and photoinduced electron transfer (PET), but ultrafast optical spectroscopy lacks the atomic sensitivity to characterize the structural evolution in the Pt dimer MMLCT states. Using time-resolved wide-angle X-ray scattering (TR-WAXS) at an X-ray free electron laser, we quantify the structural evolution in the Pt dimer MMLCT state to understand the interplay between electronic and atomic motions. Excited-state dynamics are strongly correlated to the ground-state Pt-Pt distance, which depends on the organic linker used to bridge the two Pt centers. Both methylpyridine and phenylpyridine-bridged Pt dimers exhibit mostly impulsive (< 100 fs) Pt-Pt contraction with similar amplitudes. While both dimers exhibit coherent vibrational wavepackets (CVWPs) encoded in the Pt-Pt contraction, the time-dependent evolution of the CVWPs differs between the dimers. We demonstrate that the CVWPs observed here reflect the different trajectories across the excited-state potential energy surfaces, specifically the rapid, vibronic coupling-enhanced ISC in the phenylpyridine-bridged complexes that is absent in the methylpyridine-bridged dimers. For a pyrazolate-bridged dimer, we observe a slow (100s of femtoseconds) Pt-Pt contraction. Importantly, this non-impulsive contraction is slower than PET to NDI. PET from a "non-contracted" MMLCT state has a higher driving force, which can affect the kinetics of electron transfer according to the Marcus equation. These studies are paramount towards understanding how to tune the reaction coordinate to control relevant photochemical processes.





# Molecularly Defined Multi-Metal Clusters for Solar Energy Conversion

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The goal of this program is to realize the potential of well-defined molecular-scale metal-containing clusters in the context of harvesting solar energy and light-initiated catalysis for fuels generation, Figure 1. We synthesized and characterized discrete atom-number metal-chalcogenide clusters of well-defined size and structure to tune visible light absorption, catalytic behavior, and environmental stability. Guided by computation, we pursue clusters whose structure may be tuned by the identity of the metal centers, bridging anion, capping ligands, hetero-metal centers, and overall cluster size.

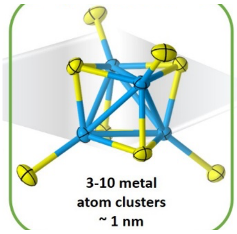

Figure 1. Molecularly-defined clusters are addressable by computation.

First, we have expanded upon a new approach to discrete-atom-number metal chalcogenide cluster synthesis, via vapor phase methods related to atomic layer deposition (ALD). ALD *within* a polymer thin film, in a process called sequential infiltration synthesis (SIS), may seed inorganic deposition in a 3D array of few-atom metal-containing clusters. The SIS process allows the precise synthesis of "magic-size" clusters in polymethylmethacrylate (PMMA) with sharp UV absorption features consistent with $In_6S_6(CH_3)_6$. Most recently, we have demonstrated the rapid synthesis of 3D-arrays of visible light absorbing discrete $Cd_xS_y$ clusters in poly(4-vinylpyridine) (P4VP) thin films. Evidence for few-atom cadmium sulfide clusters include dramatically blue-shifted optical absorption and a lack of pair correlations beyond 7 Å. Simulated $Cd_4S_4$ core cubane type clusters with heterogeneous capping ligands are most consistent with combined experimental and computational structure studies. Future studies include photophysical and solar fuel-producing studies of metal sulfide clusters embedded within the polymer thin film.

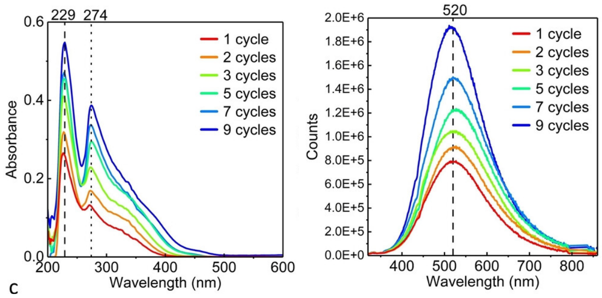

Figure 2. UV-Vis absorbance and photoluminescence spectra reveal cycle-independent cluster growth.

Next, in the interest of expanding metal-chalcogenide cluster functionality to include redox-activity, we have developed a stepwise synthesis to access $Co_6Se_8(PR_3)_6$ clusters with precisely functionalized ligands. Optical and X-ray absorption spectra of the clusters show that ligand substitution has a negligible effect on the cluster electronic structure. However, electrochemical analysis of the functionalized clusters shows three robust oxidation couples that are sensitive to ligand substitution, spanning ~600 mV. This work provides the foundation for more elaborate cluster functionalization, including linking to photocatalytic molecular modules and electrode interfaces. Ground state and time-resolved characterization tools will be used to further investigate the role of localized electronic states that result from metal-ligand and metal-metal interactions.

# A Programmable, Non-Equilibrium Electrified Ammonia Synthesis for Efficient Hydrogen Storage

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Our team aims to significantly advance our understanding of non-equilibrium chemical kinetics of ammonia ($NH_3$) synthesis from nitrogen ($N_2$) and hydrogen ($H_2$), with the ultimate goal of developing a highly efficient method of synthesizing $NH_3$ for effective storage and transport of $H_2$ (Fig. 1). This innovative technique is based on an electrified $NH_3$ synthesis process that utilizes pulsed heating and quenching (PHQ). Our most recent achievements include: (1) synthesis of a high performance FeCr alloy after screening tens of different Fe-based bimetallic catalysts, (2) development of a $LiNO_3$-based molten salt membrane reactor that selectively removes ammonia during reaction, (3) design of a one-dimensional nonequilibrium catalytic reactor with pulsed heating to investigate ammonia synthesis kinetics on iron catalysts, (4) completion of DFT-based calculations of elementary reaction energetics and barriers on Fe and doped Cu surfaces, providing detailed thermodynamic and kinetic insights, and (5) production of high-level potential energy surface mappings and first-principles rate predictions for key $NH_x$ and $N_2H_y$ reactions in the gas phase, improving understanding of ammonia pyrolysis and oxidation mechanisms. We now focus on further refinement of bimetallic catalysts, expansion of time-resolved spectroscopic studies and advanced diagnostics, while leveraging quantum mechanical and multi-scale modeling to bridge atomic-scale insights with macro-scale process optimization, and finally, pilot-scale demonstration in collaboration with industry partners, to validate feasibility and scalability of our approach.

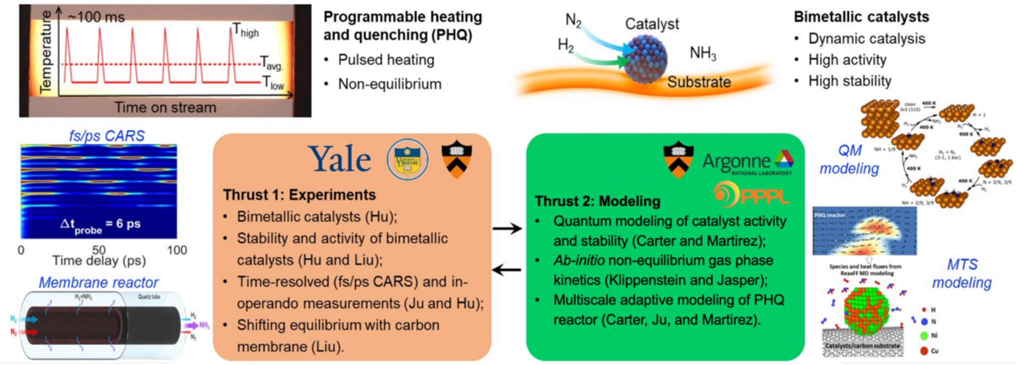

**Fig. 1** Overview of the research for the PHQ-based non-equilibrium $NH_3$ synthesis.

# Building from Molecular Catalysts to Multimetallic Assemblies: The Effects of Charge Delocalization and Intermolecular Electrostatics on Electrocatalytic Reactions

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Our work focuses on determining how the interrelated effects of charge delocalization, electronic coupling, and intramolecular electrostatics influence catalytic activity and selectivity from discrete, molecular systems to extended multidimensional catalyst architectures. We have adopted a bottom-up approach to study these effects as we build in structural complexity: from simple molecular catalysts to multimetallic assemblies, and finally towards macromolecular extended structures. In previous studies, we have studied how charge delocalization and intramolecular electrostatics influence $CO_2R$ activity and reaction selectivity by molecular catalysts, and how these effects can be used to break linear free energy scaling relationships.[1] In more recent work, we have prepared regioisomers of cobalt complexes with redox-active pyridyldiimine ligands substituted with cationic pyridinium moieties *ortho*-, *para*-, and *meta*- with respect to the rest of the Co site to determine whether electrostatic substituent effects in this class of complexes are best described as through-space electric field effects, as often assumed, or through-bond inductive effects (Figure 1a). I will also discuss some of our recent work exploring the systematic modification of the structure of multimetallic assemblies to understand the effect of electrostatic interactions and charge delocalization on per-site activity $CO_2R$ activity by bimetallic Co-Co, Co-Zn, and trimetallic Co complexes (Figure 1b). Finally, I will discuss our work successfully incorporating Co-based catalyst into larger, soluble 1D coordination polymers that show enhanced activity for the electrochemical reduction of $CO_2$ to CO (Figure 1c). We are now working to incorporate these polymeric species into hydrogels to adhere them to the surface while maintaining effective delivery of $CO_2$ and protons for effective $CO_2R$.

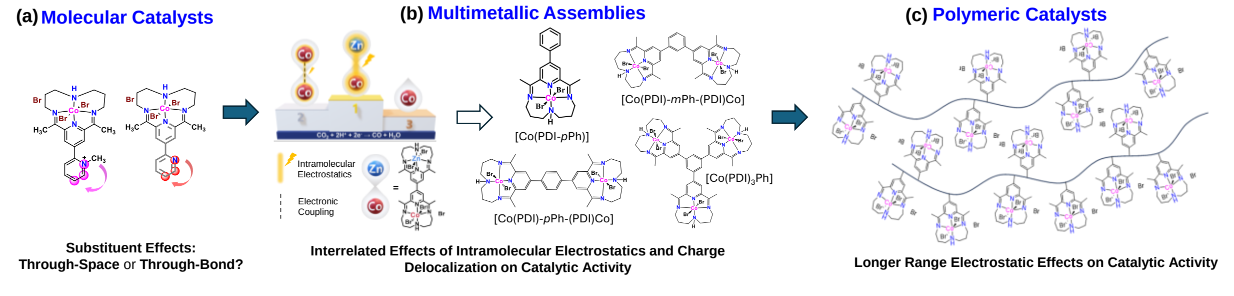

**Figure 1.** We have used a bottom-up synthesis strategy to explore how intermolecular electrostatics and charge delocalization influence catalytic activity for the $CO_2$ reduction reaction as we move from (a) molecular catalysts to (b) multimetallic assemblies, and finally to (c) extended polymeric systems.

# Probing the Reaction Coordinate for Ligand Field-state Interconversion Dynamics

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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 question of scalability and the limited potential of traditional second- and third-row chromophores to fill this void due to their elemental scarcity. A key scientific issue concerns the rapid deactivation of charge-transfer states to lower-lying, metal-centered ligand-field states, presenting distinct challenges for the development of the use of these earth-abundant analogs for a range of potential applications. Our efforts are directed at obtaining a fundamental understanding of the nature and origin(s) of these dynamics and the properties of the excited states involved through a confluence of synthetic chemistry, a range of steady-state and time-resolved spectroscopies – particularly on ultrafast time scales – and to use that knowledge toward the realization of approaches that mitigate and/or circumvent these challenges.

The presentation will highlight two of the research threads currently being pursued. The first focuses on spin-state interconversion in a Fe(II)-based polypyridyl complex that was synthetically tailored to operate in the so-called "spin-crossover" regime. This approach allowed the free energy change associated with high-spin to low-spin conversion to be determined using variable-temperature solution-phase magnetic susceptibility, thereby affording values for $\Delta G_0$ as a function of temperature from an independent measurement. The photo-induced non-radiative decay dynamics acquired for the chromophore could then be fit to semi-classical Marcus theory to yield analytically precise values for the reorganization energy ($\lambda$) and the electronic coupling between the two states ($H_{ab}$). The results we obtained call into question the validity of current formulations that are widely used for describing excited-state dynamics in this entire class of compounds.

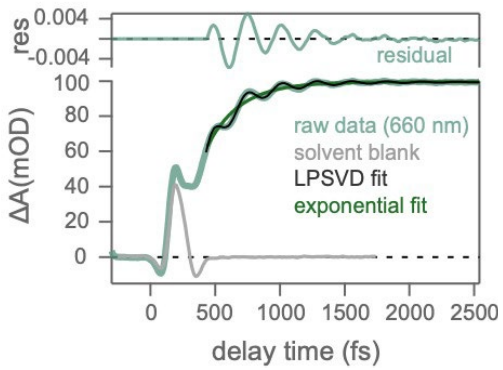

***Figure 1.*** *Ultrafast time-resolved absorption data at 660 nm for* $[Co(pyrro\text{-}bpy)_3]^{3+}$ *(where pyrro-bpy is 4,4'-di-pyrrolidine-2,2'-bipyridine) in* $CH_3CN$ *solution following ca. 45 fs excitation into the lowest energy* ${}^1A_1 \rightarrow {}^1T_1$ *ligand-field absorption at 480 nm.*

The second project concerns the use of femtosecond time-resolved absorption spectroscopy on Co(III)-based complexes to leverage excited-state vibronic coherences for the identification of degree(s) of freedom that are coupled to ultrafast intersystem crossing dynamics (Figure 1). The data reveal that, following ${}^1A_1 \rightarrow {}^1T_1$ excitation, intersystem crossing to the lowest energy excited state of the compound (${}^3T_1$) is driven by symmetry-breaking, low-frequency torsional degree(s) of freedom of the molecule (as opposed to a metal-ligand Jahn-Teller mode that presents as the dominant feature in the experimental data). The implications of this finding as it relates to the prospect of inducing reactivity from excited states other than the lowest energy excited state of the system will be presented.

# The Impact of Electric Fields on Electron Transfer at Metal Oxide-Electrolyte Interfaces

Quentin Loague, Hayden Mann, Matthew Goodwin and Gerald J. Meyer

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This impact of electric fields on light driven interfacial electron transfer reactions is of direct relevance to the mission of the DOE Basic Energy Sciences [1,2]. In this research two key objectives are actively being pursued. The first objective involves quantifying the impact of electric fields on the absorption spectra of transition metal complexes. A striking observation in these electroabsorption spectra are resolved features in the low energy region where $S_0 \rightarrow T_1$ transitions are expected and indeed observed with third row transition metals. The electroabsorption spectra appear to amplify transition(s) in this region and the most recent studies revealed a surprising sensitivity to the identity of the diimine ligands [2]. 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 quite small for the iron complexes. Ongoing work seeks to more accurately quantify the polarizability changes with a new higher-order electroabsorption spectrometer and to quantify excited state relaxation with a newly designed electrophotoluminescence apparatus. Preliminary data on a ligand-to metal charge transfer Zr(IV) complex will be presented.

The second key objective involves quantification of interfacial electron transfer kinetic parameters within the electric double layer. Analysis of kinetic data measured as a function of the driving force allows determination of the fundamental electron transfer parameters necessary for predictive models. In collaboration with the Galoppini group, three rigid-rod sensitizers based on phenylene ethynylene bridges were anchored to conductive tin-doped indium oxide (ITO), Figure 1. Both excited state injection and charge recombination kinetics were quantified as a function of the thermodynamic driving force, $-\Delta G^o$. With the assumption that the reorganization energy, $\lambda$, and the electronic coupling matrix element, $H_{ab}$, are applied potential independent, estimates of $H_{ab}$ and $\lambda$ were extracted [1]. Ongoing studies are focused on the impact of temperature on the bridge and electron transfer.

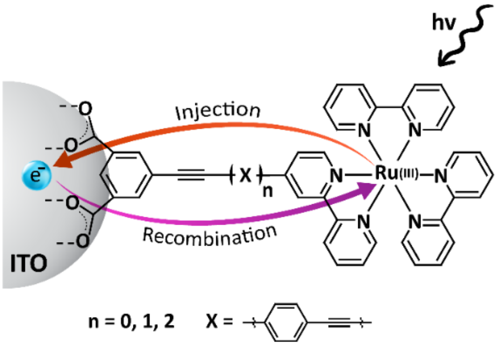

**Figure 1.** Excited state injection and charge recombination within the ITO electric double layer utilizing rigid-rod complexes that bear 0, 1, or 2 phenylene ethynylene units synthesized in the Galoppini research group.

## DOE Solar Photochemistry Sponsored Publications 2024

1. **Structural Gating Enhances Long-Distance Light Driven Interfacial Electron Transfer.** Loague, Q.; Heidari, M.; Mann, H.; Danilov, E.; Castellano, F.N.; Galoppini, E.; Meyer, G.J. *ACS Central Science* **2024**, *11*, 2132-2144.
2. **Impact of Diimine Ligands 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.

# Tuning Optoelectronic Properties of Transition Metal Sulfide Nanomaterials

Debjit Ghoshal,[1] Logan M. Wilder,[1] Taylor J. Aubry, [1] Carter S. Gerke, [2] Goutam Paul,[1] Srikrishna Sagar, [1] O. Quinn Carvalho, [1] Jonathan R. Thurston,[3] Michael F. Toney,[4] Michelle A. Smeaton, [1] Lauren Hurley,[5] Cole Shank,[1] Nina Hooper,[1] Jeiwan Tan,[1] Kory Burns,[6] Andrew J. Ferguson,[1] Ann L. Greenaway, Jeffrey L. Blackburn, [1] Jao van de Lagemaat, [1] Elisa M. Miller[1]

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The research in my group focuses on tuning optoelectronic properties of 2D transition metal dichalcogenides (TMDCs) towards various applications, such as microelectronics, sensors, and energy conversion processes. The first research project highlights a breakthrough in precision doping of 2D monolayers of $MoS_2$. 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 $MoS_2$. The mechanism involves the oxide layer trapping photoexcited holes, leaving long-lived electrons to drive surface reactions at sulfur vacancies, leading to stable dedoping (Figure 1). The stability of this process, which withstands high temperatures and vacuum conditions, demonstrates suitability for commercial semiconductor fabrication. Kelvin probe force microscopy (KPFM) measurements confirm shifts in the Fermi level during dedoping, while photoluminescence (PL) analysis reveals enhancements resulting from illumination. These techniques open the door to wafer-scale, multi-logic devices that seamlessly integrate TMDCs into practical applications. Next steps include tuning the underlying oxide for further mechanistic control.

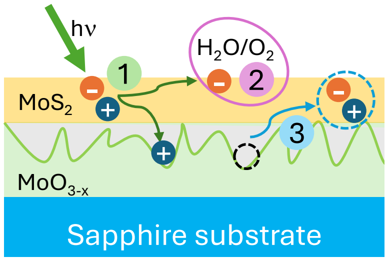

*Figure 1. Schematic mechanism of photo-dedoping. The oxide layer traps photoexcited holes upon illumination (1), leaving behind long-lived electrons that enable passivation reactions with ambient air molecules at S vacancies (2), and the trapped holes slowly recombine with electrons (3).*

My research also focuses on using 2D materials for energy conversion. The electrochemical nitrate reduction reaction ($NO_3$RR) presents a promising route to convert ammonia ($NH_3$) from nitrate for fuel and fertilizer applications. This study investigates a polycrystalline vanadium sulfide ($VS_X$) catalyst, derived from annealed solvothermally grown $VS_2$, which exhibits exceptional activity (2.3 ± 0.6 mg·cm–2·h–1 @ –0.92 V vs RHE) and Faradaic efficiency (69 ± 6% @ –0.69 V vs RHE) for $NO_3$RR in a neutral pH electrolyte. Grand-canonical density functional theory (GC-DFT) simulations identify sulfur vacancies in $VS_2$ as key active sites for $NO_3^-$ adsorption and $NH_4^+$ production, where $NO_3^-$ outcompetes $H^+$ for adsorption. The GC-DFT shows multiple favorable reaction mechanisms at undercoordinated V sites. This work highlights the role of material engineering in enhancing $NO_3$RR activity and provides insights into the mechanism and active site characterization for ammonia synthesis using vanadium sulfides. With this understanding, we will next explore how coupling of $VS_X$ with $MoS_2$ or carbon nanotubes influences the photoelectrochemical reaction mechanism for $NH_3$ generation.

# Redox Potentials of Conjugated Chains

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Brookhaven National Laboratory
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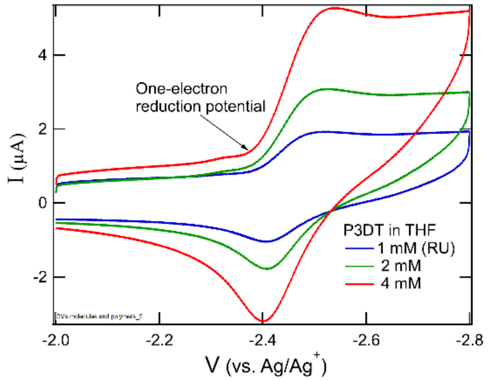
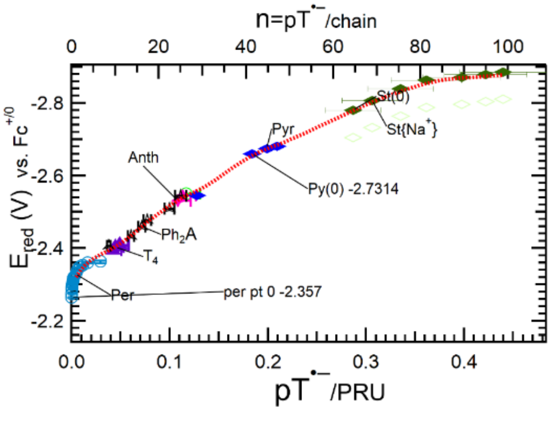
Charge transfer in conjugated polymers is the basis of organic photovoltaics (OPV) so knowledge of energies for adding a hole or electron, the "HOMO" and "LUMO" energies, is essential. Researchers measure "HOMO" and "LUMO" energies in almost every new polymer considered for photovoltaic or electrooptical applications by cyclic voltammetry (CV), differential pulse voltammetry (DPP) or and related electrochemical methods. For reversible reduction or oxidation of small molecules CV gives peaks, which are at or near the one-electron oxidation or reduction potentials. But for conjugated polymers the peaks are indistinct or absent as seen in CV's at left for reduction of poly(3-decylthiophene-2,5-diyl) (P3DT) with an average length n=225 thiophene repeat units (RU). Work from some laboratories estimate HOMO and LOMO levels not from peaks but from onsets as suggested in Figure 1. A label on the Figure reports the one-electron reduction potential, $E^{0'}(P3DT^{0/-1})$ determined in this work.



This poster describes experiments to learn simultaneously the number of charges injected into a polymer chain and the potential for injecting each charge using chemical reductions in redox titrations that inject electrons into P3DT from titrants that are radical anions of aromatic molecules, D, having known one-electron reduction potentials, $E^0$. At each stage of the titration the redox potential is determined by $E^0$ of these titrants and measured concentrations of D and $D^{\bullet-}$ using the Nernst equation, written here as eq 1, for the example of perylene$^{\bullet-}$ (Per$^{\bullet-}$) as a titrant.

$$E = E^{\circ}(Per) + \frac{RT}{F} ln\left(\frac{[Per^{\bullet-}]}{[Per\ ]}\right) \qquad (1)$$

This paper reports experiments that determine precise one-electron reduction potentials for P3DT as an example polymer and find that the broad and ill-defined peaks bear little relation to the one-electron reduction potential, which occurs close to the onset of the CV wave. Using a series of electron donors the figure at right reports that over a range of ~700 mV 95 electrons are injected per each ~225 RU P3DT molecule, squeezing each charge to occupy ~2 RU, raising the question whether conjugated chains can store large numbers of charges. The results also confirm that the one-electron redox potential is near the onset of the CV wave and lets us understand why.



# High-Resolution Photo-SECM Studies of 2D Photocatalysts

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This project is aimed at using nanoelectrochemical techniques for nanoscale characterization of activity and heterogeneity of photocatalysts. We mapped reactivity and charge separation in two-dimensional $MoS_2$ photocatalysts by different modes of photo-scanning electrochemical microscopy (photo-SECM) and demonstrated an extremely high imaging resolution (about 1-2 nm) in the tunneling mode.[1] In Fig. 1B,C, a nanotip was brought within the tunneling distance from two overlapping $MoS_2$ triangles (produced in Elisa Miller's lab at NREL) and scanned laterally above them to obtain a tunneling photo-SECM image. The source of the tip current was photoelectrocatalytic HER at the illuminated $MoS_2$ surface. This technique is sufficiently sensitive to differentiate between a single layer $MoS_2$ triangle and a bilayer based on the differences in the lateral charge transfer rate.

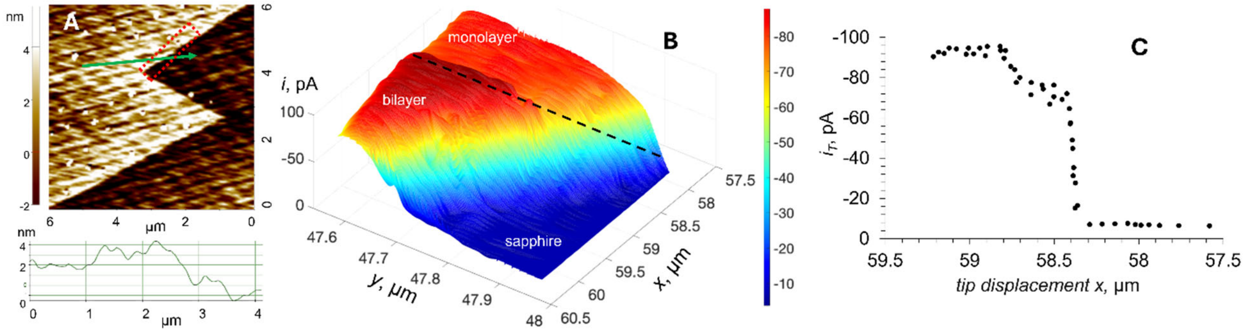

**Fig. 1.** AFM (A) and tunneling photo-SECM (B) images of two partially overlapping $MoS_2$ monolayer triangles. (A) The dotted rectangle in A shows approximately the area mapped by photo-SECM, and the green arrow indicates the scan direction in the corresponding cross section. (B) SECM image obtained under illumination in 1 mM $HClO_4$ solution in 0.1M KCl with a 60 nm Pt tip. $E_T$ = -0.7 V vs Ag/AgCl. (C) Lateral line scan along the dashed line in B.

In collaboration with the Fan group (Dalian Institute of Chemical Physics) we combined photo-SECM with spatially resolved surface photovoltage (SPV) techniques based on Kelvin probe force microscopy to obtain the first evidence of charge separation at the semiconductor/insulator interface ($MoS_2$ triangles on $SiO_2$ support).[2] The photogenerated holes migrated to the $SiO_2$ surface and travelled laterally over distances exceeding 2 µm, while electrons remained localized within a few-layer thick $MoS_2$ triangle. These experiments showed that an insulating substrate can effectively facilitate separation of electrons and holes in semiconductors.

In the future, we will use amperometric and potentiometric tunneling modes of photo-SECM for nanoscale characterization of charge-transfer processes in semiconductor/co-catalyst systems.

1. T. Bo, D. Ghoshal, L. M. Wilder, E. M. Miller and M. V. Mirkin, High-Resolution Mapping of Photocatalytic Activity by Diffusion-Based and Tunneling Modes of Photo-Scanning Electrochemical Microscopy. *ACS Nano*, **2025**, *19*, 3490−3499.
2. Z. Wang, Q. Huang, C. Ni, T. Bo, F. Fan, and M. V. Mirkin, Photoelectrochemical Imaging of Charge Separation Between $MoS_2$ Triangles and Insulating $SiO_2$ Support. *J. Am. Chem. Soc.* **2025**, *DOI:10.1021/jacs.5c02136.*

# Designing Proton Wires Based on Multiple Proton Coupled Electron Transfer

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Inspired by the proton coupled electron transfer (PCET) process involving the $\text{Tyr}_Z$-His190 pair of photosystem II, a polybenzimidazole phenol system has been used to illustrate E*n*PT processes involving one-electron oxidation of the phenol (E) accompanied by translocation of *n* number of protons (*n*PT) along the attached polybenzimidazole wires. These processes are called multi-proton coupled electron transfer processes (MPCET).[1] **Figure 1** illustrates a system designed to undergo an E5PT process (red arrows show proton translocations). The substitution of the benzimidazole by perfluorobutyl groups ($C_4F_9$) is used to increase the solubility and the phenol's redox potential. For context, in a system designed to undergo an E3PT process, the substitution by of one $C_4F_9$ group increases the MPCET potential by 50 mV. In a related system where the terminal proton acceptor (TPA) contains two fluorine atoms (**Figure 2**), the MPCET potential is further increased by 90 mV. In this example, infrared spectrochemistry (IRSEC) clearly shows the protonation of the imine TPA upon electrochemical oxidation of the phenol via monitoring the intensity of the iminium band at 1665 cm$^{-1}$. The driving force for the hypothetical intermediate steps of the MPCET process were evaluated theoretically to quantify the effects of $C_4F_9$ substitution.[1] The steps involving $C_4F_9$ substituted benzimidazole are thermodynamically neutral, yet for unsubstituted systems, each step of the MPCET process has a driving force >100 mV. Regardless of a lack of driving force for intermediate steps, even when substituting $C_4F_9$ groups in adjacent benzimidazoles, the MPCET process can be experimentally verified if the H-bonded network is intact, and an overall thermodynamically downhill process is achieved by the judicious choice of the TPA. Recently, we have been experimenting with PCET in protein environments.[2] Constructs consisting of a four-helix bundle enclosing a Mn-porphyrin with a covalently attached BIP docked to a high-potential bacterial reaction center (BRC) have been assembled. Exciting the BRC reversibly oxidizes Mn(II)-Por to Mn(III)-Por; in turn, it oxidizes the BIP, which undergoes a PCET process detected by the decreased pH in the bulk. This is a promising result for developing hybrid artificial photosynthetic constructs in which energy-conserving processes could be reengineered and optimized.

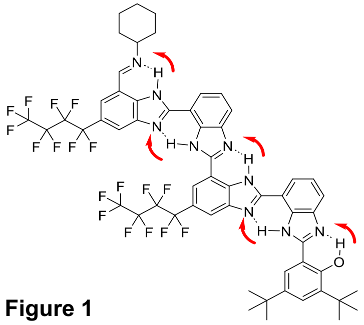
Figure 1

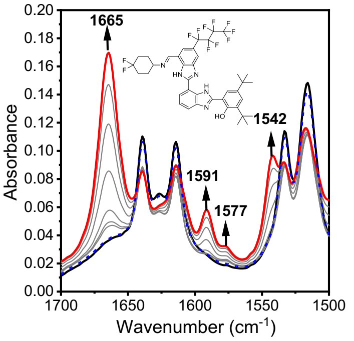

Figure 2

(1) Odella, E.; Wadsworth, B. L.; Mora, S. J.; Goings, J. J.; Huynh, M. T.; Gust, D.; Moore, T. A.; Moore, G. F.; Hammes-Schiffer, S.; Moore, A. L. Proton-Coupled Electron Transfer Drives Long-Range Proton Translocation in Bioinspired Systems. *J. Am. Chem. Soc.* **2019**, *141* (36), 14057-14061. DOI: 10.1021/jacs.9b06978.

(2) Williams, J. C.; Faillace, M. S.; Gonzalez, E. J.; Dominguez, R. E.; Knappenberger, K.; Heredia, D. A.; Moore, T. A.; Moore, A. L.; Allen, J. P. Mn-porphyrins in a Four-Helix Bundle Participate in Ohoto-Induced Electron Transfer with a Bacterial Reaction Center. *Photosynth. Res.* **2024**, *162* (2-3), 1-14. DOI: 10.1007/s11120-023-01051-9.

# Using Ligand Design and Photon Flux to Direct Multi-electron, Multi-substrate Reaction Pathways at Interfaces

D. Nishiori, L. K. Hensleigh, E. Ikediuwa, E. A. Reyes Cruz, N. Armada, N. P. Nguyen, I. Peterson, and G. F. Moore

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This work targets an improved understanding of the basic energy science governing photo-driven, multi-electron, multi-proton chemical transformations via molecular-level research in the condensed phase and at interfaces. Herein, we report applications of extended electronic conjugation as an approach for building *"good"* fuel-forming catalysts that exhibit low overpotential and high catalytic turnover frequency (see **Figure 1**).[1] These constructs thus break the traditional trade-off between these two metrics. We also extend concepts and related analysis techniques for the benchmarking of fuel-forming catalysts to studies involving photoelectrosynthetic assemblies, where, in addition to electrons and chemical substrates, photons are required as reagents (see **Figure 2**).[2,3] Our results show how light flux can be used to control local pH at light-absorbing semiconductor interfaces and steer reaction pathways. Discoveries in this area include how buffers can serve as alternate proton donors in photoelectrochemical reactions and outcompete water as a reactant. In unpublished and ongoing work, we also explore how design considerations for preparing homogeneous catalysts—including applications of extended electronic conjugation—can be imbued in heterogeneous materials.

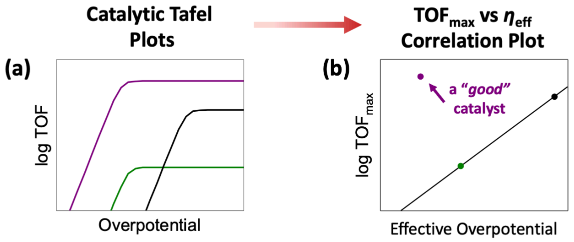

**Figure 1.** Examples of (a) catalytic Tafel plots and (b) a plot correlating the associated maximum turnover frequencies (TOF$_{max}$) and effective overpotentials ($\eta_{eff}$) required to achieve half the maximum turnover. A "*good"* catalyst appears off the correlation line, showing a traditional scaling relationship.

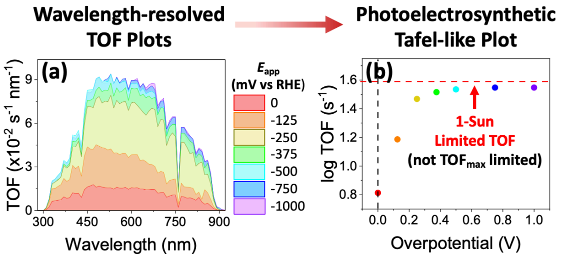

**Figure 2.** Examples of (a) wavelength-resolved turnover frequency (TOF) plots and (b) a photoelectrosynthetic Tafel-like plot constructed from integration of the plots shown in panel a.

(1) Nishiori, D.; Menzel, J. P.; Armada, N.; Reyes Cruz, E. A.; Nannenga, B. L.; Batista, V. S.; Moore, G. F. **Breaking a Molecular Scaling Relationship using an Iron-Iron Fused Porphyrin Electrocatalyst for Oxygen Reduction.** *J. Am. Chem. Soc.* **2024**, *146*, 11622-11633.

(2) Nishiori, D.; Hensleigh, L. K.; Nguyen, N. P.; Peterson, I.; Moore, G. F. **Wavelength-Resolving Catalytic Turnover Frequencies and Identifying Alternate Proton Donors in Solar-Fuel-Forming Reactions**. *ACS Catal.* **2025**, *8*, 9888-9898.

(3) Reyes Cruz, E. A.; Nishiori, D.; Wadsworth, B. L.; Nguyen, N. P.; Hensleigh, L. K.; Khusnutdinova, D.; Beiler, A. M.; Moore, G. F. **Molecular-Modified Photocathodes for Applications in Artificial Photosynthesis and Solar-to-Fuel Technologies.** *Chem. Rev.* **2022**, *122*, 16051–16109.

# Excitonic MOF Solar Cells and Photodeligation Dynamics: Orientation, Framework Flexibility, and Defect Engineering

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Department of Chemistry
Virginia Tech
Blacksburg, VA 24060

Metal–organic frameworks (MOFs) continue to emerge as versatile materials for light-harvesting applications due to their tunable structures, high porosity, and modular design. In this study, we present an integrated exploration of MOF-based photoanodes and photochemical dynamics, grounded in the development of excitonic MOF solar cells and an expanded investigation of photo-deligation processes in carboxylate-based MOFs.

Building on our previous work [J. Am. Chem. Soc. **2024**, 146, 7, 4309-4313], we demonstrate that directional orientation of MOF crystallites—achieved through tailored deposition strategies—enhances exciton transport and charge separation in MOF-based solar cells. Our excitonic devices leverage anisotropic alignment of MOF domains on conductive substrates, resulting in improved photocurrents and device reproducibility. Specifically, we prepared vertically-aligned PCN-222, a zirconium-based porphyrin framework, on titanium dioxide-coated, fluorine-doped tin oxide (FTO). To do so, a pre-surface treatment with long-chain fatty acids was needed to promote growth. We used the aligned photoanodes to construct complete solar cells with a Pt-coated FTO counter electrode. Comparisons between the vertically-aligned photoelectrodes and horizontally deposited photoelectrodes (prepared via electrophoretic deposition) clearly demonstrate an advantage to alignment control on device performance, Figure 1. Device optimization is currently underway.

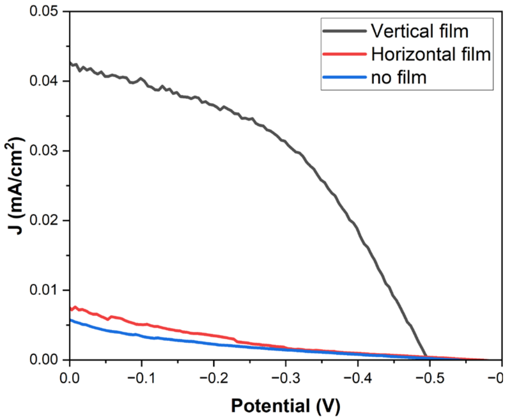

Figure 1. Current-Voltage curves for MOF excitonic solar cells, demonstrating a clear advantage to particulate alignment in performance.

Concurrently, we extend our studies on photodeligation events from carboxylate MOFs [J. Am. Chem. Soc. **2024**, 146, 1, 101-105.] to include a broader family of MIL-101 derivatives. These new systems exhibit consistent photoreactivity trends that reinforce the mechanistic insights uncovered in our earlier work. Comparative studies of rigid and flexible frameworks reveal the critical role of structural dynamics in governing ligand ejection efficiency. Namely, flexible frameworks exhibit faster bond formation and thus, faster back electron transport compared to more rigid structures of the same node and linker identity. At the same time, a targeted defect-engineering approach elucidates how crystallographic imperfections modulate both optical response and reaction pathways.

Together, these findings highlight the interplay of MOF orientation, framework flexibility, and defect architecture in shaping performance across light-harvesting and photoresponsive platforms, opening new avenues for rational design of MOF-based optoelectronic materials.

# Light-Induced Spin-Correlated Radical Pairs in Quantum Dot-Organic Molecule Conjugates

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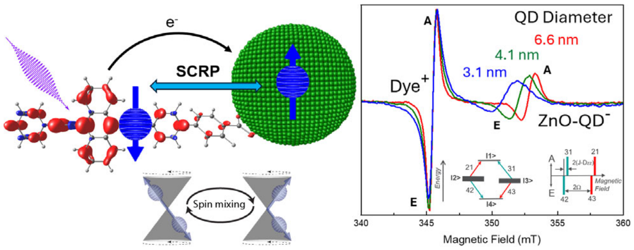
The aim of our research within the Solar Photochemistry program is to discover the fundamental mechanisms of light-induced charge separation and chemical energy conversion. For characterization of ground and excited states we use a variety of modern, high-resolution physical techniques, among them Electron Paramagnetic Resonance (EPR) spectroscopy. EPR is a powerful spectroscopic technique, which allows us to gain insight into the electronic structure, kinetics, and spin dynamics of systems containing unpaired electrons. A specialty of our group is the application of time-resolved multifrequency EPR spectroscopy with *in situ* pulsed Laser excitation, which we use to study charge and exciton transfer in organic and inorganic systems. Light-induced charge separation is a crucial step in the conversion of light energy to chemical energy. It is well known that in natural photosynthetic reaction center proteins and organic donor-acceptor systems the charge separation can result in the formation of Spin-Correlated Radical Pairs (SCRPs). Recently, SCRPs have emerged as promising candidates for quantum information science where they act as Spin Qubit Pairs (SQPs). In contrast to the well-studied organic donor-acceptor systems, there are very few electron spin measurements of photogenerated SCRPs in inorganic or hybrid organic-inorganic systems. In this work we focus on semiconducting ZnO Quantum Dots (QDs) of different sizes connected to organic molecules which act as chromophores and electron donors. Photoexcitation of these organic-inorganic conjugates results in the reversible formation of SQPs which can be probed and manipulated with EPR techniques. These hybrid systems represent a new class of spin-based qubit materials that can be photogenerated in spin-polarized states at moderate temperatures. The choice of QD, organic dye and linker offers a flexible platform for studying SQPs, allowing to tailor various properties like optical absorption, energetics, kinetics and magnetic resonance parameters. In particular, the g-factor of the electron spin in ZnO QDs is outside the range common to organic molecules and can be easily adjusted due to the quantum size effect. This results in higher spin specific addressability in these hybrid conjugates than in organic systems, which is an important requirement of functional qubit systems. Our approach provides new insight into charge transfer processes in these hybrid inorganic QD-organic molecule conjugates.



Light-induced Spin-Correlated Radical Pair (SCRP) formation in hybrid organic dye/inorganic Quantum Dot (QD) conjugates

# Photo-Induced Conformational Gating for Long-Lived Charge Separation

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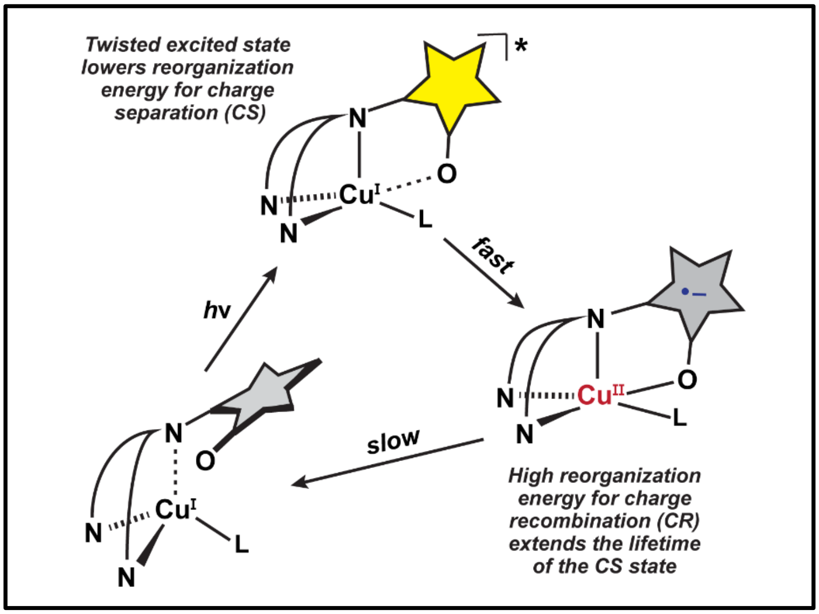

Parlaying photo-induced structural rearrangements at a chelating ligand into changes in the coordination geometry and environment around a Cu(I) ion, we are working to manipulate the reorganization energies associated with charge separation (CS) and charge recombination (CR). Specifically, these systems are designed to lower reorganization energy for CS and raise reorganization energy for CR. Our previous results revealed that (a) we have successfully developed conformationally switchable copper coordination complexes, and that (b) the fluorophore that we append to these complexes should exhibit excited state reduction potentials of ~0.8 eV. We now present our progress toward mechanistic interrogation of the link between conformational dynamics and electron transfer rates in our dynamic copper complexes, and the installation of new photo-acceptor components that are energetically and electronically tuned to generate long-lived CS states. We present structural and electrochemical characterization of a series of fluxional copper coordination complexes, and our progress towards correlating their electron transfer self-exchange rate constants (assessed by NMR linewidth broadening experiments) as a function of their inherent dynamicity (assessed by variable temperature NMR spectroscopy and DFT). Additionally, we present our results appending these complexes to a series of BODIPY photo-acceptors. Here, time-resolved photoluminescence, transient absorption, and steady state electronic spectroscopies provide evidence for the generation of the desired CS states. Generating a homologous series of these systems, progress toward assessing CS lifetimes as a function of $\Delta G_{CS}^\circ$ and $\Delta G_{CR}^\circ$ are presented. Together, both of these areas of inquiry contribute to our goal of generating long-lived CS states by leveraging the oxidation state-dependent coordination geometry changes associated with the Cu(II/I) redox couple.

# Photovoltage Generation at Gallium Phosphide Solar Hydrogen Photocathodes

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The project “Photovoltage Generation at Junctions in Heterogeneous Solar Fuel Photocatalysts and Photoelectrodes” continues investigations of photochemical charge separation at semiconductor-liquid and semiconductor-solid contacts as relevant to photoelectrochemical cells (PEC) and photocatalysts (PC) for the production of hydrogen from sunlight and water. Junctions are studied with photoelectrochemical methods and with Vibrating Kelvin Probe Surface Photovoltage Spectroscopy (VKP-SPS), which measures illumination-induced changes of the surface potential of semiconductor electrodes. In 2023 we demonstrated that the combination of VK-SPS with open circuit potential (OCP) measurements yields the electrochemical potential $E_{F,f}$ of semiconductor-electrolyte contacts. This parameter is difficult to access with standard electrochemical methods. Here we apply this methodology to p-type gallium phosphide (GaP) hydrogen evolution photocathodes to evaluate the factors that control the energy to fuel conversion efficiency. We find that the photovoltage of GaP-$H_2O$ contacts is limited by recombination at surface states. A n-CdS overlayer increases the GaP photovoltage and photocurrent due to formation of a n-p-junction, but this junction does not remove the surface states, which remain visible in surface photovoltage spectra. An electrodeposited Pt cocatalyst increases the photocurrent due to improved HER kinetics but reduces the photovoltage by causing charge recombination at the GaP/Pt interface. Added $O_2$ or $H_2$ gases reduce/increase the photovoltage by diminishing/increasing the electrostatic barrier (band bending) in the junction. This characterizes the GaP/CdS/Pt electrode as a Schottky type junction, despite the CdS overlayer. The highest performance (IPCE of 62% at 400 nm and photovoltage of 0.43 V at 250 mW $cm^{-2}$) of the GaP/CdS/Pt/$H_2O$ champion device results from a balance between efficient charge separation and fast kinetics. This shows that both thermodynamics and kinetics are important to the operation of photoelectrodes under low or zero applied bias. The work also shows that PEC and OCP data tend to underestimate the photovoltage because they do not account for changes in the electrochemical potential $E_{F,f}$ at the electrode-liquid contact. The VKP-SPV method avoids this problem by giving the photovoltage directly as the SPV signal. Ongoing and future work focuses on n-$WO_3$, n-$BiVO_4$, n-$C_3N_4$, Al:$SrTiO_3$, and oxynitrides of composition $ABO_xN_y$ (A=Sr, Ba, La, B = Ti, Nb, Ta) to answer fundamental questions about the workings of each electrode, incl. the effect of the redox potential of the electrolyte, the role of the kinetics of charge transfer, the impact of cocatalysts and of the light intensity, and role of surface defects.

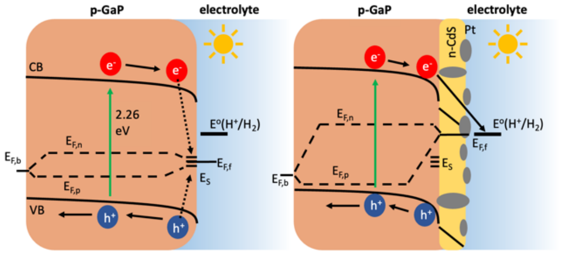

**Figure 1**. Energetics and charge separation at GaP hydrogen evolution photocathodes in aqueous electrolytes before and after surface modification with CdS/Pt. The quasi-Fermi levels and the electrochemical potentials at the back and front are shown also. From Becker, K., et al. *J. Phys. Chem. C* **2024**, *128* (40), 16915–16929.

# Elucidating Singlet Fission Spin Dynamics in Tetracene Pendent Oligomers

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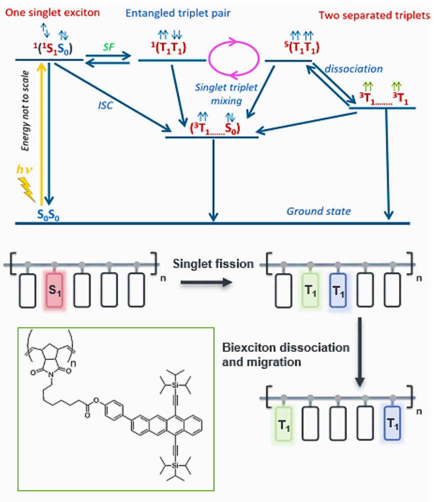
The ultimate goal of our research aims to mimic natural photosynthesis and reveal fundamental mechanisms for solar-to-chemical energy conversion which consists of capture, conversion, and storage of solar energy in high-energy molecular bonds with the production of solar fuels. Chemically designed photosynthetic systems based on molecular organic donor-acceptor entities are proficient man-made devices for direct solar energy utilization. One of the limitations of artificial photosynthetic systems is their relatively low conversion efficiency. At present this efficiency remains still well below the theoretical Shockley-Queisser limit of 33-34%.

One promising pathway to improve the efficiency of artificial photosynthetic systems is an implementation of multiple exciton generation, MEG, a process which allows to create multiple charge separated states from absorption of a single photon. One type of MEG is singlet fission (SF). SF is a process in which one organic chromophore in an excited singlet state shares its excitation energy with a second chromophore in its ground state, resulting in the generation of two excited triplet states. The correlated triplet pair is initially a pure singlet state $^1$(TT), which due to interaction between the two triplets can be converted to the quintet state $^5$(TT), and later decay into two independent triplet states. The SF process has the potential to increase quantum yields and thus the power conversion efficiency of artificial photosynthetic systems beyond the Shockley-Queisser limit. Furthermore, the generation of a doubly excited, spin correlated triplet pair state in the SF process is also interesting for Quantum Information Science applications.

The present study employs continuous and pulsed time-resolved EPR spectroscopy techniques to investigate key intermediates of SF processes in recently designed tetracene pendent oligomer systems. Generation and transformation of different spin states are explored as functions of oligomer length. Rabi nutations allow identification of spin state multiplicity, and pulsed EPR spectra obtained at different times allow visualization of spin transformations. Understanding the evolution of strongly correlated triplet states involves considering modulation of exchange interaction *J* due to exciton dynamics. This study reveals that exciton diffusion enhances mixing more efficiently in longer oligomers and is attributed to the larger diffusion space. Strategically positioned pendent groups along the backbone chain facilitate triplet migration along the pendant moieties, thereby enhancing SF efficiency.



Schematic of SF spin dynamics in tetracene pendent oligomers.

# Installation of Beneficial, Hybridized Molecule|Semiconductor States for Enhanced Photovoltage & Electron Transfer Rates

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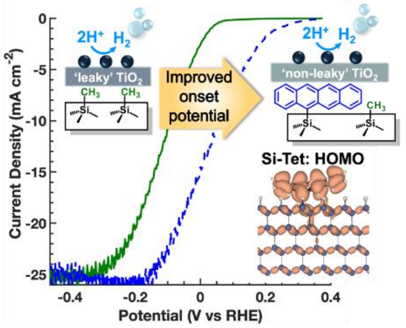
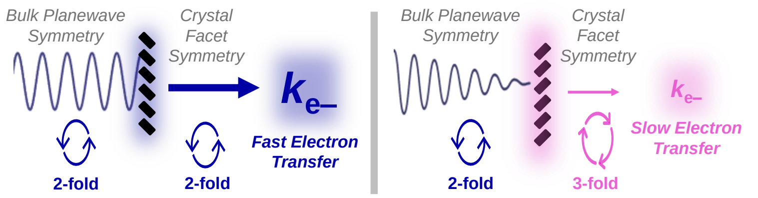
We investigate electron transfer behavior at illuminated semiconductor–electrode interfaces, targeting model systems for light-driven hydrogen evolution (HER) and solar-to-chemical energy conversion using redox couples. We modified silicon photoelectrodes with conjugated acenes (anthracene, tetracene, perylene, phenanthrene) to generate molecular acceptor states that enhance charge separation. Illuminated *J-V* measurements on *p*-type silicon functionalized with such acenes exhibit improved photovoltage. Computational studies (DFT) and group theoretical analysis using Mulliken-term–annotated band structure diagrams indicate a critical role for molecule|semiconductor energetic alignment and symmetry (mis)matches near the silicon band edges. Electrochemical data demonstrate that acene LUMOs generally align with the *p*-type silicon conduction band, while the HOMOs are buried deep in the valence band. This suggests that the molecular mode of action is the installation of increased and hybridized molecule-derived density of states at the conduction band edge. We have experimentally detected molecule-derived DOS by UPS/LEIPS, STM and solid-state voltammetry.



Group theory predicts that symmetry (mis)matches between semiconductor wavefunctions and surface atomic structure — e.g., threefold rotational atomic symmetry on hexagonal Si(111), versus twofold rotational symmetry on at Si(100) surface — determines electron density of the VB|CB at the interface. As such, variant extents of hybridization occur between the surface molecule and the silicon band structure, depending on the exact crystal facet. We hypothesize this to be one underlying reason for facet-selective electron/hole transfer. Hypotheses will be tested by studying electron transfer rates on different crystal facets. Analogous studies using covalently attached molecules acceptors.



Beyond aggregate photovoltage measurements, we will directly measure electron transfer rates across the selected molecular|semiconductor interfaces using light- and voltage-pulsed chronoamperometry. Such studies will isolate the effects of hybridization, molecular structure and symmetry. Furthermore, we will implement scanning electrochemical cell microscopy (SECCM) to map local electron transfer phenomena at differing nanoscale surface features — for example: terraces vs step-edges; functionalized vs unfunctionalized regions; and <111> vs <100> regions on the same substrate. Lastly, we seek to prove the validity of our claims and hypotheses using other Group IV semiconductor platforms, such as germanium and silicon carbide — alternative semiconductors with band-edge energetics and wavefunction symmetries distinct from silicon.

# Band gap renormalization effects on electrochemical currents at 2D semiconductor/electrolyte interfaces

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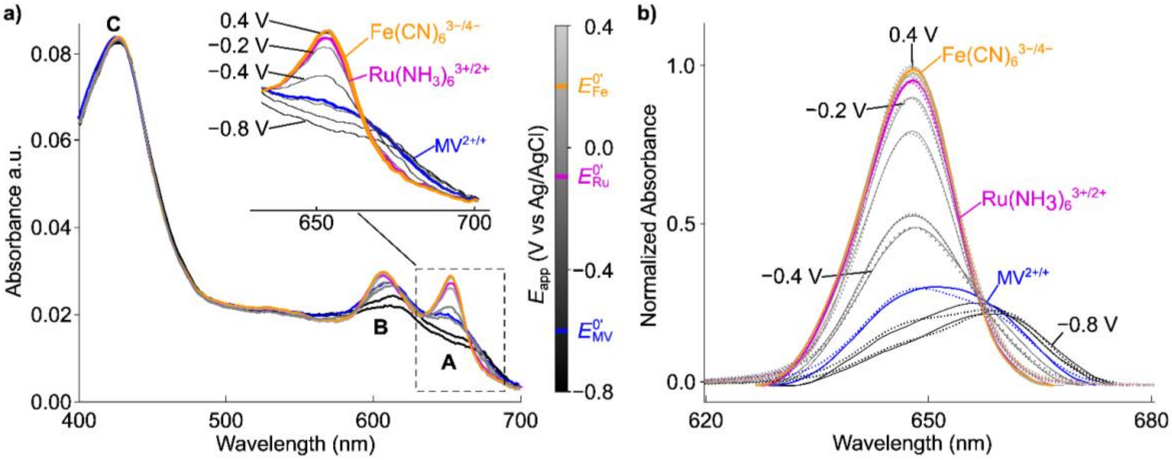
Monolayer (ML) transition metal dichalcogenides (TMDs) such as $MoS_2$ and $WSe_2$ exhibit large band gap renormalization (BGR) effects, where the electronic bandgap ($E_g$) dramatically changes with free carrier concentration ($n$). While BGR effects are known to occur under electrochemical conditions, and are likely to impact interfacial charge transfer due to its impact on energy level overlap between the semiconductor and molecular electronic states, the influence of BGR on electrochemical currents remains unexplored in the field of semiconductor electrochemistry. Here, using an unprecedented combination of in situ spectroelectrochemistry and many-body theory, we first quantify the potential-dependent BGR effect for a ML-$MoS_2$ electrode in the absence and presence of 3 outer sphere redox couples whose formal potentials ($E^{0'}$) vary by 0.8 V, and then assess how band edge movement influences current-potential behavior using cyclic voltammetry and complimentary electrochemical simulations. The key finding from this work is the electrochemistry of ML-$MoS_2$ cannot be explained by conventional models that do not invoke the BGR effect; band edge movement influences the energy state overlap between the 2D semiconductor and redox molecules in solution, leading to the observed current-voltage responses. The experimental and theoretical tools developed herein is not specific to ML-$MoS_2$ and can be applied generally to 2D semiconductors. Our future work will focus on tuning electron transfer kinetics via the BGR effect for solar energy conversion and catalysis applications.



**References:** (1) Almaraz, R.; Sayer, T.; Tews, A.; Toole, J.T.; Maldonado, S.; Montoya-Castillo, A.; Sambur, J.B. Band Gap Renormalization Causes Distinct Electrochemical Responses in Monolayer MoS2 Electrodes. **2025**, *in preparation*.; (2) Almaraz, R.; Sayer, T.; Toole, J.; Austin, R.; Farah, Y.; Trainor, N.; Redwing, J. M.; Krummel, A.; Montoya-Castillo, A.; Sambur, J. Quantifying Interfacial Energetics of 2D Semiconductor Electrodes Using *in Situ* Spectroelectrochemistry and Many-Body Theory. *Energy Environ. Sci.* **2023**, *16* (10), 4522–4529.

# Complementary Strategies for Copper(I) Charge-Transfer Photosensitizers with Long Excited-State Lifetimes

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Achieving long charge-transfer excited-state lifetimes in earth-abundant photosensitizers is a fundamental challenge that impacts solar fuels research. This poster presents three complementary strategies our group has undertaken to produce visible-absorbing, copper(I) charge-transfer photosensitizers with long excited-state lifetimes. The first two center on a class of heteroleptic three-coordinate compounds that combine β-diketiminates and isocyanides (Figure 1). We show that increasing the steric bulk of both the β-diketiminate and the isocyanide, using bulky *m*-terphenyl isocyanides, has led to excited-state lifetimes in excess of 1 μs. The second strategy with this class of complexes revolves around reversible triplet-triplet energy transfer (TTET). We have incorporated a variety of polycyclic aromatic triplet acceptors onto the isocyanide and have generalized the concept that close energetic matching of the triplet charge-transfer ($^3$CT) state and the localized $^3(\pi\rightarrow\pi^*)$ state of the triplet acceptor is a prerequisite for establishing reversible TTET and increasing the lifetime of $^3$CT, again producing excited-state lifetimes more than 1 μs.

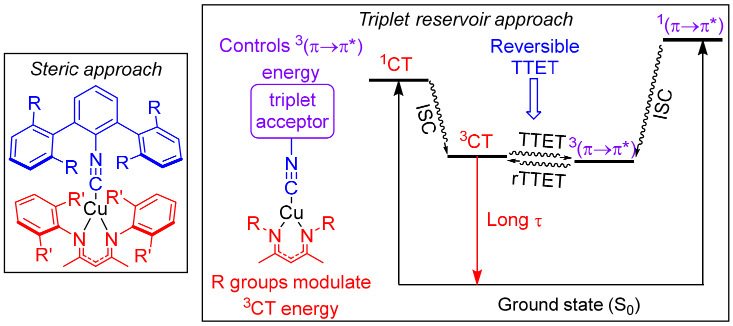

**Figure 1**

The third research effort described in this work (Figure 2) is a distinct class of heteroleptic three-coordinate copper(I) complex that functions as an effective visible-light photosensitizer. These compounds consist of hydroxyquinoline derivatives as L^X chelating ligands, capped with a sterically encumbered *N*-heterocyclic carbene (NHC). This design has resulted in two promising photosensitizers that have lifetimes as long as 80 μs and can promote a variety of photocatalytic transformations.

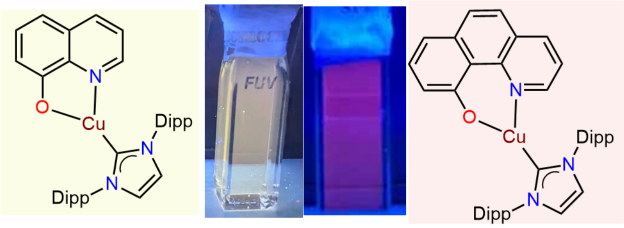

**Figure 2**

Future efforts on this project will include four-coordinate copper(I) β-diketiminate complexes supported by chelating diisocyanides, where we will adapt both the sterically-driven and triplet reservoir strategies to these new classes of compounds. In addition, inquiries into distance and orientation dependence of TTET will be undertaken, along with extension of the TTET approach to multi-metallic platforms and other classes of supporting ligands decorated with triplet acceptors.

# Driving Force and Fluence Dependent Photoinduced Charge Transfer Dynamics in Polymer-Wrapped Semiconducting Single-Walled Carbon Nanotubes (SWNTs)

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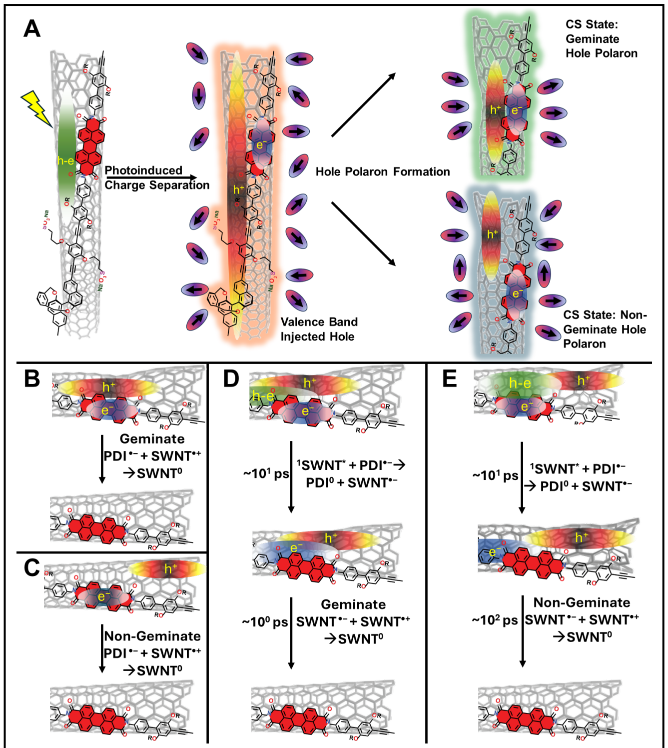

**Figure 1.** (**A**) Exciton generation, light-triggered formation of the initially prepared CS state, and subsequent polaron formation dynamics that give rise to SWNT hole polarons both geminate and nongeminate to a PDI$^{-\bullet}$. (**B-C**) Thermal charge CR reactions and (**D-E**) multibody processes that promote additional CT reactions characterized in the benchmark *R*-PBN(b)-Ph$_6$-PDI-[(6,5) SWNT] superstructure. Under low excitation fluences that produce dilute (<4 excitons per 100 nm) exciton concentrations (**B**) geminate CS states exhibit ~10$^1$ ps time scale thermal CR dynamics, while (**C**) nongeminate CS states manifest thermal CR on an ~10$^2$ ps time scale. As excitation fluence is increased into a regime (> 8 excitons per 100 nm) where excitons persist following light-triggered CS (**D-E**), a multi-body driven CT reaction – exciton driven PDI radical anion photooxidation – becomes important. (**D**) For geminate CS states, E$_{11}$ excitons mediate a decay channel for the PDI$^{-\bullet}$ population that is reflected as a fast (~10$^1$ ps) decay of the PDI$^{-\bullet}$→PDI$^{-\bullet *}$ transient absorptive signal, producing a SWNT electron polaron (SWNT$^{\bullet -}$), which recombines rapidly (< 1 ps) with its geminate SWNT hole polaron (SWNT$^{\bullet +}$) partner. (**E**) When excess excitons react with nongeminate CS states, this multi-body interaction also causes the decay of the transient PDI$^{-\bullet}$ signal on the 10$^1$ ps time scale, but instead produces a SWNT electron polaron nongeminate to a SWNT hole polaron; CR dynamics of these nongeminate SWNT$^{\bullet -}$ and SWNT$^{\bullet +}$ states occur on the order of 10$^2$ ps.

SWNT-based molecular D-A hybrid superstructures in which the spatial organization and stoichiometry of perylene diimide (PDI) electron acceptors are fixed on the nanotube surface illuminate the scope of light-triggered reactions in carbon nanotube charge transfer systems. SWNT excitation produces a photoinduced CS state characterized by an initially prepared valence band injected hole (**Fig. 1A**). SWNT lattice and solvent nuclear relaxation drive formation of hole polarons adjacent to (germinate) and nearby (nongeminate) perylene diimide radical anions. These CS states manifest independent CR dynamics; under dilute exciton conditions, **Fig. 1A-C** capture the scope of light-triggered CS and thermal CR reactions. However, commonly used pulsed laser excitation conditions that trigger SWNT photoinduced electron transfer (ET) reactions generally prepare CS states in the presence of excess, unreacted, and highly mobile excitons (**Fig. 1D-E**). In this scenario, PDI radical anions undergo a multi-body reaction with excess excitons (SWNT ${}^1E_{11}{}^*$ + PDI$^{-\bullet}$→ SWNT $E_{00}{}^-$ + PDI): the substantial SWNT exciton excited-state reduction (${}^1E^{-/*}$) potential drives formation of a neutral PDI and a SWNT electron polaron (SWNT$^{\bullet -}$). For geminate CS states (**Fig. 1D**), SWNT$^{\bullet -}$ states recombine rapidly with SWNT hole polarons (SWNT$^{\bullet +}$). For nongeminate CS states (**Fig. 1E**), the SWNT ${}^1E_{11}{}^*$ + PDI$^{-\bullet}$→ SWNT $E_{00}{}^-$ + PDI reaction produces more distant SWNT$^{\bullet +}$ and SWNT$^{\bullet -}$ states, which recombine via a mechanism that involves polaron migration. Here we further illuminate mechanistic insights for the reactions described detailed in **Fig. 1** in closely related SWNT superstructures in which both SWNT and PDI electronic structures are modulated.

# Tracking Structures of Metal Cluster Catalysts in Solution and at Soft and Hard Interfaces

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This program is developing approaches for tracking structures of metal cluster catalysts for solar fuels chemistry using operando high energy X-ray scattering (HEXS) and atomic pair distribution function (PDF) analyses. HEXS-PDF offers unique opportunities to resolve structure features across inner and outer coordination shells (0.1 to 1 nm) and intermediate length (1 nm to 50 nm) ranges. These measurements are particularly relevant for probing reaction mechanisms requiring atomic reorganization in the outer coordination sphere.

Solution Phase Photocatalysts. Molecular dynamics approaches were developed to simulate HEXS-PDF data processing and structure analysis for solar catalysts in solution using tris-(bipyridine)-ruthenium(II) chloride, $Ru(bpy)_3^{+2}$, as a model, Figure 1. This work demonstrated opportunities to use HEXS-PDF to analyze both metal coordination and solvation layer structures. Extension of PDF analyses to $[Co_4O_4](OAc)_4(py)_4$ cubane show that PDF measurements provide information on the outer coordination sphere ligand and solvation layer structures. Selective broadening of PDF peaks associated with pyridine and acetate ligands are found to reflect the layered dynamics of the cubane atomic structure and H-bonded $H_2O$ molecules.

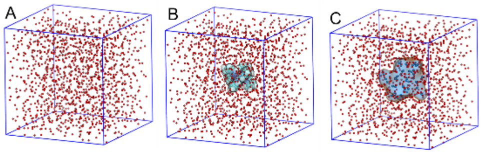

*Figure 1. Atomic modeling of solution PDF measurements. Parts A, B, C illustrate water solvent, $Ru(bpy)_3^{+2}$, and solvation layer structures, respectively.*

Interfacial Catalysts. Capabilities for tracking structures of metal clusters supported on “soft” polymer and “hard” oxide interfaces was investigated by comparing structures for platinum hydrogen-evolving catalysts formed by photo-reductive assembly from aqueous hexachloroplatinate salts on photosystem I with structures assembled by atomic layer deposition (ALD) from vapor phase Pt organometallic precursors on anodic aluminum oxide (AAO). Despite major differences between the two supports, precursors, and reductive chemistries, mechanisms for Pt catalyst assembly were found to be remarkably similar. Apart from the presence of $PtO_x$ species in the initial Pt cluster formed by a single ALD cycle, Figure 2A, the nucleating structures and growth to 3-layer, disk-shaped nanoparticles, Figure 2B, were found to be nearly equivalent. This suggests the central role that Pt chemistry plays in assembly and the opportunity to use PDF for structure analysis of interfacial solar catalysis.

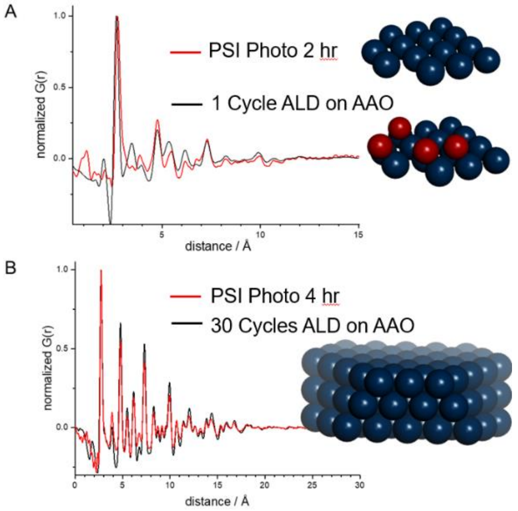

*Figure 2. (A) Similar nucleating Pt and $PtO_x$ clusters on PSI and AAO, respectively. (B) Convergence of equivalent Pt nanoparticles on PSI and AAO with prolonged growth.*

# Transition Metal Complexes as Single-Molecule Photocatalysts for $H_2$ Production with Visible/Red Light

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The generation of $H_2$ driven by sunlight has the potential to be transformative as a renewable energy source to help meet the growing global demand. In particular, materials that are able to absorb broadly from the ultraviolet to the near-infrared (NIR) spectral range and are able to utilize low-energy photons to produce hydrogen from abundant sources catalytically hold great promise in this area. The Turro group recently discovered the photocatalytic ability of dirhodium(II,II) complexes, such as *cis*–$[Rh_2(DPhF)_2(bncn)_2]^{2+}$ (bncn = benzo[*c*]cinnoline; DPhF = *N,N'*-diphenylformamidinate), to act as a single-molecule photocatalyst that is active with red and NIR irradiation in the presence of a number of acids and a sacrificial electron donor. These complexes are also electrocatalysts for $H_2$ production, and experiments and calculations revealed that the activity of these complexes appear to be localized on the bncn ligand.

In order to ascertain that the photocatalysis is also centered on bncn, we designed a series of complexes with axially-caped sites to preclude the formation of a Rh–H hydride intermediate (Figure 1a). *Cis*-$[Rh_2(DTolF)_2(bpnp)(bncn)]^{2+}$ photocatalytically produces $H_2$. In addition, *cis*-$[Rh_2(DPhF)_x(OAc)_{2-x}(bncn)_2]^{2+}$ (x = 0 – 2) electrocatalytically produce $H_2$. Both results point at a bncn-localized reaction.

We have now focused on the replacement of expensive rhodium with abundant first-row metals, specifically Cu(I) and Ni(II). We synthesized and characterized a new $Cu_2$(I,I) complex with a bridging and bncn ligand, shown in Figure 1b and characterized it using single crystal x-ray diffraction (Figure 1c). This $Cu_2$(I,I) complex exhibits absorption in the visible range attributed to a Cu(I)→bncn metal-to-ligand charge transfer (MLCT) transition that tails to ~700 nm (Figure 1d). We are now beginning to characterize the photophysical properties, electorchemistry, and photochemistry of this complex, including photocatalysis. In addition, we have already prepared $Ni_2(DPhF)_4$, which we plan to react with bncn to obtain the corresponding *cis*-$[Ni_2(DPhF)_2(bncn)_2]^{2+}$ complex. We expect that strong Ni/DPhF→bncn transitions at low energy in this complex that may allow similar bncn-localized reactivity in the excited state in the presence of acids.

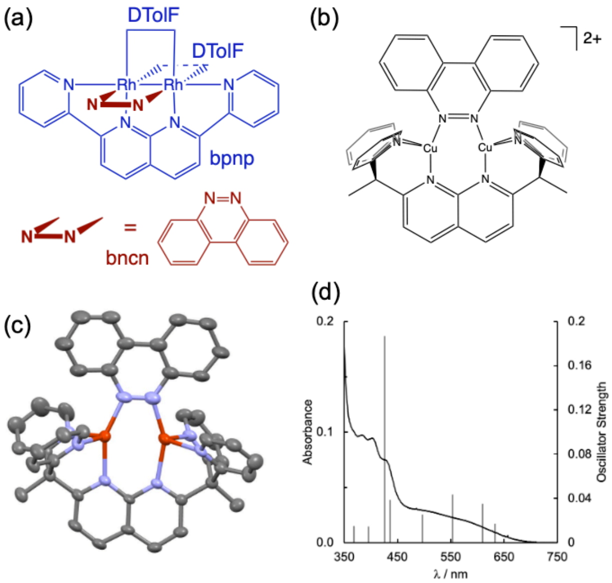

**Figure 1.** Molecular structures of (a) bncn complex with blocked axial sites, (b) new $Cu_2$(I,I)-bncn complex, (c) its crystal structure, and (d) UV-vis spectrum in $CH_2Cl_2$.

# Probing Water Oxidation Mechanisms with Atomically Defined Heterogeneous Catalysts

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This project seeks to understand water oxidation reactions on heterogeneous catalysts, especially under photochemical conditions, with the long-term goal of enabling solar water splitting with low-cost, efficient, and durable catalysts. Toward this goal, we introduced a unique catalyst system featuring active centers whose structures are resolved at the molecular level. Derived from an organometallic precursor, our heterogeneous catalyst system offers definitive information that is critical to the understanding of catalytic mechanisms, such as the number of the active sites and their molecular structures. Similar information is often difficult to obtain for traditional heterogeneous catalysts. The project further benefits from the employment of surface-enhanced infrared absorption spectroscopy (SEIRAS) for the detection of reactive intermediates. We aim to refine this technique to enable real-time, operando tracking of the reaction progress.

In this poster, we report our latest progress on two fronts. First, we show how the water oxidation kinetics is determined by the interplay of surface hole concentration and the density of active sites. Our results suggest that the transfer of surface holes to the catalytic active sites is reversible and dynamic, especially under low surface hole concentration conditions (such as under low lighting or weak driving force or both). Depending on the relative concentration of surface holes and the active site density, facile hole redistribution among different active sites may promote or inhibit water oxidation reactions. The results highlight that it is inadequate to treat complex reactions such as water oxidation as being limited by a single step. It is critically important to build new models to study the complex reactions step by step. Second, we show that high signal-to-noise ratios can be achieved in SEIRAS characterization of water oxidation intermediates using a phase-sensitive detection method. This approach exploits a lock-in amplification strategy that has worked well in other measurements but has not been applied to SEIRAS in the context of catalysis. By stimulating the system with a periodically varying electrode potential, we were able to detect water oxidation intermediates in the cycle of an Ir pyridinyl alkoxide complex, a prototypical water oxidation molecular catalyst. Together our results have established a foundation for us to fully characterize water oxidation reactions by heterogeneous catalysts under photochemical conditions, contributing to our long-term goal of enabling practical solar fuel synthesis.

# 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 for the ultimate commercialization of all-polymer solar cells. The bottleneck is due, in part, to the lack of understanding and control of 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, we report our molecular design and synthesis of ladder-type, carbonyl-functionalized oligo(*p*-phenylene)s, and theoretical calculations using density functional theory and modeling for the structure-property relationships.[4] As soon as the Laser Electron Accelerator Facility (LEAF, currently in a shutdown period for upgrading) at Brookhaven National Laboratory resumes operations, we will investigate electron delocalization in the carbonyl-functionalized oligo(*p*-phenylene)s by nanosecond time-resolved infrared spectroscopy coupled with pulse radiolysis (PR-TRIR). We thank the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences for financial support under Award #DE-SC0023329 for "Building EPSCoR State/National Laboratory Partnerships."

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# Transition Metal Hydrides for $CO_2$ Reduction

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Our work has focused on selective $CO_2$ reduction through hydride transfer and electrocatalyst development. The scope of work includes new transition metal ligand development, synthesis and characterization, reactivity studies, and thermochemical measurements.

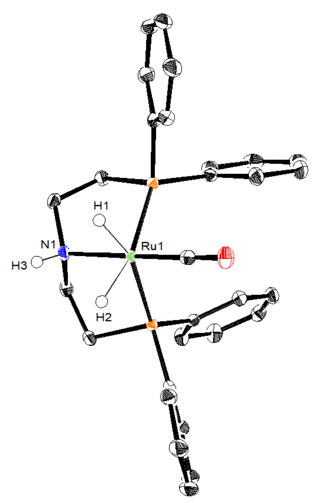

**Figure 1:** Crystal structure of $RuH_2$(MACHO)(CO). Thermal ellipsoids are drawn at 50% probability. Non-hydride and N–H hydrogen atoms and solvent molecules are omitted for clarity.

The hydrogenation catalyst RuH(MACHO)(CO)Cl has been widely utilized in reduction of C=O bonds, including $CO_2$, esters, and carbamates, where MACHO is the tridentate ligand with the formula $HN(CH_2CH_2PR_2)_2$ and R is a phenyl group. While the catalyst has been studied for over a decade, the active hydride intermediates have never been isolated or characterized. We successfully synthesized both the *cis*- and *trans*-dihydride complexes determined their unique $^{31}P\{^1H\}$ NMR spectroscopic resonances. The former was also structurally characterized by single crystal X-ray analysis (Figure 1). Both dihydrides react with $CO_2$ to form formate under mild conditions (1 atm and room temperature). To determine the most likely active species under hydrogenation conditions, we collaborated with Dr. Linehan and Dr. Appel at PNNL to perform high-pressure NMR to analyze the compound under operando hydrogenation conditions. Interestingly, both the *cis*- and *trans*- dihydride isomers were observable under hydrogenation conditions. However, the *trans*-dihydride appears to react more rapidly than the *cis*-dihydride. Evaluation of their relative hydricity is underway.

We concurrently wanted to explore one of the few iron-based homogeneous catalysts active for $CO_2$ hydrogenation to methanol. A prior report described $CO_2$ hydrogenation to methanol by a purported iron tris(pyrazole)methane catalyst. The authors proposed but did not isolate a hydride intermediate or the parent compound. We attempted to synthesize this compound and its respective hydride intermediate. To our surprise, we were unable to isolate the iron compound with only one tridentate ligand. To overcome this challenge, we synthesized a more sterically encumbered version of the ligand with isopropyl functionalities, which achieved the desired structure.

In order to access new catalytic motifs, this project has also focused on the development of new ligands. These include bipyridines and terpyridines with cationic functionalities and water-soluble bidentate phosphine ligands.

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

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Artificial photosynthetic system designs have deep roots in our understanding of how natural photosynthesis works, borrowing key elements such as the energetic Z-scheme, and coupling water oxidation to $CO_2$ reduction chemistry. Natural systems take advantage of catalytic cascades to build complex molecules from simple building blocks, and using cascades is a logical step to improve the efficiency and selectivity of conversion of solar energy into complex chemicals in artificial systems. The chemical reactions used for such conversion involve multi-electron/proton processes for making new bonds and molecules, and require the precise control of flow of charges and molecular reactants to be selective. A fundamental challenge of controlling reaction sequence is that progress in the reaction relies on stochastic events, and electron transfers leading to charge accumulation at catalytic sites are random in time on heterogeneous surfaces. As a result, cascaded catalysts operate "open loop": the chemical activity of the second site in the cascade is uncoordinated with that of the first. The fundamental scientific questions are (1) *how can molecular-level processes initiated by multiple types of energy carriers be tightly coordinated, and* (2) *how can photo-driven catalytic sequences be controlled to ensure that only the desired products are formed.*

<u>Understanding the role of heterogeneous catalytic sites for controlling reactions:</u> One of the important outcome in this aim is the discovery of distinctive functions of the catalytic surfaces in heterogeneous PEC systems and their control of the chemical network (Varley, 2025).

<u>Detecting chemical changes with temporal and spatial sensitivity:</u> We are also developing X-ray spectroscopy methods with modulation excitation with electrochemical bias (Garcia-Esparza, 2025) and light to control chemical processes and significantly increase the detection efficiency, using the water oxidation reaction with $IrO_2$ grown on $TiO_2$ substrate as a model system (**Figure 1**, Simon, manuscript in preparation).

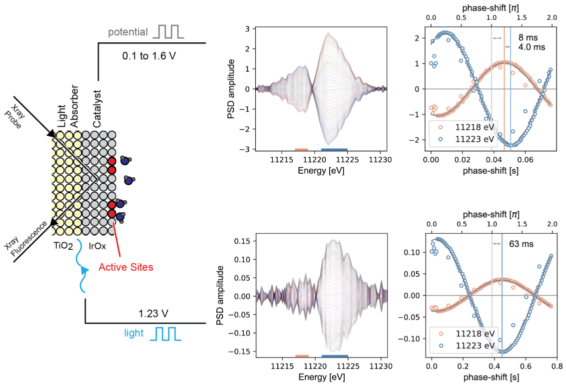

**Figure 1:** XAS measurements under potential and light modulation on Ir-oxide catalyst coupled to $TiO_2$ photoabsorber. Top panels: Ir oxidation under modulated potential at 13 Hz. bottom: Ir oxidation under constant 1.23 V and UV light modulation at 1.3 Hz. The delay of the energies shown relative to each other and the stimulus at 1π is indicated.

## DOE Solar Photochemistry Sponsored Publications:

1. J. B. Varley, N. Govindarajan, J. W. Ager. *J. Phys. Chem. Lett.* 2025, 16, 2, 604–610.
2. A. Garcia-Esparza, P. Simon, J. Yano, *et al*. *Energ. Env. Sci.* 2025 (<u>doi.org/10.1039/D5EE01068C</u>)

# Chiroptics and spin selectivity in helicenes and twistacenes

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This poster will describe our results in the following two areas. Firstly, to create PDI based helicenes and twistacenes capable of transporting spin-polarized electrons over micron length scales. Secondly, to quantify spin polarization and spin-selective transport in helicene and twistacene macromolecules through direct imaging, leveraging ultrafast microscopies we pioneered.

These materials have extraordinary properties as materials. The helicenes have the largest chiroptic response of any molecular species. The twistacenes helicity is dynamic and can be controlled by light and chemical/electrochemical reductions. The electrochemistry of the twistacene derivatives was recently published (1). The spin dependent transfer from TMDCs was recently communicated (2). These molecules can be attached to surfaces and measurements with magnetized substrates, and these monolayers excel in CISS measurements (3). Figure 1 to the right displays the CISS measurments on these monolayer films. Spectroscopy reveals that thin films of these materials support spin transport over long distances. This study will be important in the field of CISS given the high currents and large amounts of CISS in these devices. Even more exciting is our 4th publication (out for review), which details twistacene polymers and the study of spin polarization using TMDCs.

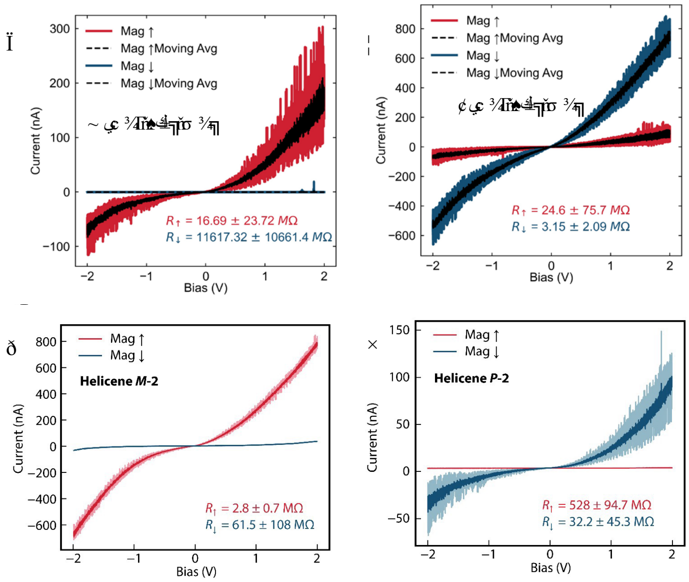

**Figure 1. Conductive AFM Results** Magnetic field dependent CAFM traces for M-helicene trimer (a), P-helicene trimer (b), M-Helicene dimer (c), and P-helicene dimer (d), comparing the 4 molecules. Magnetic field up is in red and magnetic field down is in blue, showing similar trends between all samples based on helix core chirality.

(1) “Near-Infrared, Organic Chiroptic Switch with High Dissymmetry Factors,” S. T. Bao, S. Louie, H. Jiang, Q. Jiang, S. Sun, M. L. Steigerwald, C. Nuckolls, Z. Jin *J. Am. Chem. Soc.* **2023**, 146 (1), 51–56.

(2) “Spin-Polarized Charge Separation at Two-Dimensional Semiconductor/Molecule Interfaces”, Yufeng Liu, Taketo Handa, Nicholas Olsen, Colin Nuckolls, Xiaoyang Zhu, *J. Am. Chem. Soc.* **2024**, *146*, 10052–10059.

(3) “Spin-Filtering with Surface-Active Helicene- and Twistacene-Based Perylene Diimides”. Haoyu Jiang, Daniel Čavlović, Qifeng Jiang, Fay Ng, Si Tong Bao, Evan J. Telford, Michael L. Steigerwald, Xavier Roy, Colin Nuckolls, Jeffrey M. McNeill. *J. Am. Chem. Soc.* **2025**. ASAP.

# High throughput measurement of activity descriptors for electrocatalytic materials

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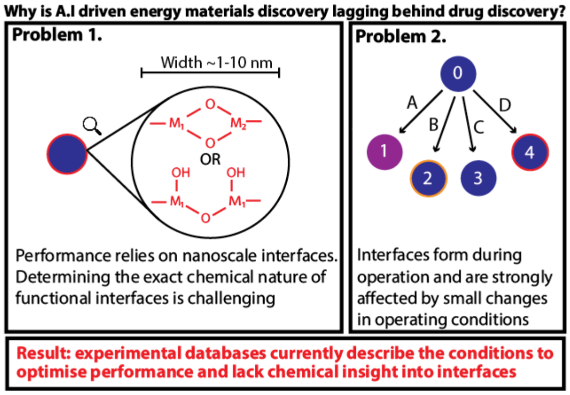
Mitigating anthropogenic climate change requires the rate of discovery of future materials for carbon neutral chemical industry to be accelerated. Net Zero Strategy involves gigawatt-scale hydrogen combined with the capture and utilisation of megatons of $CO_2$ by 2030[1], driven by 70 GW of installed solar capacity[2] by 2035. Such targets aim to drive decarbonisation at pace and scale. However, they also require new processes and materials, which retain performance, yet are cheaper, benign, and environmentally sustainable. Machine learning (ML) is driving advances at pace and scale in the linked fields of structural biology[3] and drug discovery[4], yet to date has not driven a commensurate acceleration in energy materials discovery. Accurate predictions the chemical nature (3d-strcture) of proteins from amino acid sequences are achieved through training on vast experimental datasets of sequence-structure pairs. As structure dictates function, this high dimensional structure space can be used to predict the physical parameters that describe performance.[5] Performance in energy materials is often dependent on a nano-scale interface that only emerges under operational conditions, with chemical nature that is highly sensitive to operational conditions. Insight into these materials is typically obtained using operando spectroscopies and microscopies to extract structures and descriptors, which can be used to understand performance. A bottleneck in scaling this approach to produce materials databases containing deep chemical insight arises because the most powerful approaches to exploring and filtering materials design spaces (e.g. high throughput (HT) synthesis, ex-situ characterisation, simulation, Bayesian inference/optimisation and ML) are performed at a scale which is incompatible with the glacially slow workflows of operando spectroscopies; the gold standard in determining activity descriptors, as structure/function relationships often only become apparent under operational conditions. As a result, large experimentally derived databases on energy materials map compositions and experimental conditions to performance and tend to lack deep chemical and structural insight.[6]



**Why is A.I driven energy materials discovery lagging behind drug discovery?**

**Problem 1.**

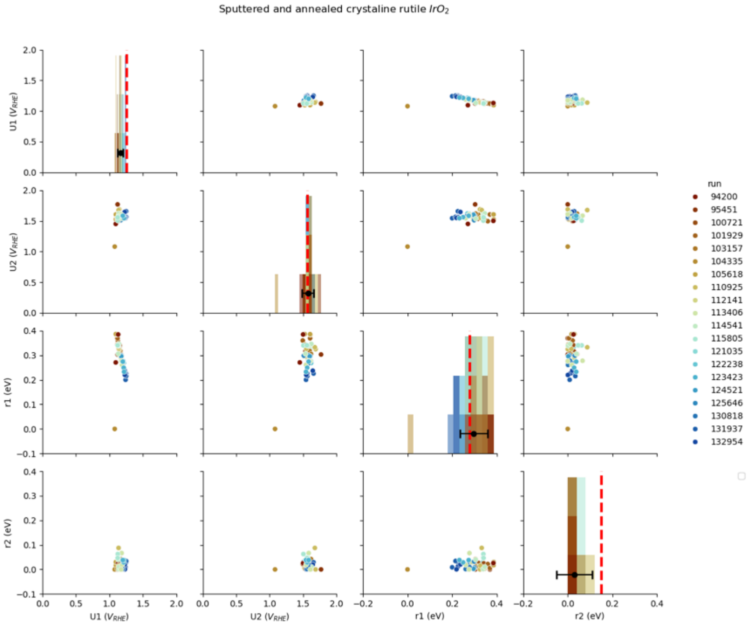
Performance relies on nanoscale interfaces. Determining the exact chemical nature of functional interfaces is challenging

**Problem 2.**

Interfaces form during operation and are strongly affected by small changes in operating conditions

**Result: experimental databases currently describe the conditions to optimise performance and lack chemical insight into interfaces**

To help address this problem we have designed a high throughput operando spectroscopy system capable of extracting two descriptors thought to be crucial to predicting the activity of materials used to catalyze the oxygen evolution reaction (OER). This reaction provides a source of protons and electrons for transformations of carbon dioxide as well as industrially relevant chemicals such as olefins. A good catalyst will bind its substrate strongly enough to provide an alternative pathway for the reaction to proceed but not so strongly as to become poisoned. Further, in electrocatalytic reactions, interactions with ions that are attracted to the polarized electrode are critical and can vary as catalytic intermediates are generated at the surface. These two parameters (binding potential, $U^0$, and interaction energy $r$) are extremely challenging to extract in real OER catalysts, which exhibit dynamic surface evolution. Recently it has been shown that potential resolved optical spectroscopy (spectroelectrochemistry, SpEC) can extract these parameters for real electrochemical interfaces on a small scale. By automating SpEC and designing an analysis workflow driven by unsupervised machine learning we have been able to reliably extract binding potentials for an $IrO_2$ benchmark system, where these parameters are well known. This strong result provides the foundations for a larger study aiming to generate a large database of experimentally derived activity descriptors



# Catalysts May Not Be What They Seem to Be …
# Where the Action Is– The Solution-Catalyst Interface

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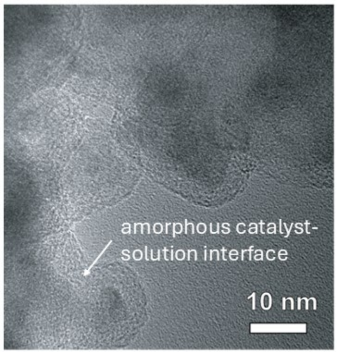
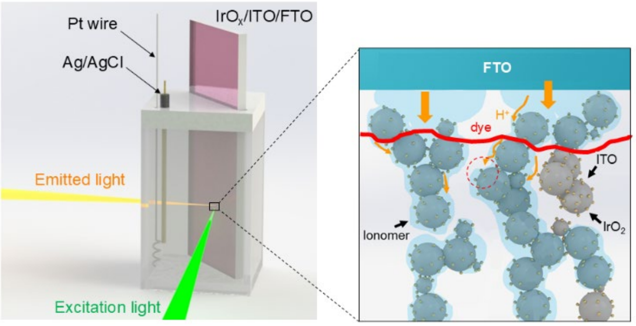
Energy conversion reactions comprise proton-coupled electron transfer (PCET) steps that occur at the interface between the catalyst surface and solvent. It is the interfacial environment that supplies the solvation to enable the coupling of the electron to the proton, providing an imperative for understanding the nature of the interface during catalysis. We have focused on how interfacial properties control two catalytic reaction: the oxygen evolution reaction (OER) and the carbon dioxide reduction reaction (CDR).



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

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 in the working environment is tenuous at best as a higher current density at a lower overpotential may simply be due to 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 often to be the case for first-row, mixed-metal oxide OER catalysts using lanthanide-incorporated cobalt/nickel oxides. More generally, increased catalytic activity in metal doped (alloyed) OER catalysts is often attributed to a number of reasons including strain on the catalyst lattice, favorable inter-mediate energetics due to optimized metal–oxygen covalency, defect-induced reactivity enhance-ments, favorable entropic contributions (i.e. high entropy catalysts), and cooperative multimetallic active sites. However, our studies suggest that most observations of enhanced activity may be due increased number of active sites in the catalyst interface.



Operando method to determine local pH within a porous electrode microenvironment

In addition to the catalyst interface, the solvent at the catalyst interface must also be considered in assessing catalytic activity. 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 p$K_a$, 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 the CDR reaction at nanostructured electrodes.

In summary – a pristine catalyst in a bulk solution is not representative of the catalyst-solution interface … where catalysis occurs in the working environment.

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1. 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.
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Operando pH Measurements of OER within a Porous Oxygen Evolving Electrode. Z. Yan, D. M. Loh, R. Sun and D. G. Nocera