Proceedings of the

Forty-Second DOE Solar Photochemistry P.I. Meeting

Virtual Meeting
June 2-4, 2021

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

FOREWORD

The 42^{nd} 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 as an online meeting June 2-4, 2021. These proceedings include the meeting agenda and abstracts of the presentations.

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. Travel restrictions caused the meeting to be cancelled in 2020 and held via Zoom in 2021. The meeting agenda has been adjusted a bit this year to accommodate the online format, including the addition of a few multi-PI presentations from large national laboratory projects and a series of lightning talks about single investigator and small group projects.

The meeting this year also features a few invited presentations. Bill Tumas will tell us about the BES Roundtable on Liquid Solar Fuels that he chaired in August 2019. The workshop goal was to identify research opportunities to overcome scientific and technical barriers in the generation of liquid solar fuels via artificial photosynthesis. Two other invited presentations will be given by Solar Photochemistry PIs who also serve as director of an Energy Frontier Research Center (EFRC). Greg Scholes leads the Bioinspired Light-Escalated Chemistry (BioLEC) EFRC that has the mission "To employ light harvesting and advances in solar photochemistry to enable unprecedented photoinduced cross-coupling reactions that valorize abundant molecules." Matt Beard leads the Center for Hybrid Organic Inorganic Semiconductors for Energy (CHOISE) that seeks "To enable unprecedented synthetic control over the emergent phenomena of spin, charge, and light-matter interactions, in tailored organic-inorganic perovskite-inspired systems for energy science."

I would like to express my thanks to Nate Neale who spends part of his time as a detailee for the Solar Photochemistry Program, assisting with numerous critical behind-the-scenes tasks including the preparation of this meeting agenda and abstract book. Special appreciation also goes to Teresa Crockett of Basic Energy Sciences, as well as Connie Lansdon and her colleagues at the Oak Ridge Institute for Science and Education for their assistance with meeting logistics. Finally, I am 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
Chemical Sciences, Geosciences,
and Biosciences Division
Office of Basic Energy Sciences

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42^{nd} DOE SOLAR PHOTOCHEMISTRY
P.I. MEETING

June 2-4, 2021

Virtual Meeting

All times EDT
Please Note – **Session start times fixed; Talk times estimated within each Session**

PROGRAM

Wednesday, June 2

SESSION I
Opening Session

11:00 a.m. News from DOE-BES Chemical Sciences, Geosciences, and Biosciences Division
Bruce Garrett and **Chris Fecko**, DOE Office of Basic Energy Sciences

11:40 a.m. BES Roundtable on Liquid Solar Fuels – Summary Presentation
Bill Tumas, National Renewable Energy Laboratory

SESSION II
Lab Programs

12:00 p.m. Fundamental Mechanisms for Solar Energy Conversion in Artificial Photosynthesis
David M. Tiede, **Lin X. Chen**, **Oleg Poluektov**, **Karen L. Mulfort**, **Alex B. F. Martinson**, and **Richard D. Schaller**, Argonne National Laboratory
George C. Schatz, Northwestern University
Felix N. Castellano, North Carolina State University
Xiaosong Li, University of Washington
Amy Cordones-Hahn, SLAC National Accelerator Laboratory
Ksenija D. Glusac, University of Illinois at Chicago

1:00 p.m. Break

SESSION III
PI Highlights: Singlet Fission and Triplet Dynamics

1:30 p.m. Singlet Fission
Josef Michl, University of Colorado Boulder

1:35 p.m. Femtosecond Stimulated Raman Spectroscopy–Guided Screening Leads to Efficient Singlet Fission in Rubrene Derivatives
Renee R. Frontiera, University of Minnesota

1:40 p.m. Structure-Function Relationship in a Flexible Perylene Diimide Tetramer Illustrating Singlet Exciton Fission
Theodore Goodson III, University of Michigan

1:45 p.m. Symmetry-Breaking Charge Separation in Molecular Crystals
Michael R. Wasielewski, Northwestern University

1:50 p.m. Dexter Energy Transfer Mechanisms
David N. Beratan, Duke University

1:55 p.m. Towards Efficient Up- and Down-Conversion with Nanocrystals Light Absorbers
Ming Lee Tang, University of California Riverside

2:00 p.m. Controlling Singlet Fission by Molecular Contortion
Xiaoyang Zhu and **Colin Nuckolls**, Columbia University

SESSION IV
PI Highlights: Supramolecular Assemblies

2:05 p.m. Quasi-Particle Dynamics in Electronically and Morphologically Homogeneous Single-Walled Carbon Nanotubes
Michael J. Therien, Duke University

2:10 p.m. A Paradigm Shift Inspired by Nature: Supramolecular Assemblies for Solar-Energy Harvesting
Dorthe M. Eisele, City University of New York

2:15 p.m. Light Harvesting "Antenna" Behavior in Chromophoric Metal-organic Frameworks
Joseph T. Hupp, Northwestern University

2:20 p.m. Integrated Arrays for Panchromatic Light Harvesting and Long-Lived Charge Separation
Dewey Holton and **Christine Kirmaier**, Washington University
David F. Bocian, University of California Riverside
Jonathan S. Lindsey, North Carolina State University

2:25 p.m. Energy Transfer, Charge Separation, and Photo-driven Water Oxidation at Metal Organic Framework Interfaces
Amanda Morris, Virginia Tech

2:30 p.m. Toward a 10% efficient light-driven proton pump
Shane Ardo, University of California Irvine

SESSION V
PI Highlights: Ultrafast Electron Transfer

2:35 p.m. Interplay of Vibrational Wavepackets During an Ultrafast Electron Transfer Reaction
Gregory D. Scholes, Princeton University

2:40 p.m. Exciton Dissociation, Transport, and Interactions in Two-Dimensional Heterostructures
Libai Huang, Purdue University

2:45 p.m. Vibrational Coupling and Conformational Dynamics in Interfacial Electron Transfer
Lars Gundlach, University of Delaware

2:50 p.m. Three Approaches for Enhancing the Efficiency of Plasmon Induced Hot Electron Transfer
Tianquan Lian, Emory University

2:55 p.m. Correlated Spectroscopic and Structural Probes of Charge Transport in Lead Halide Perovskites
Erik M. Grumstrup, Montana State University

3:15 p.m. Break

SESSION VI
New Projects: Molecular Chromophores and Catalysts

3:45 p.m. Single-Molecule Photocatalysts for H2 Production with Red Light
Claudia Turro, The Ohio State University

4:00 p.m. Understanding and Controlling Multielectron, Multisubstrate Reactions Involving Complex Architectures and Interfaces
Gary F. Moore, Arizona State University

4:15 p.m. Design and Structural Analysis of Covalent Organic Frameworks as CO_2 Photoreduction Catalysts
Jier Huang, Marquette University

4:30 p.m. Probing Water Oxidation Mechanisms on Heterogeneous Catalysts
Dunwei Wang and **Matthias Waegele**, Boston College

4:45 p.m. Observation of a Potential-Dependent Switch of the Water-Oxidation Mechanism on Cobalt-Oxide-Based Catalysts (5-min PI Highlight)
Gary W. Brudvig, **Victor S. Batista, Robert H. Crabtree,** and **Charles A. Schmuttenmaer**, Yale University

5:00 p.m. Close for the day

Thursday, June 3

SESSION VII
EFRC Highlights

11:00 a.m. BioLEC EFRC: Taking Inspiration from Nature to Power Up Catalysts
Gregory D. Scholes, Princeton University

11:30 a.m. CHOISE EFRC: Center for Hybrid Organic Inorganic Semiconductors for Energy
Matthew C. Beard, National Renewable Energy Laboratory

SESSION VIII
Lab Programs

12:00 p.m. Fundamental Studies of Redox Processes and Catalysis Relevant to Artificial Photosynthesis and Organic Photovoltaics
Matthew J. Bird, **Javier J. Concepcion**, **Andrew R. Cook**, **Mehmed Z. Ertem**, **Etsuko Fujita**, **David C. Grills**, **Gerald F. Manbeck**, **John R. Miller**, and **Dmitry E. Polyansky**, Brookhaven National Laboratory

1:00 p.m. Break

SESSION IX
PI Highlights: Molecular Chromophores and Catalysts

1:30 p.m.	Excitations and Relaxations of Ruthenium Dyes in Natural Sunlight **Frances A. Houle**, Lawrence Berkeley National Laboratory
1:35 p.m.	Next Generation Cuprous Phenanthroline MLCT Photosensitizers **Felix N. Castellano**, North Carolina State University
1:40 p.m.	Impact of Electric Fields on Charge Transfer Excited States **Gerald J. Meyer**, University of North Carolina
1:45 p.m.	Functionally Active Linker Design for Photoactive Molecules at Semiconductor Interfaces **Elena Galoppini** and **Robert A. Bartynski**, Rutgers University
1:50 p.m.	Controlling Interfacial Charge Separation Energetics and Kinetics **Jared H. Delcamp**, University of Mississippi
1:55 p.m.	Controlling Charge-Transfer Reactions with Cobalt Complexes **Thomas W. Hamann**, Michigan State University
2:00 p.m.	Sensitizers for Solar Fuels Production: (carbene)M(amide) Complexes (M = Cu, Ag, Au) **Mark Thompson** and **Stephen Bradforth**, University of Southern California
2:05 p.m.	Redefining the Reaction Coordinate for Light Capture and Excited-state Dynamics of First-row Transition Metal-based Charge-transfer Chromophores **James K. McCusker**, Michigan State University
2:10 p.m.	Photohydrides: Mechanism-Guided Development of Molecular Photoelectrocatalysts **Alexander J. M. Miller**, University of North Carolina, Chapel Hill
2:15 p.m.	Towards Molecular Water Oxidation Electrocatalysts with More Favorable Stability/Activity Profiles **Doughlas B. Grotjahn** and **Diane K. Smith**, San Diego State University
2:20 p.m.	Mechanisms for CO_2 Reduction Modelled with Metal Carbonyl Clusters **Louise A. Berben**, University of California Davis
2:25 p.m.	Environment and nature of adjacent metals as critical reactivity and photo-induced ET factors in polyoxometalate-based water oxidation catalysts **Craig L. Hill**, **Tianquan Lian**, and **Djamaladdin G. Musaev,** Emory University

2:30 p.m. Selective & Reversible CO_2/HCO_2^- Conversion with Thermodynamic and Kinetic Control
Jenny Y. Yang, University of California Irvine

2:35 p.m. Mixed-Metal Oxide Energy Conversion Catalysts for Integration with Photoabsorbers
Daniel G. Nocera, Harvard University

SESSION X
PI Highlights: Electron Transfer and Proton-Coupled Electron Transfer

2:40 p.m. Multiproton-Coupled Electron Transfer Across Hydrogen-Bond Networks
Ana L. Moore and **Thomas A. Moore**, Arizona State University

2:45 p.m. Theories of Homogeneous and Electrochemical Electron Transfer in Complex Media
Dmitry V. Matyushov, Arizona State University

2:50 p.m. Using Voltammetry to Probe Mechanisms of Surface-Anchored Molecular Catalysts
Jillian L. Dempsey, University of North Carolina

2:55 p.m. Experimental and theoretical evaluation of surface functionalization and interfacial charge transfer kinetics of 2-D layered materials
Nathan S. Lewis, Caltech

3:15 p.m. Break

SESSION XI
New Projects: Semiconductor Photoelectrodes

3:45 p.m. Advancements in AI for Accelerating Discovery of Solar Fuels Materials
John M. Gregoire, Caltech
Carla P. Gomes, Cornell University
Jeffrey B. Neaton, Lawrence Berkeley National Laboratory

4:00 p.m. Exploiting Disordered Photonics for Light Trapping in Photoelectrochemical Energy Conversion Applications
Robert H. Cordian, University of Arkansas

4:15 p.m. Molecular regulation of charge transfer at organic semiconductor electrodes
Erin L. Ratcliff, University of Arizona

4:30 p.m. Atomistic Characterization of Physical and Chemical Characteristics of Metal/Semiconductor Interfaces on Functioning Photocatalysts
Suljo Linic, University of Michigan

5:00 p.m. Close for the day

Friday, June 4

SESSION XII
Lab Programs

11:00 a.m. Charge Transfer Processes in Metal Halide Perovskite Based Light Harvesting Assemblies
Prashant V. Kamat, Notre Dame Radiation Laboratory

11:20 a.m. Spin-Exchange Auger Up-Conversion for “High-Energy” Photochemistry
Victor I. Klimov, Los Alamos National Laboratory

11:40 a.m. Correlating Nuclear and Electronic Dynamics
Graham R. Fleming, Lawrence Berkeley National Laboratory

12:00 p.m. Solar Photoconversion in Molecular, Nanoscale and Semiconductor Systems
Garry Rumbles, **Jeffrey L. Blackburn**, **Elisa M. Miller**, **Nathan R. Neale**, **Justin C. Johnson**, **Jao van de Lagemaat**, and **Matthew C. Beard**, National Renewable Energy Laboratory

1:00 p.m. Break

SESSION XIII
New Projects: Semiconductor Nanoparticles and Systems for Solar Energy Conversion

1:30 p.m. Probing Interfacial Charge Transfer in Heterostructured Nanomaterials using Ultrafast X-ray Spectroscopy
Renske van der Veen, University of Illinois Urbana Champaign

1:45 p.m. Ultrafast carrier dynamics in monolayer MoS_2 photoelectrodes
Justin B. Sambur, Colorado State University

2:00 p.m. Light Harvesting in Semiconductor Quantum Dots
Warren F. Beck, Michigan State University
Benjamin G. Levine, Stony Brook University
Gregory Van Patten and **Mengliang Zhang**, Middle Tennessee State University

2:15 p.m. From Captured CO_2 to Value-added Chemicals: A Photochemical Approach
Ksenija D. Glusac, **Lin X. Chen**, **David Kaphan**, **Alex B. F. Martinson**, **Karen L. Mulfort**, **David M. Tiede**, and **Peter Zapol**, Argonne National Laboratory
Amy Cordones-Hahn, SLAC National Accelerator Laboratory

2:30 p.m. Toward Selective Photocatalytic Conversion of Methane to Methanol by a Colloidal Quantum Dot: Spatio-Temporal Reaction Control and in Situ Methanol Protection Schemes
Emily A. Weiss, Northwestern University

3:00 p.m. Break

SESSION XIV
PI Highlights: Semiconductor Nanoparticles for Solar Energy Conversion

3:30 p.m. Modular Nanoscale and Biomimetic Assemblies for Photocatalytic Hydrogen Generation
Kara L. Bren, **Todd D. Krauss**, and **Ellen M. Matson**, University of Rochester

3:35 p.m. Excited State Dynamics of Photoexcited Charge Carriers in Metal Halide Perovskites: Time-Domain Ab Initio Studies
Oleg Prezhdo, University of Southern California

3:40 p.m. Excited State Surface Chemistry of Colloidal Quantum Dots for Photocatalysis
John B. Asbury, Penn State University

3:45 p.m. Elucidating how semiconductor nanocrystals drive enzymatic N_2 reduction
Paul W. King, National Renewable Energy Laboratory
Gordana Dukovic, University of Colorado Boulder
John W. Peters, Washington State University
Lance C. Seefeldt, Utah State University

3:50 p.m. Metal-Tipped and Electrochemically Wired Semiconductor Nanocrystals: Modular Constructs for Directed Charge Transfer
Neal R. Armstrong, **Jeffrey Pyun**, and **S. Scott Saavedra**, University of Arizona

3:55 p.m. New Systems for Multiple Exciton Creation and Collection
Bruce Parkinson, University of Wyoming

SESSION XV
PI Highlights: Semiconductor Photoelectrochemical Approaches to Solar Fuels

4:00 p.m. Photoelectrochemical Nitrogen Reduction to Ammonia on Cupric and Cuprous Oxide
Kyoung-Shin Choi, University of Wisconsin

4:05 p.m. Managing pH Gradients in Photoelectrochemical Solar Fuel Production
Thomas E. Mallouk, University of Pennsylvania

4:10 p.m. Nanoscale mapping of photoelectrochemical reactivity by SECM
Michael V. Mirkin, City University of New York

4:15 p.m. Toward a Realistic Description of Oxidation at the Semiconductor/Liquid Interfaces
Sylwia Ptasinska, Notre Dame Radiation Laboratory

4:20 p.m. Investigating material properties and electronic dynamics of photovoltaic and photocatalytic thin films in situ using nuclear resonance spectroscopies
Benjamin T. Young, Rhode Island College
Dugan Hayes, University of Rhode Island

4:25 p.m. Using Inverted Surface Photovoltage to Measure Space Charge Regions in Nanostructured Solar Fuel Photocatalysts
Frank E. Osterloh, University of California, Davis

4:30 p.m. Quantitative Analysis of Voltammetric Responses of Adsorbed Redox Species on Semiconductor Electrodes
Stephen Maldonado, University of Michigan

4:35 p.m. Quantitative Analysis of Voltammetric Responses of Adsorbed Redox Species on Semiconductor Electrodes
Stephen Cronin, University of Southern California

4:40 p.m. Nanoscale Properties and Design of Catalyst/Semiconductor Interfaces
Shannon W. Boettcher, University of Oregon

4:45 p.m. Closing Comments
Chris Fecko, DOE Office of Basic Energy Sciences

5:00 p.m. Adjourn

BES Roundtable on Liquid Solar Fuels

Bill Tumas
National Renewable Energy Laboratory
Golden, CO 80401

Sunlight is Earth's most abundant energy resource. Remarkable advances in photovoltaic technologies are allowing society to better capitalize on this resource for electricity generation. Harnessing the power of the sun to produce energy-rich chemicals directly from abundant feedstocks such as water, carbon dioxide (CO_2), and nitrogen (N_2) promises a plentiful supply of sustainable, transportable, and storable solar fuels to meet future US energy needs. Furthermore, solar fuels can provide pathways for efficient chemical energy storage to complement existing electrical energy storage. Solar fuels can also produce diverse chemicals, products, and materials with low environmental impact.

Solar fuels generation—often termed artificial photosynthesis—involves the direct conversion of solar energy to chemical energy using man-made materials and chemical processes. Significant progress has been made to boost the efficiency of solar-driven hydrogen production. Much less progress has been made in the area of liquid solar fuel, an approach that requires chemically transforming CO_2 and other small molecules into promising fuel targets. Hydrocarbons and/or oxygenates produced from CO_2 conversion will be compatible with existing fuels infrastructure. They could also be valuable for production of commodity chemicals and materials. The generation of ammonia and other nitrogen-containing species, which can be used as fuels, fertilizers, and other commodities, presents an opportunity to exploit an extremely abundant feedstock—atmospheric N_2.

The science that underlies solar fuels generation using an artificial photosynthesis approach builds upon decades of sustained fundamental research. Basic research on phenomena in organic and inorganic systems—as well as on the complex biological conversion of sunlight into chemical energy by natural photosynthesis—is advancing the molecular-level understanding of important physical and chemical phenomena such as light absorption, charge generation, electrocatalysis, thermal catalysis, ion and mass transport, and product separations. Light-driven generation of liquid solar fuels requires the coordinated action of a number of phenomena. These processes occur over vastly different time and length scales. Further progress in developing artificial systems for liquid solar fuels production will require new knowledge and advances to control and link individual processes. Components and systems will need to retain their structural and functional properties under operating conditions in real-world environments for significant time periods. Research must identify and advance the scientific principles necessary to achieve selective and efficient fuels production through integration of molecular and material components while ensuring durability.

Basic Energy Sciences held a Roundtable on Liquid Solar Fuels in August 2019 to examine fundamental challenges and research opportunities for generating energy-rich liquids from abundant feedstocks using sunlight as the only energy input. Four Priority Research Opportunities were identified to address critical physical and chemical phenomena required for selective, stable, and efficient direct liquid solar fuels production using an artificial photosynthesis approach. The full report is available at https://science.osti.gov/bes/Community-Resources/Reports.

Fundamental Mechanisms for Solar Energy Conversion in Artificial Photosynthesis

David M. Tiede[1], Lin X. Chen[1,4], Oleg Poluektov[1], Karen L. Mulfort[1], Alex B. F. Martinson[2], Richard D. Schaller[3,4], George C. Schatz[4], Felix N. Castellano[5], Xiaosong Li[6], Amy Cordones-Hahn[7], Ksenija Glusac[1,8]

[1]Chemical Sciences and Engineering and [2]Materials Sciences Divisions, [3]Center for Nanoscale Materials, Argonne National Laboratory; [4]Chemistry Department, Northwestern University;

[5]Chemistry Department, North Carolina State University; [6]Chemistry Department, University of Washington; [7]SLAC, Stanford University; [8]Chemistry Department, University of Illinois at Chicago

The overarching research goal of the Argonne group is to achieve a fundamental understanding of the mechanisms, structures, and design features needed for efficient coupling of light-generated excited-states to multiple-electron, proton-coupled water-splitting and fuels catalysis. This challenge is addressed using a photochemically tiered approach that couples modular synthesis with methods for tracking the electronic and structural dynamics in light-generated excited states, measured on multiple temporal and spatial scales, from atomic motions in model systems to in-situ and operando conditions relevant to solar-to-fuels energy conversion. The program is organized into research objectives focused on understanding fundamental processes along the full trajectory of solar-to-fuels conversion: 1) tracking structural dynamics of the initial excited states of solar energy converting systems in terms of electron density distribution, vibronic coherence, and more importantly the key reaction coordinates to influence photochemical outcome; 2) designing vectorial charge transfer (CT) in donor-acceptor assemblies and the role for spin state dynamics in controlling charge separation (CS) processes, and understanding how these can be manipulated to drive long-range, multi-step charge separation processes; and 3) the use of CT and CS to initiate multi-electron, multi-step hydrogen evolution (HER) and oxygen evolution (OER) reactions, and the testing of mechanisms for linking single electron excited states to multi-step fuels catalysis. The program highlights the combination of advanced (supra)molecular and atomic layer synthesis approaches to achieve modular artificial photosynthetic architectures with the tracking of fundamental mechanisms for solar-to-fuels energy conversion using continuous and time-resolved X-ray spectroscopy and reciprocal space techniques, multi-frequency and time-resolved electron paramagnetic resonance (EPR), and transient optical spectroscopies. The program resolves fundamental mechanisms needed to design efficient solar energy-to-fuels conversion.

Tracking Excited State Structural Dynamics for Solar Energy Converting Systems

Generation of electronic excited states via solar photons is the first step leading to various photochemical reactions. Studies have revealed that the excited state trajectories before thermal equilibrium are foundational for predicting, and ultimately steering, subsequent reaction steps. Tracking these excited state trajectories requires a mapping of the potential energy (PE) levels and nuclear motions across the excited state landscape. Accordingly, we have initiated two collaborative research team projects to develop advanced laser spectroscopy and ultrafast X-ray light source (e.g., LCLS, APS) approaches for interrogating electronic and nuclear dynamics across excited state landscapes. These programs combine effort in molecular/material synthesis, structural dynamics characterization, and theory. The main aims are 1) identifying key reaction coordinates in photochemical reactions, 2) steering the reaction via different external sources, and 3) rationalizing and predicting photochemical outcomes. Solar energy conversion model systems have been studied, such as transition metal complexes and molecules-nanoparticle/cluster hybrids. We investigate nuclear coordinates responsive to the electron density shift in the excited states, the rate/amplitude/phase of coherent nuclear motions as well as their influence on energy and charge migration within and between light activated systems. These research activities are illustrated by the two examples here.

Evanescent Excited State Dynamics of Photoluminescent Pt(II) dimers Probed by Coherent Vibrational Wavepackets. Femtosecond intersystem crossing (ISC) dynamics were probed by Pt-Pt stretching coherent vibrational wavepacket motion from the metal-metal-to-ligand-charge-transfer (MMLCT) excited states in Pt(II) dimers (Figure 1A). Structure-dependent coherent wavepacket behavior, e.g., dephasing time and oscillation amplitudes (Figure 1B), were examined by quantum mechanical calculations on the excited-state potential energy surfaces (PESs) (Figure 1C). When the conical intersections of the PESs for the S_1 (^{1}MMLCT) and the triplet intermediate T_2 states and for the T_2 and T_1(^{3}MMLCT) states are near the Franck-Condon region along the reaction coordinate, the vibrational coherence transfer takes place, resulting in prolonged vibrational dephasing times beyond the ISC time (Figure 1B). The conserved vibrational coherence revealed a previously unknown evanescent ISC pathway in Pt(II) dimers. Concurrently, the time evolution of Pt-Pt distance in the excited state has been visualized as shortening followed by oscillations using ultrafast X-ray solution scattering (Figure 1D) to build the structural basis for calculating the impact of vibrational motions on the excited state paths. These results will enable further investigation of the effects of electronic and nuclear coherence in photoinduced electron transfer with covalently attached electron acceptors (Figure 1E).

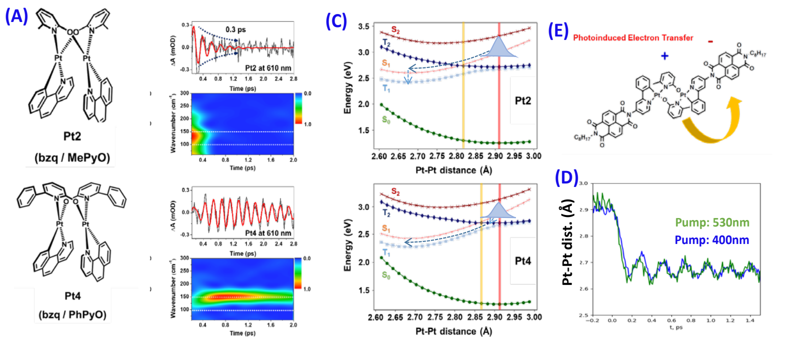

Figure 1. A) Structures of two Pt-dimers; B) coherent vibrational wavepacket dynamics detected by broad band fs transient absorption spectroscopy; C) calculated PESs showing conical intersections for S_1/T_2 and T_2/T_1 to explain dual intersystem cross pathways. D) ultrafast solution X-ray scattering revealed the time evolution of the Pt-Pt distance change, showing that the Pt-Pt shortening in <100 fs and ~0.1 Å Pt-Pt distance oscillations; E) effects of vibronic coherence in photoinduced electron transfer is under investigation.

Unveiling Dynamics in Bridged Bimetallic Complexes Using Ultrafast Optical and X-ray Spectroscopies. Hetero-bimetallic systems are model platforms for studying directional charge transport in artificial photosynthetic systems (Figure 2A). However, tracking charge migration through molecular systems especially those including metal centers has been a challenge because the optical features of the metal centers oftentimes overlap and are relatively weak. In this study, optical and X-ray spectroscopy are used to

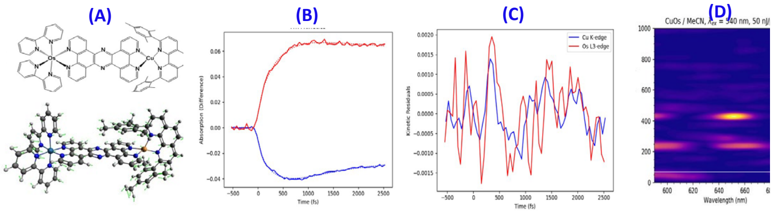

Figure 2. A) Structure and vibrational vectors of 60 cm^{-1} for the Os-Cu complex; B) excited state structural dynamics detected from the X-ray transient absorption difference spectra at Os L_{III}-edge and Cu K-edge, respectively (using SACLA); C) the concerted oscillatory signals at two metal centers shown by electron density changes due to the mode depicted in A) which was also detected by broad band transient absorption spectra, shown in D) (60 cm^{-1} marked by a while line).

interrogate the ultrafast dynamics of a bridged Cu(I)/Os(II) complex (Figure 2B). The MLCT excited-states for both the Cu and Os exhibit similar early-time kinetics; further, concerted coherent vibrations are observed that involve both metal centers (Figures 2C&D). This study shows how electronic coupling between two transition metal centers can be mediated by the delocalized bridging ligand vibrational modes, even at the earliest times following photoexcitation.

Designing Vectorial Charge Transfer and Spin Dynamics in Donor-Acceptor Excited States.

Building from the resolution of ultrafast structural and PE dynamics initial excited states, this program is investigating mechanisms for achieving vectorial charge transfer inorganic and organic donor-acceptor assemblies, and understanding how these can be manipulated to drive long-range, multi-step charge separation processes.

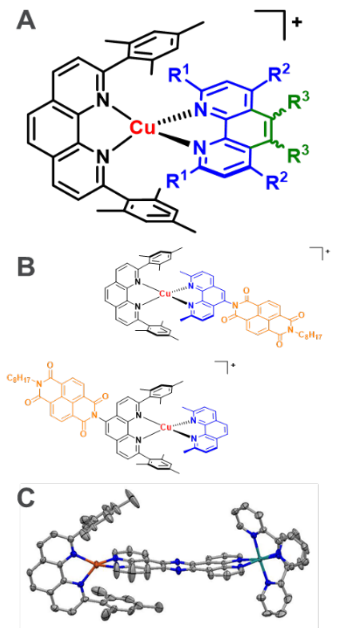

Figure 3. A) General chemical structure of the CuHETPHEN module. Blocking phen ligand in black, secondary phen ligand in blue. B) Chemical structures of CuHETPHEN-NDI dyads. C) Crystal structure of hetero-bimetallic CuHETPHEN—$Ru(bpy)_3^{2+}$ complex.

Inorganic Donor-Acceptor Complexes. Concepts for achieving directional charge transfer from heteroleptic coordination complexes are being investigated by the development of heteroleptic Cu(I)bis(1,10-phenanthroline) (CuHETPHEN) complexes and their integration into donor-acceptor dyads and multimetallic assemblies (Figure 3). Benchmarking studies of CuHETPHEN model complexes show that modification of the phenanthroline ligand sterics adjacent to the Cu(I) center dramatically influences the excited state lifetime, allowing us to tune the ^{3}MLCT lifetime across orders of magnitude. A series of molecular dyads composed of a CuHETPHEN electron donor with a naphthalene diimide electron acceptor linked to either the blocking ligand or secondary ligand has allowed us to observe that initial electron transfer occurs with near quantum unity toward the blocking ligand and that charge separation is facilitated by minimal steric substitution adjacent to the Cu(I) center. A series of homo- and heterobimetallic assemblies linking CuHETPHEN modules with $Ru(bpy)_3^{2+}$ modules was synthesized and investigated by time-resolved optical and X-ray spectroscopies and allowed us to map the complex photoinduced energy and electron transfer pathways between both metal centers and the conjugated bridging ligand. These studies are establishing the foundational knowledge needed for the integration of CuHETPHEN complexes into photocatalyst architectures.

Organic Donor-Acceptor Assemblies. In a complementary approach, we are investigating the mechanisms, length, and time scales for light-induced CS in conjugated organic donor-acceptor systems. Our recent work to investigate CS distances used pulsed EPR techniques, high-frequency (130 GHz) D-band EPR in combination with pulsed ENDOR techniques, and DFT calculations to unravel electronic structure of light-induced positive polaron and triplet exciton states of specially synthesized short PTB7-type oligomers. This work is demonstrating opportunities to extend these architectures for photo-HER.

Connecting Light-Excited States to Multi-Step Fuels Catalysis.

Photo-HER. As an approach for the design of molecular catalysts that efficiently function as electron acceptors from light-excited states and drive proton-to-hydrogen reduction, this program investigates how manipulations of catalysts at the atomic level impact activity and mechanism, and with a particular focus on mononuclear Co(II) catalysts. We have designed and synthesized a family of Co(II)poly(pyridyl) catalysts which incorporate redox-active bipyridine groups linked by nitrogen groups, both components which can participate in electron and proton transfer steps in the catalytic cycle (Figure 4). Photocatalysis measurements show that these catalysts are highly active for aqueous proton reduction at moderate pH levels, with one variation reaching almost 2 x 10^4 turnovers of H_2 when photo-driven by $[Ru(bpy)_3]^{2+}$ using ascorbate as an electron relay and a phosphine compound as the terminal electron donor. Measurements of the electrocatalytic activity were used to investigate key steps in the mechanism of proton reduction, and from a detailed analysis of these experiments we propose a mechanism for catalytic proton reduction to H_2 that involves both intramolecular proton and electron transfer steps between the macrocycle ligand to the cobalt center. Multi-frequency EPR/ENDOR spectroscopy was used to determine the key magnetic parameters of relevant nuclei for these molecular catalysts (e.g. ^{59}Co, ^{14}N, and ^{31}P). Coupled with computational (DFT) analysis, we can identify specific molecular conformations, the spin density distribution on cobalt and ligand atoms, and interactions with coordinating solvent molecules. The combination of HER activity and mechanistic analyses, EPR spectroscopy, and DFT-calculated electronic structure has revealed trends in electronic structures of the mononuclear cobalt catalysts that are critical for next-generation catalyst designs.

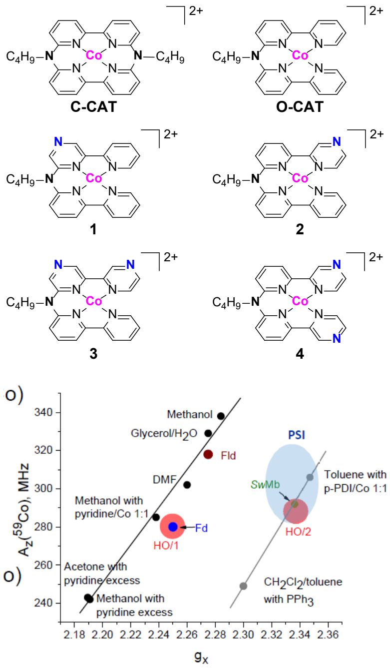

Figure 4. Top: molecular structures of Co(II) HER catalysts. Bottom: correlation of EPR parameters A_Z with g_X for cobaloxime catalysts tuned by differing solvent environments.

Photo-OER. We are investigating X-ray approaches for resolving atomic and electronic structures and mechanisms for light driven OER catalysis from water as an electron source for solar-to-fuels conversion. As summarized in Figure 5, our X-ray scattering and atomic pair distribution function (PDF) analyses on an amorphous cobalt oxide OER catalyst formed by electrochemical deposition in the presence of phosphate, CoOx-Pi, and the cobalt cubane model OER complexes have resolved metal atom redox-state dependent structure, while X-ray spectroscopy has a identified LMCT and MMCT transitions in both CoOx-Pi and Co-cubane. These data, together with the optical properties, suggests opportunities for light excitation of metal-oxo CT transitions to trigger atom-centered oxidation related to precursors for catalysis. Accordingly, we will report on the discovery of light-induced electrochemical responses in the CoOx-Pi OER catalyst.

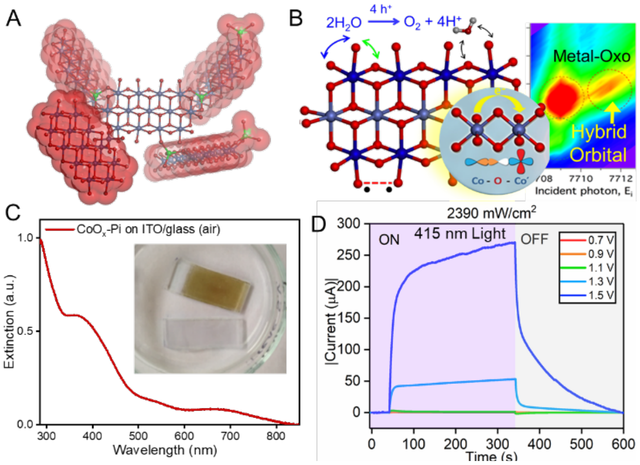

Figure 5. Atomic structure (A), representation of X-ray detected LMCT and MMCT electronic structure (B), UV-VIS absorption (C), and photo-electrochemical properties (D) of the amorphous cobalt oxide OER catalyst.

Singlet Fission

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We have continued a rational search for new singlet fission chromopores, treating both (i) their molecular structure and (ii) their crystal packing. As a new chromophore, we have studied alkylated 2,3-diamino-1,4-naphthoquinones. We found that they produce triplets via a short-lived charge-separated state intermediate formed in the first picosecond. Such states are frequently considered favorable for singlet fission, but use of isotopically labelled derivatives showed that in our case they yield triplets by intersystem crossing using the radical pair mechanism. This casts doubt on the frequently made assumption that in the absence of special structural features (such as $n\pi^*$ transitions or heavy atoms), very fast triplet formation implies singlet fission mechanism. As for (ii), an investigation of the photophysics and the widely differing crystal structures of a dozen variously fluorinated 1,3-diphenylisobenzofurans has been completed. About half of them perform singlet fission and the other half form excimers. These results have been rationalized using the previously developed computer program SIMPLE, based on an evaluation of interactions within pairs of molecular neighbors. The results revealed that more than two molecules need to be considered simultaneously and we are now extending the search for all optimal geometries (local maxima of singlet fission rate) of a molecular pair to all optimal geometries of a group of three molecules. The first step, programming of a Smolyak fit to a polynomial, has been completed, and we are now coding a search for all local maxima of the polynomial. An examination of crystal engineering methods for modifying crystal structures in desirable directions has started.

Femtosecond Stimulated Raman Spectroscopy–Guided Screening Leads to Efficient Singlet Fission in Rubrene Derivatives

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Ultrafast vibrational spectroscopies provide the ability to follow structural changes on timescales relevant for solar energy conversion. Our lab uses femtosecond stimulated Raman spectroscopy (FSRS) to identify the relevance of specific nuclear motions and vibrational or vibronic coherences in electron transfer and singlet fission processes. Building off of previous DOE-funded work on singlet fission[1-3], here we use the structural insights provided by FSRS in order to rationally design new derivatives for fast and efficient singlet fission.

A major bottleneck in the singlet fission and organic photovoltaic fields is the challenge of designing or discovering new molecules which will improve photophysical properties, while not altering other parameters such as crystal packing or solubility which can hinder overall device performance. Traditionally, spectroscopic measurements have not provided much insight for rational design of new chromophores, but rather have been used to understand why an existing system works well. Here, we show how spectroscopy-guided screening within a set of rubrene derivatives can effectively select for optimal photovoltaic properties. Specifically, we use FSRS to create a predictive model for the design and identification of rubrene derivatives that show an order-of-magnitude increase in singlet fission rates with concurrent drop in energy loss due to structural reorganization during the fission process. Our work shows that spectroscopy-informed molecular design can be realized in rubrene-based singlet fission materials.

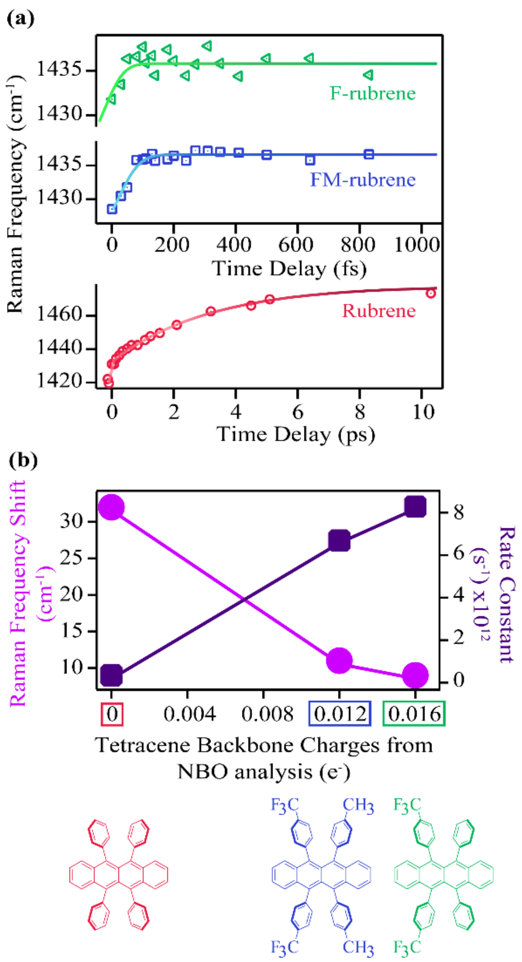

Figure 1. Vibrational spectroscopy guides rational design of more efficient singlet fission chromophores. (a) Vibrational frequency shifts associated with correlated triplet pair separation. (b) Structural rearrangements are inversely correlated with fission rate.

1. Bera, K., Douglas, C. J., Frontiera, R. R., *J. Phys. Chem. Lett.*, **2017**, 8 (23), 5929–5934. 2. Hart, S. M., Silva, W. R., Frontiera, R. R. *Chem. Sci.*, **2018**, 9, 1242-1250. 3. Bera, K.*, Kwang, S. Y.*, Frontiera, R. R. *J. Phys. Chem. C*, **2020**, 124, 46, 25163-25174.

Structure–Function Relationship in a Flexible Perylene Diimide Tetramer Illustrating Singlet Exciton Fission

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For organic photovoltaics (OPVs), we seek to characterize novel materials with a potential to improve the power conversion efficiency (PCE). Some organic systems exhibit the process of intramolecular singlet exciton fission (iSEF). This process leads to the production of two electron–hole pairs for each absorbed photon of an OPV device. Recent studies show that linker flexibility is crucial in activating iSEF in perylene diimide (PDI) systems. Here, we present our latest results which compare the photophysical properties of two flexible PDI tetramers, α and β. While β–functionalization leads to strong co–facial π–π interactions which favor the formation of excimers, an almost perpendicular geometry is obtained for α. Although the double triplet and triplet energy calculations show that iSEF is energetically unfavorable for both chromophores, a high triplet quantum yields of 124% is obtained for α in chlorobenzene. However, the excimers observed for β trap singlet excitons inhibiting iSEF, and hence a triplet yield of 17% is observed. For α, excimers were not found to form and excited state coupling mechanisms contribute to the illustration of the large triplet yield in this system. These results provide structure-function properties useful in the design of new iSEF organic systems.

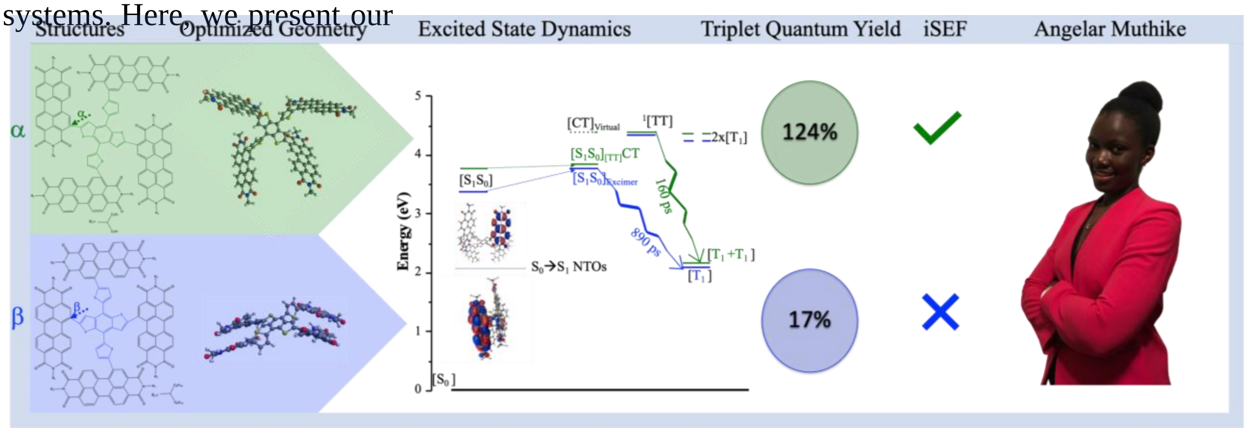

Figure 1: *Structures, optimized geometries, excited state dynamics and the obtained triplet yields for both α and β tetramers showing the presence or lack of iSEF. On the right is a picture of Angelar K. Muthike, the graduate student who led this study.*

References:

1. Muthike, A.K.; Carlotti, B.; Madu, I.K.; Jiang, H.; Kim, H.; Qinghe, W.; Yu, L.; Zimmerman, P.M.; Goodson, T. III. Submitted, *Chem. Mater.* **2021.**
2. Carlotti, B.; Madu, I.K.; Kim, H.; Cai, Z.; Jiang, H.; Muthike, A.K.; Yu, L.; Zimmerman, P.M.; Goodson, T. III. *Chem. Sci.* **2020**, 11, 8757-8770.

Symmetry-Breaking Charge Separation in Molecular Crystals

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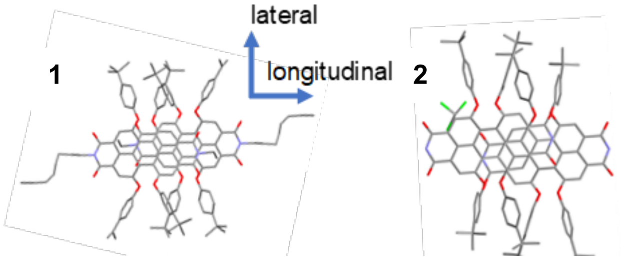
Project Scope: Our research focuses on 1) singlet fission to substantially enhance light harvesting efficiency in polycrystalline and single crystal molecular solids; 2) the fundamental structural, electronic, and energetic requirements for efficient photo-driven charge generation using symmetry-breaking charge separation (SB-CS) in molecular crystals and self-assembled nanostructures; 3) integrating photosensitizers based on radical ions that act as super-redox agents with catalysts to give the high chemical potentials needed to drive energy-demanding chemistry.

Recent Results: Generation of electron-hole pairs via SB-CS in photoexcited assemblies of organic chromophores is a potentially important route to enhancing the open-circuit voltage of photovoltaics. While most reports of SB-CS have focused on molecular dimers in solution, where the solvent polarity can be manipulated, we have shown that SB-CS in thin solid films of **1** and **2**. Single crystal structures of these molecules reveal that while both compounds show π-π stacking in thin films, **2** is more slip-stacked than **1** and has intermolecular hydrogen bonds to its neighboring molecules (Fig. 1). Transient absorption spectroscopy shows that **1** exhibits strong mixing between its singlet excited state and a charge transfer state (Fig. 1A, yielding an excimer-like state and a weak $PDI^{\bullet-}$ band at 780 nm resulting from formation of the CT state, while **2** undergoes nearly quantitative SB-CS (Fig. 1B). Although these films are nonpolar, PDI has a strong quadrupole moment that increases as the length of the alkyl group attached to its imide position decreases. Thus, PDI molecules can essentially "solvate" each other, and **1** may experience an overall less polar environment than **2**, partially rationalizing why SB-CS occurs more readily in **2** than in **1**. Self-solvation may stabilize the CT state and enable ultrafast SB-CS.



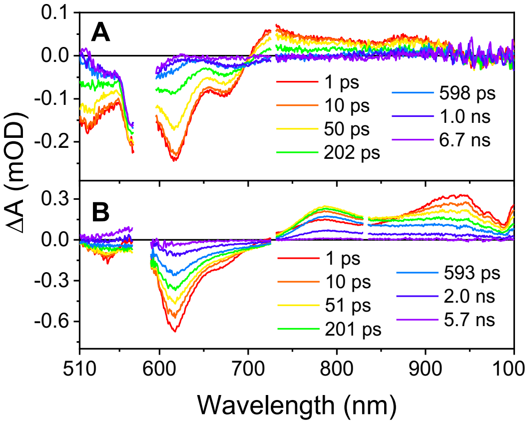


Fig. 1. The crystal structures of **1** (X = 4-t-BuPhO; R = n-C_8H_{17}) and **2** (X = 4-t-BuPhO; R = H). fsTA spectra of polycrystalline films of **1** (A) and **2** (B).

Future Plans: We will employ X-ray structural techniques at the APS at Argonne to characterize molecular structures and assemblies. We will also use femtosecond transient optical and time-resolved EPR measurements to determine the dynamics of energy and charge transfer in molecular solids to obtain detailed information essential to understanding how to design integrated molecular systems for photochemical solar energy conversion.

Dexter Energy Transfer Mechanisms

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Scope: An ability to control and direct the flow of triplet excitons through molecular and nanostructured assemblies, and especially across molecule-nanoparticle interfaces, is anticipated to have wide-ranging impact in energy science. The migration of triplet excitons is essential for exciton fission and fusion reactions, which are of great interest for enhancing the performance of solar cells. This project develops and applies theoretical approaches to understand and control the flow of triplet excitation energy, through Dexter energy transport (DET) and other mechanisms, in molecular and nanostructured assemblies.

Recent results: **(1)** We developed an approach to perform DET coupling-pathway decompositions (Fig. 1) and thus to understand the origins of Dexter coupling interactions at the nanoscale [1,2]. The strategy is based, in part, on the computation of HOMO-HOMO and LUMO-LUMO overlaps (Fig. 2). This approach allows us to understand features of molecular structure that control Dexter couplings and the associated transport kinetics. **(2)** Recent experiments find time-resolved electron paramagnetic resonance (TR-EPR) signatures of triplet excitons in molecules with weak spin-orbit couplings, raising the question of how the triplet excited states are generated. Our theoretical analysis finds that the TR-EPR triplet signals arise from triplet populations created directly by the photoexcitation, rather than from intersystem crossing from an excited singlet state [3]. **(3)** We have also made progress on designing and simulating polymers with extended triplet exciton states and in simulating the electronic structure of small molecules adsorbed on semiconducting nanoparticle surfaces [4].

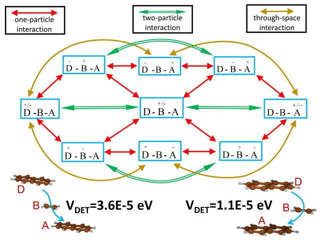

Figure 1. Dexter pathways in a DBA stacked structure.[2]

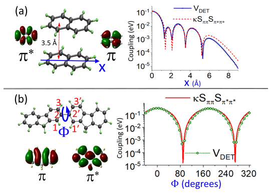

Figure 2. Approximations to the Dexter couplings from the product of HOMO-HOMO and LUMO-LUMO overlap factors.[2]

Future plans: Our plans involve understanding DET across quantum dot-molecule interfaces, exploring triplet energy transport in molecular and nanoparticle networks, and developing practical electronic structure methods to assist in the design, interpretation, and direction of electronic excitation energy in molecule-quantum dot assemblies.

References: **1**. S. Bai, P. Zhang, P. Antoniou, S.S. Skourtis, and D.N. Beratan, "Quantum interferences among Dexter coupling pathways," Faraday Discuss., 216, 301-318 (2019). **2.** S. Bai, P. Zhang, and D.N. Beratan, "Predicting Dexter energy transfer interactions from molecular orbital overlaps," J. Phys. Chem. C, 124, 18956-18960 (2020). **3.** S. A Mavrommati, S.S. Skourtis, "Initial-State Preparation Effects in Time-Resolved Electron Paramagnetic Resonance Experiments," J. Chem. Phys., 152, 044304 (2020). 4. S.A. Mavrommati and S.S. Skourtis, "Molecular wires for efficient long-distance triplet energy transfer," in preparation (2021).

Towards Efficient Up- and Down-Conversion with Nanocrystals Light Absorbers

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Tianquan Lian[3], Sean Roberts[4], and Ming Lee Tang[1,2]

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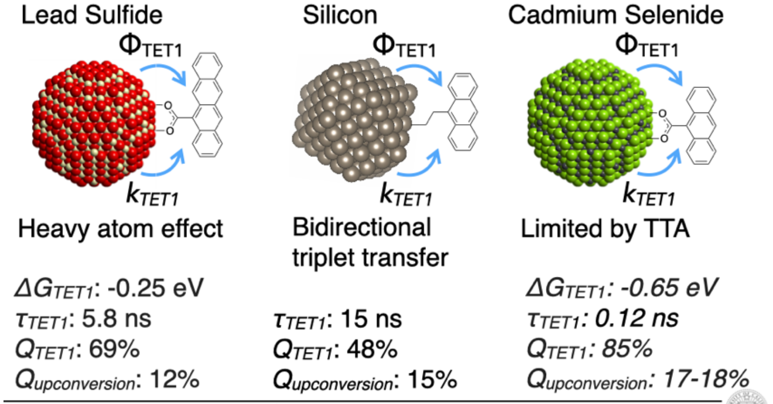
The overarching theme is to establish the physical rules governing efficient triplet energy transfer at the nanoscale, in order to efficiently control light-matter interactions. In particular, we focus on photosensitized triplet states for efficient energy conversion, with the ultimate goal of increasing solar cell conversion efficiency with materials like nanocrystals and conjugated organic molecules. These next generation materials can strongly couple to light to generate long-lived spin-triplet excitons. For example, tetracene undergoes singlet fission quantitatively and nanocrystals can photosensitize triplet states with due to their small exchange term.



τ_{TET1} is normalized for the rate of one NC to one transmitter;
ΔG_{TET1} is from the abs maxima of direct gap chalcogenide NCs.

We have examined many nanocrystal-molecule interfaces shown on the left. For the II-VI materials, with support from the Solar Photochemistry program, we have established that upper limit for triplet-triplet annihilation-based photon upconversion efficiencies ~20%. The use of defect-free nanocrystals, strongly bound transmitter ligands, energy gradients, etc., all contribute to lengthening donor lifetime, whether in the form of inorganic nanocrystal exciton lifetime, or transmitter ligand triplet lifetime[1]. This motivated a foray into Si nanocrystals, which naturally proffer a microsecond lifetime while being earth-abundant and environmentally benign, compared to Cd or Pb based nanocrystals. As shown in the figure above, we were the first to use Si nanocrystals to photosensitize molecular triplet states[2]. The covalent nature of the Si-transmitter bond provides an avenue to use the diversity in organic bonds to control conductivity and exciton delocalization. As an example, Si nanocrystal functionalization with anthracene and perylene results in drastically different triplet energy transfer rates because the transmitter ligands differ in the energetics of their lowest triplet excited state[3]. In the future, we will investigate different synthetic routes to installing interesting transmitter ligands for the purposes of enhancing the quantum yields of singlet fission and photon upconversion.

DOE Solar Photochemistry Sponsored Publications 2021

1. Z. Xu, Z. Huang, T. Jin, T. Lian, **M. L. Tang** "Mechanistic understanding and rational design of quantum dot/mediator interfaces for efficient photon upconversion", *Acc. Chem. Res.*, 12, 36558, **2021**. (invited, selected for journal cover).
2. P. Xia, E. K. Raulerson, D. Coleman, C. S. Gerke, L. Mangolini, **M. L. Tang**, S. T. Roberts, "Achieving Spin-triplet Exciton Transfer between Silicon and Molecular Acceptors for Photon Upconversion" *Nature Chem.*, 12, 137, **2020**.
3. T. Huang, T. Koh, J. Schwan, T. Tran, P. Xia, L. Mangolini, **M. L. Tang**, S. T. Roberts, " Bidirectional Triplet Exciton Transfer Between Silicon Quantum Dots and Perylene Molecules in a Red-to-Blue Photon Upconversion System" **2021** (in press).

Controlling Singlet Fission by Molecular Contortion (DE-SC0014563)

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The PIs have successfully developed the new strategy of controlling singlet fission from molecular contortion, synthesized new candidate molecules, and carried out in-depth analysis of key mechanistic issues in this process. Within the HOMO-LUMO (H-L) approximation, the singlet energy is $E_{S1} = E_0 + K_0$ and the triplet energy is $E_{T1} = E_0 - K_0$, where E_0 is the HOMO-LUMO excitation energy and K_0 is the HOMO-LUMO two-electron exchange energy. In a single particle picture and tight-binding approximation, E_0 is proportional to the inter-atomic exchange integral. For the two-electron exchange interaction in the lowest electronically excited state, K_0 is given by

$$K_0 = \langle H(1)L(2) \left| \frac{1}{r_{12}} \right| H(2)L(1) \rangle \qquad (1).$$

This term is usually positive and, thus, S_1 is higher in energy than T_1. For singlet fission, the enthalpy change is $\Delta E_{SF} = 2E_{T1} - E_{S1} = E_0 - 3K_0$. Tuning E_0 requires a change to the inter-atomic exchange integral and the extent of π-delocalization in a conjugated chromophore. This result in a change in S_1 and T_1 energies collectively. Contortion destabilizes the π bond and reduces E_0 and thus S_1 and T_1 energies by similar amounts, with little change to K_0. This can bring an otherwise endoergic singlet fission process to exoergic or less endoergic. The contortion strategy allowed the PIs to accelerate singlet fission in two molecular systems. In perylene diimide, the PIs decreased E_0 by straining the molecule and tuned singlet fission energetics from endoergic to iso-energetic. As a result, the singlet fission rate was increased by two orders of magnitude over that of the unstrained molecule. In perylene thin films, singlet fission does not happen due to a large endoergicity. This endoergicity could be decreased by half and singlet fission could be turned on in thin films of strained perylenes (Fig. 1).

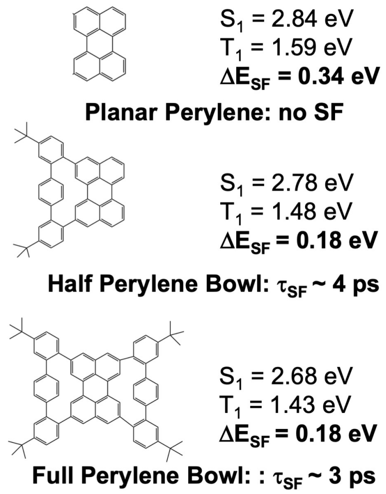

Fig. 1. Switching on singlet fission in perylene by molecular contortion. Singlet fission does not occur in perylene thin films due to the large endo-ergicity. Molecular contortion reduces the endo-ergicity and turns on singlet fission, with time constants of 3-4 ps in solid thin films.

Quasi-Particle Dynamics in Electronically and Morphologically Homogeneous Single-Walled Carbon Nanotubes

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The formation of quasiparticles, such as polarons, excitons, and trions, is crucial to solar energy conversion reactions of single-walled carbon nanotubes (SWNTs), as these species respectively carry charge, excitation energy, and spin. Unraveling the spectroscopic and dynamic properties of these quasiparticles in SWNTs has proved challenging due to the electronic and morphological heterogeneity of commonly interrogated SWNT samples. We have developed families of highly charged, chiral anionic semiconducting polymer-SWNT superstructures in which the polymer wraps at periodic and constant morphology (**Fig. 1A**). These polymers define tools to modulate SWNT electronic properties, provide expansive solubility, and organize functional organic moieties at predefined intervals along the SWNT surface. These robust superstructures enable multiple rigorous separation procedures that permit isolation of highly enriched single diameter, length-sorted metallic and semiconducting SWNTs; recent advances along these lines include the development of new approaches that separate SWNT enantiomers (**Fig. 1B**). These uniquely engineered, consistent nanoscale carbon nanotube superstructures define assemblies with which to probe quasi-particle spectroscopic signatures and dynamics (**Fig. 1C-D**) and light-triggered energy conversion reactions, as well as tools to unmask how these spectral signatures and dynamics depend upon absolute SWNT electron- or hole-doping levels.

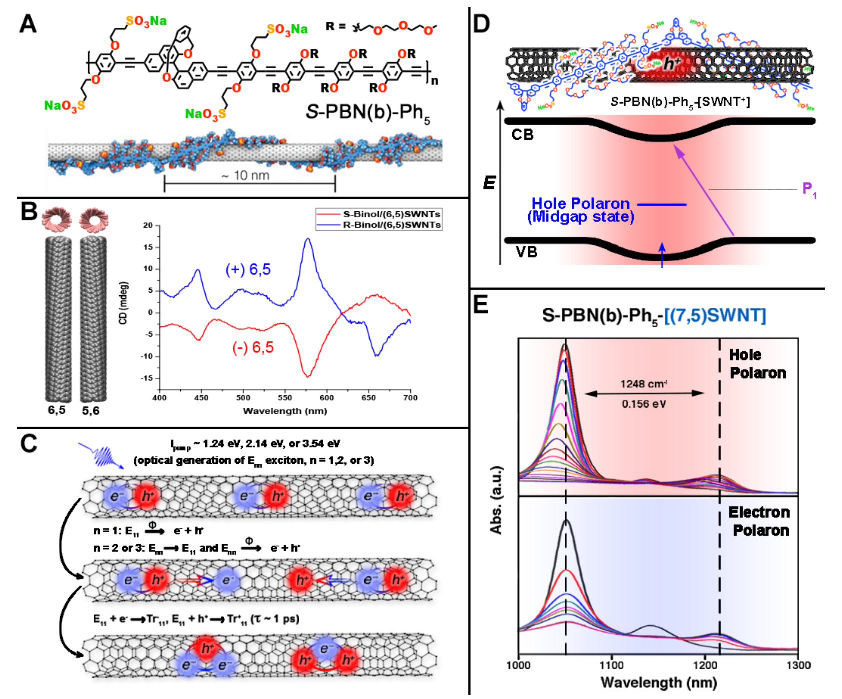

Figure 1. (A) Prototypical chiral semiconducting arylenethynylene polymer-wrapped SWNT assembly. (B) Cartoon and representative CD spectra of enantioenriched (+)(6,5)SWNT and (-)(6,5)SWNT enantiomers. (C) Ultrafast trion formation in neutral SWNTs following: (i) optical production of E_{nn} excitons (n = 1, 2, or 3), (ii) exciton dissociation into unbound h^+ and e^-, and (iii) exciton migration to h^+ or e^- polaron sites and trion formation. (D) Schematic illustration depicting hole polaron midgap states associated with ***S*-PBN(b)-Ph$_5$-[(6,5) SWNT]** superstructure. The band bending depicted is generated over the SWNT spatial domain consistent with the polaron delocalization length (~2.8 nm). (E) Electronic absorption spectra of ***S*-PBN(b)-Ph$_5$-[(7,5) SWNTs]** showing the characteristic hole- and electron-polaron absorptive features.

A Paradigm Shift Inspired by Nature: Supramolecular Assemblies for Solar-Energy Harvesting

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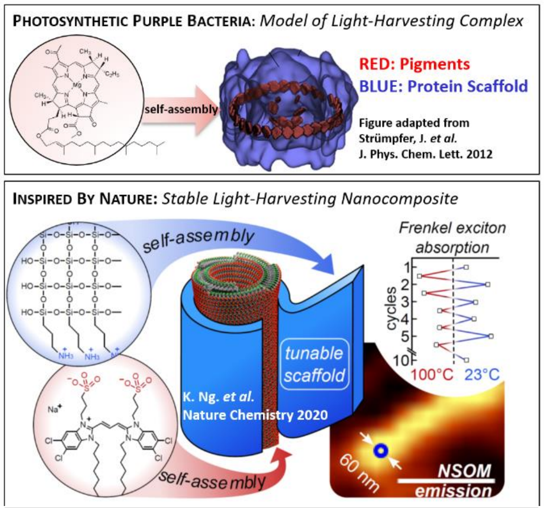
[3]Chemistry, New York University; [4]Chemistry, Queens College; Eisele@EiseleGroup.com

The future of sustainable energy technologies requires not only highly efficient but also robust light-harvesting (LH) materials, especially as rising global temperatures (increase of extreme weather events such as excessively high temperatures) threaten the efficiency of existing photovoltaic installations. Unlike current solar energy conversion technologies, natural photosynthetic organisms [1] have clearly evolved beyond these challenges, capturing and transporting solar energy both robustly and efficiently even under extreme environmental stress. In photosynthetic organisms, the first step (that is, light harvesting) involves the interaction between light energy and the light-harvesting antenna, which are composed of delicate, weakly bound structures known as supramolecular assemblies (**Fig.-TOP**). Delocalized Frenkel excitons—coherently shared excitations among molecular chromophores—are responsible for the remarkable efficiency of supramolecular light-harvesting assemblies within those photosynthetic organisms. However, the translation of nature's successful design principles to applications in optoelectronic devices has been limited by the fragility of the supramolecular structures used and the delicate nature of Frenkel excitons.

We present a proof-of-concept demonstration that the intrinsic barriers towards functionalization of supramolecular assemblies can finally be overcome; through *in situ* cage-like scaffolding of individual supramolecular LH nanotubes [2], we designed highly stable supramolecular nanocomposites [3] with discretely tunable (~4.7-5.0 nm), uniform (±0.3 nm), cage-like scaffolds (**Fig.-BOTTOM**). High-resolution cryoTEM, spectroscopy, and near-field scanning optical microscopy (NSOM) revealed supramolecular excitons within cage-like scaffolds are robust, even under extreme heat stress. Together, these results indicate that our novel supramolecular nanocomposite system is a successful, critical first step towards the development of practical bio-inspired LH materials for solar-energy conversion technologies as well as a basis for future fundamental investigations that were previously not possible, such as dilution of supramolecular assemblies required for single-molecule imaging or precise tunability of scaffold dimensions for controlled functionalization of hybrid model systems, such as plasmonic-excitonic (plexcitonic) systems.



***TOP**: Nature's successful design principle for solar energy harvesting involves delicate supra-molecular assemblies that are embedded within a dynamic, non-rigid protein (or lipid) scaffold. **BOTTOM**: Proof-of-concept demonstration that shows how to overcome barriers to functionalize artificial supra-molecular assemblies.*

[1] Scholes, G.D., *et al. NatureChem*. 2011; [2] Eisele, D.M., *et al.*, *NatureChem*. 2012; Eisele, D.M., *et al.*, *NatureNanotech*. 2009; Eisele, D.M., *et al.*, *PNAS* 2014; [3] Ng, K. *et al. NatureChem.* 2020

Light Harvesting “Antenna” Behavior in Chromophoric Metal-organic Frameworks

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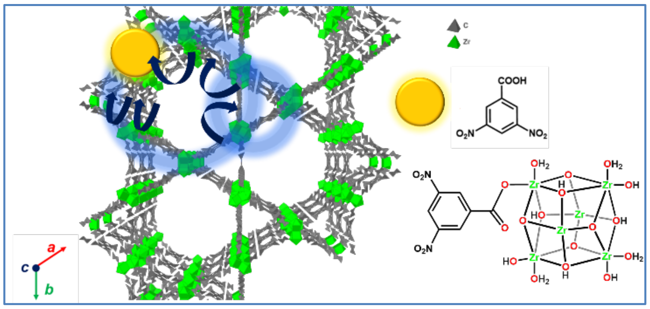
Structural or conceptual synthetic analogues of natural photosynthetic light-harvesting complexes (LHCs) hold promise as entities capable of both efficient collection of visible-region solar photons and rapid & efficient delivery of stored solar energy to energy-converting electrodes or chemical catalysts. Porous, crystalline metal-organic frameworks (MOFs) are promising supramolecular scaffolds for this purpose. This Lightning Talk will focus on the “antenna behavior” of chromophore assemblies comprising crystallographically well-aligned organic linkers within a zirconium-based MOF, NU-1000. The behavior was probed primarily via amplified emission quenching using either an electron donor (ferrocene carboxylate) or an electron acceptor (3,5-dinitrobenzoate) as a redox quencher.[1] We used solvent assisted ligand exchange as a means of siting/immobilizing desired quencher molecules directly within the extended chromophoric structures. We found that a photogenerated molecular exciton (spanning about four linkers) can sample ~300 chromophoric linkers over the course of a 1.2 ns lifetime – behavior which translates to a single-step energy-transfer or exciton-hopping time of a few picoseconds.

NU-1000 is an example of a framework featuring **csq** topology**.** This topology aligns transition-dipole moments for the compound’s tetraphenylpyrene linkers and yields incipient H-aggregate behavior for the spatially separated linkers. NU-901, a framework of identical chemical composition to NU-1000, but with components instead arranged to yield an **scu** topology, exhibits incipient J-aggregate behavior and, consequently, wider visible-region spectral coverage.

A tiny change in linker structure, *i.e.* shifting the phenyl groups from the 1,3,6, and 8 carbons of pyrene to the 4,5,9, and 10 carbons, engenders a completely different framework topology, the **she** topology. This framework, termed NU-601, features linkers, that in every direction, are oriented orthogonally to their nearest neighbors. The consequences are: a) localization of photo-excited states on single linkers, b) a several-fold increase in fluorescence lifetime, but c) much slower energy transfer, such that only a dozen linkers are sampled over the lifetime of the emissive singlet excited-state, with the efficacy of the framework as an antenna being considerably diminished. The combined findings are reasonably well described, at least qualitatively, by venerable Forster theory and contemporary extensions. Thus, paths to superior framework-based antenna structures for photochemical energy conversion, via coupling to electrodes and/or catalysts, are relatively straightforward to envision. Outside the scope of the Lightning Talk, but also directly relevant to solar energy conversion, we find large topological variations as well for rates of *charge* transfer.



1. Subhadip Goswami, Jierui Yu, Sameer Patwardhan, Pravas Deria, Joseph T. Hupp *ACS Energy Letters* **2021**, *6,* 848-853.

Integrated Arrays for Panchromatic Light Harvesting and Long-Lived Charge Separation

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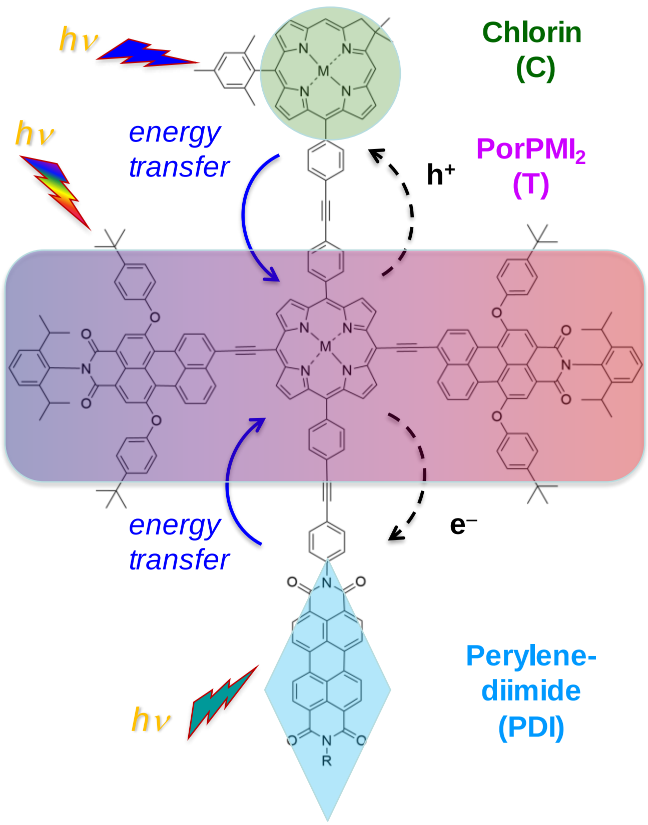
A long-term objective of our program is to design, synthesize, and characterize tetrapyrrole-based molecular architectures that absorb sunlight across the visible and near-infrared spectrum, funnel energy, and separate charge (hole, electron) with high efficiency and in a manner compatible with current and future solar-energy conversion schemes. Here, one area of our recent work is highlighted.



Panchromatic absorbers are potentially valuable for use in molecular-based energy-conversion schemes. To this end, we have prepared and characterized a number of dyads and triads comprised of a tetrapyrrole (porphyrin, chlorin, bacteriochlorin, or phthalocyanine) and one or more dyes (boron-dipyrrin, perylene, or terrylene) that afford intense absorption ($\varepsilon_{avg} \geq 50{,}000$ M^{-1} cm^{-1} across the violet to red spectral regions along with long (several nanoseconds) singlet excited-state lifetimes even in polar media. One such construct is the triad highlighted in the blue-red rectangular box in the figure. This triad is comprised of two perylene-monoimdes strongly coupled to a porphyrin, the latter being either the zinc chelate (M = Zn^{2+}) or the free base form (M = $2H^+$).

A goal has been to assemble a single architecture that exhibits panchromatic absorption, transfers energy to the lowest excited state, and contains additional components for excited-state electron transfer and ground-state hole transfer. We have studied a number of pentads (and subunits) in which the central panchromatic-absorber triad is elaborated with (i) a perylene-diimide (PDI; cyan diamond, bottom) that serves as an electron acceptor, and (ii) a chlorin (C; green circle, top), again with M = Zn^{2+} or $2H^+$, that serves as a hole trap. The pentad in which the central porphyrin is a free base and the chlorin is the zinc chelate, affords rapid efficient energy transfer and charge separation, and a long-lived (microseconds) charge separation across the dyad involving ZnC^+ and PDI^-.

Energy Transfer, Charge Separation, and Photo-driven Water Oxidation at Metal Organic Framework Interfaces

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The Morris research group has explored in detail energy transfer and water oxidation catalysis in metal organic frameworks (MOFs). Through systematic investigations of 3D structure and molecular identify, we have uncovered critical design rules for the optimization of artificial photosynthetic interfaces. With respect to energy transfer, we recently determined the effect of spin-orbit coupling on energy transfer efficiency. We incorporated three chromophores that exhibit different spin-orbit interactions into the backbone of a zirconium-based MOF, UiO-67. In all three cases, the excited state lifetime of chromophore in MOF depended on the doping concentration indicating a presence of the self-quenching mechanism. Given that the chromophores are affixed at distances greater than 10 Å, such self-quenching was attributed to a Förster resonant energy transfer (FRET). However, this is somewhat counterintuitive considering that the FRET from triplet emissive states of chromophores requires a conservation of spin. We ascribe such behavior to the appreciable degree of spin-orbit coupling present in the studied chromophores, as evident with the direct correlation between spin-orbit coupling constants and energy transfer descriptors, quenching constant, and Förster radius. Remarkably, the Förster radius obtained for OsDCBPY-doped UiO-67 of 88 Å represent one of the longest distances reported for MOF materials.

With the design rules we have uncovered, we are now making strides toward combining light harvesting and water oxidation catalysis. We are focused on the development of metal organic framework (MOF) interfaces – MOF-MOF, MOF-semiconductor, MOF-conductor with the goal of optimizing growth to promote desired function. For example, we investigated the well-studied water oxidation catalyst ([Ru(tpy)(dcbpy)OH$_2$]$^{2+}$, where tpy = 2,2′:6′,2″-terpyridine) in UiO-67 grown on a layer of WO$_3$. The new MOF/WO$_3$ photoanode can produce oxygen at 1V applied potential under white light illumination, compared to 1.71 V required for the electrochemical approach alone. The lower reaction barrier is only observed under illumination, suggesting that photoexcited WO$_3$ plays a key role in oxidizing the catalyst to the active state. Additionally, preliminary results indicate the possibility of driving the reaction at a thermodynamic underpotential, a first for MOF-based water oxidation.

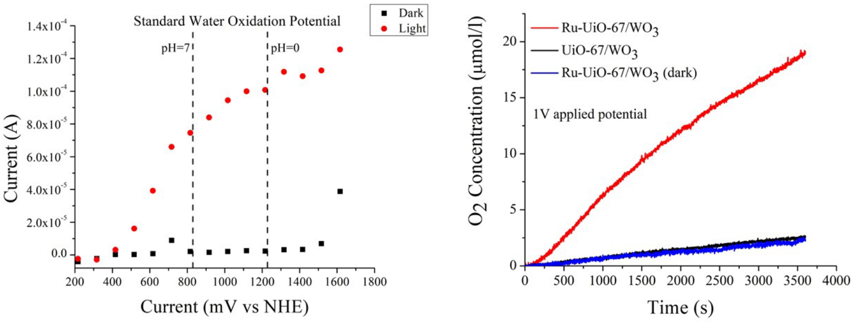

Figure 1. (Left) Current as a function of applied potential indicates water oxidation may be possible at an underpotential. (Right) Oxygen production at 1V applied potential below the 1.71 V required for a purely electrochemical approach.

Toward a 10% Efficient Light-Driven Proton Pump

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Junctions that form at interfaces of electronic semiconductors can lead to space–charge regions that result in diode behavior through current rectification. Space–charge regions are not unique to semiconductor interfaces and also form at and across ion-exchange membranes, with properties that can be tuned by varying the concentration of ions in contacting phase(s). This project aims to leverage this fact to demonstrate effective light-driven proton pumps. Toward this, a photoacid dye-sensitized cation-exchange membrane was interfaced with an anion-exchange membrane to form a dye-sensitized bipolar membrane that when fashioned into a membrane–electrode assembly analogous to a fuel cell, exhibited excellent diode performance. Unexpectedly, "reverse" photovoltaic action was observed, proposed to be due to dynamics of the polymeric materials. Mechanistic details gleaned using nanosecond transient absorption spectroscopy indicate that state-of-the-art photoacids only photogenerate protons as the mobile charged species. Because our dye-sensitized cation-exchange membranes are infiltrated with protons, this means that minority-carrier hydroxides are not able to elicit photovoltaic action by standard minority-carrier-dominated charge separation. Detailed-balance simulations were performed using a model that includes proton-transfer processes based on the Förster cycle and with rate constants that follow Brønsted theory. The maximum photovoltage calculated for sunlight absorption over 10 nm was ~330 mV, with a maximum power conversion efficiency into H^+(aq) and OH^-(aq) of ~10%. In future work, we aim to synthesize new photoacids and/or photobases that are predicted to exhibit larger power conversion efficiencies and use bind them in protonic diodes for light-driven H_2 pressurization.

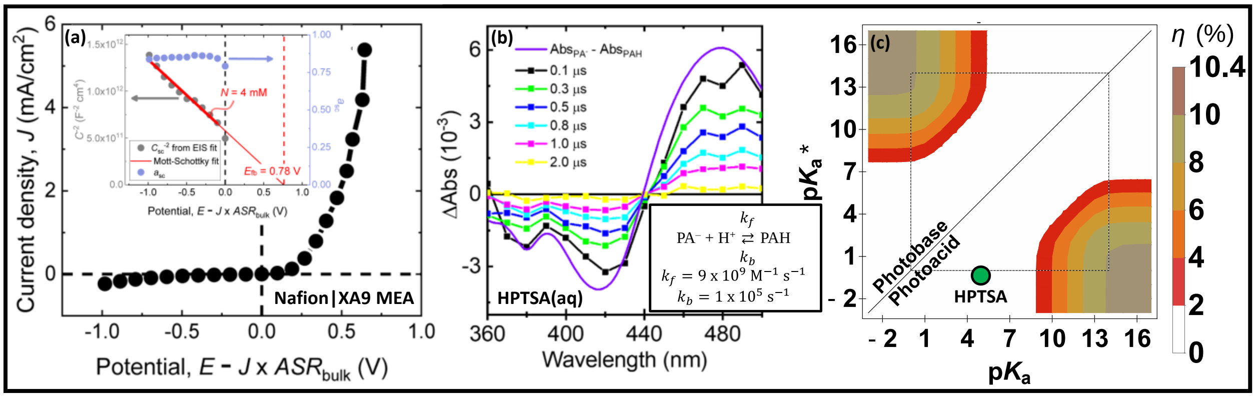

Figure 1. (a) *J*–*E* data for a Nafion|XA9 bipolar-membrane–electrode assembly (MEA) protonic diode, illustrating net water dissociation (reverse bias) and net water formation (forward bias). Inset: Capacitances (C_{sc}) and ideality factors (a_{sc}) of the space–charge region extracted from best-fits of EIS data to a nonideal Randles equivalent circuit model, and reported as a Mott–Schottky plot with extracted values indicated for the fixed-charge density in the space–charge region (N) and flatband potential (E_{fb}). **(b)** Transient absorption spectroscopy spectra, after 355 nm pulsed-laser excitation (0.6 mJ/pulse), that resolve the ground-state reprotonation of deprotonated ethylene-diamine-modified 8-hydroxypyrene-1,3,6-trisulfonic acid trisodium salt (HPTSA) photoacid dissolved in aqueous electrolyte at pH ≈ 4. Inset: Dominant reaction and rate constants extracted from best-fits of kinetic data at several pH values in the range (3, 6). **(c)** Ideal detailed-balance sunlight-to-protonic power conversion efficiencies (η), assuming pH = 7, Brønsted proton-transfer theory for a Förster cycle, and a fill factor equal to 0.75, and with properties of HPTSA indicated (green circle).

Interplay of Vibrational Wavepackets During an Ultrafast Electron Transfer Reaction

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Electron transfer reactions facilitate energy transduction and photoredox processes in biology and chemistry. Recent findings show that molecular vibrations can enable the dramatic acceleration of some electron transfer reactions, and control it by suppressing and enhancing reaction paths. Here, we report ultrafast spectroscopy experiments and quantum dynamics simulations that resolve how quantum vibrations participate in an electron transfer reaction. We observe ballistic electron transfer (~30 fs) along a reaction coordinate comprising high-frequency promoting vibrations. Along another vibrational coordinate, the system becomes impulsively out of equilibrium as a result of the electron transfer reaction. This leads to the generation (by the electron transfer reaction, not the laser pulse) of a new vibrational coherence along this second reaction coordinate in a mode associated with the reaction product. These results resolve a complex reaction trajectory composed of multiple vibrational coordinates that, like a sequence of ratchets, progressively diminish the recurrence of the reactant state.

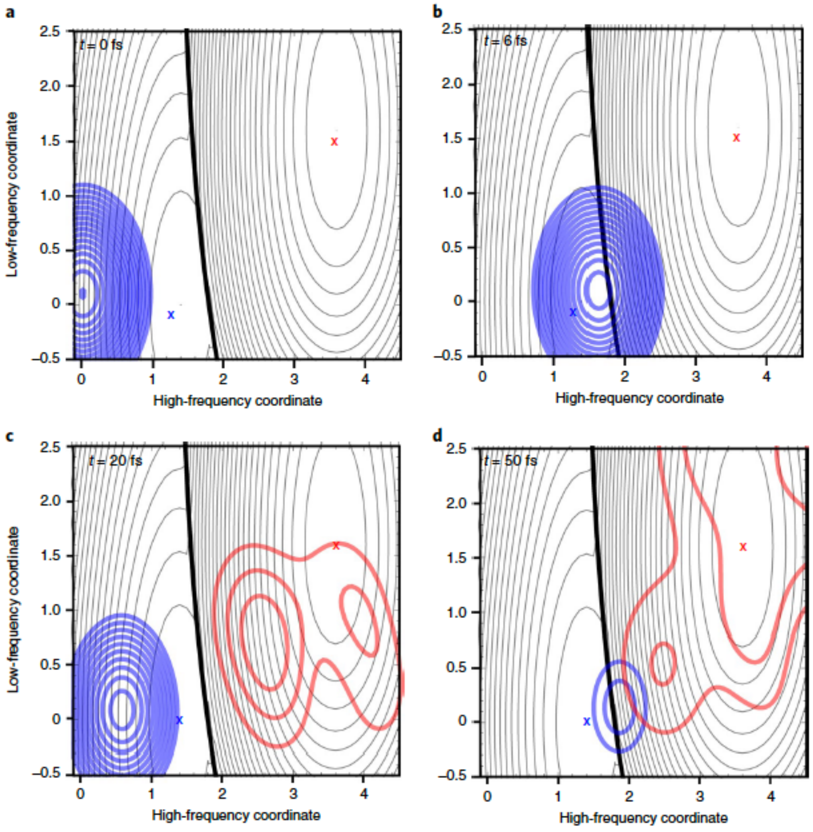

Figure. Schematic of the wavepacket dynamics during the initial 50 fs [Reproduced from: Rafiq, et al. *Nature Chemistry* (2021) 13, 70–77].

Exciton Dissociation, Transport, and Interactions in Two-Dimensional Heterostructures

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Overview: The overarching goal of this project is to build the fundamental knowledge base for energy transport at 2D interfaces. Here we demonstrate two-dimensional (2D) heterostructures, including those based on transition metal dichalcogenides (TMDCs) and hybrid perovskites, as a programmable platform to achieve efficient charge separation and energy transport.

Charge Separation and Long-Range Energy Transport at Interfaces: We have recently demonstrated the control of charge and energy transfer processes at 2D interfaces. One example is type II heterostructures constructed from 2D perovskite layers and semiconducting organic ligands. Charge transfer between thiophene-based semiconducting ligands and lead halide inorganic sublattices have been measured to be ~ 10 ps with charge-separated state lifetime > 1 ns (*1*). By adjusting the quantum well thickness of the inorganic layer, efficient triplet energy transfer and charge transfer exciton formation have been observed in pyrene-perovskite heterostructures (**Fig. 1a**). Another example is heterostructures formed with MoS_2 layers and single-walled carbon nanotubes (SWNTs) (**Fig. 1b**, in collaboration with Dr. Blackburn at NREL). The energy band offset and electron-hole separation can be tuned by varying the number of MoS_2 layers, leading to charge transfer time ranging from 100s of fs to 100s of ps. Transport of the interfacial charge-separated state (with lifetime > 10 ns) over µm length scale is directly imaged by transient absorption microscopy (TAM). The long-lived charge separation coupled with long-range energy transport points toward the potentials of these new 2D heterostructures for solar cell applications.

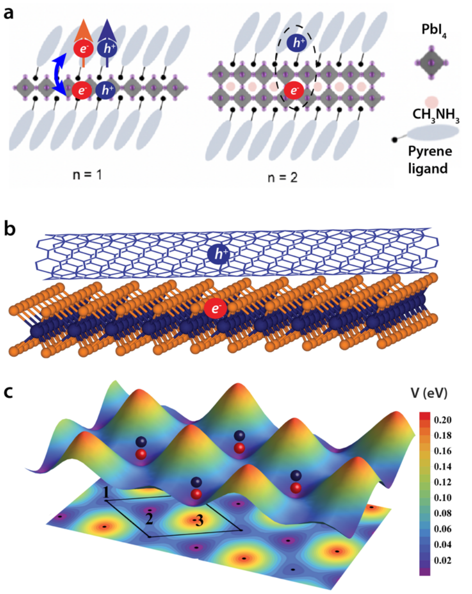

Figure 1. Two-dimensional heterostructures as a programmable platform for interfacial charge separation and energy transport (a): energy transfer and charge separation in 2D perovskite-semiconducting organic ligand heterostructures. (b) MoS_2-SWNT heterostructures. (c) Moiré excitons in a WS_2-WSe_2 heterostructure.

Nonlinear exciton interactions at 2D interfaces: Exciton-exciton interactions can be significantly enhanced in low-dimensional materials due to the reduced dielectric screening. We have demonstrated strong many-body effects between charge-transfer excitons hosted in moiré potentials in WS_2-WSe_2 heterostructures (**Fig. 1c**) (*2*). By imaging the exciton population with simultaneously high spatial and temporal resolutions, this study revealed the competition between the moiré potentials and repulsive exciton–exciton interactions. In another study on 2D hybrid perovskites (*3*), our ultrafast microscopy measurements showed that the unique dielectric properties of these materials can effectively suppress undesirable exciton-exciton annihilation.

References: 1. S. Deng et al., J. Chem. Phys. 152, 044711 (2020). 2. L. Yuan et al., Nat. Mater. 19, 617-623 (2020). 3. S. Deng et al., Nat. Comm. 11, 1-8 (2020).

Vibrational Coupling and Conformational Dynamics in Interfacial Electron Transfer

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This project aims at exploring the interaction between charge transfer, molecular vibrations and conformational changes in interfacial electron transfer (IET). The overarching goal is to understand and ultimately exploit these interactions to control charge transfer and charge recombination dynamics between molecular sensitizers and semiconductor surfaces.

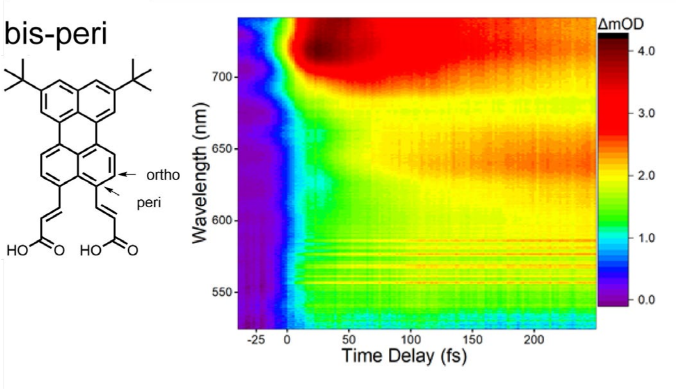

Figure 1: Structure and transient absorption map of one of the sensitizers, a di-tert-butyl perylene chromophore bound to TiO_2 via two acrylic acid linkers substituted in adjacent peri positions..

To address these questions, a set of single and dual-linker perylene based model sensitizers with identical acrylic acid linkers in different substitution positions, developed by Galoppini, was investigated.[1] IET dynamics from these sensitizers to mesoporous anatase was measured by femtosecond white-light transient absorption.[2] The structure and an example transient absorption map of one of the dual linker sensitizer are shown in Figure 1. The two most striking results from this study are: exceptionally pronounced vibronic modulation of IET, and a strong effect of conformational changes on IET rates. Molecular mechanics simulations of the bis-peri sensitizers by Rego predicted that only one linker binds covalently to the surface of TiO_2, while the second linker binds weakly via hydrogen-bonding interactions. The study showed that, surprisingly, IET from bis-peri was significantly slower than that from peri. Theory attributes this behavior to small conformational changes caused by steric interactions. Comparison between a bis-ortho and ortho sensitizer showed, as expected, that the dual-linker sensitizer injected faster than the single-linker variant. The Influence of the substitution position on IET was much smaller than expected based on the difference in the static electronic structure. This study shows that small conformational changes and vibrational coupling can have a significant influence on IET even on the femtosecond time scale. The addition of linkers that differ in bonding strength and serve different functions opens up new avenues for controlling IET dynamics.

1) *Synthesis and Properties of Perylene-Bridge-Anchor Chromophoric Compounds,* R. Harmer, H. Fan, K. Lloyd, S. Doble, J. Avenoso, H. Yan, L. G. C. Rego, . Gundlach, and E. Galoppini, J. Phys. Chem. A 2020 124 (31), 6330-6343

2) *Conformational and Binding Effects on Interfacial Electron Transfer from Dual-Linker Sensitizers,* H. Yan, J. P. Avenoso, S. Doble, R. Harmer, L. G. C. Rego, E. Galoppini, and L. Gundlach, J. Phys. Chem. C 2021 125 (16), 8667-8676

Three Approaches for Enhancing the Efficiency of Plasmon Induced Hot Electron Transfer

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Our research program contains three specific aims: 1) understanding the mechanism of long distance charge separation and recombination in semiconductor nanoplatelet/metal heterostructures. 2) understanding multiple electron transfer from quantum-confined semiconductor nanocrystals to molecule catalysts for efficient H_2 generation, 3) understanding how the dynamics and efficiency of plasmon induced hot electron transfer at plasmonic metal/metal oxide interfaces depend on the metal, semiconductor and their interaction. we have made significant progresses in all three specific aims of the proposed research plan, as well as on quantum dot-sensitized triplet-triplet annihilation based photon upconversion through a collaborative project with Ming-Lee Tang.

Plasmonic hot carrier photocatalysis utilizes hot electrons and/or holes generated by plasmon decay to drive catalytic chemical transformations and may offer multiple potential advantages. However, the reported quantum efficiencies of plasmonic photocatalysts are often low, which limits their practical applications. In this presentation, we will summarize our recent progress in developing approaches for improving the efficiency of plasmon induced hot electron transfer at metal/semiconductor interface (which is the focus of specific aim 3). The first strategy for enhancing plasmon induced hot electron transfer (HET) is to control the material's morphology, such as the nanoparticle (NP) size and shape, to improve surface damping and create stronger metal-semiconductor electronic coupling for faster HET. This approach has been demonstrated experimentally recently in colloidal quantum-confined Au-tipped CdS nanorod (CdS-Au NR) heterostructures. The QE of HET can be increased from ~1% to ~18% when the size of Au NPs decreases from 5.5 nm to 1.6 nm (Nano Letters, 2020). The second strategy is to introduce a plasmon-induced interfacial charge-transfer transition (PICTT) pathway in which plasmon decays by directly exciting an electron into the conduction band of the semiconductor, circumventing the competition with hot-electron relaxation (Fig. 1a). With these two approaches, we achieve unprecedentedly efficient plasmon-induced hot electron transfer in Ag NP sensitized nanoporous anatase TiO_2 thin films. With decreasing Ag NP sizes, the efficiency of HET increases, and for the smallest Ag NPs (1.7 ± 1.2 nm), the efficiency reaches as high as 53 ± 2% at 400nm excitation (Fig. 1b, ACS Photonics, 2021). Our findings suggest that decreasing plasmonic particle size is an effective approach to improve the efficiency of plasmon-induced HET. Finally, as a third approach, we have studied hot electron transfer in semiconductor based plasmonic materials, in which the presence of bandgap may suppress charge recombination loss.

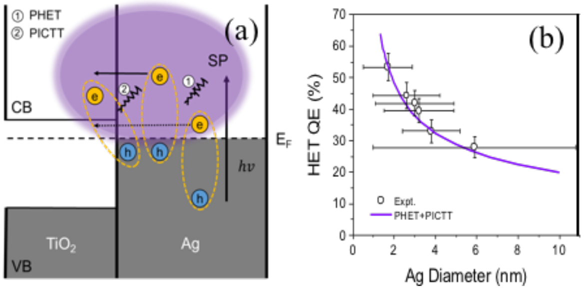

Figure 1. (a)Two-pathways for plasmon induced hot electron transfer at Ag/TiO_2 interface. (b) Plasmon induced hot electron transfer efficiency increases at smaller Ag size.

Correlated Spectroscopic and Structural Probes of Charge Transport in Lead Halide Perovskites

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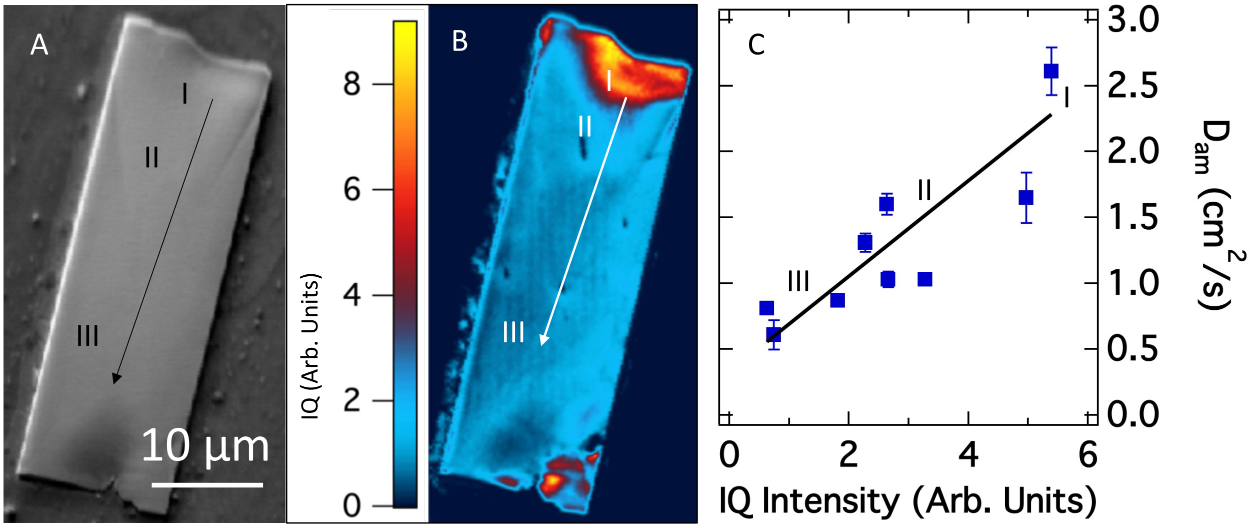
Efficient charge carrier transport is an important parameter for the application of lead halide perovskites in energy conversion motifs. Although lead halide perovskites have been extensively studied for nearly a decade, the extent to which structural and chemical defects affect excited-state transport are not well understood. To address this knowledge gap, we have been working to correlate direct measures of charge carrier transport to both structural and spectroscopic probes at the length scales where heterogeneity in lead halide perovskites manifests. In particular, we have combined ultrafast pump-probe microscopy and electron backscattering diffraction to directly correlate charge carrier transport with the local diffraction pattern contrast, an indicator of crystal quality. Spatial correlation of these measurements strongly suggests that even on individual single crystal $CsPbBr_3$ domains (Panel A), microscopic variability in the crystal quality (as measured by EBSD pattern contrast; Panel B) profoundly impacts the efficiency of charge carrier transport (as parameterized by the ambipolar diffusion coefficient; Panel C). More recent work has worked toward determining the specific structural defects responsible for the observed behavior by correlating the dislocation density, again measured by EBSD, to the local ambipolar diffusion coefficient.



1. Hickey, C. L.; Grumstrup, E. M. *Nano letters* **2020,** 20, (7), 5050-5056.

Single-Molecule Photocatalysts for H_2 Production with Red Light

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Single-molecule photocatalysts that are able to act as both the light absorber and catalyst within the same chromophore are extremely rare. The few such systems reported to date suffer from decomposition resulting in low turnover numbers (TONs) and the requirement of ultraviolet light for activation. In addition, traditional photosensitizers used in dye-sensitized solar cells are limited by their poor absorption of low energy visible light, such that the extension of their absorption profiles to include these spectral regions is important to improve the output of these devices.

Dirhodium(II,II) paddlewheel complexes with formamidinate bridging ligands have been shown by our research group to exhibit absorption profiles that extend throughout the visible region that extend into the near-IR with singlet metal/ligand-to-ligand (^{1}ML-LCT) excited states (τ_S ~8-10 ps) that decay to the corresponding ^{3}ML-LCT states (τ_T ~ 0.5 to 33 ns).[1] The properties of these complexes modulated by the ligation sphere and their excited states charge transfer with electron donors and acceptors in solution and semiconductors will be discussed. Within this class of complexes, *cis*–$[Rh_2(DPhF)_2(bncn)_2](BF_4)_2$ (bncn = benzo[c]cinnoline, DPhF = N,N'-diphenylformamidinate; **1**, Figure 1a), was found to act as a single-molecule photocatalyst for H_2 production upon irradiation with 670 nm (TON = 170 in 24 h; Figure 1b) and 735 nm light.[2]

Complex **1**, can be reduced chemically or electrochemically to generate the singly- and doubly-reduced complex, $[\mathbf{1}]^{-1}$ and $[\mathbf{1}]^{2-}$, respectively. The addition of acid to solutions of $[\mathbf{1}]^{2-}$ led to the production of one equivalent of H_2, whereas little reactivity was observed for **1** and $[\mathbf{1}]^{-1}$ in the presence of acid. These results, along with those from electrocatalysis and measurements of the excited state energies, redox potentials, and charge transfer for **1** and $[\mathbf{1}]^{-}$, led to the mechanism shown in Figure 1c. Mechanistic aspects of the reduction of H^+ to H_2 by $[\mathbf{1}]^{2-}$ will be discussed, along new complexes and their attachment to NiO for the photoelectrosynthesis of H_2.[3]

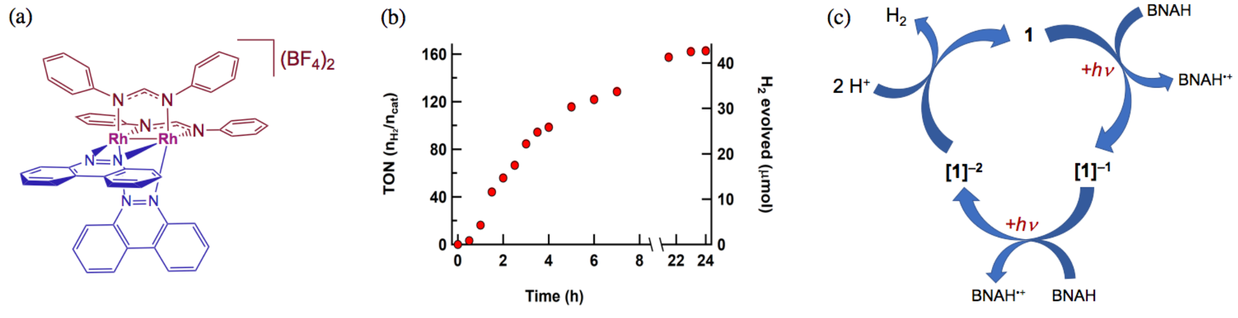

Figure 1. (a) Molecular structure of **1**, (b) TON (moles H_2/moles of **1**) as a function of irradiation time (λ_{irr} = 670 nm), BNAH (0.03 M), TsOH (0.1 M), and (c) photocatalytic cycle.

1. (a) Lin, S.; Turro, C. *Chem. Eur. J.* **2021**, *27*, 5379. (b) Huang, J.; Gallucci, J. C.; Turro, C. *Chem. Sci.* **2020**, *11*, 9775.

2. Whittemore, T. J.; Xue, C.; Huang, J.; Gallucci, J. C.; Turro, C. *Nature Chem.* **2020**, *12*, 180.

3. Huang, J.; Sun, J.; Wu, Y.; Turro, C. *J. Am. Chem. Soc.* **2021**, *143*, 1610.

Understanding and Controlling Multielectron, Multisubstrate Reactions Involving Complex Architectures and Interfaces

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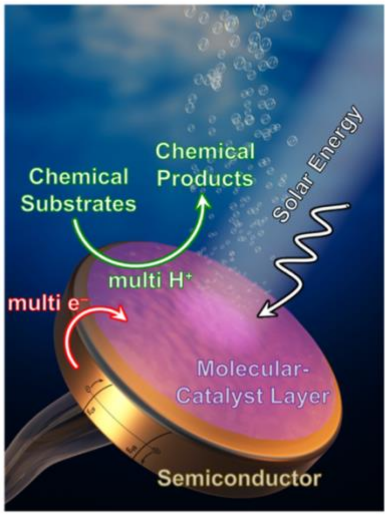

Figure 1. Schematic illustration of a molecular catalyst-modified photoelectrode. Figure adapted from cover image of reference 2.

Catalysts provide low-energy pathways for driving chemical transformations and are utilized in applications ranging from manufacturing fuels and fine-chemicals to controlling the bioenergetics essential to all living organisms. Although the ability to catalyze fuel-forming reactions using sunlight as an energy source has been demonstrated, finding ways to more effectively interface catalysts with light-absorbing materials remains challenging as there is not enough understanding of how charge carriers move through these systems. This research targets an improved understanding of the fundamental science governing such photo-driven transformations through molecular-level research in the condensed phase and at interfaces (**Figure 1**).[1-4] Our objectives include: (1) synthesizing catalysts with tailored electronic states that promote both electron-transfer and proton-transfer processes, (2) developing methods to interface these catalysts with light-absorbing semiconductors, and (3) enhancing fundamental understandings of the interplay between light absorption, charge transfer, and catalysis. While structurally more complex than their isolated components, the hierarchical materials used in this research move beyond traditional model systems and toward studying the basic energy science of using solar photochemistry to produce fuels and other industrially relevant chemicals.

1. Khusnutdinova, D.; Wadsworth, B. L.; Flores M.; Beiler, A. M.; Reyes Cruz, E. A.; Zenkov, Y.; Moore, G. F. **Electrocatalytic Properties of Binuclear Fused Cu(II) Porphyrins for Hydrogen Evolution**. *ACS Catal.* **2018**, *8*, 9888-9898.
2. Wadsworth, B. L.; Beiler, A. M.; Khusnutdinova, D.; Reyes Cruz, E. A.; Moore, G. F. **Interplay between Light Flux, Quantum Efficiency, and Turnover Frequency in Molecular-Modified Photoelectrosynthetic Assemblies**. *J. Am. Chem. Soc*. **2019**, *141*, 15932-15941.
3. Wadsworth, B. L.; Nguyen, N. P.; Nishiori, D.; Beiler, A. M.; Moore, G. F. **Addressing the Origin of Photocurrents and Fuel Production Activities in Catalyst-Modified Semiconductor Electrodes**. *ACS Appl. Energy Mater*. **2020**, *8*, 7512-7519.
4. Nguyen, N. P.; Wadsworth, B. L.; Nishiori, D.; Reyes Cruz, E. A.; Moore, G. F. **Understanding and Controlling the Performance-Limiting Steps of Catalysts-Modified Semiconductors**. *J. Phys. Chem. Lett.* **2021**, *12*, 199-203.

Design and Structural Analysis of Covalent Organic Frameworks as CO_2 Photoreduction Catalysts

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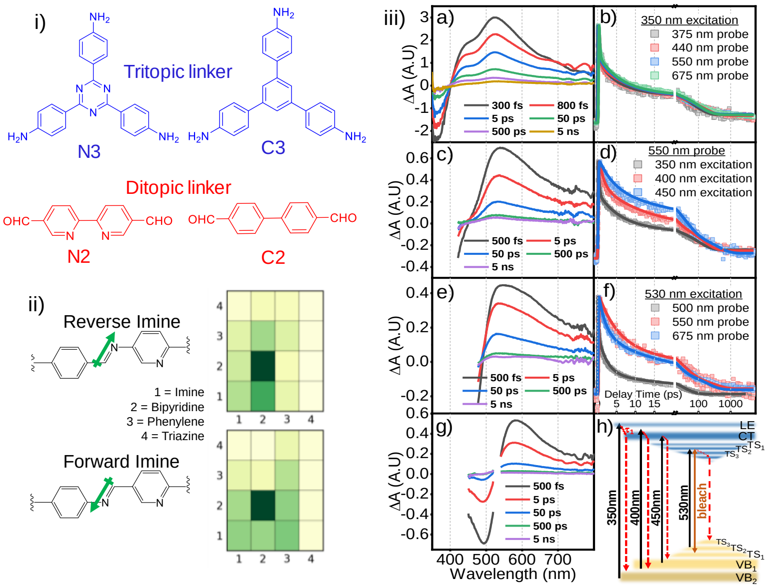
2D covalent organic frameworks (COFs) have demonstrated as promising photocatalytic materials for solar energy conversion due to their inherent porosity, large surface area, and accessible organic building blocks that enables flexible structural design. However, a majority of the work focuses on the design, synthesis, and characterization of the photocatalytic activity of COFs, leaving the fundamental aspects of how the intrinsic structure of COFs impacts their photophysical and photocatalytic properties underexplored; yet they are key to further develop these COFs to be exploited in photocatalytic applications. We aim to address this challenge using an interdisciplinary approach that combines innovative material design and synthesis, fundamental mechanistic studies, theoretical prediction, and photocatalytic performance evaluation.

In this talk, I will present our recent comprehensive computational analysis and optical transient absorption study on the light absorption, charge transfer (CT), and intralayer/interlayer exciton transport behaviors of a set of 2D COFs built from selective combinations of tritopic and ditopic monomers (Figure i), which allows precise tuning of the COF structure to uncover the direct correlation of COF structure with their photophysical properties. We find that monomer selection only moderately affects the charge transfer (CT) behavior of the COFs. Instead, linker chemistry has a profound impact on CT by acting as an electron mediator and imparting a directionality to CT (Figure ii). Moreover, we discover two distinct valence bands, which is responsible for the two CT regimes and energy dependent exciton dynamics observed experimentally (Figure iii). These results not only reveal that the linker chemistry should be recognized as the most important factor to consider in the development of COF photocatalysts but also unravel the direct correlation of COF structural environment with their light harvesting and CT properties that ultimately determine their photocatalytic function.



Figures. i) The tritopic and ditopic monomers used to form the 2D COFs; ii) Electron/Hole correlation plot showing the impact of imine linkage direction on CT of N2N3 COF. Excitation wavelength dependent transient absorption spectra of N2N3 (a, c, e, g), probe dependent kinetics (b, d. f), and the proposed two valence band model (h).

Probing Water Oxidation Mechanisms on Heterogeneous Catalysts

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As the first step of natural photosynthesis, water oxidation liberates electrons and protons from H_2O that are important for downstream reactions such as hydrogen or CO_2 reduction. To enable solar water splitting as a practical technology for solar energy harvesting and storage, it is especially important to carry out the reaction on heterogenous catalysts. While many catalysts have been studied and shown active toward this reaction, it remains elusive to find one that are both active *and* durable. At the heart of the issue is the lack of knowledge on the catalyst structures at the active site. As a result, the mechanisms by which water is oxidized on heterogeneous catalysts are poorly understood. Our project seeks to address this critical issue. We aim to provide clarity to the structure-property relationship within the context of water oxidation by heterogeneous catalysts. To realize our goals, we introduce two key innovations. The first one concerns the catalyst platform, which consists of well-defined active centers. The catalyst is derived from heterogenized molecular catalysts, which is obtained by anchoring organometallic complexes onto solid-state supports and then replacing the organic ligands with -O, -OH, and H_2O, effectively producing a material whose structure is atomically resolved. The second innovation of our project is to carry out detections of water oxidation intermediates under operando conditions using complementary techniques that include spectroelectrochemistry and synchrotron-based X-ray absorption spectroscopy. Taken together, we are presented with an opportunity to test important hypotheses concerning water oxidation on heterogeneous catalysts that were previously difficult to study.

During the first year of the project, we have made exciting progress with a surprising observation of potential-dependent mechanistic switch of water oxidation. In this set of experiments, we were inspired to establish a kinetic model of water oxidation. The mechanisms we sought to differentiate were water nucleophilic attack (WNA) and intramolecular oxygen coupling (IMOC). Simplistically, when the rate-determining step (RDS) is O-O bond formation, WNA would be more sensitive than IMOC to the water activity. Using a unique water-in-salt system, where the water activity can be suppressed to below 1.0 with a high salt concentration, we observed the IMOC mechanism is more prominent at low driving force, but the WNA mechanism becomes more prevailing at high driving force (Figure 1). The results shed new light on the complexity of water oxidation mechanisms and may find implications in the study of the reaction as a function of the driving forces.

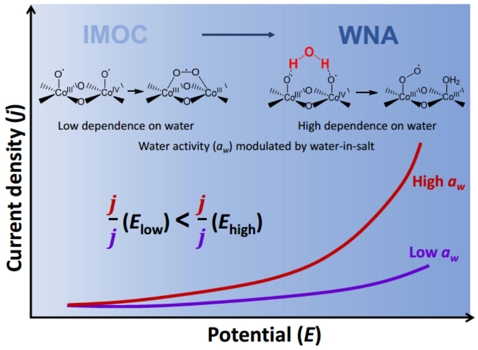

Figure 1: Switching between water nucleophilic attack (WNA) and intramolecular oxygen coupling (IMOC) mechanisms was observed when the driving force is changed.

Observation of a Potential-Dependent Switch of the Water-Oxidation Mechanism on Cobalt-Oxide-Based Catalysts

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Department of Chemistry and Energy Sciences Institute
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The goals of this collaborative research project are the development of high-potential photoanodes for water-oxidation chemistry and the characterization of interfacial processes for accumulation of multiple oxidizing equivalents on catalytic complexes. We focus on molecular assemblies that are robust under oxidative conditions. Ongoing work is aimed at the design and synthesis of photoanodes based on metal oxides functionalized with water-oxidation catalysts and high-potential panchromatic photosensitizers for light-driven water oxidation.

O–O bond formation is a key elementary step of the water-oxidation reaction. However, it is still unclear how the mechanism of O–O coupling depends on the applied electrode potential. Using water-in-salt electrolytes, we systematically altered the water activity, which enabled us to probe the O–O bond-forming mechanism on heterogeneous Co-based catalysts as a function of applied potential (1). We discovered that the water-oxidation mechanism is sensitive to the applied potential: At low overpotential, the reaction proceeds through an intramolecular oxygen coupling mechanism, whereas the water nucleophilic attack mechanism prevails at high overpotential. The observed mechanistic switch has major implications for the understanding and control of the water-oxidation reaction of heterogenized catalysts.

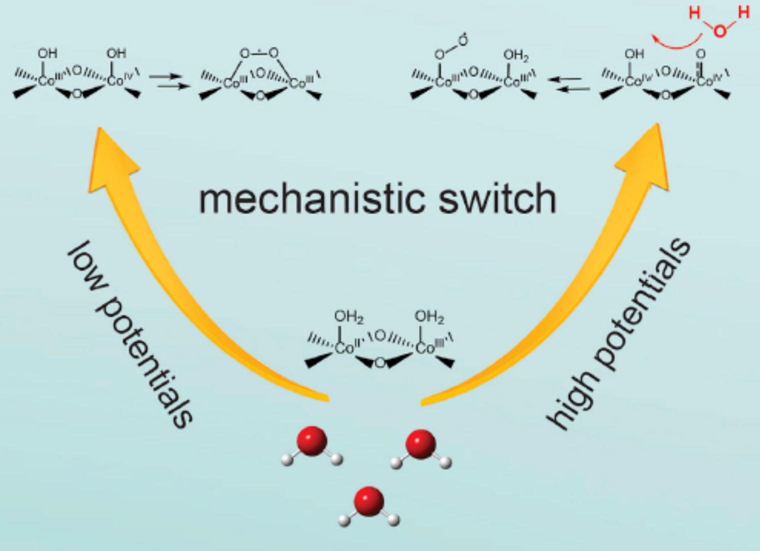

Figure 1. Proposed water-oxidation mechanisms by heterogeneous Co phosphate catalysts: intramolecular oxygen coupling (left) and water-nucleophilic attack (right).

1. C. Lang, J. Li, K. R. Yang, Y. Wang, D. He, J. E. Thorne, S. Croslow, Q. Dong, Y. Zhao, G. Prostko, G. W. Brudvig, V. S. Batista, M. Waegele and D. Wang (2021) Chem **7**, in press (https://doi.org/10.1016/j.chempr.2021.03.015).

BioLEC EFRC: Taking Inspiration from Nature to Power Up Catalysts

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BioLEC is an EFRC that brings experience in the realm of solar photochemistry to bear on the field of organic synthesis, using biological systems to inform our strategy. I will discuss how we conceived of the Center, how it now functions, what has worked well, and challenging questions we had to settle. Some of those questions include what chemistry do we focus on, and how is it energy relevant? Can organic chemists talk to physical chemists? More specifically, what is the intermediate 'fertile' research ground that will engage team science? Lastly, I will describe just a few scientific stories that come from BioLEC research.

Twenty-five percent of the world's GDP [Gross Domestic Product] is linked to the chemical industry, in which catalysts are used to assist in the manufacture of everyday chemicals. The industry accounts for 10% of total global energy consumption, and generates 7% of the world's greenhouse gases annually.[1] The BioLEC (Bioinspired Light-Escalated Chemistry) EFRC aims to use light to supercharge catalysts, enabling them to power reactions more effectively and efficiently. The Center's mission is to use light-powered catalysts to generate specific and valuable chemical products from more stable starting materials, including waste matter like sawdust or plastic bags. To achieve this, low-energy starting materials need to effectively be 'pushed uphill' on the energy landscape to higher energy products (Figure 1).

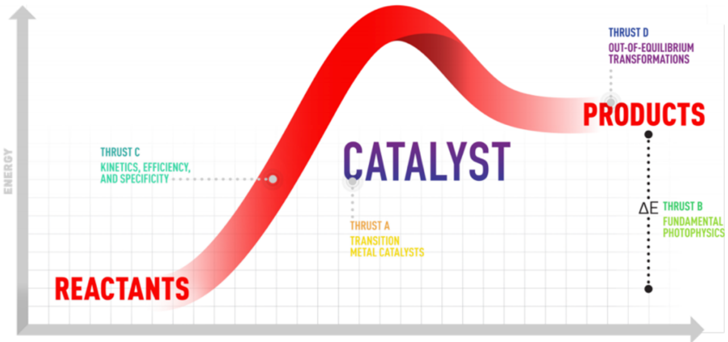

Figure 1. Multiple research thrusts tackle the challenges that must be overcome to accomplish the BioLEC mission.

Photoredox catalysis, the basis of many of the reactions used in BioLEC, has been revolutionizing organic syntheses in the pharmaceutical and fine chemical industries for over a decade. Photoredox offers considerable reductions in required energy, enabling normally high-pressure and high-temperature reactions to occur under more mild conditions with visible light illumination. At BioLEC we couple this approach with solar photochemistry and light-harvesting, and seek to apply the approach to reactions that will upcycle waste materials for energy-relevant applications.

Several of our projects focus on improving the current understanding of photoredox catalysis, which is currently lacking, and using this understanding to improve efficiencies and yields. For instance, charge recombination after excitation of a photoredox catalyst can severely limit yields. We mobilized expertise and facilities from almost half the groups within BioLEC to implement a

Photosystem II inspired solution to this problem: we used proton-coupled electron transfer (PCET)-based ligands to limit charge recombination by coupling a chemical model of the tyrosine-histidine residue responsible for PCET in Photosystem II to an Ir(III) photocatalyst. This new structure decreased the rate constant for charge recombination following photoinitiated electron transfer to methyl viologen by an order of magnitude over the uncoordinated photocatalyst. Limiting charge recombination in this way enabled an eight-fold increase in reaction quantum yield for photocatalyzed phthalimide ester reduction.[2]

A biohybrid approach can also enable exquisite control over the structure of products. For instance, the pharmaceutical and agrochemical industries often require precise control over each distinct stereocenter in a complex molecule, a feat that can be challenging and time consuming using traditional asymmetric synthesis. Although stereoconvergent processes have the potential to streamline and simplify synthetic routes, they are currently limited by a narrow scope of inducibly dynamic stereocenters that can be readily epimerized. At BioLEC, we used photoredox catalysis to enable the racemization of traditionally static, unreactive stereocenters through the intermediacy of prochiral radical species. This technology was applied in conjunction with biocatalysts such as ketoreductases and aminotransferases to realize stereoconvergent syntheses of stereodefined γ-substituted alcohols and amines from β-substituted ketones.[3]

At BioLEC we seek to use multiple photons to excite catalysts and push reactants thermodynamically uphill. We recently reported a new photophysical approach to initiate free-radical polymerization, which is widely used in manufacturing and conventionally initiated using UV light. UV excitation consumes considerable energy and can cause reagent degradation, so our approach uses visible-light photons, which are absorbed by zinc tetraphenylporphyrin molecules in a solution, promoting them to their triplet excited states. These triplet states are significantly longer-lived than singlet excited states, giving the excited molecules more time to find each other and collide, at which time the energy of two excitations combines to generate an upper singlet excited state on one molecule. This highly excited molecule is also strongly reducing, and readily transfers an electron to a monomer in solution, initiating free-radical polymerization. An additional benefit results from how easy it is to control the visible-light illumination to initiate the reaction: the team showed it is straightforward to generate well-defined macroscopic and microscopic polymer gel objects with this approach.[4]

1. https://www.globalefficiencyintel.com/new-blog/2018/chemical-industrys-energy-use-emissions
2. Hannah J. Sayre, Hunter H. Ripberger, Emmanuel Odella, Anna Zieleniewska, Daniel A. Heredia, Garry Rumbles, Gregory D. Scholes, Thomas A. Moore, Ana L. Moore, Robert R. Knowles, submitted.
3. Jacob S. DeHovitz, Yong Yao Loh, Jacob A. Kautzky, Kazunori Nagao, Andrew J. Meichan, Motoshi Yamauchi, David W. C. MacMillan, Todd K. Hyster, *Science* **2020**, *369*, 1113—1118.
4. Nancy Awwad, Evgeny O. Danilov, Felix Castellano, *Chem* **2020**, *6(11)*, 3071—3085.

Center for Hybrid Organic Inorganic Semiconductors for Energy

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Center for Hybrid Organic-Inorganic Semiconductors for Energy (CHOISE): Targeting unprecedented synthetic control over the emergent phenomena of spin, charge, and light-matter interactions, in tailored organic-inorganic perovskite-inspired systems for energy science.

Hybrid organic/inorganic semiconductors (HOIS) offer tremendous opportunities to control fundamental properties that underpin energy technologies. While currently there are enormous worldwide efforts exploring, exploiting and improving a narrow class of HOIS (lead-halide perovskites, such as methylammonium lead iodide ($MAPbI_3$)), primarily for photovoltaic (PV) applications, CHOISE seeks to transcend this initial focus on PV research and develop a deeper understanding and control of their fundamental properties. Inherent in these unique hybrid systems is the dichotomy between organic/molecular moieties and inorganic/extended systems. As a result, they exhibit properties that are not solely a juxtaposition of the inorganic and organic sub-units, but instead exhibit emergent or synergistic phenomena, with the concomitant ability to control and design new properties by judicious *choice* of the inorganic and organic components. Semiconductor physics has revolutionized our world in the past century due to investments in fundamental studies of quantum mechanics and solid-state physics. Unfortunately, this knowledge is insufficient to completely describe HOIS. Complex coupling among inorganic and organic components drive unique (and often collective) dynamic phenomena involving light, matter, and energetic species such as spins, charge carriers, and phonons. Thus, *the mission of CHOISE is to accelerate discovery and elucidate design principles that enable unprecedented control over emergent properties involving spin, charge and light-matter interactions*, *which are of interest for the next generation of energy technologies*.

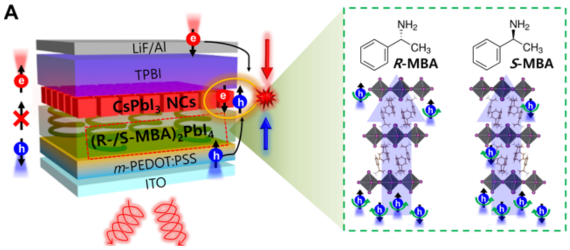

Figure 1. Spin-LED consisting of a chiral-metal halide hole-transport layer and a non-chiral metal-halide light emitting layer.

In this presentation, I will discuss a few studies of controlling the charge carrier dynamics, light/matter interactions, and spin populations. With respect to controlling spins we have studied and developed a novel class of chiral hybrid semiconductors based upon layered metal-halide perovskite 2D Ruddlesden-Popper type structures.[1-5] These systems exhibit chiral induced spin selectivity (CISS) whereby only one spin sense can transport across the film and the other spin sense is blocked. We have demonstrated >80% spin-current polarization and high spin-injection efficiency from the chiral layer into a nanocrystal layer. To demonstrate our control, we developed novel spin-based light emitting diodes (LEDs) using non-chiral nanocrystals as the light emitting layer (**Fig. 1**). The spin-LEDs emit circularly polarized light (CPL) with 2.5% descrimination at room temperature without the use of magnetic fields. We also demonstrate spin-PV systems, half-spin valves, and the circular photogalvanic effect

(CPGE). The CPGE effect is governed by Rashba splitting. We are developing design rules of how the organic component can induce structural distortions in the inorganic component that give rise to Rashba splitting. We developed a chiral copper-halide system that selectively adsorbs CPL with a high discrimination factor and demonstrate how these systems can be used to detect CPL with 20% discrimination factors.[6]

With regard to light and charge we have developed spectroscopic probes to understand charge transport at and near surfaces and interfaces.[7-8] We have used these probes to develop various 2D/3D interfaces for efficient charge management[9-11] as well as serving to protect the underlying 3D system from water ingress. For layered systems we are interested in controlling both in-plane and out-of-plane transport. Two systems highlight our studies of how to increase the out-of-plane charge transport while maintaining the advantage of the 2D layers. One system consists of using the organic components to template a more favorable arrangement of the inorganic layers (**Fig. 2**) and thus increase out-of-plane transport. The other systems contains a quasi-2D layer with attributes of both 3D and 2D. In another effort, some 2D layered systems exhibit a broadband emission that is more intense then the free-exciton emission. We studied the broadband emission in tin-doped Pb 2D layered systems. We find that the hole is first trapped at the Sn-site (<5 ps) followed by electron localization to form the self-trapped exciton.[12] Finally, CHOISE researchers discovered that a novel interface between single-walled carbon nanotubes and metal-halide NCs exhibits a low-threshold persistent photoconductivity at room temperature that could enable optical memory and brain-inspired neuromorphic information processing.[13]

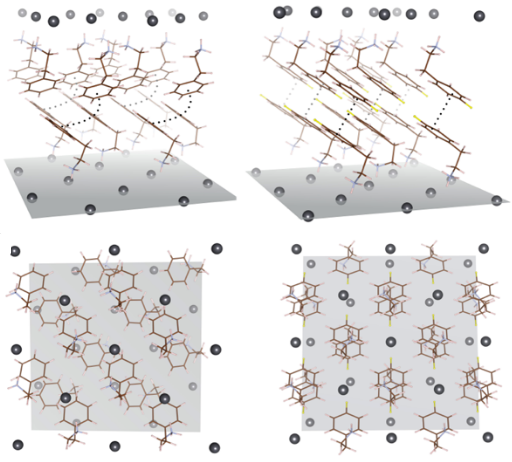

Figure 2. Templating of the inorganic sheets by the organic cations leads to an increase in the out-of-plane charge transport.

We are studying NCs of metal-halide perovskite semiconductors as photocatalysts for light-driven chemical transformations.[14-16] For photocatalytic applications these NCs are highly photoactive, support charge-separation and migration and have low surface defect densities. We have studied their use as photo-redox systems to drive C-C bond formation reactions. Recently we are taking advantage of the ease of cation substitution at the surface of the NCs to develop a photocatalyst that undergoes multiple sequential inner-sphere photo-oxidation events. A diamine substrate is bound to surface Cu^{+1} cations, which attract holes from the valence band of the NCs and promotes sequential oxidization of the bound diamine to form a N-N heterocycle.

1. Wang, J., et al., *ACS Nano* **2021,** *15* (1), 588-595
2. Kim, Y.-H., et al., *Science* **2021,** *371* (6534), 1129.
3. Lu, H., et al., *JACS* **2020,** *142* (30), 13030-13040.
4. Lu, H., et al., *Science Adv.* **2019,** *5* (12), eaay0571.
5. Jana, M. K., et al., *Nat Commun* **2020,** *11* (1), 4699.
6. Hao, J., et al., *ACS Nano* **2021,** *15* (4), 7608-7617.
7. Habisreutinger, S. N., et al., *ACS Energy Lett.* **2019,** *4* (8), 1872-1879.
8. Zhai, Y., et al., *ACS Energy Lett.* **2020,** *5* (1), 47-55.
9. Xue, J., et al., *Science* **2021,** *371* (6529), 636.
10. Zhang, F., et al., *JACS* **2019,** *141* (14), 5972-5979.
11. Tong, J., et al., *Science* **2019,** *364* (6439), 475
12. Li, T., et al., *ACS Energy Lett.* **2020,** *5* (2), 347-352.
13. Hao, J., et al., *Sci. Adv.* **2021,** *7* (18), eabf1959
14. Zhu, X., et al., *JACS* **2019,** *141* (2), 733-738.
15. Lu, H., et al., *JCP* **2019,** *151* (20), 204305.
16. Wang, K., et al., *ACS Energy Lett.* **2020,** *5* (2), 566-571

Fundamental Studies of Redox Processes and Catalysis Relevant to Artificial Photosynthesis and Organic Photovoltaics

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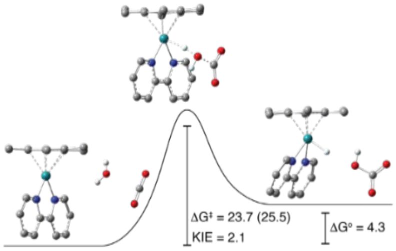
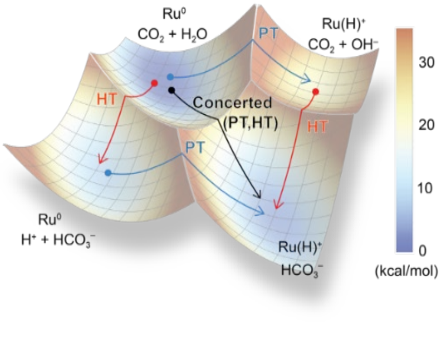
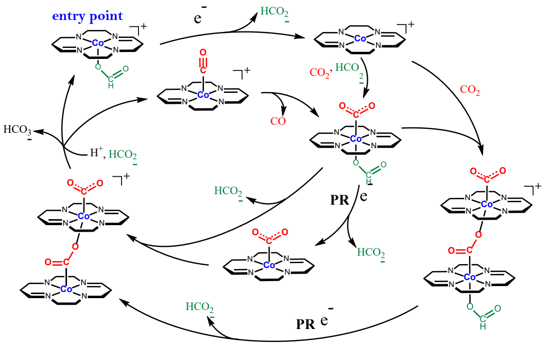
Research in this program pursues fundamental understanding of molecular systems and processes important for solar energy conversion to fuels in artificial photosynthesis (AP) or to electricity in organic photovoltaics (OPV). Studies aimed at both AP and OPV applications pursue efficient light absorption and charge separation, and AP studies also seek to effectively couple charge separation to CO_2 reduction and/or water oxidation catalysis. In both areas, a detailed understanding of redox processes and energetics is of paramount importance. We discuss our progress in AP first, focusing on reductive catalysis in section **1** and oxidative catalysis in section **2**. We then discuss in section **3** our progress in understanding redox state energetics, important to both AP and OPV processes, using pulse radiolysis methods to complement what can be learned by electrochemistry.

1. **Reductive catalysis by metal complexes for CO_2 conversion.** We address two key aspects in CO_2 reduction: protonation pathways of relevant catalytic intermediates in organic solvents **(1a)** and the role of bimetallic interactions in enhancing catalytic activity **(1b)**. For these studies, we use advanced experimental techniques such as pulse radiolysis time-resolved IR spectroscopy (PR-TRIR) and IR spectroelectrochemistry (IR-SEC) in combination with density functional theory (DFT) calculations.

1a. The generation of solar fuels from CO_2 reduction requires the delivery of both electrons and protons. Therefore, understanding how protonation of key catalytic intermediates and products takes place is of the utmost importance. In the electrochemical generation of a Ru(II) hydride ($[Ru(HMB)(bpy)(H)]^+$, HMB is hexamethylbenzene; bpy is 2,2′-bipyridine) by reduction of its Ru(II) precursor ($[Ru(HMB)(bpy)(CH_3CN)]^{2+}$) followed by protonation, in acetonitrile solutions, the movement of protons from weak Brønsted acids, such as water and methanol, is coupled with the concerted transfer of its negatively charged counterpart to carbon dioxide (CO_2) – a process termed here proton-coupled group transfer – to stoichiometrically produce a metal-hydride complex and a carbonate species. These previously unidentified pathways play important roles in CO_2 and proton reduction catalysis by enabling the generation of key intermediates such as hydrides and metallocarboxylic acids, while their broad applicability may provide alternative approaches in the electrosynthesis of chemical commodities via alkylation and carboxylation reactions.[1]



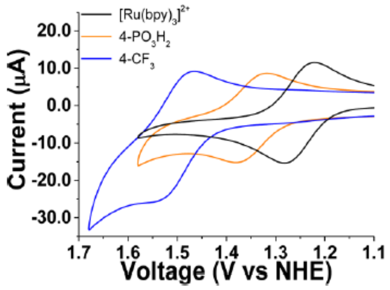




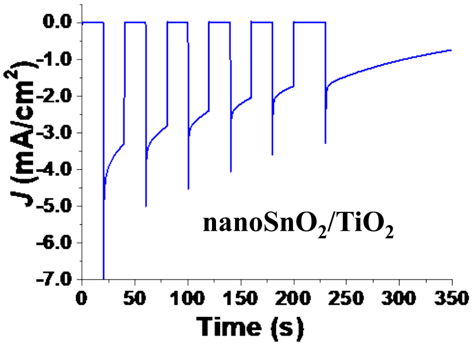
1b. The use of two metal centers working in synergy with similar or complementary functions can potentially lead to a significant reduction in overpotentials, enhance catalytic activity and/or selectivity and enable access to cascade strategies where each metal center catalyzes a different step in the conversion of CO_2 to a fuel. We have identified bimetallic reactivity of two metal centers as the primary route for CO_2 reduction promoted by $[Co(HMD)]^{2+}$, based on experimental characterization of every step of the catalytic cycle using pulse radiolysis time-resolved IR spectroscopy (PR-TRIR), corroborated by density functional theory (DFT) calculations and IR spectroelectrochemistry (IR-SEC). We demonstrate that this reactivity enables access to elementary steps with lower energy requirements, resulting in overall catalysis being kinetically more facile as compared to the monometallic pathway. The presence of a coordinating species, e.g., formate anion, appears to assist in the formation of the bimetallic intermediate.[2]

2. **Integrated molecular systems for water splitting.** We are focusing on principles of energetics, coupling and assembly of molecules to enable functional AP assemblies at interfaces. We have made substantial progress on integrated systems for water splitting, specifically in Dye-Sensitized Photoelectrosynthesis Cells (DSPEC) **(2a)** and in new approaches to obtain good DSPEC performance at desirable low pH conditions **(2b)**.

2a. We described a new approach for the preparation of water oxidation photoanodes in a DSPEC for water splitting. It is based on a chromophore (C)−catalyst (Cat) assembly prepared by a self-assembled bilayer on a mesoporous SnO_2/TiO_2 core/shell electrode, FTO|SnO_2/TiO_2|-C−Cat. A key feature in the resulting assembly is the in situ “synthesis” by utilization of noncovalent interactions between long alkyl substituents of the chromophore and catalyst components. The photoanode carries out photoelectrochemical water oxidation for more than 3 h with ∼86% faradaic efficiency for oxygen generation. At pH 7 under 1 sun illumination, the photoanode reaches a photocurrent density of ∼2.2 mA/cm^2 with an incident photon to current efficiency of 29% at 450 nm. With an injection yield of only ∼42%, the efficiency of the cell, excluding the losses at the core/shell interface, is a remarkable 67%.[3]

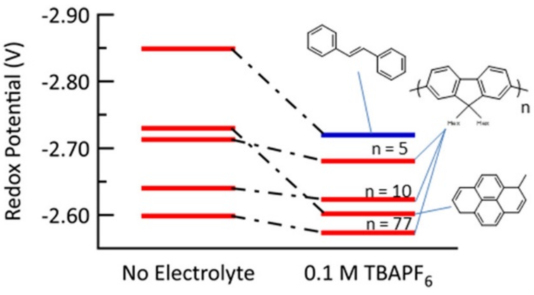


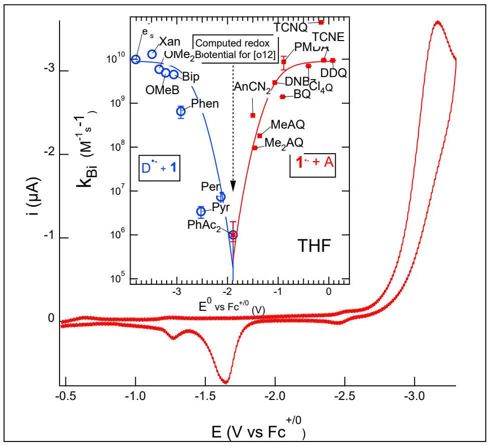
2b. Most DSPEC studies to date have been carried out at pH values between 4.5 and 8.0 where the injection efficiency of commonly used chromophores into the conduction band of wide bandgap semiconductors such as TiO_2 is below 50%. In addition, stability of catalysts, chromophores and anchors also decrease as the pH is increased. But photochemical water oxidation at low pH requires chromophores with adequate photophysical properties and high redox potentials capable of oxidizing the catalysts. We synthesized a series of homoleptic Ru(II) polypyridyl complexes and evaluated their performance in photochemical water oxidation at pH 1 using persulfate as the sacrificial electron acceptor was evaluated. These chromophores incorporate CF_3 or PO_3H_2 groups to increase the $Ru^{III/II}$ standard potentials to 1.3−1.6 V versus NHE, while their homoleptic nature retains photophysical properties (absorption spectra, lifetimes, emission energies, emission quantum yields) comparable to $[Ru(bpy)_3]^{2+}$. With $[(bda)Ru(isq)_2]$ (bda is 6,6′-dicarboxylate-2,2′-bipyridine; isq is isoquinoline) as the catalyst, the chromophores promote visible-light driven water oxidation with high activity at low pH. The chromophores carried out the light absorption, charge migration, and proton transfer roles of P_{680}, Tyr161, and His190 in Photosystem II on a single molecule and are good candidates for photoelectrochemical water oxidation at low pH in dye-sensitized photoelectrochemical cells.[4] We recently carried out studies, for the first time, on DSPEC performance and stability at pH 1 with these new chromophores. The results are remarkable with photocurrents reaching record values (compared to studies at any pH) of 4.5 mA/cm^2 at sustained photocurrents above 2.0 mA/cm^2 for minutes (manuscript in preparation).



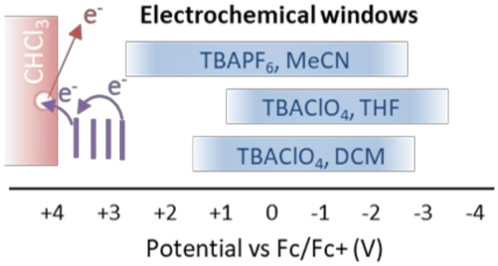
3. Redox potentials and highly oxidizing species: beyond electrochemistry

3a. Redox potentials are important to understanding the AP processes described above, as well as in OPV applications. However, electrochemical measurement of such potentials usually requires 0.1M electrolyte, which shifts potentials by unknown amounts, is not present in the environment of either AP or OPV. We have used pulse radiolysis transient equilibration methods (left figure) to determine the shifts of redox potentials due to the presence of supporting electrolyte. The method is generally[5] applicable to weakly polar fluids producing results complementary to those we found earlier by free energy cycles.[6] We are also using a new pulse radiolysis method to determine redox potentials of conjugated polymers, which are important in OPV but often difficult to measure electrochemically due to ambiguous redox waves. The method lets us determine a unique one electron redox potential for a given polymer motif regardless of the chain length and can be performed in nonpolar solvents, representative of molecular films (ongoing work). We have also recently applied pulse radiolysis methods to determine reversible potentials in molecules where cyclic voltammograms seem not to have a clear reverse wave. Here (right figure) for reduction of o-12 carborane a massive structural change makes it difficult to learn the potential by voltammetry. Measurement of electron transfer reactions by pulse radiolysis (inset) determined the actual reversible potential.[7]





3b. We have also applied pulse radiolysis methods to measure the energetics of highly oxidizing species. Such species are hard to study by electrochemical methods due to electrolyte breakdown and other factors. For highly positive potentials oxidized products frequently decompose, but identification of reversible oxidations in pulse radiolysis (right figure) of chloroform gives new insight into those potentials.[8]



4. Related studies of molecular processes at the Accelerator Center for Energy Research

This program operates the Accelerator Center for Energy Research (ACER), where the pulse radiolysis studies described in Sections 1b and 3 were conducted. ACER studies have also characterized triplet motion in conjugated chains to yield information about the speed of triplet diffusion along the chains.[9] ACER also provides a unique capability for studies of short-lived intermediates and kinetics in other collaborative studies. For instance, our collaborative work at ACER in the BioLEC EFRC is investigating energetics and spectroscopically characterizing short-lived radical ions that cannot be characterized electrochemically. In that EFRC, we are also exploiting pulse radiolysis at ACER for mechanistic studies of important organometallic photocatalytic cross-coupling reactions, such as oxidative addition to reactive Ni(I) intermediates. In other work funded under an SCGRS collaboration (M. Thompson, student), pulse radiolysis studies elucidated charge delocalization in molecules that exhibit symmetry-breaking charge transfer, which may help minimize energy loss in solar cells and photocatalysis. The work specifically examined radical ions of dimer molecules with 90-degree dihedral angles.

Ongoing and future work includes measurements of triplet ion pairs, dependence of bimolecular electronic couplings on molecular size and characterizing non-radiative charge recombination pathways in OPV materials.

1. Sampaio, R. N.; DiMarco, B. N.; Concepcion, J. J. , "Proton-Coupled Group Transfer Enables Concerted Protonation Pathways Relevant to Small Molecule Activation", *submitted*.
2. Polyansky, D. E.; Grills, D. C.; Ertem, M. Z.; Ngo, K. T.; Fujita, E. "The Role of Bimetallic Interactions in Enhancement of Catalytic CO_2 Reduction by a Macrocyclic Cobalt Catalyst", *submitted*.
3. Wang, D.; Wang, L.; Brady, M. D.; Dares, C. J.; Meyer, G. J.; Meyer, T. J.; Concepcion, J. J., "Self-Assembled Chromophore–Catalyst Bilayer for Water Oxidation in a Dye-Sensitized Photoelectrosynthesis Cell", *J. Phys. Chem. C* . **2019,** *123* (50), 30039-30045.
4. Wang, L.; Shaffer, D. W.; Manbeck, G. F.; Polyansky, D. E.; Concepcion, J. J., "High-Redox-Potential Chromophores for Visible-Light-Driven Water Oxidation at Low pH", *ACS Catal.* **2020,** *10* (1), 580-585.
5. Bird, M. J.; Pearson, M. A.; Asaoka, S.; Miller, J. R., "General Method for Determining Redox Potentials without Electrolyte", *J. Phys. Chem. A* **2020,** *124* (26), 5487-5495.
6. Bird, M. J.; Iyoda, T.; Bonura, N.; Bakalis, J.; Ledbetter, A. J.; Miller, J. R., "Effects of electrolytes on redox potentials through ion pairing", *J. Electroanal. Chem.* **2017,** *804*, 107-115.
7. Miller, J. R.; Cook, A. R.; Simkova, L.; Pospisil, L.; Ludvik, J.; Michl, J., "The Impact of Huge Structural Changes on Electron Transfer and Measurement of Redox Potentials: Reduction of ortho-12-Carborane", *J. Phys. Chem. B* **2019,** *123* (45), 9668-9676.
8. Bird, M. J.; Cook, A. R.; Zamadar, M.; Asaoka, S.; Miller, J. R., "Pushing the limits of the electrochemical window with pulse radiolysis in chloroform", *Phys. Chem. Chem. Phys.* **2020,** *22* (26), 14660-14670.
9. Cook, A. R.; Girimonti, A.; Sreearunothai, P.; Asaoka, S.; Miller, J. R., "Dynamic broadening alters triplet extinction coefficients in fluorene oligomers and polymers", *J. Chem. Phys.* **2020,** *152* (2), 024901.

Excitations and Relaxations of Ruthenium Dyes in Natural Sunlight

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Ruthenium dyes are useful sensitizers to transform light into other forms of energy because of their ability to absorb in the visible region and inject electrons into a semiconductor support, generating electricity or stimulating chemical reactions. We are examining how these dyes couple into full energy conversion systems using multiscale reaction-diffusion modeling to link timescales from fs to sec and length scales from nm to µm. To construct the dye photophysical mechanism, we use stochastic chemical kinetics modeling to analyze spectroscopic data from our collaborators at the University of North Carolina, M. K. Brennaman, P. G. Giokas, D. F. Zigler, A. M. Moran, J. M. Papanikolas, G. J. Meyer and T. J. Meyer.[1] We have developed a full scheme for the coincident absorptions, emissions, and excited state relaxations that are observed in transient absorption and photoluminescence experiments for a series of six tris(2,2'-bipyridine)ruthenium(2+) (Ru-P) derivatives in solution. Predictive rate coefficients for each transition are estimated by requiring that the simulated spectroscopic data be in quantitative agreement with experimental data for all the dyes. The calculations reveal that the rate coefficients are all in the range of 10^{13} s^{-1} except for final relaxations from the triplet to the ground state, indicating that decay rates are dominated by populations. Ultrafast non-radiative relaxation from the singlet excited state manifold is an important process, resulting in an intersystem crossing efficiency to the triplet manifold in the range of 50%. By combining the data from the transient spectroscopies with an analysis of the linear absorption spectra,[2] we obtain the detailed Jablonski diagram shown in Figure 1.

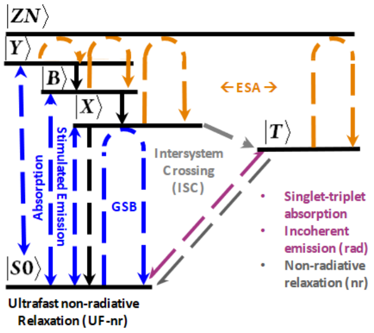

Figure 1. Photophysics of Ru-P dyes. ESA are excited state absorptions. GSB is ground state bleach.

Using this scheme, we examine dye photophysical processes for this dye family under continuous illumination by natural sunlight, which is directly relevant to solar energy conversion systems.[2] Starting with dyes supported on a transparent semiconductor where no charge injection can occur, we calculate event statistics showing that each dye undergoes about 160 events s^{-1}, and that half are radiative relaxations. ESAs do occur even under low light flux, at the ppm-event level. We are currently using this scheme and transient absorption measurements to obtain detailed information on the timing and rate coefficients for charge injection into TiO_2 in sunlight. We are also evaluating the interplay between the photophysics and slower chemical reactions in photoanodes such as dye cycling by I^- in solar cell systems using detailed electrolyte chemistry,[3] and water oxidation by molecular Ru catalysts in photoelectrochemical synthesis cells. The resulting mechanistic modules will be incorporated in full dye-sensitized system models.

(1) Cheshire et al, J. Phys. Chem. B (2020) DOI: 10.1021/acs.jpcb.0c03110
(2) Cheshire and Houle, J. Phys. Chem. A (2021), accepted for publication
(3) Houle, Chem. Sci. (2021) DOI: 10.1039/d1sc00384d

Next Generation Cuprous Phenanthroline MLCT Photosensitizers

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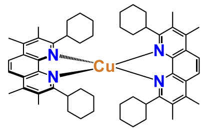
Three newly conceived Cu(I) *bis*(phenanthroline) metal-to-ligand charge transfer (MLCT) photosensitizers (**1-3**) featuring 2,9-cyclohexyl subunits flanked by 3,8-methyl steric supports have been prepared. Complete synthesis, structural characterization, and electrochemistry, in addition to static and dynamic photophysical properties of these chromophores are reported on all relevant time scales. Figure 1 presents the UV-Vis and static photoluminescence (PL) spectra as well as the PL intensity decays of **1-3** recorded in CH_2Cl_2. The combined ground- and excited-state properties of **1** echo those previously observed for the $[Cu(dsbtmp)_2]^+$ (**4**), whereas **2** and **3** display PL properties and excited-state lifetimes that markedly outperform the benchmark **4**, Table 1. Cyclic voltammetry experiments in CH_3CN indicate systematic variation of the metal-based one-electron oxidation and first one-electron ligand-based reduction as a function of heteroatom substitution on the cyclohexyl moieties, Table 1. The resulting energy gap variation appears to be responsible for the increased lifetimes and PL quantum yields observed in **2** and **3**. Ultrafast transient absorption spectroscopy enabled the assignment of the singlet-triplet intersystem crossing time constants in **1-3**. This contribution demonstrates that the substituent variation within the cyclohexyl platform represents an effective means to create tailor-made long-lifetime Cu(I) photosensitizers with deterministic photophysical properties, precisely designed for solar photochemistry applications.



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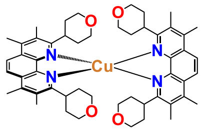

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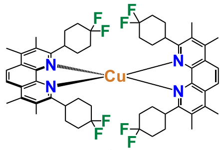

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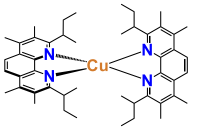

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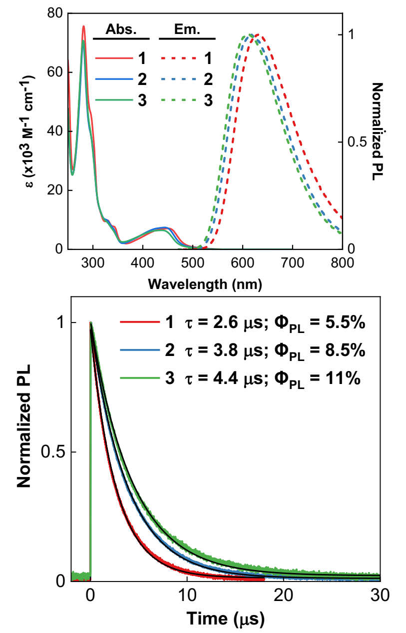

Figure 1. UV-Vis absorption and PL spectra (top) and the PL intensity decays of **1-3** measured in degassed CH_2Cl_2 at RT.

Table 1. Summary of the Photophysical and Electrochemical Properties of **1-4**.

Molecule	τ (μs)^a	Φ_{PL} (%)^a	k_r ($\times10^4$ s^{-1})^a	k_{nr} ($\times10^5$ s^{-1})^a	E_{ox} (V)^b	E_{red} (V)^b	E^* (V)^b
1	2.6	5.5	2.1	3.6	0.43	-2.38 -2.60	-1.77
2	3.8	8.5	2.2	2.4	0.59	-2.26 -2.41	-1.64
3	4.4	11	2.4	2.0	0.67	-2.21 -2.42	-1.58
4	2.8	6.3	2.3	3.4	0.42	-2.38 -2.59	-1.78

^{a}Data obtained in deaerated CH_2Cl_2. ^{b}Data obtained in deaerated CH_3CN (potentials measured *vs* $Fc^{+/0}$).

Impact of Electric Fields on Charge Transfer Excited States

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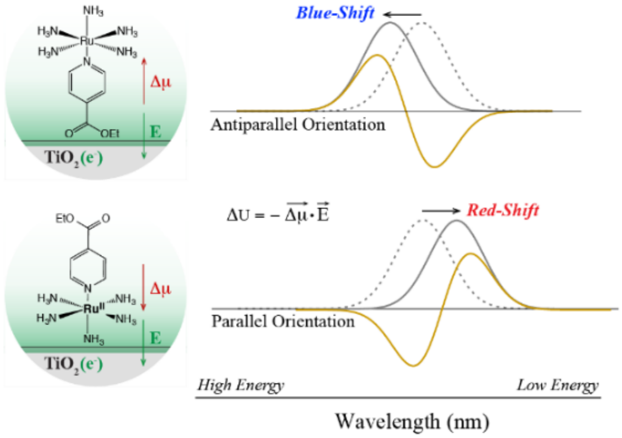
Dye-sensitized solar cells have received considerable attention since the advent of the mesoporous metal oxide thin films described by Grätzel and O'Regan [1]. Fundamental interest in light driven interfacial electron transfer in these materials is motivated by applications in electrical power generation and in solar fuels production [1,2]. Our present DOE-funded research is focused on the role electric fields play in dye-sensitized electron transfer. Molecular dyes based on $(d\pi)^6$ transition metal complexes and organic pigments report on the field magnitude and direction at dye-sensitized TiO_2 interfaces [2]. Pulsed laser excitation has been particularly valuable as it provides kinetic data for ion-migration (screening) and dye reorientation that occur in response to the transient electric field. In particular, the $[Ru(NH_3)_5(eina)]^{2+}$ sensitizer shown binds to TiO_2 through the ethyl ester group of the eina ligand. Pulsed laser excitation resulted in excited state injection and spectral changes consistent with the sensitizer flipping over so that the amines interacted with the oxide surface [3]. Interestingly, when the field was removed the molecules flipped back over with dynamics that were time resolved and sensitive to sensitizer deuteration. Quantification of the electric field strength required knowledge of the change in dipole moment that accompanies light absorption. A traditional Stark apparatus has been assembled for this purpose. A surprising observation was the appearance of low energy features in the Stark spectra of $[M(bpy)_3]^{2+}$, where M = Fe, Ru, and Os, that were very weak or absent in the electronic spectra [4]. These features have been assigned to the $\Delta S \neq 0$ population of a high spin Franck-Condon excited state. The implications of these findings for solar energy conversion and for fundamental aspects of charge transfer excited states will be discussed [2].



References:

[1] *"A Low-Cost, High Efficiency Solar Cell Based on the Dye- Sensitized Colloidal TiO_2 Films"* O'Regan, B.; Grätzel, M. *Nature* **1991**, *353*, 737.

[2] "*Perspectives in Dye Sensitization of Nanocrystalline Mesoporous Thin Films*" Hu, K.; Sampaio, R.N.; Schneider, J.; Troian-Gautier, L.; Meyer, G.J. *J. Am. Chem. Soc.* **2020**, *142*, 16099.

[3] "*Flipping Molecules Over on TiO_2 Surfaces with Light and Electric Fields"* Sampaio, R.N.; Li, G.; Meyer, G.J. *J. Am. Chem. Soc.* **2019**, *141*, 13898.

[4] "*Stark Spectroscopic Evidence that a Spin Change Accompanies Light Absorption in Transition Metal Polypyridyl Complexes"* Maurer, A.B.; Meyer, G.J. *J. Am. Chem. Soc.* **2020**, *142*, 6847.

Functionally Active Linker Design for Photoactive Molecules at Semiconductor Interfaces

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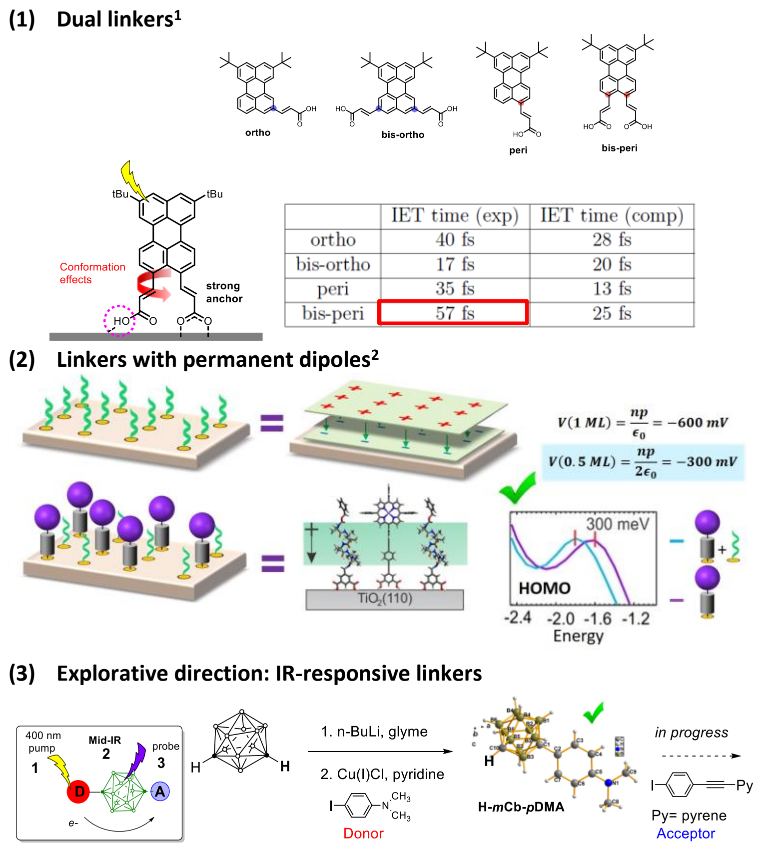
The lightning talk will outline progress in our research program investigating organic chromophores bound to oxide semiconductor interfaces, an area that remains at the center of intense research in solar photochemistry. The program focuses on developing, and studying, molecular components that link the photoactive portion of the molecule to the surface. These are designed to have intrinsic properties that can be used to influence interfacial photochemical reaction pathways (i.e. "functionally active linkers"). Our approach involves a combination of synthesis and surface science, and it is complemented by collaborations to study the photophysical properties of these systems and provide a theoretical underpinning to the experiments.

The three areas of focus that will be presented, schematically shown in Figure 1, include: **(1)** Developing dual linker design with conformation and environment-sensitive surface attachments to control photoinduced charge transfer pathways;[1] **(2)** Using linkers with permanent dipoles to manipulate energy levels between the photoactive unit and the semiconducting substrate;[2] **(3)** We are working towards an exploratory direction involving stimulus-responsive linkers, where charge transfer can be promoted by excitation with infrared radiation.



	IET time (exp)	IET time (comp)
ortho	40 fs	28 fs
bis-ortho	17 fs	20 fs
peri	35 fs	13 fs
bis-peri	57 fs	25 fs

Figure 1. Schematic representation of key results in each research direction.

References: **(1)**. (a) *Synthesis and Properties of Perylene-Bridge-Anchor Chromophoric Compounds* Fan, H.; Lloyd, K.; Doble, S.; Avenoso, J.; Yan, H.; Rego, L.; Gundlach, L.; Galoppini, E. *J. Phys. Chem. A* **2020**, *124*, 6330–6343; DOI: 10.1021/acs.jpca.0c04609. (b) *Conformational and Binding Effects on Interfacial Electron Transfer from Dual-Linker Sensitizers* Yan, H.; Avenoso, J.; Doble, S.; Harmer, R.; Rego, L.; Galoppini, E.; Gundlach, L. *J. Phys. Chem. C* **2021**, *125*, 8667-8676; DOI: 0.1021/acs.jpcc.0c11299. **(2).** *Helical Peptides Design for Molecular Dipoles Functionalization of Wide Band Gap Oxides* Chen, Y.; Viereck, J.; Harmer, R.; Rangan, S.; Bartynski, R.A.; Galoppini, E. *J. Am. Chem. Soc.* **2020**, *142*, 3489-3498; DOI:10.1021/jacs.9b12001.

Controlling Interfacial Charge Separation Energetics and Kinetics

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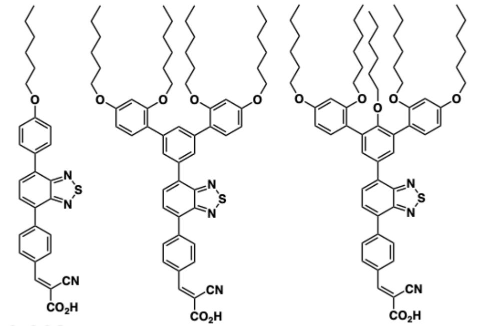
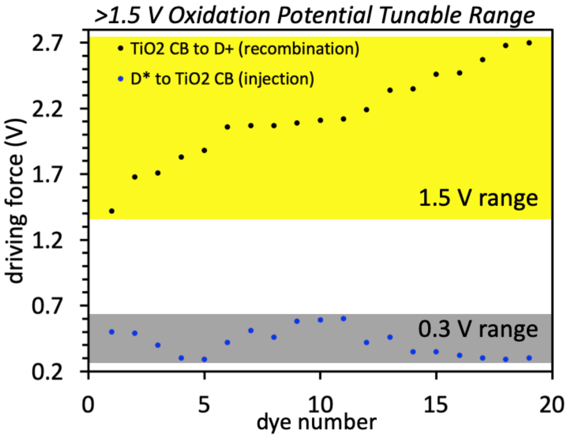
Strong photoinduced oxidants capable of injecting electrons into a metal oxide semiconductor such as TiO_2 with maximal oxidizing potency from visible light photons are needed for a range of applications including uses in dye-sensitized solar cells, dye-sensitized photoelectrochemical cells, and photocatalysis. This presentation will focus on the design and properties of donor-π bridge-acceptor organic chromophores for this purpose. The donor groups are comprised of weak aryl ether donors in place of commonly used triarylamines for more positive oxidation potentials while retaining directional charge transfer. The π-bridge groups are comprised of benzothiadiazole and thienopyrroledione bridges to maintain positive oxidation potentials while facilitating efficient electron transfer from the donor to acceptor regions. The acceptor group is comprised of a benzene-cyanoacrylic acid group known for efficient electron transfer to TiO_2. The donor group design is a primary focus since this group plays a key role in sustaining charge separation after the electron transfer reaction from a reducing species. In this work, $Fe(bpy)_3^{2+}$ is used as an example reducing species with a significantly positive oxidation potential. Several iterations of the donor group design are probed to allow for maximal interfacial charge separation lifetimes of up to 0.2 s as observed via electrochemical impendence spectroscopy measurements. The observed long interfacial charge separation lifetime is made possible through exceptional surface protection of electrons in TiO_2 from $Fe(bpy)_3^{3+}$ by judiciously designed donor groups with multiple insulting alkyl chains.



0.003 s **0.02 s** **0.2 s**

increasing charge separated lifetime of electrons in TiO_2 from $[Fe(bpy)_3]^{3+}$ (~1.9 V recombination driving force)



References: 1) Curiac, C.; Rodrigues, R. R.; Watson, J. Hunt, L. A.; Devdass, A.; Jurss, J. W.; Hammer, N. I.; Fortenberry, R. C.; Delcamp, J. H. "Iron Redox Shuttles with Wide Optical Gap Dyes for High Voltage Dye-Sensitized Solar Cells" *Submitted* April **2021**. 2) *ACS Appl. Energy Mater.* **2019,** *2*, 5547. 3) *Angew. Chem. Int. Ed.* **2018,** *57*, 5472.

Controlling Charge-Transfer Reactions with Cobalt Complexes

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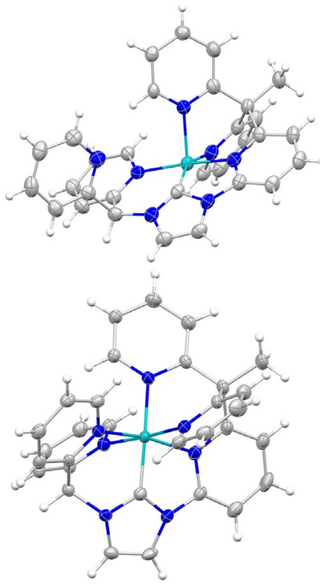
All solar photochemical conversion systems involve fundamental processes of light absorption, charge separation and charge collection. Dye-sensitized solar cells (DSSCs) represent an excellent platform highlighting the subtle interplay of various electron-transfer reactions that give rise to charge separation and collection following light absorption by molecular chromophores. This lighting talk will highlight one recent result of our design and investigation of cobalt-based redox shuttles in the context of DSSCs.

In previous work, we have found that the spin state of Co(II) redox couples has a dramatic effect on the inner-sphere reorganization energy, λ_{in}, associated with oxidation to Co(III), and thus electron-transfer kinetics. For example, the self-exchange rate constants of low-spin Co(II) to low-spin Co(III) octahedral complexes are roughly 4 orders of magnitude faster than high-spin Co(II) to low-spin Co(III) octahedral complexes. We have been pursing routes to exploit this relationship by developing new low-spin Co(II) complexes which are capable of more efficient (reduced energy penalty) kinetics in DSSCs which can lead to improved energy conversion efficiencies.

We have synthesized a new family of strong-field hexadentate ligands in order to induce low-spin Co(II) complexes that are stable with tunable redox potentials. By introducing 0, 1 or 2 dimethyl amino groups onto the PY5Im ligand backbone (PY5Im, PY5ImDMA1 and PY5ImDMA2 respectively), the redox potentials of the Co(II/III) couples shift from -0.19 V to -0.29 V to -0.43 V vs Fc+/Fc respectively. The series are all low-spin Co(II) complexes, as confirmed by Evan's method, due to strong sigma donation of the NHC carbene unit of the ligand. Interestingly, crystal structures of the complexes show a geometry change from distorted square pyramidal in the Co(II) complexes to octahedral in the Co(III) complexes. This unusual geometry change is attributed to a strong Jahn-Teller distortion due to the low-spin d7 electronic configuration. We will discuss the implications of this geometry change on the electron-transfer kinetics of cobalt metal centers by utilizing cross-exchange reaction measurements with ferrocene derivatives as well as preliminary data on these new redox couples employed in DSSCs.



Top: $[\mathrm{Co(PY5Im)}]^{2+}$
Bottom: $[\mathrm{Co(PY5Im)}]^{3+}$

Relevant publications:

Raithel, A.L., Kim, T.Y., Nielsen, K., Staples, R.J., Hamann, T.W.; "Low-Spin Cobalt(II) Redox Shuttle by Isocyanide Coordination" *Sustainable Energy & Fuels* **2020** 4, 2497 - 2507

Baillargeon, J., Xie, Y., Raithel, A.L., Ghaffari, B., Staples, R.J., Hamann, T.W.; "Spin-Doctoring Cobalt Redox Shuttles for Dye-Sensitized Solar Cells" *Inorganic Chemistry* **2018**, 57 (18), 11633–11645

Sensitizers for Solar Fuels Production: (carbene)M(amide) Complexes (M = Cu, Ag, Au)

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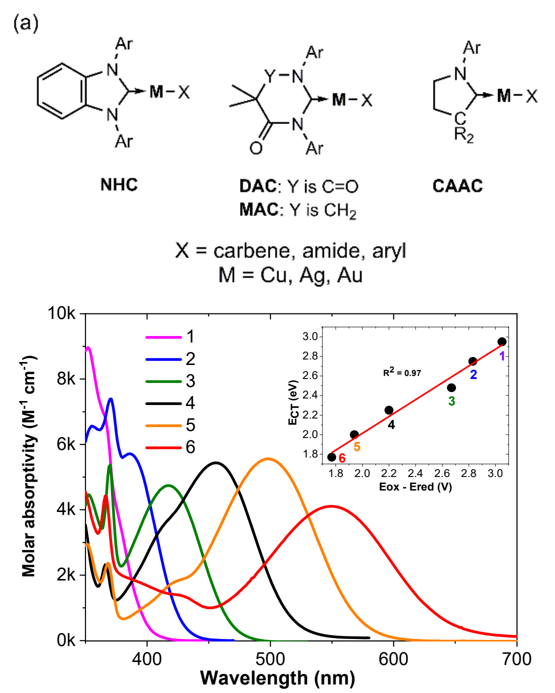
We have developed a large family of monovalent coinage metal sensitizers [i.e. (carbene)M(amide), cMa, see Figure] that absorb throughout the visible spectrum, have lifetimes in the 1-10 μs range and emission quantum efficiencies in the 0.8-1.0 range for blue-to-yellow emitters (light absorption up to 550 nm). The Energy Gap Law leads to enhanced nonradiative rates for the lower energy materials, so sensitizers with excited state energies in the red give $\Phi_{PL} < 0.3$, but still give measured lifetimes in the μs regime. These materials have high excited state redox potentials and absorb light in the visible range with ε of 10^3-10^4 $M^{-1}cm^{-1}$. At the start of our new DOE BES program, we had these materials in hand, and had characterized their steady state photophysical properties.* Our first step in the DOE program has been to evaluate them as sensitizers for photoelectrochemical processes.



(a) Structures of (carbene)$M^{(I)}$(donor) compounds, (b) Absorption spectra of DAC/MAC-based materials in THF. Inset shows the linear correlation of the redox gap with the ICT energy.

Our initial studies of these cMa materials showed that they give reversible reduction, but irreversible oxidation waves. Suitable substitution of the amide moiety gives cMa complexes reversible redox waves in non-coordinating solvents, but still gives poor reversibility for oxidation in acetonitrile and DMF. Irradiation of these cMa complexes in both polar and nonpolar solvents leads to the formation of an interligand charge transfer (ICT) state, which emits via thermally assisted delayed fluorescence (TADF). We have previously measured the ISC rate for this ICT state and found that it is in the 100-200 ps regime for the Cu and Ag complexes and ~ 20 ps for the Au complexes.

Our next step is to use time resolved photophysical measurements to follow the progression from the initial excited state to the ^{3}ICT. Our initial interest is in what role the metal ion plays in this process since it appears the ICT transition is being promoted driectly. We are using transient absorption (TA) spectroscopy to follow the temporal evolution of the excited state, with the triplet, cation and anion spectra being measured by pulse radiolysis (PR) at Brookhaven National Labs. We are using TA and PR methods to study the instability of the oxidized cMa complexes in polar solvents. Lastly, we are preparing macrocyclic versions of the cMa complexes to increase their stability toward ligand loss or exchange. We will discuss our most recent results at the meeting.

* S. Shi, *et al.*, *J. Am. Chem. Soc.* **2019**, *141*, 3576; R. Hamze, *et al.*, *J. Am. Chem. Soc.* **2019**, *141*, 8616.

Redefining the Reaction Coordinate for Light Capture and Excited-state Dynamics of First-row Transition Metal-based Charge-transfer Chromophores

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Our research program is focused on understanding and ultimately redefining the photophysical properties of first-row transition metal complexes with an eye toward applications reliant on photo-induced electron transfer. The desirability of shifting to the first transition series is tied to the high natural abundance of these elements; for material-intensive applications such as light capture in solar energy conversion strategies, this represents an enormous advantage with regard to scalability relative to chromophores based on much rarer elements such as ruthenium and iridium. A critical impediment to realizing this goal rests in fundamental differences in the electronic structures of compounds in the first row of the transition block as compared to their heavier congeners:[1] overcoming these challenges lies at the heart of our ongoing efforts.

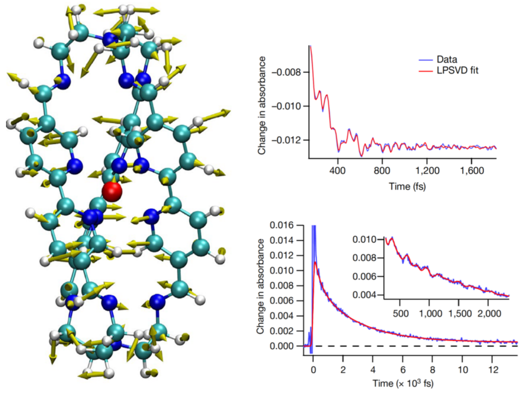

Figure 1. *Fe(II) polypyridyl chromophore used for exploring the connection between vibronic coherence and synthetic control of excited-state dynamics. The ca. 100 fs lifetime of the initially formed MLCT excited state revealed coherent oscillations (top right) which allowed for visualization of the motions coupled to excited-state evolution (left). Insertion of Cu(I) ions in the apical positions above and below the central Fe atom attenuated these motions, leading to a ~25-fold increase in MLCT lifetime (lower right). From ref. 2.*

Work supported through the Solar Photochemistry Program keys on two themes: (1) identification and manipulation of the reaction coordinate associated with the ultrafast conversion of electron transfer-active charge-transfer excited states to more redox-inert ligand-field excited states, and (2) the creation of new coordination platforms that allow for independent synthetic control of electronic energies and absorption cross-section. In the former, we have demonstrated that vibronic coherence can help identify degrees of freedom coupled to excited-state evolution of a chromophore, information that can then be used to synthetically modify the chromophore to alter its photophysical behavior. In this case, ultrafast evolution from the MLCT manifold of an Fe(II)-tris-bipyridyl compound to its lower-energy ligand-field states was coupled to large amplitude motion of the ligand superstructure (Figure 1). Restriction of these specific degrees of freedom via ligation to Cu(I) ions resulted in a 25-fold increase in the MLCT lifetime.[2]

The second area is hallmarked by the development of a new class of heteroleptic Fe(II) complexes in which the dual tasks of light capture and ligand-field modulation are simultaneously addressed within a single compositional motif. Data acquired on a three compounds - $[Fe(phen)_3]^{2+}$ (**1**), $Fe(phen)_2(CN)_2$ (**2**), and $[Fe(phen)_2(C_4H_{10}N_4)]^{2+}$ (**3**) - reveals a systematic modulation of electronic state energies via destabilization of the ligand-field states while maintaining the fidelity of the compound's absorption cross-section. The net result is a nearly 100-fold increase in MLCT-state lifetime of the carbene complex (**3**) relative to that observed for $[Fe(phen)_3]^{2+}$.[3]

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[1] McCusker, J.K. *Science* **2019**, *363*, 484. [2] Paulus, B.C.; Adelman, S.L.; Jamula, L.L.; McCusker, J.K. *Nature* **2020**, *582*, 214. [3] Paulus, B.C.; Nielsen, K.A.; Tichnell, C.R.; Carey, M.C.; McCusker, J.K. *J. Am. Chem. Soc.* **2021**, *143*, in press.

Photohydrides: Mechanism-Guided Development of Molecular Photoelectrocatalysts

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Metal hydride complexes that absorb visible light to drive fuel-forming chemical reactions hold promise for solar fuel synthesis.[1] Recent research has identified strategies to tune photochemical pathways between H_2 evolution and hydride or hydrogen atom transfer. One approach to promote hydride transfer involves intercepting photogenerated hydride intermediates with high concentrations of organic substrate.[2] An alternative strategy, in focus here, harnesses excited states with M–H antibonding character to promote hydride or hydrogen atom transfer. We hypothesized that first-row transition metal hydrides would be ideal candidates, despite the lack of well-defined photochemistry of 3d metal hydride complexes. Here we present on new photochemistry of nickel bis(diphosphine) hydride complexes.

As shown in **Figure 1**, isolated nickel hydrides generate H_2 upon visible light illumination. This is a unique example of photochemical H_2 evolution from a nickel hydride. Mechanistic studies are consistent with a short-lived excited state having substantial Ni–H bond weakening due Ni–H σ* antibonding character, implicating H_2 evolution via hydrogen atom transfer. Such a mechanism should be amenable to reactions beyond H_2 evolution. Indeed, photolysis of nickel bis(diphosphine) hydride complexes in the presence of the persistent radical TEMPO• leads to suppression of H_2 evolution and hydrogen atom transfer to generate TEMPO–H in high yield. These findings provide a platform for fundamental studies of nickel hydride photochemistry and thermochemistry-guided applications in fuel-forming electrochemical reductions at low overpotential.

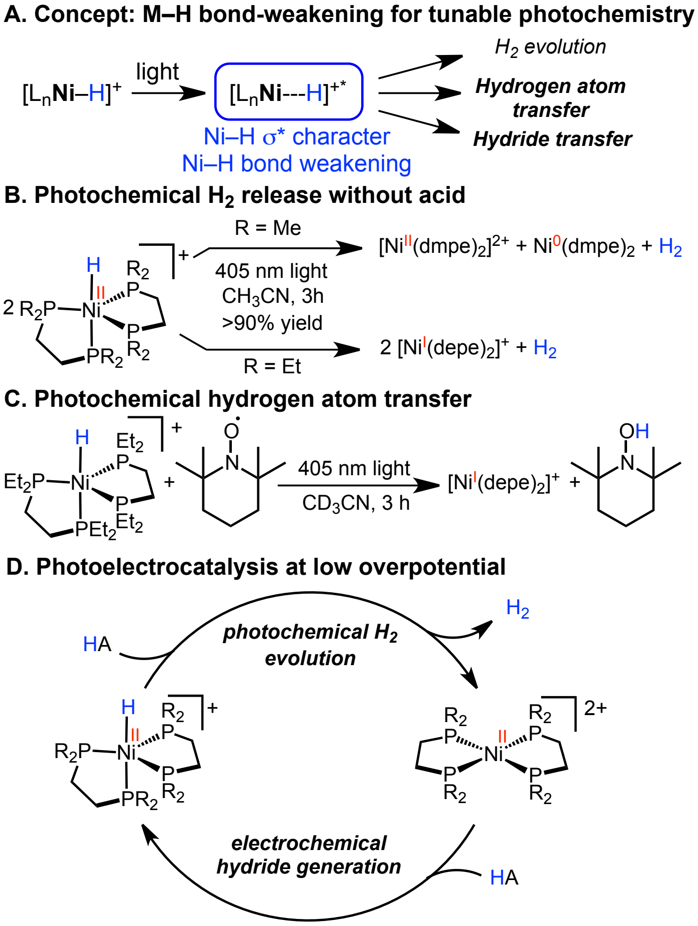

Figure 1. Conceptual scheme of nickel hydride photochemistry and reactivity demonstrating H_2 evolution and hydrogen atom transfer.

[1] Brereton, K. R.; Bonn, A. G.; Miller, A. J. M. *ACS Energy Lett.* **2018**, *3*, 1128.
[2] Barrett, S. M.; Stratakes, B. M.; Chambers, M. B.; Kurtz, D. A.; Pitman, C. L.; Dempsey, J. L.; Miller, A. J. M. *Chem. Sci.* **2020**, *11*, 6442.

Towards Molecular Water Oxidation Electrocatalysts with More Favorable Stability/Activity Profiles

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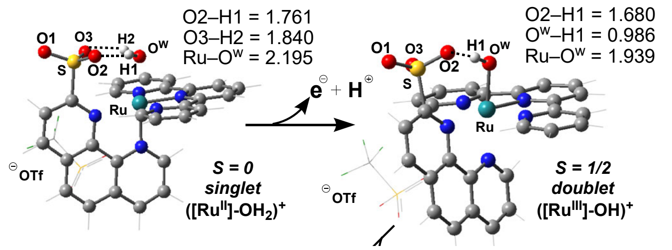
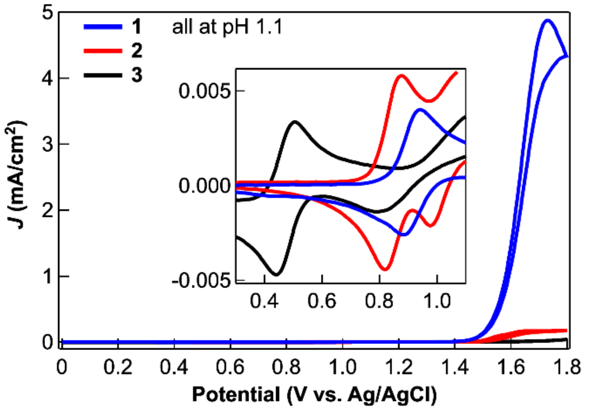
Our overall goals are to (1) slow the rate of water oxidation electrocatalyst (WOEC) degradation, (2) enable molecular WOEC activity in acid, and (3) create and refine new methods for characterizing WOEC stability. We have made progress in all three areas but focus on the second one for this talk.



DFT-calculated structures of our sulfonate-bearing catalyst **1** (left) and the proposed first intermediate



Comparison of **1** with Sun's catalyst **2** and Meyer's catalyst **3** that is like **1** but without the sulfonate group in the active site. Concentrations 0.125 mM.

Whereas other homogeneous water oxidation catalysts are less active in acid, here we report a catalyst (**1**) that maintains high electrocatalytic turnover frequency at pH values as low as 1.1 and 0.43 ($k_{cat} = 1501 \pm 608$ s^{-1} and 831 ± 254 s^{-1}, respectively). Moreover, current densities ranged from 15 to 50 mA cm^{-2} mM^{-1} comparable to those reported for state-of-the-art heterogeneous catalysts and 30 to 100 times greater than those measured here for two prominent homogeneous catalysts (Sun's catalyst **2** and **3**, the analog of **1** without the sulfonate) at pH 1.1 and 0.43. The catalyst also exhibits excellent durability when chemical oxidant Ce^{IV} is used (7400 turnovers). Some of the fastest molecular WOEC with pendent carboxylates or phosphonates give rates 8000-10,000 s^{-1}, but these data were obtained at pH 7 or higher, where the pendent base remains active. *In contrast, sulfonate complex* ***1*** *appears to be unique in that it maintains high activity under acidic conditions.* Sulfonate complex **1** is 30-45 times faster than **3** without the sulfonate, even though the pH dependence of the II/III couples are very similar. Preliminary computational studies suggest that the unusual active-site sulfonate group acts a proton relay even in strong acid, as intended.

More recent studies examine other related complexes with active-site sulfonates, as well as begin to evaluate the electrostatic effects of sulfonate groups or other anions near an active site.

Mechanisms for CO_2 Reduction Modelled with Metal Carbonyl Clusters

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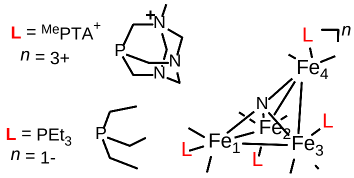
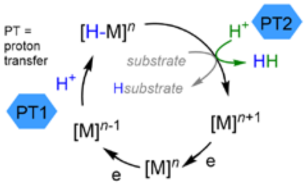
This project uses metal carbonyl clusters (MCC's), which have delocalized bonding and electronic structures, as models for mechanisms in nanoparticle and heterogeneous (electro/photo)catalysis. The intermediate size of MCC's, between molecules and nanoparticles, preserves access to the powerful characterization tools of molecular chemistry to enable atomic level detail in characterization of structures, reactivity, and mechanism. The scope of the project includes: i) mechanistic insights into the role of electrostatic effects in the catalyst microenvironment with iron clusters as a platform, and ii) expanding access to next generation catalysts with concerted electron, proton transfer mechanisms using cobalt clusters.

We developed synthetic approaches to include cations in the secondary coordination sphere (SCS) of iron clusters, and to include up to *four* uncharged or cationic groups. We have so far employed that series of MCC's to quantify the electrostatic effect of the cationic SCS on electrochemical measurements; electrostatic contributions to redox potential are up to 600 mV when four cations adorn the SCS. Those electrostatic contributions affect all catalysts when linear free energy relationships (LFER) are used to benchmark, or rationalize behavior of a (electro/photo)catalyst: ie. redox potential alone does not reflect catalyst thermochemical properties in some cases.



An effective approach to speeding up proton transfer (PT) by molecular catalysts is manipulation of the SCS with proton relays and these enhance overall H_2 evolution rates by orders of magnitude: all PT steps get faster. In contrast, heterogenous electrocatalysts have band structures that promote facile PT concerted with electron transfer (ET), known as the Volmer mechanism, for fast catalysis. Just as proton relays statistically enhance PT rates in molecular or biological catalysis, we have recently shown that the multiple metal-metal bonds in cobalt clusters afford increased sites for PT that enhance hydride formation rates up to 10^9 M^{-1} s^{-1}. We showed that the rate for the first proton transfer step (PT1), which generates a hydride intermediate on $[Co_{13}C_2(CO)_{24}]^{4-}$ and $[Co_{11}C_2(CO)_{23}]^{3-}$, is limited only by diffusion of protons through solution. We also showed that rates for PT2 can be controlled independently, over five orders of magnitude, from the fast rate for PT1 and range from $10^5 – 10^9$ $M^{-1}s^{-1}$.



HER takes two proton transfer (PT) steps. On cobalt clusters we control the PT2 rate while PT1 is fast & diffusion limited.

Our future efforts are directed toward i) elucidation of the role of a cationic catalyst microenvironment on the mechanism of hydride formation and hydride transfer in HER and CO_2RR; and ii) capitalizing on the controllable chemistry of PT2 with cobalt clusters to obtain reaction pathways and mechanistic information where C-H bond formation with CO_2 occurs.

This work was published in: *J. Am. Chem. Soc.* **2020**; *ChemElectroChem* **2021***; *J. Phys. Chem. Lett.* **2021**. * *Special Issue in Memory of JM Savéant.*

Environment and Nature of Adjacent Metals as Critical Reactivity and Photo-Induced ET Factors in Polyoxometalate-Based Water Oxidation Catalysts

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Impact of metals adjacent to the active site metal on water oxidation catalysis and electronic structure. In the last 2 years we achieved the first highly-selective installation of two different 3d metals in water oxidation catalysts (WOCs). For example, the internal Co(II) centers in the polyoxometalate (POM) WOC, $[Co_4(PW_9O_{34})]^{10-}$ (**Co_4**) were replaced with other metals including Ni(II), $[Co_2Ni_2(PW_9O_{34})]^{10-}$ (**Co_2Ni_2**). **Co_2Ni_2** is a tenfold faster WOC than **Co_4** and has profoundly different electronic structure. Understanding structure-activity profiles of these 3d-metal-oxides is critical for design of the best related heterogeneous mixed-metal WOCs. This past year, we have demonstrated that synchrotron X-ray anomalous scattering (XRAS) can be effectively used to quantify the transition metal positions and occupancies in **Co_2Ni_2** (blue-ball outside and green-ball inside sites are ~97% Co and ~97% Ni, respectively, Fig. 1). We hypothesize that XRAS could also facilitate quantification of occupancies of similar-Z-value metals in other multi-metal solar fuel catalysts. Also this year, we have used XANES, EXAFS and other techniques (collaboration with our ANL colleagues) to obtain site-specific structural (geometrical and electronic) information on these solar-fuels catalysts in their intermediate oxidation/reduction states. These investigations, consistent with our DFT studies, reveal dramatic differences in electronic structures of **Co_2Ni_2** and **Co_4**, as well as in their intermediate oxidation states. We have shown that these changes closely correlate with the difference in their reactivities.

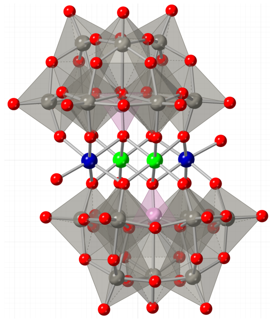

Fig. 1. X-ray structure of **Co_2Ni_2**. Blue balls, active-site Co; green balls, Ni(II); gray octahedra, WO_6; pink tetrahedra, PO_4.

Solar photoredox chemistry of POM salts with water and other donors/solvents. Our recent computational studies on chemical and photophysical properties of the $[PW_{12}O_{40}]^{3-}[M^+(H_2O)_{16}]_3$, M = Li, Na, K, and Cs POMs have enabled us to uncover a critically important role of counter-cations in water oxidation activities of these POMs, which we propose to be another key factor for designing improved light-driven WOCs. We have shown that (a) the visible-region electronic excitations of these complexes are *predominantly solvent-to-POM charge transfer transitions* (i.e. intermolecular CT), and (b) the ratio of intermolecular CT to intramolecular transitions increases with the increasing atomic number of the alkali metals (Fig. 2).

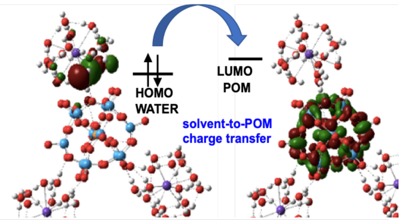

Fig. 2. Visible-region CT from water on alkali-metal-counterions to POM.

In addition, we have continued development of an all-atom theory of ET at nanocrystal/molecule interfaces much needed by our solar-research community. To account for electronic configuration mixing, we extended our previously reported all-atom hybrid BA-LCAO/DFT approach by including the electron/hole and exciton-exciton interactions.

Selective & Reversible CO_2/HCO_2^- Conversion with Thermodynamic and Kinetic Control

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Reversible catalysis is a hallmark of energy-efficient chemical transformations, but can only be achieved if the changes in free energy of intermediate steps are minimized and the catalytic cycle is devoid of high transition-state barriers. Using these criteria, we demonstrate reversible CO_2/HCO_2^- conversion catalyzed by $[Pt(depe)_2](PF_6)_2$ (depe = 1,2-bis(diethyl-phosphino)ethane). Direct measurement of the free energies associated with each catalytic step accurately predicts a slight bias towards CO_2 reduction. We demonstrate how the experimentally measured free energy of each step directly contributes to the < 50 mV overpotential (Figure 1, top). We also find that for CO_2 reduction, H_2 evolution is negligible and the Faradaic efficiency for HCO_2^- production is nearly quantitative. A free-energy analysis reveals H_2 evolution is endergonic, providing a thermodynamic basis for highly selective CO_2 reduction.[1]

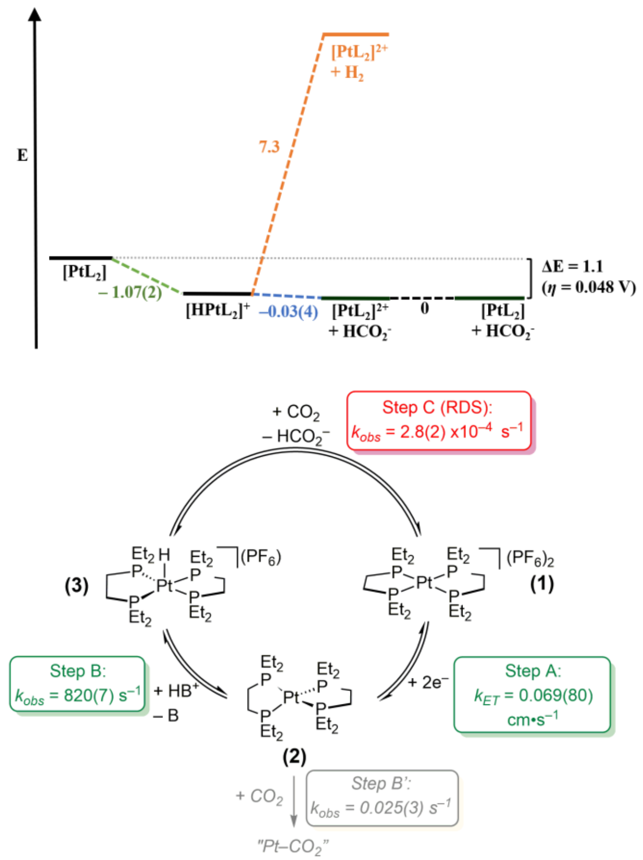

Figure 1. (top) Energy landscape under catalytic conditions (pK_a of 29.0, 1 atm CO_2) at –1.64 V vs $Fe(C_5H_5)_2^{+/0}$ in CH_3CN. Energetic values are in kcal/mol unless otherwise indicated. (bottom) Proposed catalytic cycle and corresponding rates of reactions for electrocatalytic CO_2 reduction to HCO_2^- by $[Pt(depe)_2](PF_6)_2$ (**1**). Conditions: 5 mM **1**, 100mM $CH_2(TBD)_2$•HPF_6, 1 atm CO_2.

$[Pt(depe)_2](PF_6)_2$ electrocatalyzes the reversible conversion between CO_2 and HCO_2^- with high selectivity and low overpotential but low rates. A comprehensive kinetic analysis indicates the rate determining step for CO_2 reduction is the reactivity of a Pt hydride intermediate to produce HCO_2^- (Figure 1, bottom).[2]

We also describe a thermodynamic analysis on organometallic CO_2 reduction and new catalyst design strategies for selectivity at mild potentials inspired by the enzyme formate dehydrogenase (FDH).[3]

1. Cunningham, D. W.; Barlow, J. M.; Velazquez, R. S.; Yang, J. Y., *Angew. Chemie, Int. Ed.* **2020,** *59* (11), 4443-4447.
2. Cunningham, D. W.; Yang, J. Y., *Chem. Commun.* **2020,** *56* (85), 12965-12968.
3. Yang, J. Y.; Kerr, T. A.; Wang, X. S.; Barlow, J. M., *J. Am. Chem. Soc.* **2020,** *142* (46), 19438-19445.

Mixed-Metal Oxide Energy Conversion Catalysts for Integration with Photoabsorbers

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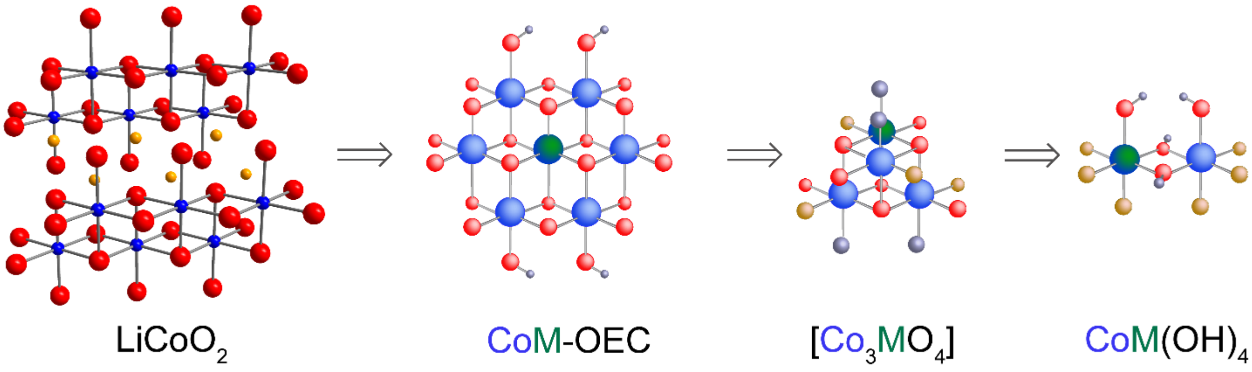
Dimensional reduction of first-row transition metal oxides gives rise to metalate oxygen evolving catalysts (M-OECs) that exhibit high OER activity. Further dimensional reduction generates $[M_4O_4]$ cubanes, which comprise head-to-tail catenates of the minimalist dimetal M_2O_4 unit. All structures contain this essential M_2O_4 subunit that is able to support OER. The approach of dimensional reduction affords an atomistic-level understanding of the structure-activity relationships of OER catalysts and offers a roadmap for rational catalyst design. Indeed, crystalline metal oxides, long thought to be OER catalysts, have been shown in the working solution environment to possess aggregates of metalate M-OEC clusters on the surface oxide; it is these M-OECs that are the active sites for OER in these conventional oxides.

Dimensional reduction provides a path for increasing edge sites, which have been shown to be essential for OER. Across the series, edge site reactivity at the M_2O_4 subunit is retained. A suite of X-ray Absorption Spectroscopy measurements performed at the APS at Argonne National Laboratory, together with electronic spectroscopic and electronic structure studies, have shown that the balance between the Hubbard (U) and ligand field (Δ) energies of neighboring M edge sites is an important determinant of OER. When $U > \Delta$, hole equivalents are driven to oxygen to engender significant oxyl radical character, which promotes the critical O–O bond forming step. Work is currently focused on correlating the O2p level and mixed-metal composition of the various dimensionally reduced structures with U/Δ. The O2p energy level, along with oxide lattice strain and edge site populations, are being assessed as predictive descriptors to guide ML search protocols. In parallel, a new class of ML-based semi-local DFT functionals are under investigation to capture the crucial exchange interactions in the various dimensionally reduced OER structures.



A dimensionally reduced Co OER catalyst series. Chemical structures of $LiCoO_2$, and molecular mixed-metal cobalt structures: CoM-OEC metalate cluster, Co_3MO_4 cubane and dinuclear $CoM(OH)_4$ DPEN complex (blue, red, brown, yellow and gray spheres denote Co, O, N, Li and H atoms, respectively). The Co-OEC is a dimensionally reduced molecular fragment of the extended $LiCoO_2$ structure. In turn, the cubane and then further, the dinuclear Co DPEN complex, are further reduced, retaining the essential Co_2O_4 subunit to support OER.

Multiproton-Coupled Electron Transfer Across Hydrogen-Bond Networks

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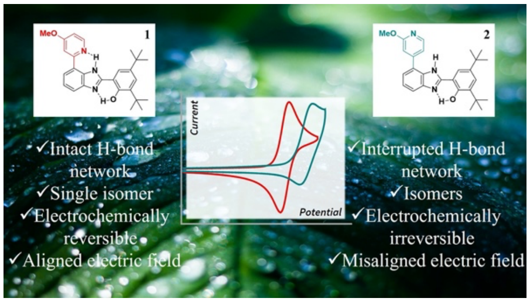
Constructs consisting of a phenol, a Grotthuss-type hydrogen-bond network based on a polybenzimidazoles (bridge), and a terminal proton acceptor (TPA) demonstrate long-range (~16Å) proton translocation upon oxidation of the phenol.[1] The addition of successive benzimidazole moieties to the bridge results in decreasing redox potential of the phenoxyl radical/phenol couple by 60 mV per benzimidazole unit. We interpret this as evidence that benzimidazole-based bridges are non-innocent participants in the PCET processes.[2] This is confirmed by structural modification of the bridge, where the drop in redox potential is modulated by selected substituents on the benzimidazoles.

The essential role of a well-defined hydrogen-bond network in achieving chemically reversible electrochemical oxidation/reduction was investigated with the models shown in the Figure. With compound **1**, experimental and theoretical evidence indicates an overall chemically reversible two-proton coupled electron-transfer process (E2PT). In contrast, with compound **2** electrochemical oxidation of the phenol results in an overall chemically irreversible E2PT process. Insights into the electrochemical behavior of these systems are provided by theoretical calculations of the electrostatic potentials and electric fields at the site of the transferring protons for the forward and reverse processes.



To initiate an E1PT process photochemically we prepared a benzimidazole-phenol (BIP) unit covalently attached to a tripentafluorophenyl-porphyrin (BIPPF$_{15}$). An ultrafast photoinduced process enabled us to observe by 2DEV spectroscopy and long-range-corrected hybrid DFT theoretical techniques the evolution of an initial, partly charge-transferred state to full charge separation on the 120 fs time scale.[4]

1. Odella, E., *et al.*, "Proton-Coupled Electron Transfer Drives Long-Range Proton Translocation in Bioinspired Systems." *J. Am. Chem. Soc.* **2019**, *141*, 14057-14061.
2. Odella, E., *et al.*, "Proton-Coupled Electron Transfer across Benzimidazole Bridges in Bioinspired Proton Wires." *Chem. Science* **2020**, *11*, 3820-3828.
3. Guerra, W. D., *et al.* "Role of Intact Hydrogen-Bond Networks in Multiproton-Coupled Electron Transfer." *J. Am. Chem. Soc.* **2020**, *142,* 21842-21851.
4. Yoneda, Y., *et al.* "Electron–Nuclear Dynamics Accompanying Proton-Coupled Electron Transfer." *J. Am. Chem. Soc.* **2021**, *143*, 3104-3112.

Theories of Homogeneous and Electrochemical Electron Transfer in Complex Media

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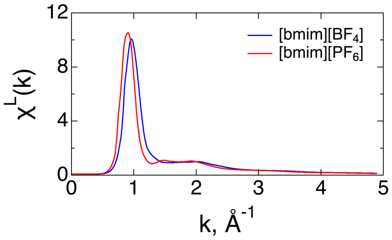
The focus of solar photochemistry research has been continuously shifting toward the use of complex heterogeneous media and interfaces. The bulk materials currently employed include many dynamically dispersive, slowly relaxing media, such as polymers, glasses, and ionic liquids. With additional complexity, these media offer new opportunities for controlling charge transport. We have developed theories and computational formalisms to describe electron transfer in nonpolar solvents and in ionic liquids. Traditional theories are not applicable to both media: violations of their basic assumptions are found in both cases. Spectroscopy of charge-transfer bands supports unexpectedly large reorganization energies in nonpolar media and asymmetry between forward and backward charge transfer.



From the viewpoint of spectroscopic probes, ionic liquids are often characterized as weakly polar media and one anticipates that the standard phenomenology of charge transfer in polarizable media should apply. Yet ionic liquids are conducting materials with formally an infinite dielectric constant. These contradicting facts cast doubt on the standard picture. Characterizing the response of an ionic liquid and its fluctuations driving charge transfer requires specifying both the length and time scales. These questions were addressed by combining a microscopic formal theory with extensive molecular dynamics simulations to connect to Stokes shift dynamics of optical dyes reported in ionic liquids. These media possess an alternating structure of opposite sign ions. This structural motif is reflected in a sharp peak of the charge density structure factor (see Figure). We find that continuum theories of solvation are invalid for ionic liquids. The reorganization energy of charge transfer depends on the observation window (nonergodic): it rises sharply for longer observation times consistent with the relaxation time of collective charge fluctuations. The rise of the reorganization energy is so steep that only sufficiently fast reactions can take place in ionic liquids.

Nonpolar solvents are increasingly applied in applications to solar energy conversion because they avoid large trapping solvation energies of polar solvents. Despite this interest, no quantitative theory has been proposed. Traditional theories predict no charge transfer in nopolar solvents since zero reorganization energy stipulated by continuum theories also means no fluctuations driving the energy levels to resonance. In contrast, we have prosed a new mechanism of charge transfer in nonpolar media based on modulations of induction interactions by density fluctuations. Measurements of absorption and emission charge-transfer bands in cyclohexane have confirmed this basic mechanism, but also showed (i) different reorganization energies in the charge-neutral and charge-separated states (ii) and higher values of reorganization energy than predicted by the theory. Both the enhancement of the reorganization energy and asymmetry are explained by contraction of the solvation shell caused by charge transfer. Nonlinear theories are required for a quantitative description.

Using Voltammetry to Probe Mechanisms of Surface-Anchored Molecular Catalysts

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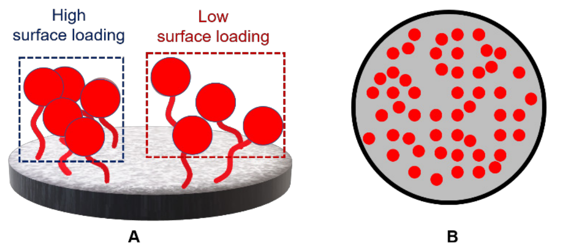
The integration of molecular catalysts that mediate electrochemical fuel production with light-harvesting materials is a major challenge for solar fuel production. A further challenge is to understand how the activity, durability, and selectivity of immobilized catalysts are influenced by the microenvironment at the electrode–catalyst interface. Understanding the mechanisms—and associated kinetics—of both catalysis and catalyst deactivation pathways provides a clear means to address these challenges. Towards this, our lab is developing the application of cyclic voltammetry to probe reaction mechanisms of immobilized molecular catalysts.

Redox-active ferrocene molecules have been anchored to both amorphous carbon and glassy carbon electrodes. Robust covalent attachment is enabled through a newly developed *in situ* Grignard reaction between brominated alkyl ferrocene derivatives and chlorine-terminated carbon surfaces. On amorphous carbon, the redox-active monolayers exhibit diagnostic electrochemical features expected for surface-confined species, but substantial peak splitting is observed and the full-width at half maxima is larger than expected. Analysis of these data reveals lateral interactions between non-uniformly distributed ferrocene headgroups give rise to these deviations and suggest that intrinsic disorder in the underlying carbon electrode. Systematic variation of the alkyl spacers and surface loadings reveals that conformational flexibility of the anchored ferrrocene provides a mechanism to elude repulsive and unbalanced lateral interactions. Rigid linkages provide direct information about the underlying disorder in the material.



(**A**) Schematic diagram of aC-$(CH_2)_n$-Fc showing the surface distribution of Fc for a high surface loading and a low surface loading with a flexible alkyl chain linker allowing the Fc molecules to dynamically approach the surface. (**B**) A two-dimensional projection of the top view of the functionalized aC electrode showing the non-random distribution of Fc molecules on the surface.

When alkyl ferrocene derivatives are anchored to glassy carbon, the voltammetric responses are consistent with reduced disorder. However, non-uniform distribution of the ferrocene on the surface is detected from asymmetry in the voltammograms, which becomes more pronounced at higher scan rates. Voltammograms recorded as a function of surface coverage are consistent with a model wherein populations of “clustered” and “isolated” ferrocenes are both present on the sample. Ferrocene in each sub-population experiences a different local environment. Ongoing work in this project is investigating model complexes that undergo proton-coupled electron transfer, as well as CO_2 reduction catalysts, anchored to these carbon electrodes.

Dhar, D.; McKenas, C. G.; Huang, C.-W.; Atkin, J. M.;* **Dempsey, J. L.;*** Lockett, M. R.* Quantitative effects of disorder on chemically modified amorphous carbon electrodes. *ACS Applied Energy Materials* **2020**, *3*, 8038–8047.

Experimental and theoretical evaluation of surface functionalization and interfacial charge transfer kinetics of 2-D layered materials

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We have developed a new method to functionalize transition metal dichalcogenides involving reductant-actived functionalization processes of exfoliated materials and have analyzed the process both experimentally and theoretically. An increase in covalently bound methyl group coverage on *ce*MoS_2, from <25-30% up to 65% per MoS_2 (i.e. 32% of sulfurs), was observed using a reductant-activated method to functionalize 1T′ *ce*MoS_2 with alkyl halides via intercalation and exfoliation. Using DFT with grand canonical potential kinetics, we found that one type of sulfur on 1T′-MoS_2 is preferentially functionalized (low-S) over the other type (high-S) between 0.3 to –0.9 V vs SHE, effectively restricting functionalization to half of the sulfurs and a substantial decrease in the reaction free energy was observed methylating next to two groups vs zero or one. These factors help to explain the experimental coverage limit of 65% per MoS_2. Reductant-activated functionalization can also be used to control and increase methyl coverage on WS_2, although both experimental and theoretical results indicate that WS_2 methylation is less thermodynamically favorable than on MoS_2 at potentials within 0.3 to –0.9 V vs SHE.

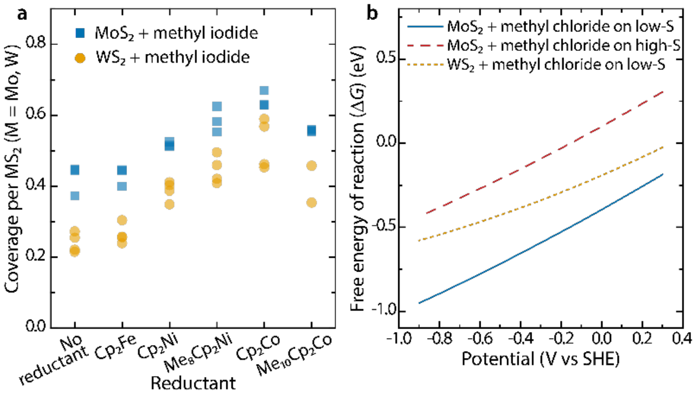

Figure 1. (a) Methyl coverage per MoS_2 or WS_2 under various reductant-activated conditions. (b) Calculated potential-dependent reaction free energy for MoS_2 and WS_2 methylation.

In addition, we are using scanning electrochemical cell microscopy to probe the interfacial charge transfer kinetics at monolayer, bilayer and multilayer grapheme and other 2-D layered materials. These measurements will allow definition of the coupling length in the electrode that is effective for interfacial charge transfer processes to one-electron outer sphere redox systems. This is a key parameter in simple electron-transfer theory involving the application of the Fermi Golden Rule to nonadiabatic interfacial charge transfer processes and the approach will allow experimental determination of this quantity. The nanoscale electrochemical methods are needed to mitigate effects of enhanced charge transfer at grain boundaries confounding interpretation of the experimental results and comparison with theory. Measurements are being performed over a range of redox potentials, substrate thicknesses, and with materials having a wide range of their densities of states at the Fermi level to provide a fundamental understanding of the factors that control such interfacial charge transfer processes.

Advancements in AI for Accelerating Discovery of Solar Fuels Materials

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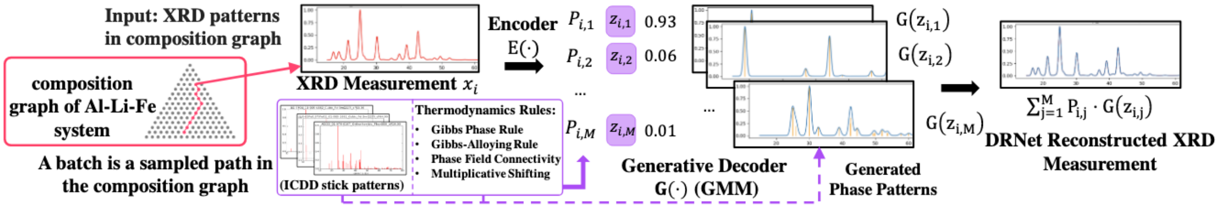
The Energy Materials Chemistry Integrating Theory, Experiment and Data Science (EM-CITED) project is a multidisciplinary research effort focused on accelerating discovery of scientific knowledge via incorporation of data science and artificial intelligence in materials chemistry research. The project aims to advance materials chemistry-aware data science to unify theory and experiment knowledge streams. Our presentation will describe recent advancements in AI for materials chemistry based on the understanding and prediction of metal oxide photoanodes.

In the pursuit of theory-guided discovery of solar fuels photoanodes, identification of the phases formed in combinatorial libraries is a research bottleneck for associating experimental data to electronic structure calculations. A related challenge is that often photoactivity within a given composition system is optimized with a mixture of phases, where modelling the role of each phase requires a "phase map" of the molar fraction and identity of each phase in each photoanode sample. While x-ray diffraction (XRD) provides high throughput characterization of the phase distribution, for example as a function of composition within a 3-cation metal oxide library, automatic interpretation of the XRD patterns to produce the phase map is a long-standing challenge of materials science. While humans and algorithms can evaluate the validity of a solution through application of rules related to the thermodynamics of phase diagrams, full integration of the rules into phase mapping algorithms has not been possible to-date. This problem is emblematic of a broader class of AI problems wherein machine learning is needed to recognize patterns within the dataset and logical reasoning is needed to constrain the learning to produce meaningful solutions. We established Deep Reasoning Networks (DRNets, see figure below) to seamlessly integrate learning and reasoning, which has enabled automated phase mapping of datasets whose solutions have not been solvable by any other means.

We have also advanced machine learning prediction of the properties of materials for which no training data is available. While the high throughput experiments produce large volumes of data in the composition spaces that have been synthesized to-date, these compositions comprise a small fraction of those that could be synthesized. For composition spaces where no synthesis has occurred, predicting properties based on existing data requires algorithms to learn interactions among the elements from existing data to predict what will happen when the elements are mixed in new ways. This poses a substantial challenge for machine learning models that we have addressed with hierarchical correlation learning, a new framework that outperforms state of the art for predicting optical absorption in new composition spaces.



Exploiting Disordered Photonics for Light Trapping in Photoelectrochemical Energy Conversion Applications

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Photoelectrochemical (PEC) solar energy conversion applications rely on chemical reactions driven by photogenerated minority carriers (electrons or holes) at a semiconductor-liquid junction. The optical, electronic, and chemical transport processes characteristic of these PEC reactions occur on independent and generally disparate length scales. Fabricating electrodes with hierarchical structure can optimize the performance for each of these processes simultaneously. However, the optimal structure for one process is generally at odds for another. Our research focuses on disordered, hierarchically structured materials as the basis for PEC photoelectrodes. Disordered materials with dielectric contrast on the length scales of the wavelength of light can trap light in localized modes. The simplicity of the fabrication alone makes this approach a particularly attractive one for engineering light trapping into scalable photoelectrode structures. We have recently introduced an approach to synthesizing disordered colloidal composites (SiO_2 and polystyrene) and selectively removing the polystyrene spheres from the assembly. This allows us to fabricate defects in disordered or random assemblies of SiO_2 nanospheres called photonic glasses to function as resonant optical cavities. We have demonstrated that we can functionalize these structures with a thin semiconductor to improve the rate of PEC water oxidation, for example. This approach can also generate the multiscale structure necessary for uniting the many important transport length scales for PEC energy conversion into a single, simple material.

In this talk, we will introduce our combined theoretical and experimental approach to building photoelectrodes based on disordered photonic scaffolds as a way to dramatically improve light absorption and quantum yield in thin-film semiconductors. One significant issue is that disordered materials can only be defined by ensemble or statistical parameters (pore diameter, scatterer diameter, relative volume fractions) rather than as precise structures, which results in a real, physical variance intrinsic to the ensemble structure. Simulations of the properties of a given ensemble (local light absorption, for example) require a large number of examples for generating statistically accurate measurements for those properties. We will describe our recent efforts to use neural network emulation to explore the absorption properties of defects in a simplified, disordered photonic glass. [1] We will outline how these algorithmic predictions can be used to identify the most efficient ensemble configuration for a given semiconductor photoelectrode. Finally, we will discuss recent experimental photoelectrode constructions synthesized via atomic layer deposition and electrodeposition. [2,3]

[1] R. H. Coridan, Chem. Commun. **56**, 10473 (2020).
[2] Z. Ma, K. Piętak, J. Piątek, J. R. DeMoulpied, A. Rokicińska, P. Kuśtrowski, R. Dronskowski, S. Zlotnik, R. H. Coridan, and A. Slabon, Chem. Commun. **56**, 13193 (2020).
[3] J. M. Lowe, Q. Yan, M. Benamara, and R. H. Coridan, J. Mater. Chem. A **5**, 21765 (2017).

Molecular Regulation of Charge Transfer at Organic Semiconductor Electrodes

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The goal of this work is to seek fundamental new understanding of the mechanisms governing charge transfer and charge transport at organic semiconductor/electrolyte interfaces that underpin the development of new molecular catalysts and generation of fuels from sunlight. This talk will focus on electrochemical impedance and spectroscopy-based methodologies for assessing charge transport properties in conductive polymer electrodes.

The realization of all-organic semiconductor systems that capture light energy and convert it into chemical energy requires a detailed understanding of structure-property relationships governing the interconnected dynamics of photo-generation, transport, and electron transfer across multiple interfaces. Dark electrochemical processes must be understood before increasing the complexity via light-matter interactions. Generally, organic semiconductors will only undergo charge transfer (Faradaic) when electrically conductive (adequate polarons are present); charge-supporting ions from the electrolyte are necessary to support polarons with the organic semiconductor (non-Faradaic). A major challenge is the complexity arising from the hybrid electronic-ionic conduction of the semiconductor. At low doping fractions, long-range Coulombic forces dominate and counterions reside in amorphous domains while electronic charges are supported in the crystallites. At higher doping fractions, electrical and ionic charges can cross between domains, assisted via aggregate relaxation pathways. Critically, each of these regions have spectroscopic signatures which can enable understanding of structure-property relationships.

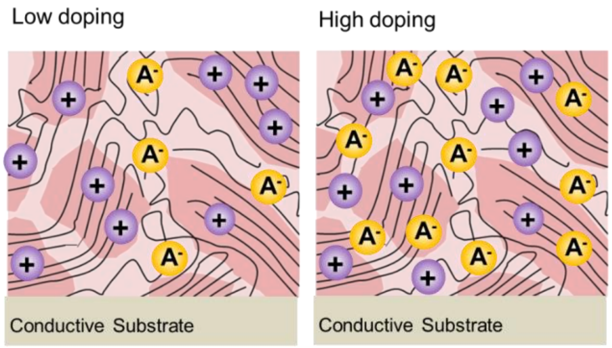

Figure. Schematics of the microstructure of a semicrystalline conductive polymer film, such as poly(3-hexylthiophene-2,5-diyl) (P3HT) at low (left) and high (right) electrochemical doping conditions, where (+) indicates polarons and (A-) represents counterions. Shaded regions are areas of ordered structure, with amorphous regions unshaded.

Using prototypical poly(3-alkylthiophenes), an enthalpic model that describes the conformational relaxation of the polymers with increasing doping will be presented and supported with steady-state and impedance-based spectroelectrochemical approaches. Preliminary results using color impedance spectroscopy will be provided, allowing for discernment between Faradaic and non-Faradaic processes in the energy and frequency domain.

Atomistic Characterization of Physical and Chemical Characteristics of Metal/Semiconductor Interfaces on Functioning Photocatalysts

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Materials that have received the most attention in photocatalysis (including solar water splitting) contain a semiconductor light absorber and an attached metal electrocatalyst. The interface between the semiconductor and electrocatalyst plays a pivotal role in the efficiency of these systems. The physical and chemical properties of the catalyst/semiconductor interface for functioning photoelectrocatalysts; however, are poorly understood. I will discuss our work on shedding light on this interface by developing appropriate atomistic models that allow us to understand underlying physical factors that affect the performance of these systems.

Specifically, we performed rigorous electrochemical measurements, atomistic imaging and characterization, as well as computational modeling to describe the interface of a functioning semiconductor (silicon) and nanoparticle electrocatalysts (Ni) in photoelectrochemical water oxidation (figure 1). We found that the interface is highly dynamic under operating conditions and that the evolution of the interface plays a critical role in (1) minimizing the electron/hole recombination by influencing the charge carrier fluxes (2) increasing the barrier height of the junction, and (3) improving the stability of the system.[1–3] I will discuss the critical physical mechanisms that contribute to these three factors. Overall, these findings are important for understanding and optimizing nanoparticle catalyst/ semiconductor interfaces which are ubiquitous in photoelectrocatalysts.

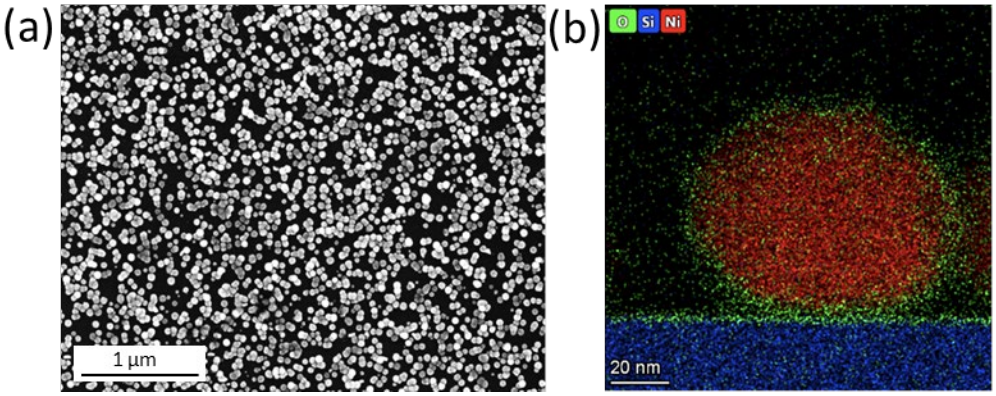

Figure 1: (a) SEM micrograph showing electrodeposited Ni with average diameter of 70 nm on top of a Si substrate. (b) EDS/STEM cross-sectional micrograph showing an individual Ni nanoparticle with an oxide layer at the Ni/Si interface.

References:

1. Hemmerling, J., Quinn, J. & Linic, S. *Advanced Energy Materials* **10**, 1903354 (2020).
2. Hemmerling, J. R., Mathur, A. & Linic, S. *Acc. Chem. Res.* **54**, 1992–2002 (2021).
3. Quinn, J., Hemmerling, J. & Linic, S. *ACS Catal.* **8**, 8545–8552 (2018).

Charge Transfer Processes in Metal Halide Perovskite Based Light Harvesting Assemblies

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Perovskite nanocrystals such as $CsPbBr_3$ have drawn immense interest for solar cells and display devices because of their high emission quantum yield and composition-dependent bandgap tunability. We have now probed the excited state interaction between $CsPbBr_3$ and methyl viologen (MV^{2+}), an electron acceptor probe molecule to explore the charge transfer properties of perovskite nanocrystals.

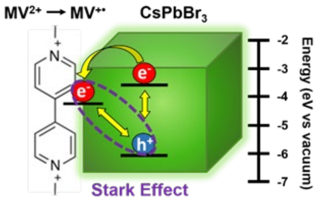

Figure 1. Photoinduced electron transfer between $CsPbBr_3$ and methyl viologen.

Surface chemistry plays an important role in dictating the excited state interactions of semiconductor nanocrystals with charge-shuttling redox molecules. We explored the impact of $CsPbBr_3$ nanocrystal surface modification on the excited state interactions with methyl viologen (MV^{2+}) for three different ligand environments: prototypical oleic acid/oleylamine (OA/OAm) ligands, $PbSO_4$-oleate capping, and didodecyldimethyl ammonium bromide (DDAB) ligands. The electron transfer rate constants as measured from transient absorption spectroscopy vary in the range of $1.2–3.6\times10^{11}$ s^{-1} for different ligand environments. For DDAB-$CsPbBr_3$ NCs the efficiency of electron transfer ($\Phi_{e\text{-}T}$) remained high (73%), despite relatively weaker binding between the NCs and MV^{2+}.

When $CsPbBr_3$–MV^{2+} nanocrystal suspension was excited with a 387 nm laser pulse we observed initially (<20 ps) a quick transient bleach recovery. However, at longer times we observed a residual bleaching, which is in contrast to the longer time (up to 1.6 ns) recovery seen in the absence of MV^{2+}. Interestingly the magnitude of the sustained bleach increased with increasing concentration of MV^{2+}, thus confirming its direct influence on the excited state dynamics. The holes and electrons residing in $CsPbBr_3$ and $MV^{+\bullet}$ remain as a bound pair and create a dipole, contributing to long-lived bleach.

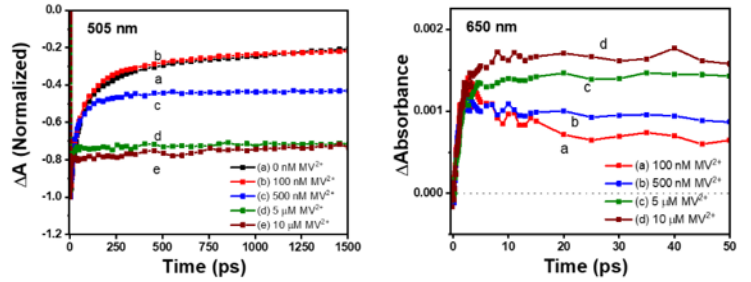

Figure 2. Transient bleach recovery of $CsPbBr_3$ at 505 nm (Left) and corresponding $MV^{+\bullet}$ formation at 650 nm (Right) for concentrations of 0 – 10 μM MV^{2+}. Laser excitation was at 387 nm.

With increasing MV^{2+} concentration we observed a greater fraction of long-term bleach as more of such dipoles are formed following laser pulse excitation (Figure 2 Left). The existence of a $CsPbBr_3(h)$–$MV^{+\bullet}$ pair in our investigation (Figure 2 Right) demonstrates its dipole character as the electrons and holes remain in the bound state and influence the overall dynamics of the semiconductor. The longer life of this charge-separated state should be of interest to further utilize them for photocatalytic oxidation and reduction reactions.

Two-dimensional (2D) lead halide perovskites with better chemical stability and tunable dimensionality offer new opportunities to design optoelectronic devices. We have probed the transient absorption behavior of Ruddlesdon-Popper 2D lead halide (bromide and iodide) perovskites of different dimensionality, prepared by varying the ratio of methylammonium:phenylethylammonium cation. With decreasing dimensionality ($n = \infty \rightarrow 1$), we observed a blue shift in transient absorption bleach in agreement with the trend observed with the shift in the excitonic peak. The lifetime of the charge carriers decreased with decreasing layer thickness (n). The dependence of charge carrier lifetime on the 2D layers as well as the halide ion composition shows the dominance of excitonic binding energy on the charge carrier recombination in 2D perovskites (Figure 3). The excited-state behavior of 2D perovskites elucidated in this study shows the importance of layer dimensionality (n) to tune desired optoelectronic properties.

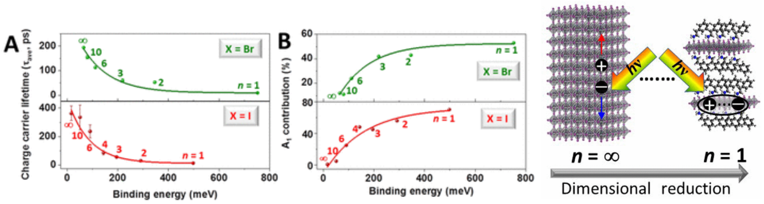

Figure 3. (A) Dependence of charge carrier recombination lifetime (τ_{ave}) and (B) contribution of fast decay component (A_1) of bleach recovery versus binding energy of 2D perovskites. Scheme on the right shows the charge separation and exciton formation in excited perovskites.

Future efforts will include design of $CsPbBr_3$/CdS heterostructures that can exhibit stability in polar environments while still inducing electron transfer under bandgap excitation, and elucidation of the spacer cation role in stabilizing the excited state of 2D perovskites. Fundamental understanding of excited state processes will pave the way to improve the charge transfer efficiency of light harvesting assemblies.

Related Readings:

(1) DuBose, J. T.; Kamat, P. V. Probing Perovskite Photocatalysis. Interfacial Electron Transfer between $CsPbBr_3$ and Ferrocene Redox Couple, *J. Phys. Chem. Lett.* **2019,** *10*, 6074-6080.
(2) Samu, G. F. *et. al*, Electrochemical Hole Injection Selectively Expels Iodide from Mixed Halide Perovskite Films. J. Am. Chem. Soc. 2019, 141, 10812-10820.
(3) Kobosko, S. M.; DuBose, J. T.; Kamat, P. V. Perovskite Photocatalysis. Methyl Viologen Induces Unusually Long-Lived Charge Carrier Separation in $CsPbBr_3$ Nanocrystals, *ACS Energy Lett.* **2020,** *5*, 221-223.
(4) DuBose, J. T.; Kamat, P. V. Surface Chemistry Matters. How Ligands Influence Excited State Interactions between $CsPbBr_3$ and Methyl Viologen, *J. Phys. Chem.* **2020,** *124*, 12990-12998.
(5) Cho, J.; DuBose, J. T.; Kamat, P. V. Charge Carrier Recombination Dynamics of Two-Dimensional Lead Halide Perovskites, *J. Phys. Chem. Lett.* **2020,** *11*, 2570-2576.
(6) Cho, J.; DuBose, J. T.; Kamat, P. V. Charge Injection from Excited $Cs_2AgBiBr_6$ Quantum Dots into Semiconductor Oxides, *Chem. Mat.* **2020,** *32*, 510-517.
(7) DuBose, J. T.; Kamat, P. V. TiO_2-Assisted Halide Ion Segregation in Mixed Halide Perovskite Films, *J. Am. Chem. Soc.* **2020,** *142*, 5362-5370.
(8) DuBose, J. T.; Mathew, P. S.; Cho, J.; Kuno, M.; Kamat, P. V. Modulation of Photoinduced Iodine Expulsion in Mixed Halide Perovskites with Electrochemical Bias, *J. Phys. Chem. Lett.* **2021,** *12*, 2615-2621.
(9) Cho, J.; DuBose, J. T.; Mathew, P. S.; Kamat, P. V., Electrochemically induced iodine migration in mixed halide perovskites: suppression through chloride insertion. *Chem. Comm.* **2021**, 57, 235-238.
(10) Kamat, P. V.; Kuno, M., Halide Ion Migration in Perovskite Nanocrystals and Nanostructures. *Acc. of Chem. Res.* **2021**, 54, 520-531.

Spin-Exchange Auger Up-Conversion for “High-Energy” Photochemistry

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In order to drive “high-energy” photoreduction reactions one needs materials with a sufficiently high conduction band (CB) that matches the reduction potential of a particular chemical transformation. Such materials, however, are expensive and/or not chemically stable. Further, since they exhibit large bandgaps, their activation requires high-energy, ultraviolet (UV) photons that are scarce in the solar spectrum. A possible approach to address this challenge is by using advanced “up-conversion” schemes that raise the energy of the reactive electron by combining energies of multiple absorbed photons. Importantly, employing this method one can, in principle, achieve the desired effect not only with UV but also with visible and infrared (IR) photons that are much more abundant in the solar spectrum.

One approach to up-conversion entails the use of Auger-type energy transfer initiated by absorption of two photons that generate two CB electrons (Fig. 1a). One of these electrons relaxes into a vacant valence band (VB) hole state, transferring its energy to the second electron. As a result, the acceptor electron is promoted to a higher-energy “hot” CB state or even ejected (or “emitted”) into a surrounding “vacuum” (Fig. 1a) if the electron affinity (E_a) is less than the bandgap (E_g). In principle, the “photoemission” process can be very useful in “high-energy” photochemistry as it can be exploited for generating solvated electrons that possess a large reduction potential of almost -3 eV. This potential is sufficient to drive many challenging reactions that are difficult to perform using standard photocatalytic approaches.

Recently, we demonstrated the feasibility of extremely efficient electron up-conversion using spin-exchange Auger interactions enacted by paramagnetic “quantum” defects [1]. In particular, by incorporating spin-5/2 manganese (Mn) ions into CdSe quantum dots (QDs), we achieved ultrafast (~200 fs) up-hill Auger energy transfer, which corresponded to an unusually high energy gain rate (r_{gain}) of ~25 eV ps^{-1}, a 20-fold enhancement compared to Auger processes due to “direct” Coulomb interactions. The comparison of r_{gain} with the energy-loss rate (r_{loss}) due to phonon emission indicated that in Mn-doped QDs, r_{gain} outpaced r_{loss} by a factor of ~7. This is in sharp contrast to undoped QDs, where r_{gain} is lower than r_{loss} by at least a factor of 3 [1].

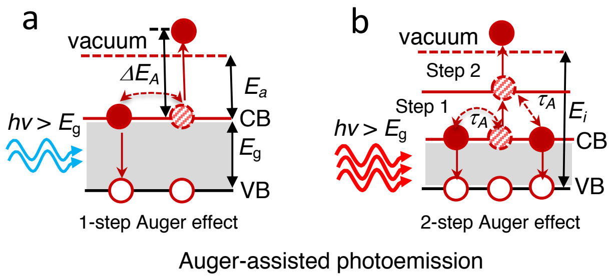

Figure 1. (a) When the electron affinity (E_a) is smaller than the bandgap (E_g), Auger-assisted photoemission can be triggered by absorption of two low-energy photons with $h\nu \approx E_g$ that generate two CB electrons. (b) When E_a is greater than E_g photoemission requires multiple consecutive Auger-excitation steps, as depicted here for a two-step process initiated by absorption of three photons.

The energy gained by a CB electron during single-step Auger recombination (ΔE_A, Fig. 1a) is ~1E_g. Usually, it is not sufficient to eject an electron from a QD (that is, to ionize it) as E_a is normally greater than E_g. In ref. [1], we achieved ionization by combining ΔE_A with a kinetic energy of the "hot" electron excited in a QD using a UV pump pulse. This process took advantage of extremely fast rates of spin-exchange Auger transitions, which allowed for ejecting an energetic hot electron before it had a chance to lose its kinetic energy *via* phonon emission.

Recently, we developed a new doping procedure using which we were able to boost the doping level to $\langle N_{\mathrm{Mn}} \rangle > 10$ of Mn ions per dot on average [2] versus $\langle N_{\mathrm{Mn}} \rangle \approx 0.5$ in ref. [1]. We used these samples to demonstrate for the first time highly efficient two-step Auger photoemission driven not by UV but visible light pulses [3] (Fig. 2). Due to greatly enhanced spin-exchange interactions, photoexcitation of our heavily doped QDs leads to virtually instantaneous formation of a 'hybrid' multiexciton comprising an intrinsic QD exciton and one or more excited Mn ions. This multiexciton state experiences very fast (~200 fs) spin-exchange Auger recombination, which leads to de-excitation of one of the Mn ions accompanied by the formation of a high-energy hot electron. This electron is then re-excited one more time *via* energy transfer from another Mn ion, which results in its ejection to outside "vacuum." This two-step Auger up-conversion process leads to a photoemission efficiency of >3%, which exceeds the value achieved in previous experiments on generation of solvated electrons with activated diamond surfaces [4]. Importantly, with our Mn-doped QDs, these efficiencies are realized with visible light, while the measurements of ref. [4] utilized high energy UV photons.

These results indicate a considerable promise of the discovered phenomena in advanced photoconversion. In particular, ultrahigh energy gains associated with spin-exchange interactions can be exploited for realizing high-efficiency carrier multiplication mediated by magnetic impurities. Spin-exchange Auger up-conversion can be also of considerable utility in "hot-carrier" photovoltaics that would take advantage of a large kinetic energy of hot electrons produced by energy transfer from multiple excited Mn states. In addition, Auger-assisted photoemission can be used for high-efficiency generation of solvated electrons with visible photons, which could allow for driving challenging "high-energy" photochemistry.

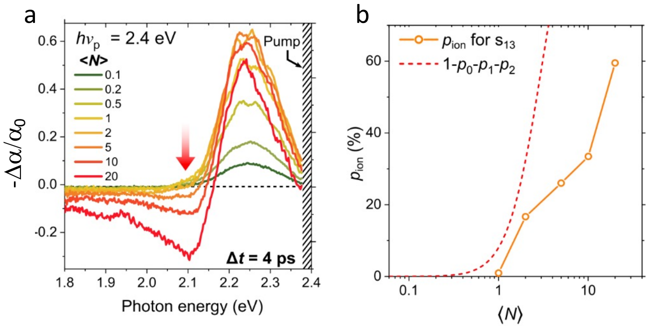

Figure 2. (a) Transient absorption spectra of Mn-doped CdSe QDs with $\langle N_{\mathrm{Mn}} \rangle = 13$ as a function of pump level shown in terms of the average per-dot excitonic occupancy, $\langle N \rangle$ ($\Delta\alpha/\alpha_0$ is the pump-induced absorption change normalized by linear absorption). A photoinduced feature (PA) at ~2.1 eV (red arrow) emerging at $\langle N \rangle > 3$ (onset of three-photon absorption) is a signature of QD ionization; it results from a Stark shift of the band-edge transition. (b) Based on the PA amplitude, the ionization probability reaches 60% at $\langle N \rangle = 20$ (circles).

[1] R. Singh, W. Liu, J. Lim, I. Robel, V.I. Klimov, Hot-Electron Dynamics in Quantum Dots Manipulated by Spin-Exchange Auger Interactions, Nat. Nanotech., 14 (2019) 1035-1041.

[2] H. Jin, M. Goryca, M.T. Janicke, S.A. Crooker, V.I. Klimov, Exploiting Functional Impurities for Fast and Efficient Incorporation of Manganese into Quantum Dots, J. Am. Chem. Soc., 142 (2020) 18160-18173.

[3] C. Livache, H. Jin, O.V. Kozlov, W.D. Kim, I. Fedin, V.I. Klimov, High-efficiency photoemission from magnetically-doped quantum dots driven by multi-step, spin-exchange Auger ionization, submitted (2021).

[4] D. Zhu, L. Zhang, R.E. Ruther, R.J. Hamers, Photo-illuminated diamond as a solid-state source of solvated electrons in water for nitrogen reduction, Nat. Mater., 12 (2013) 836-841.

Correlating Nuclear and Electronic Dynamics

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The newly developed method of two-dimensional electronic-vibrational (2DEV) spectroscopy has a number of advantages for the study of complex molecular systems undergoing ultrafast dynamics [1]. It provides remarkably enhanced spectral resolution compared to electronic absorption spectra, and uniquely contains a cross correlation between solvation dynamics and vibrational spectral diffusion, making the spectra very sensitive to changes in electronic structure. 2DEV spectra, through the involvement of both electronic and vibrational transition moments, are also very sensitive to vibronic mixing and can provide maps of the role of specific vibrations in enabling efficient energy flow over moderate-sized energy gaps in light harvesting complexes.

In this talk I will illustrate these aspects of 2DEV spectra by an example from a synthetic proton-coupled election transfer system [2], energy transfer in the LHCII light harvesting complex [3], and if time permits new data on the primary charge separation mechanisms in the Photosystem II reaction center. Future plans include multiple (up to four) proton transfers, analysis of PSII reaction center and PSII core complex 2DEV spectra under environmental perturbations.

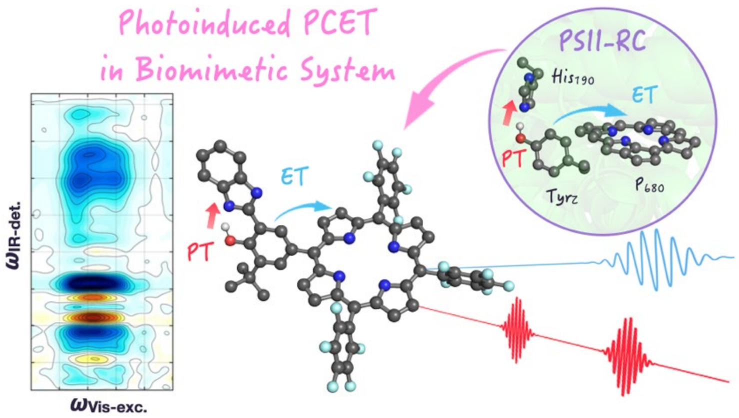

Figure 1: Photoinduced PCET in Biomimetic System

The role of quantum effects in natural photosynthesis had been extensively debated and the application of quantum light spectroscopy (entangled pairs of photons) has the potential to provide significant new insights. Single photon pairs can approximate real sunlight and the ability to excite with heralded single photons can directly address the long-running question of whether data from ultrafast spectroscopy is directly relevant to natural sunlight conditions. Perhaps remarkably the initial event of optical absorption has not been clearly studied. I will describe our initial experiments demonstrating that optical absorption of light does indeed occur in a single quantum jump [4]. Single photon pairs can breach the time-frequency Fourier transform limit, and enable many new control parameters for spectroscopy. If time permits I will sketch some possible experiments.

REFERENCES

1. E.A. Arsenault et al. J Chem Phys Perspective in press (2021)
2. Y. Yoneda et al. JACS 143, 3104-3112 (2021)
3. E.A. Arsenault et al. Nat Comm 11, 1460 (2020)
   E.A. Arsenault et al. Nat Comm 11, 6011 (2020)
4. Q. Li et al, in preparation

Solar Photoconversion in Molecular, Nanoscale and Semiconductor Systems

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The BES Solar Photochemistry core program at NREL focuses on fundamental research of solar photoconversion in molecular, nanoscale and semiconductor systems to capture, control and convert solar radiation with high efficiency into electrochemical potential for electricity, chemicals, or fuels. The project is operated under three focus areas (Thrusts), with an overview of the goals and objectives of each presented briefly below. We will also discuss some unique experimental tools that have been developed over the years for transient photoreflectance (TPR) spectroscopy; time-resolved microwave conductivity (TRMC); transient terahertz spectroscopy (TRTS); UHV deposition of molecules, polymers and quantum dots; nonthermal plasma synthesis; and the synthesis and separation of single-walled carbon nanotubes and 2D transition metal dichalcogenides. The presentation will conclude with three highlights from each of the Thrusts.

Organic and Molecular Semiconductors: Our goal is to develop a fundamental understanding of interfacial photoinduced electron transfer processes at molecular, nanoscale and organic interfaces. Specific organic systems that are examined include conjugated polymers, single-walled carbon nanotubes, and molecular thin films. Our goal is to track the photophysics of both singlet and triplet excitons in the condensed phase and examine the factors that control charge generation, transport, and recombination. We have a special interest in understanding the role of charge delocalization on the generation and recombination processes. We use interchromophore coupling in molecular thin films to promote and understand factors that control efficient singlet fission and the subsequent dissociation to free carriers.

Quantum-Confined Semiconductors: The objective is to control the optical and electronic properties of quantum-confined semiconductors through doping, coupling of the core electronic structures to surface-bound ligands or interactions with plasmonic nanoparticles to direct and transduce energy. Through rational design, synthesis, and spectroscopy, our aim is to understand and control the photophysical properties of quantum-confined structures. We aim to examine the role of composition, morphology, ligands, and plasmonic interactions in mediating charge dynamics and charge transfer processes; the chemistry required to produce asymmetric, functional nanostructures; and nanoscale heterojunctions and arrays to control the flow of energy and charge.

Semiconductor-Electrolyte Interfaces: We examine how interfacial chemistry and microenvironments affect the thermodynamics and kinetics of charge separation and redox chemistry at (photo)electrocatalyst-electrolyte interfaces. The goal is to understand surface modification, phase, defects, surface (re)construction, and co-catalysts in semiconductor-electrolyte systems. By determining the thermodynamics and kinetics at semiconductor-electrolyte junctions using new spectroscopic techniques, we can understand how charge transfer can be used to manipulate (photo)electrocatalysis. For example, we explore the role of charge dynamics and energy flow in cooperative plasmonic photocatalysts coupled to reaction chemistry and hope to use this knowledge to retain the maximum amount of the photon excess free energy in fuel-forming reactions on photoactive systems. Other systems of interest include nanostructured and bulk crystals, 2D semiconductors and catalysts, and interfacial surface modification thereof.

Thrust 1: Slow Charge Transfer from Pentacene Triplet States at the Marcus optimum

Understanding the factors that control photoinduced electron transfer (PET) in the solid-state is a central goal of Thrust 1 of the NREL solar photochemistry program. Specifically, examining whether the Marcus formulation is an appropriate model for describing the PET process, and whether this model is appropriate for singlet states generated by direct photoexcitation, or triplet states that evolve from a singlet-fission process. By sensitizing thin films of conjugated polymers[1], crystalline molecules[2], and single-walled carbon nanotubes[3] we have investigated the impact of the driving force on the PET process and observed clear evidence of the Marcus inverted region in each case.

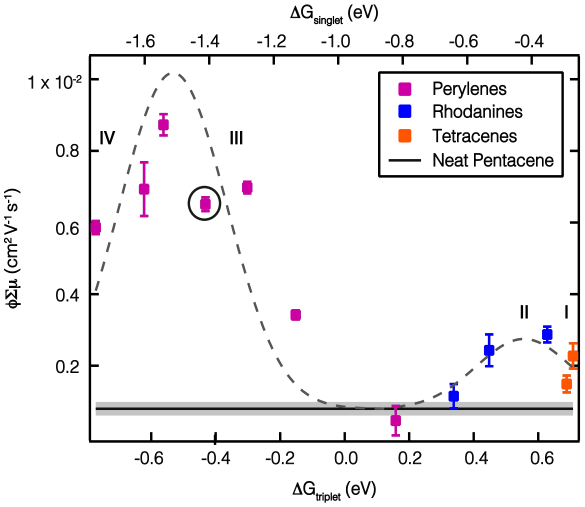

Figure 2 - Trends in charge yield as a function of driving force, displaying two distinct optimum values that are consistent with a Marcus formulation for electron transfer from both the singlet and the triplet excited states of pentacene. (The twelve acceptors were provided through collaborations with KAUST (KSA); Colorado State University; and the University of Kentucky. Full details here[2]).

We will briefly overview these previous studies and then describe the recent investigation of the dissociation of triplet states produced from singlet fission (SF) in polycrystalline films of pentacene. Twelve acceptor molecules with reduction potentials that span a range of 1.5 eV were used to control the driving force for electron transfer. We used femtosecond transient absorption spectroscopy to track singlet and triplet decay in pentacene concurrent with acceptor anion formation and correlated the dynamics with results from transient microwave conductivity (TRMC), which probed the production of mobile holes after exciton dissociation. We observed separate optima in the charge yield as a function of driving force for singlet and triplet excitons, including inverted regimes for the dissociation of both states (see Figure 2). But even at the optimal driving force, the rate constant for charge transfer from the triplet state is surprisingly small, ~10^7 s^{-1}, presenting a previously unidentified obstacle to the design of efficient SF solar cells. However, we also show that molecular acceptors can provide a strategic advantage to SF solar cells by suppressing singlet dissociation at optimal driving forces for triplet dissociation.

Thrust 2: Modulating Quantum Dot Energetics via Doping

We have been exploring doping semiconductor quantum dots (QDs) and its impact on the QD primary photochemical events including charge generation, separation, and recombination. In one example, colloidal PbSe QDs were post-synthetically doped with In^{3+} as the substitutional dopant. We found that incorporating In^{3+} results in a gradual bleaching of the interband first-exciton transition and

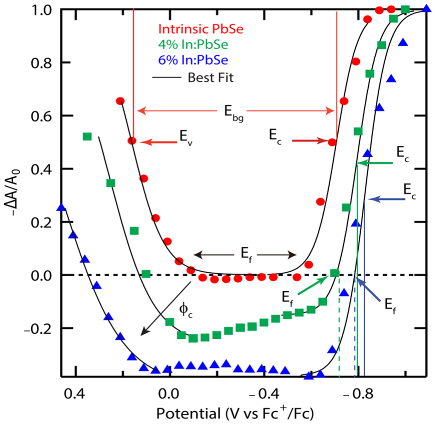

Figure 1 - Normalized differential excitonic absorption of intrinsic PbSe (red-circles), 4% In:PbSe (green-squares), and 6% In:PbSe (blue-triangles) QD thin films as a function of electrochemical bias.

concurrently the appearance of a size-dependent, intraband absorption, suggesting the controlled introduction of delocalized electrons into the QD band edge states.[4] . The optical properties of the In:PbSe QDs were comparable to n-type PbSe QDs generated from remote cobaltocene reduction, confirming that In^{3+} is an electronic n-type dopant. Spectroelectrochemical measurements also demonstrated characteristic n-type signatures, including both an induced absorption within the electrochemical bandgap and a shift of the Fermi-level toward the conduction band with increased In^{3+} content (Figure 1). Finally, In^{3+} dopants can be reversibly removed from the PbSe QDs, whereupon the first exciton bleach is recovered. Our results demonstrate that PbSe QDs can be controllably n-type doped via impurity doping.

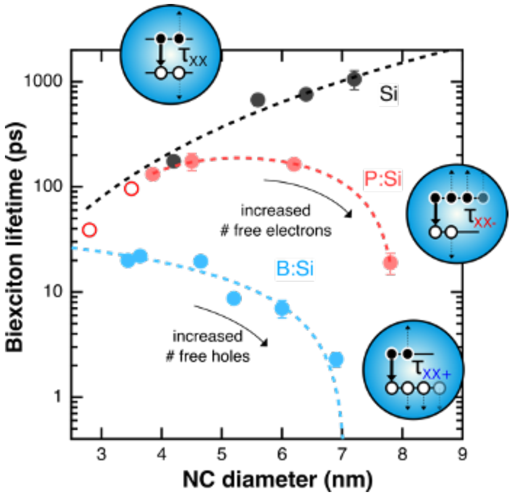

Figure 3 - Lifetimes of a charge-neutral biexciton τ_{XX} in intrinsic Si QDs (black disks), and charged biexcitons τ_{XX-} in P:Si (red disks) and τ_{XX+} in B:Si (blue disks). The red open circles are τ_{XX-} values for P:Si systems with amorphous surfaces.

Other examples of doping effects are silicon quantum dots (Si QDs) with high concentrations (~10^{20} cm^{-3}) of either p-type (B:Si) or n-type (P:Si) dopants. For the P:Si QDs, additional electrons in the Si lattice lowered the density of states in the conduction band, decreasing the strength of the Auger interaction. Also, the biexciton lifetime (τ_{XX}) of P:Si QDs at varying doping densities did not follow the volumetric dependence ($\tau_{XX} \propto r^3$) normally observed for other QD semiconductors.[5]

In subsequent work, we found that both B:Si and P:Si QDs exhibit size-dependent τ_{XX}.[6] We confirmed our prior observations for larger (>4 nm) P:Si QD, but observed that small-sized (<4 nm) n-doped P:Si QDs had negatively charged biexciton lifetimes (τ_{XX-}) comparable to charge-neutral τ_{XX} in intrinsic, undoped Si QDs (Figure 3). In contrast, p-doped B:Si QDs exhibited positively charged biexciton lifetimes (τ_{XX+}) that were always faster than τ_{XX} in undoped Si QDs regardless of size (Figure 3). This suggests that below a critical size (~4.5 nm for P:Si), electrons are not "free" but are localized. Holes, on the other hand, are never localized and always interact with excitons for B:Si QDs above ~2.5 nm in diameter (based on extrapolation).

Thrust 3: Plasmon-Driven Hot Carrier Effects in 2D Transition Metal Dichalcogenides for (Photo)electrochemical Catalysis

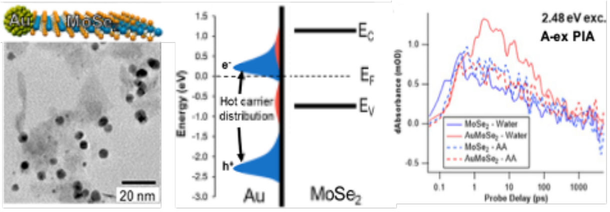

Figure 4 - Left: Experimental system for studying hot carrier injection in gold/TMDC composites. Middle: Hot carrier distribution after optical excitation. Excitation at high energies allows for hot holes to inject into $MoSe_2$. Right: TA of $MoSe_2$ and gold-decorated $MoSe_2$ indicating hot carrier transfer from the gold to the $MoSe_2$.

Many alternative catalytic materials are being studied for important photoelectrochemical reactions; however, their activity and performance often lag behind noble metals. Coupling novel catalysts with strongly resonant states in plasmonic materials presents a route for controlling and enhancing catalytic reactions. This work is aimed at understanding excited carriers in hybrid metal–transition metal dichalcogenide (TMDC) systems using transient absorption (TA),[7] in-situ reflectance,[8] spectro-electrochemistry, X-ray/ultraviolet

(XPS/UPS) photoelectron spectroscopy, and theory. TA studies show that gold nanoparticles grown *directly* on WSe_2 and $MoSe_2$ nanosheets give rise to a new long-lived photoinduced absorption (PIA) feature that is quenched by a hole capture agent (ascorbic acid) indicating hole injection into the TMDC (Figure). This long-lived PIA signal only arises when Au interband transitions are excited, which have been shown to selectively produce hot holes in gold. XPS/UPS revealed the valance bands of the selenide TMDCs are positioned to capture the hot hole while those of the sulfides are too deep, elucidating key differences between these semiconductors. These observations show that charge separation at a metal−semiconductor interface can be used to extend the lifetime of hot holes. Harnessing these plasmonically generated long-lived carriers could be valuable to solar-driven catalysis.[7]

Furthermore, we employed model plasmonic metal-TMDC systems that show strong (~100 meV) plasmon–exciton coupling, unique coherent exciton-exciton coupling of the A and B excitons[8] in MoS_2 as well as very strong (300 meV) coupling of the C-exciton (Figure). These coupled states are long-lived and allow for the manipulation of both the energetics and quantum mechanical character of the excited state, and potentially the production of highly energetic carriers that can be used in fuel-forming reactions. Electrochemical measurements show the production of photocurrent from these states.

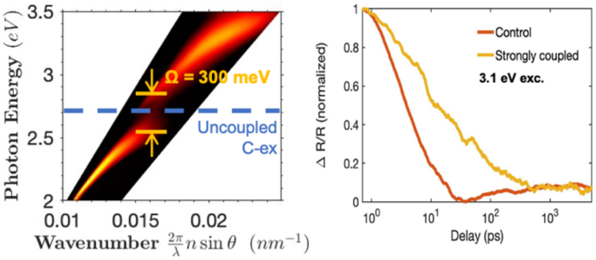

Figure 5 - Left: Exciton-plasmon dispersion showing strong coupling at the C-exciton. Right: Transient reflectance of uncoupled and strongly coupled MoS_2 indicating enhanced excitation lifetime.

References

(1) Coffey, D. C.; Larson, B. W.; Hains, A. W.; Whitaker, J. B.; Kopidakis, N.; Boltalina, O. V.; Strauss, S. H.; Rumbles, G. An Optimal Driving Force for Converting Excitons into Free Carriers in Excitonic Solar Cells. *J. Phys. Chem. C* **2012**, *116*, 8916–8923. https://doi.org/10.1021/jp302275z.

(2) Pace, N. A.; Korovina, N. V.; Clikeman, T. T.; Holliday, S.; Granger, D. B.; Carroll, G. M.; Nanayakkara, S. U.; Anthony, J. E.; McCulloch, I.; Strauss, S. H.; Boltalina, O. V.; Johnson, J. C.; Rumbles, G.; Reid, O. G. Slow Charge Transfer from Pentacene Triplet States at the Marcus Optimum. *Nat. Chem.* **2019**, *100*, 1–8. https://doi.org/10.1038/s41557-019-0367-x.

(3) Ihly, R.; Mistry, K. S.; Ferguson, A. J.; Clikeman, T. T.; Larson, B. W.; Reid, O. G.; Boltalina, O. V.; Strauss, S. H.; Rumbles, G.; Blackburn, J. L. Tuning the Driving Force for Exciton Dissociation in Single-Walled Carbon Nanotube Heterojunctions. *Nat. Chem.* **2016**, *8*, 603–609. https://doi.org/10.1038/nchem.2496.

(4) Lu, H.; Carroll, G. M.; Chen, X.; Amarasinghe, D. K.; Neale, N. R.; Miller, E. M.; Sercel, P. C.; Rabuffetti, F. A.; Efros, A. L.; Beard, M. C. N-Type PbSe Quantum Dots via Post-Synthetic Indium Doping. *J. Am. Chem. Soc.* **2018**, *140*, 13753–13763. https://doi.org/10.1021/jacs.8b07910.

(5) Limpens, R.; Neale, N. R. Free Electron-Driven Photophysics in n-Type Doped Silicon Nanocrystals. *Nanoscale* **2018**, *10*, 12068-12077. https://doi.org/10.1039/C8NR02173B.

(6) Limpens, R.; Pach, G. F.; Mulder, D. W.; Neale, N. R. Size-Dependent Asymmetric Auger Interactions in Plasma-Produced n- and p-Type-Doped Silicon Nanocrystals. *J. Phys. Chem. C* **2019**, *123*, 5782–5789. https://doi.org/10.1021/acs.jpcc.9b00223.

(7) Dunklin, J. R.; Rose, A. H.; Zhang, H.; Miller, E. M.; van de Lagemaat, J. Plasmonic Hot Hole Transfer in Gold Nanoparticle-Decorated Transition Metal Dichalcogenide Nanosheets. *ACS Photonics* **2020**, *7*, 197–202. https://doi.org/10.1021/acsphotonics.9b01393.

(8) Rose, A. H.; Dunklin, J. R.; Zhang, H.; Merlo, J. M.; van de Lagemaat, J. Plasmon-Mediated Coherent Superposition of Discrete Excitons under Strong Exciton–Plasmon Coupling in Few-Layer MoS2 at Room Temperature. *ACS Photonics* **2020**, *7*, 1129–1134. https://doi.org/10.1021/acsphotonics.0c00233.

Probing Interfacial Charge Transfer in Heterostructured Nanomaterials using Ultrafast X-ray Spectroscopy

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The increasing demand for renewable and low-cost energy has triggered a vast amount of research aimed at developing, characterizing and optimizing materials that can efficiently convert sun light into useful chemical energy in the form of electricity or chemical fuels. A promising approach for third-generation solar cells is to replace metal-organic dyes by purely inorganic substances with strong optical absorption and extended long-term stability. So-called quantum dot sensitized solar cell (QDSC) materials have gained much attention in recent years based on the advantageous physicochemical properties of semiconducting quantum dots (QDs) as sensitizers, as well as their promising potential to increase the conversion efficiency beyond the Shockley-Queisser limit of ~33% by making use of hot-electron transfer routes and multiple exciton generation.

Despite extensive research on QDSC materials, several key questions remain unanswered and the mechanisms of ultrafast charge transfer phenomena are heavily debated. The research project presented here aims at resolving these pertaining questions by elucidating the time scales and mechanistic origins of the crucial steps of photoinduced interfacial charge separation and adverse carrier trapping and recombination routes in chemically linked and epitaxially grown QD/MO heterostructured nanomaterials. The proposed research will take the form of the following specific objectives: **(1)** Establish the first *direct* element-specific probing of (hot) electron/hole dynamics, and unambiguous disentanglement of all relaxation processes; **(2)** Identification and atomic-scale characterization of electron/hole trap sites in the acceptor and donor moieties; **(3)** Determination of the structural changes associated with interfacial charge transfer and testing theoretical electron transfer models for heterostructured nanomaterials; **(4)** Comparing the charge transfer dynamics between chemically linked and epitaxially connected QD/MO materials and exploring the factors favoring hot-electron transfer routes in these systems.

Our experimental approach is based on various forms of ultrafast X-ray spectroscopy implemented at synchrotron and X-FEL facilities. Ultrafast X-ray spectroscopy is ideal to fulfill the above-listed objectives since it is element-specific such that charge density changes and structural distortions in the donor and acceptor moieties can be followed selectively, and it delivers not only the local geometric structure of the system under study (by means of EXAFS), but also the underlying electronic structure changes (using XANES). Furthermore, its time resolution (~70 ps at synchrotrons, ~100 fs at X-FELs) is ideal to study charge transfer processes in the weak- and strongly-coupled electron transfer regimes, respectively. The results from these studies, if successful, will lead to a detailed fundamental understanding of the factors driving photoinduced electron transfer in QDSC materials and will enable the identification of ways to improve the efficiency of QD-based solar cell devices.

In this presentation, I will provide an overview of the motivation and plans of this project and present the first results obtained for ultrafast X-ray spectroscopy on photoexcited epitaxial ZnO nanorods.

Ultrafast Carrier Dynamics in Monolayer MoS_2 Photoelectrodes

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The fundamental problem that limits the solar energy conversion efficiency of semiconductors such as CdTe and Si is that all excess solar photon energy above the band gap is lost as heat. Avoiding thermalization energy losses is of paramount significance for solar energy conversion because hot-carrier-based systems theoretically achieve 66% efficiency, which breaks the detailed balance limit of 33%. Of all the candidate materials, 2D semiconductors such as monolayer (ML) MoS_2 have unique physical and photophysical properties that could make hot-carrier energy conversion possible. The overall goal of this project is to acquire fundamental knowledge of interfacial energetics and hot-carrier dynamics in 2D semiconductors under working solar photochemistry conditions. The knowledge gap in the field that our research will address is that the electronic states of 2D materials move with carrier density, due to either light absorption or an applied electrochemical potential. The energy level movements are significant because the real fundamental driving force for charge transfer ($\Delta G^{0\prime}$) is unclear for a given reaction and applied potential. In principle, quantifying $\Delta G^{0\prime}$ under working conditions opens up the possibility to tune the hot carrier extraction rate relative to the cooling rate. In the first six months of this project, our research team has employed photocurrent spectroscopy, steady-state absorption spectroscopy, and in situ femtosecond transient absorption spectroscopy as a function of applied potential to characterize underlying steps in a ML MoS_2 photoelectrochemical cell (Figure 1). The rich data set informs us on the timescales for hot-carrier generation/cooling and exciton formation/recombination, as well as the magnitudes of changes in exciton energy levels, exciton binding energies, and the electronic band gap. At negative potentials before the steady-state photocurrent onset for iodide oxidation, hot-carriers form C-excitons within 50 fs. When a steady-state photocurrent flows due to photoelectrochemical iodide oxidation, C-exciton formation diminishes, suggesting that hot carriers are extracted from ML MoS_2 before they cool to form C-excitons. These findings open the possibility of tuning the hot-carrier extraction rate relative to the cooling rate to ultimately utilize hot-carriers for solar energy conversion applications.

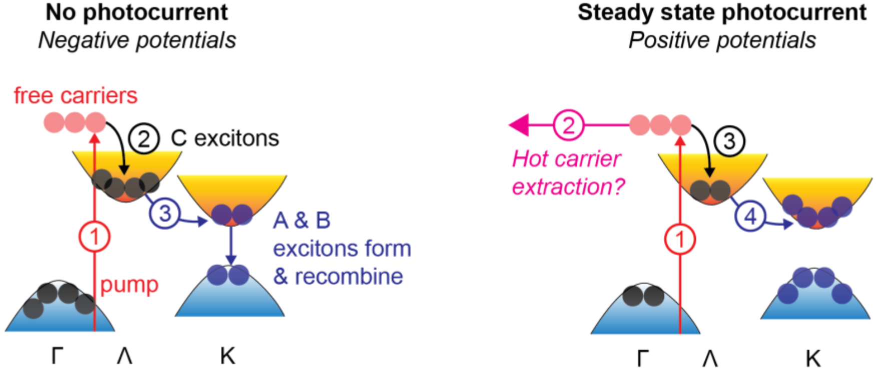

Figure 1. Fundamental processes in a photoelectrochemical cell made from ML MoS_2.

Light Harvesting in Semiconductor Quantum Dots

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Semiconductor quantum dots (QDs) are potentially useful as synthetically tunable mid-visible light-harvesting structures in photocatalysis applications, but at present they perform inefficiently because they exhibit much faster exciton relaxation processes than expected given their large intraband energy spacings. Rapid cooling of hot carriers in QDs, involving fast intraband relaxation pathways mediated by an Auger mechanism, results in a significant loss of captured energy. The role of surface states and the presence of organic capping ligands in the mechanism of hot carrier cooling, however, remains to be fully elucidated. Developing a detailed mechanistic understanding of the influence of organic capping ligands on the dynamics of recombination and cooling in QDs is an essential precursor to the rational design of materials for light harvesting and photocatalysis.

We propose that the spectroscopy and dynamics of QDs can be better understood in terms of a *vibronic exciton model*, in which extensive quantum coherent mixing of the electronic and vibrational states of the core semiconductor nanoparticle with those of its surface capping ligands accounts for the absorption and photoluminescence properties. The preliminary results provide the first evidence that coherent vibronic wavepacket motions control the rate of cooling of carrier states to the band edge via a nonadiabatic mechanism directed by mid-frequency branching modes derived from the surface ligands. An important implication of these findings is that the QDs present an opportunity to learn how the structural features of an energy material can be manipulated to optimize its function through control of its coherence properties.

Planned Research. The vibronic exciton hypothesis will be tested by combining state-of-the-art approaches for the synthesis and structural characterization of QDs (Van Patten, Zhang) with two-dimensional electronic spectroscopy (Beck) and electronic structure calculations (Levine).

Aim 1: Prepare CdSe QDs with a range of surface-capping ligands intended to vary the mode of bonding and coupling to the core wavefunction, and then characterize the surface coordination before and after exchange of ligands using mass spectrometry and NMR spectroscopy.

Aim 2. Determine the impact of QD–ligand bonding character on hot carrier cooling and vibronic coherences using broadband two-dimensional electronic spectroscopy.

Aim 3. Determine the mechanisms that promote hot carrier cooling in QDs at the atomistic level.

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

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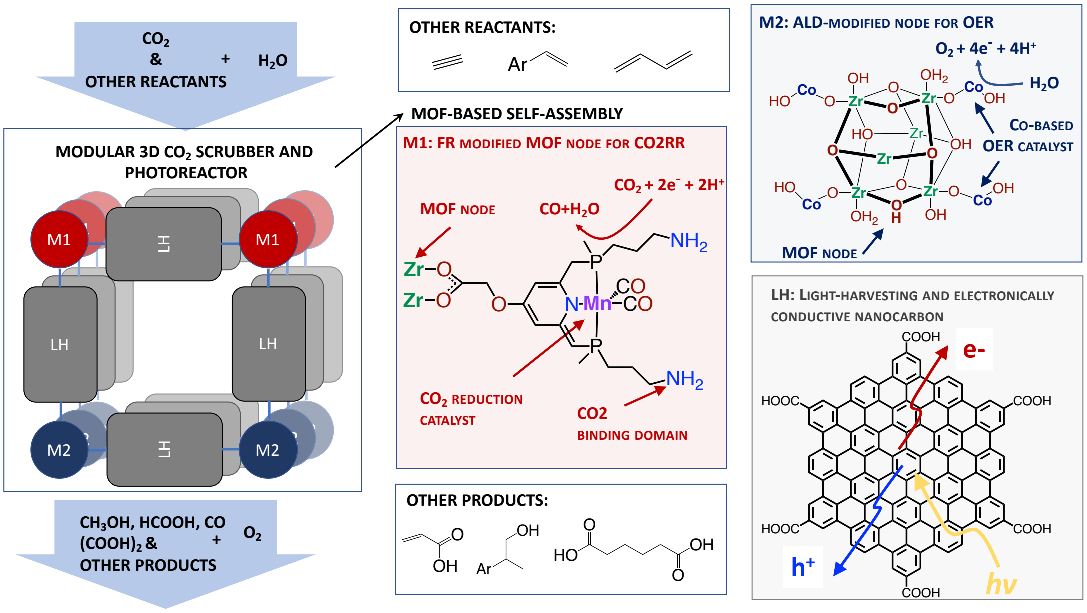
Carbon dioxide is an abundant and inexpensive reagent that, if captured from the air, can serve as a source of value-added chemicals. However, efficient approaches toward direct-air capture (DAC) of CO_2 rely on the formation of strong chemical bonds with the capturing reagent, which require prohibitively large energy inputs when CO_2 release is needed, rendering the overall capture process impractical. To circumvent this challenge, we investigate a photoreactive capture approach that combines the DAC of CO_2 with its direct conversion into value-added chemicals, such as methanol, acrylic acid derivatives and oxalic acid, using visible light as an energy input. This molecular reactor is composed of a porous, three-dimensional architecture, where light-harvesting, CO_2-capturing and catalytic moieties are assembled into a metal-organic framework (MOF), which provides high surface area for efficient DAC, precise orientation of chromophores for successful light harvesting and catalyst deposition needed for selective and fast synthesis of relevant products.



The chemical processes is driven using light as an energy source and water as an electron and proton source (through the oxygen evolution reaction). Chemically tunable catalytic sites are deposited at the MOF nodes using atomic layer deposition or functionalization reactions to contain CO_2 binding motifs as well as the catalytic metal site in the close proximity and optimal geometry for desired CO_2 reduction reaction to useful chemicals. The light harvesting is accomplished using MOF ligands composed of nanocarbon-based chromophores with tunable absorption frequencies (due to quantum confinement effects) and high electrical conductivity (due to high degree of π-conjugation).

Toward Selective Photocatalytic Conversion of Methane to Methanol by a Colloidal Quantum Dot: Spatio-Temporal Reaction Control and *in Situ* Methanol Protection Schemes

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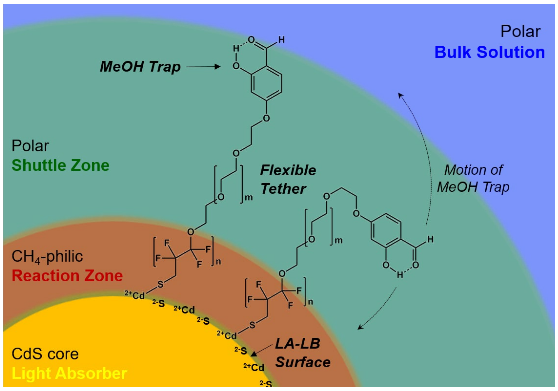

Figure 1. ***Design of a QD-Ligand Catch-React-Trap-Release Photocatalyst.*** The reaction zone comprises densely packed, chemically inert fluorinated alkyl chains to stabilize CH_4 and bring it to the QD surface to adsorb on Lewis acid-Lewis base pairs. The QD absorbs visible-light to produce $OH^{\bullet}$ or $^{1*}O_2$ and, subsequently, a series of uncharged intermediates of the CH_4 oxidation process. Upon CH_3OH formation, the activated aldehydes that terminate the fluorinated ligands add to the CH_3OH molecules to form acetals. Through random motion combined with a driving force to enter a more polar region of the monolayer, these ligands shuttle the protected CH_3OH away from the QD surface. Water molecules that diffuse into the shuttle region activate the release of the CH_3OH into the bulk.

The selective conversion of methane to molecules other than CO_2 is a grand challenge of Chemistry, from both an energy-and-environment standpoint and a fundamental standpoint. Methane, the principal component of natural gas, is abundant and devastatingly polluting. Methane is responsible for 20% of anthropogenic global warming. Its greenhouse gas effect is a factor of 20 greater than that of the same mass of CO_2. It is stubbornly inert such that its transformations are hard to control. Under conditions where reactions of methane are fast enough to be of interest, the formation of CO_2 is so favorable that production of useful chemicals, like ethane and methanol, is not economically feasible. One could claim that chemically activating methane, but then *stopping* that reactivity mid-stream, to obtain a partially oxidized, useful product like methanol is the ultimate demonstration of chemical control.

The aim of this project is to realize such control through colloidal photocatalysis, a mixture of high-energy excited state chemistry, selective adsorption and activation on the surfaces of colloidal semiconductor quantum dots (QDs), and controlled diffusion of molecules to and away from the surface of the QD, **Figure 1**. We aim to achieve spatio-temporal control of the complex partial oxidation of methane by designing a nanoscale, *confined* diffusion-reaction system triggered by fast photo-induced electron and energy transfer events. Specifically, we will (i) design a QD-ligand complex to adsorb methane in a distorted geometry to lower the energy barrier for H-atom abstraction, (ii) demonstrate the use of QDs to photo-generate high-energy species ($^{1*}O_2$, $OH^{\bullet}$, S^{1-}) to perform H-atom abstraction from methane, and (iii) design ligands for the QD that will chemically protect the target product methanol through reversible acetal formation, shuttle methanol away from the "reaction zone" at the QD surface, and release the methanol into bulk solution, selectively terminating the methane oxidation reaction at methanol.

Modular Nanoscale and Biomimetic Assemblies for Photocatalytic Hydrogen Generation

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Our goal for this collaborative project is to improve the photochemical production of H_2 by nanocrystalline quantum dots (QDs) through the addition of molecular and bio-inspired catalysts and compounds. The development and study of these catalytic systems yields new insights into the physical and chemical properties of QDs, which remain poorly characterized.

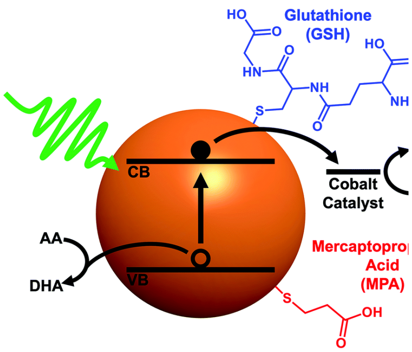

Figure 1: System for photochemical H_2 production using a cobalt catalyst.

We recently developed an extremely efficient (photon-to-H_2 quantum yield of 28%) and robust photocatalytic hydrogen (H_2) production system with CdSe QDs capped with the tripeptide glutathione (GSH) and a cobalt catalyst which yielded 210,000 mol H_2 per mol Co(II) over 91 hours. Electrochemical studies suggest that the active proton reduction catalyst is a $Co_x(GSH)_y$ complex formed *in situ*. Importantly, this method of forming the complex with GSH circumvents previously reported catalyst poisoning by thiolate ligands. When compared to a system with a similar ligand, mercaptopropionic acid (MPA) (Fig. 1), the GSH-capped QDs were found to be twice as efficient which shows that the peptide functional groups play an active role in facilitating proton reduction.

We have also been interested in improving proton reduction yields by accelerating hole transfer from QDs. Given the large effective mass of a hole relative to that of an electron in CdSe, hole transfer is substantially slower than electron transfer and can often be rate-limiting for photochemical systems. We report that polyoxovanadate (POV)-alkoxide clusters act as redox mediators to remove photogenerated holes from the QD (Fig. 2). Adding these clusters to CdSe QDs inhibits charge recombination and improves the H_2 yield by ~125%. We also note that the size and electrostatics of the QD ligands have a large impact on H_2 yields and suggest that optimizing the ligand shell is crucial for allowing the clusters to associate with the QD. Continuing our work with these POV-alkoxides, we have recently been studying methods to optimize charge transfer between the QDs and clusters. We have found that the negative charge of the POV-alkoxide clusters facilitates electrostatic association with positively charged metal ions on the surface of the QD which improves charge transfer. These results have implications for utilizing the oxidative equivalents from QDs, a necessary step for the production of solar fuels from water.

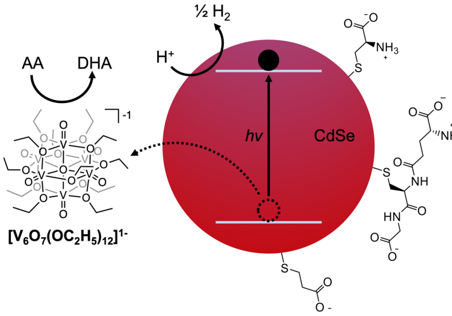

Figure 2: Polyoxovanadate-alkoxide clusters as redox mediators.

Excited State Dynamics of Photoexcited Charge Carriers in Metal Halide Perovskites: Time-Domain Ab Initio Studies

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Considering realistic aspects of perovskite structure,[1] including defects,[2] we demonstrated that soft lattice and localization of defect states rationalize defect tolerance in both hybrid organic-inorganic[3-4] and all-inorganic[5] perovskites, that point defects benign in bulk create midgap states at grain boundaries and require passivation,[6] that moderate disorder rationalizes the unusual temperature dependence of carrier lifetimes,[7] that edges[8] and grain boundaries[9] can help exciton dissociation and extend carrier lifetimes, how photoinduced lattice expansion influences perovskite optoelectronic and charge carrier properties,[10] and how peroxide chemistry influences perovskite stability and charge lifetimes.[11] We also studied metal oxides,[12-16] 2D[17-21] and plasmonic[22] materials, few atom catalysts,[23-25] and QD.[26]

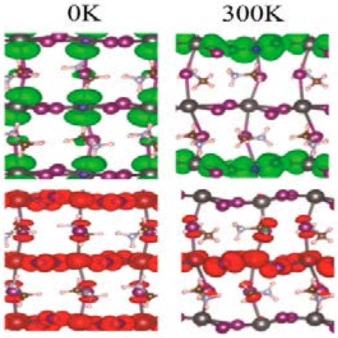

Fig. 1 Fully delocalized at 0K, electron and hole become partially localized at 300K. Their overlap decreases and lifetime increases, in contrast to usual semiconductors.

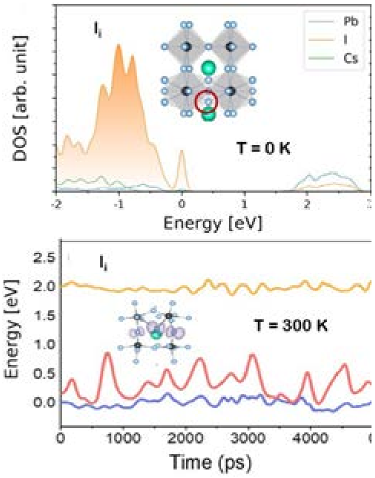

Fig. 2 Perovskites are softer than traditional semiconductors and adapt to defects, decoupling them from free carriers. Iodine interstitial energy that appears shallow at 0K fluctuates significantly at 300K. Other soft semiconductors with well-defined periodicity can be defect tolerant.

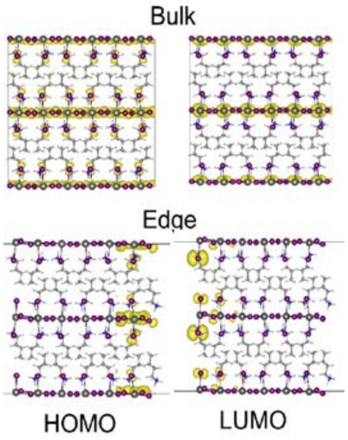

Fig. 3 Edges in 2D and grain boundaries in 3D perovskites separate charges and extend their lifetimes. They can also act as trap states, and therefore, should be passivated or annealed. Defects that are benign in bulk can be detrimental at edges

1. *J. Phys. Chem. Lett.* **2020,** 11, 7066
2. *J. Phys. Chem. Lett.* **2019,** 10, 3788
3. *Sci. Adv.* **2020**, 6, eaaw7453
4. *J. Chem. Phys.* **2020**, 152, 064707
5. *Angew. Chemie* **2020**, 59, 6435
6. *ACS Energ. Lett.* **2020**, 5, 3813
7. *J. Phys. Chem. Lett.* **2019,** 10, 6219
8. *J.Am. Chem. Soc.* **2019**, 141, 15557
9. *J. Phys. Chem. Lett.* **2019,** 10, 1617
10. *J.Phys.Chem. Lett.* **2019,** 10, 5000
11. *J.Am. Chem. Soc.* **2019**, 141, 5798
12. *J. Phys. Chem. Lett.* **2021,** 12, 2191
13. *J.Am. Chem. Soc.* **2020,** 142, 4136
14. *J. Chem. Phys.* **2020,** 152, 024706
15. *J.Am.Chem.Soc.* **2019**, 141, 20222
16. *J.Phys.Chem. Lett.* **2019,** 10, 2676
17. *J. Chem. Phys.* **2020,** 153, 154701
18. *J.Phys.Chem. Lett.* **2019,** 10, 7732
19. *PCCP.* **2019**, 21, 23198
20. *J.Phys.Chem. Lett.* **2019,** 10, 6151
21. *J.Phys.Chem. Lett.* **2019,** 10, 1083
22. *Nano Lett.* **2019**, 5, 3187
23. *J. Mat. Chem. A* **2020,** 8, 12485
24. *J.Phys.Chem. Lett.* **2019,** 10, 7009
25. *ACS AMI* **2019**, 11, 9629
26. *PNAS* **2020**, 117, 11940

Excited State Surface Chemistry of Colloidal Quantum Dots for Photocatalysis

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Ultrafast vibrational spectroscopy in the mid-infrared spectral range was used to probe the dynamics of organic ligands on the surfaces of PbS quantum dots in their excited electronic states. The ligand shell around colloidal quantum dots mediates the electron and energy transfer processes that underpin photocatalytic processes at their surfaces. The measurements revealed that the surface chemistry of carboxylate anchoring groups of oleate ligands passivating PbS quantum dots undergo significant changes when the quantum dots are excited to their excitonic states. The changes of surface chemistry of oleate ligands were directly probed using time-resolved mid-infrared spectroscopy that records the evolution of the vibrational frequencies of their carboxylate groups following excitation of the electronic states. The transient vibrational spectra represented in **Figure 1** (left) highlight the changes in vibrational features for a range of PbS quantum dot sizes. The transient spectra reveal a ground state bleach (negative-going peak with pink shaded region) of carboxylate groups bonded to PbS surfaces with a bidentate chelating geometry. There is a corresponding increase of absorption where carboxylates bonding via bridging and unidentate geometries absorb (positive-going peaks with blue and grey shading). These features were well-correlated with the mid-infrared absorption (FTIR) spectrum of the PbS quantum dot films.

The right-side of **Figure 1** illustrates the changes in carboxylate bonding geometry that occur in the excited states of the PbS quantum dots. The changes in vibrational spectra revealed a reduction of the Pb-O coordination of carboxylate anchoring groups to lead atoms at the quantum dot surfaces. The dynamic surface chemistry of the ligands may have increased their surface mobility in the excited state, enhancing the ability of molecular species to penetrate the ligand shell and undergo energy and charge transfer processes that depend sensitively on distance. Future work will use this capability to explore how dynamic surface chemistry can be used to enable new reactivity for hard to achieve chemical transformations and photocatalytic processes on quantum dot surfaces.

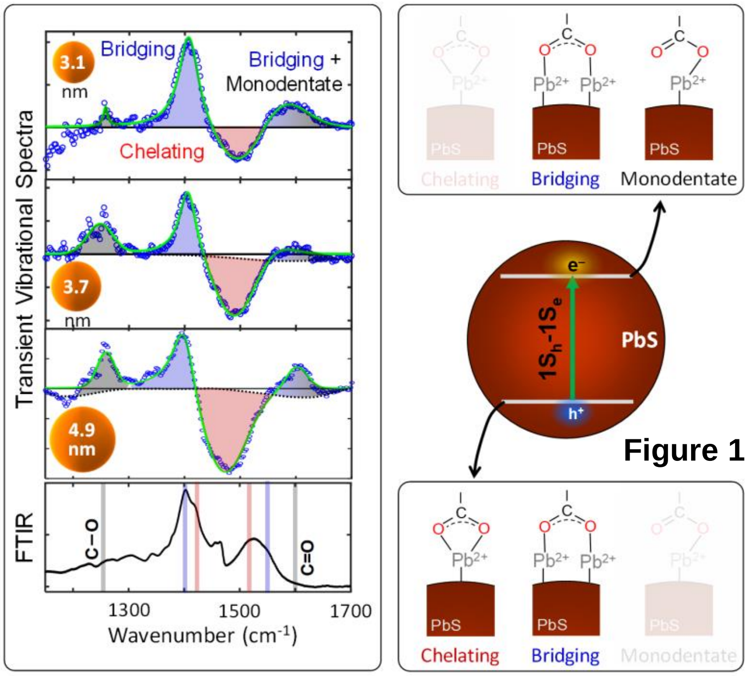

Figure 1

Elucidating How Semiconductor Nanocrystals Drive Enzymatic N_2 Reduction

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Project Scope: The activation and reduction of dinitrogen (N_2) to ammonia (NH_3) is one of the most energy demanding and difficult chemical reactions. *Nitrogenase* is an enzyme complex that catalyzes this reaction by coupling ATP hydrolysis by the Fe protein to drive the sequential delivery of electrons to the MoFe protein for N_2 reduction. We have demonstrated that the biochemical reaction cycle can be replaced by a photochemical reaction cycle in complexes of nitrogenase MoFe protein with cadmium sulfide (CdS) nanocrystals (NC), to enable light-controlled N_2 reduction. This is remarkable because reduction of N_2 to $2NH_3$ by nitrogenase is an immensely complicated catalytic process that involves transfer of 8 electrons and 8 protons. The goal of this project is to elucidate how the complex and specific interactions that lead to biological N_2 reduction are replaced in this artificial hybrid system and to outline the kinetic and energetic requirements for nanocrystal-driven photochemical N_2 reduction by MoFe protein.

Recent Results: This short talk will focus on recent work using transient absorption (TA) spectroscopy to probe the kinetics and mechanism of photoexcited electron transfer (ET) from CdS NCs to MoFe protein. This is a critical step that provides the electrons for enzyme catalysis. The TA measurements, along with kinetic modeling, show that ET is competitive with electron relaxation in the NCs. The work suggests that, for the NCs that are bound to MoFe protein, the majority of photoexcited electrons are converted to a photochemical product (NH_3 or H_2). The information from the TA data together with analysis of enzyme structure and potential NC binding sites suggests that increasing specificity of binding will increase the control of the ET process towards the desired photochemical pathways.

In addition, we have made progress towards understanding the N_2 reduction reaction in photochemically activated MoFe protein. Electron paramagnetic resonance (EPR) spectroscopy with cryo-trapping was used to identify time-dependent changes in the MoFe protein redox states during illumination and provided access to reaction intermediates that otherwise can be difficult to resolve. Analyses of product formation as a function of excitation rate showed that the ratio of NH_3 to the side-product H_2 can be tuned by excitation rate. This work revealed that the remarkable ability of CdS nanocrystals to drive N_2 reduction stems at least in part from the high photoexcitation rates, and electron fluxes, achievable with these materials. Additional progress has been made towards measuring the binding thermodynamics between MoFe protein and CdS NCs.

Future Plans: Our future plans involve targeting the binding of NC to MoFe protein to guide electron pathways, measurements of the dependence of ET kinetics on a variety of NC structural and energetic parameters, and further work on elucidating the chemical pathways in MoFe protein.

Recent Publications: 1. *ACS Catalysis*, **2020**, *10*, 11147. 2. *J. Am. Chem. Soc*, **2020**, *142* , 14324. 3. *Ann. Rev. Phys. Chem*. **2020**, *71*, 335.

Metal-Tipped and Electrochemically Wired Semiconductor Nanocrystals: Modular Constructs for Directed Charge Transfer

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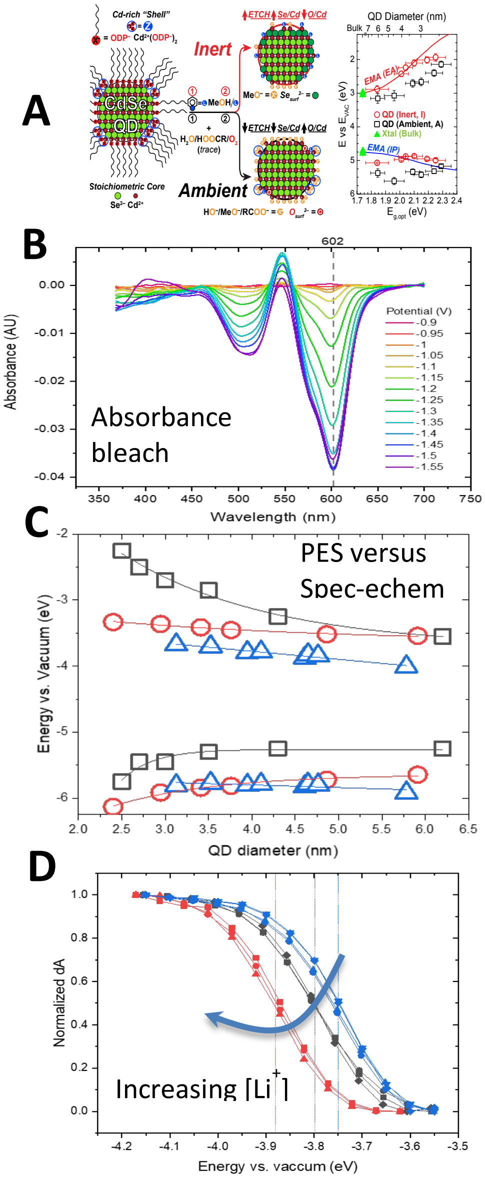
Photocatalytic and photoelectrochemical processes involving surface-tethered semiconductor nanocrystals (quantum dots, core-shell nanorods, tetrapods) are critically dependent upon the valence and conduction band energies (VBM/CBM), relative to solution electron acceptors/donors. It has become increasingly clear that the energetics of the nanocrystal are extremely sensitive to surface composition, the nature and packing density of capping ligands, the type of linker used to tether the nanocrystal monolayer or multilayer, and even the type and concentration of counterions surrounding the tethered nanoparticle at electrode/solution interfaces. (A) Our photoemission spectroscopies of monolayer-tethered CdSe QDs on Au showed that even sub-monolayers of ambient-derived contaminants can drive the VBM/CBM, as a function of QD diameter, away from energies predicted by the effective mass approximation (EMA), but that the EMA is followed conclusively if absolute surface purity and an absence of ligands is obtained (*in vacuuo*). (B,C) We have subsequently returned to spectroelectrochemical studies on ATR/waveguide substrates to examine CBM energies from absorbance bleach experiments of sub-monolayer, ligand capped CdSe QDs and seen that the EMA is approximately followed but that an additional "offset" is seen for all QD diameters owing to the apparent stabilization of the QD upon electron injection, by supporting electrolyte cations (Li^+ - D), and to a lesser extent solvent, molecular tether and the underlying electrical contact. Using these new measurement science protocols, we have even more recently shown that these spectroelectrochemical experiments can now distinguish the onset for absorbance bleach upon electron injection into CdSe@CdS NRs, for both Type I heterojunctions (CdSe seed and CdS rod are bleached at unique potentials allowing for estimation of CBM offsets between the CdSe seed and CdS rods), and quasi-Type II heterojunctions where the CBM of both the seed and rod are nearly equal. These measurement science approaches now underpin the design of new tethered photocatalysts, and thin film semiconductors for photovoltaic applications.



New Systems for Multiple Exciton Creation and Collection

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Laramie, Wyoming, 82071

We are pursuing two strategies for generating (MEG) and collecting more than one electron hole pair from solar photons in a sensitized oxide semiconductor photoelectrochemical system. The first approach uses quantum dots of the low band gap (0.19eV) III-V semiconductor indium antimonide. InSb is a promising MEG system due to its low bandgap, and much lower electron effective mass than the hole effective mass. We have successfully grown QDs of this material using our atomic layer deposition system (ALD) and are also exploring several recently published synthesis techniques for free standing InSb QDs. (Figure 1)

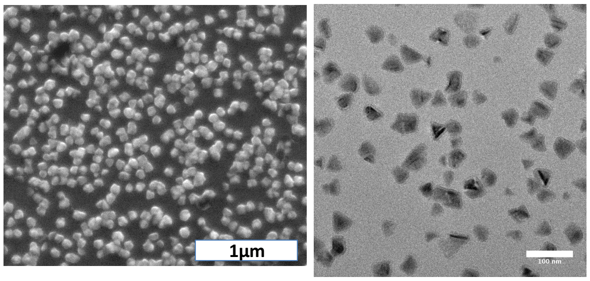

Figure 1 SEM image of crystal InSb QDs on SnO_2 with 1000 cycles of trimethyl indium and tris-dimethylamido antimony followed by 120 cycles of TiO_2 deposition (left). InSb nanocrystals deposited directly on a TEM grid. (right)

We are also investigating collecting multiple excitons from nanocrystals of $CsPbBr_3$. We will exploit a recent exciting result where *enhanced multiple exciton generation was measured via below bandgap nonlinear multiphoton absorption (MPA) in $CsPbBr_3$ QDs!* (Figure 2)

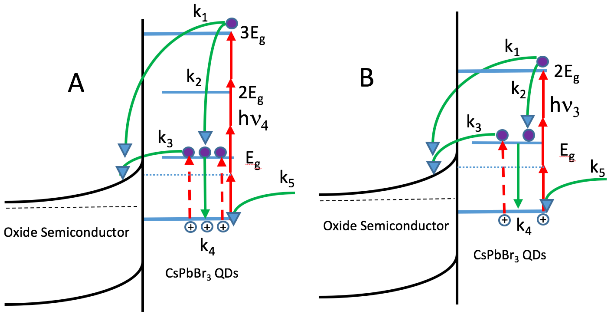

Figure 2 Schematic showing the multiphoton processes for the 4 photon/3 exciton process (A) and the 3 photon/2 exciton process (B). $h\nu_4$ and $h\nu_3$ represent photon energies of ¼ and 1/3 the energy of the third exciton level ($3E_g$) and second exciton level ($2E_g$) of the $CsPbBr_3$ nanocrystals r. The hot injection rate is k_1, the multiple exciton generation rate is k_2 the relaxed electron injection rate is k_3, the electron hole recombination rate is k_4 and the regeneration rate is k_5.

Due to issues of the solubility of nanocrystals of $CsPbBr_3$ in the electrolytes we use for single crystal sensitization, we have employed a vacuum evaporation technique followed by evaporation of protection layers to stabilize the nanocrystals and have successfully collected stable sensitized photocurrents on TiO_2 single crystals from the nanocrystals. We are currently pursuing collaborations for the non-linear pulsed laser MEG up-conversion photocurrent experiments.

Photoelectrochemical Nitrogen Reduction to Ammonia on Cupric and Cuprous Oxide

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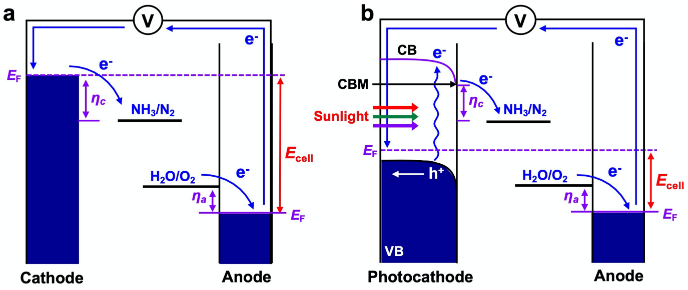
The overall objective of our project is to bring about marked advancements in the construction, understanding, and variety of high-quality, polycrystalline, oxide-based semiconductor electrodes available for use in solar fuel production. To date, we have mainly focused on the development of photoelectrodes for solar water splitting. In this presentation, we present our recent effort on solar N_2 reduction to NH_3. The photoelectrochemical N_2 reduction reaction enables the production of NH_3 under ambient conditions using water as the hydrogen source. By utilizing solar energy, photoelectrochemical N_2 reduction can significantly reduce the energy input required for electrochemical N_2 reduction (Scheme 1). To perform photoelectrochemical N_2 reduction, a p-type semiconductor with a conduction band minimum located at a more negative potential than the reduction potential of N_2 is needed as a photocathode. Considering that the reduction potential of N_2 is slightly more positive than the reduction potential of water, ideally, any photocathode used in a water splitting photoelectrochemical cell should meet this thermodynamic requirement. However, N_2 reduction is kinetically much more difficult than water reduction. This means that the photogenerated electrons in the photocathodes may be predominantly used for water reduction, resulting in a negligible Faradaic efficiency for NH_3 production. Fortunately, most photocathodes used in photoelectrochemical water splitting cells are reported to be poorly catalytic for water reduction on their own and they are almost always paired with hydrogen evolution catalysts to produce an appreciable amount of H_2. Thus, if any of these photocathodes possess surfaces that are catalytic for N_2 reduction, a relatively high FE for NH_3 production may be achieved by a photoelectrochemical N_2 reduction cell while reducing the energy input necessary for N_2 reduction.

In this study, photoelectrochemical N_2 production was investigated using CuO and Cu_2O photocathodes that are known to be poorly catalytic for water reduction. When tested under simulated solar illumination with isotopically labeled $^{15}N_2$ in 0.1 M KOH solution, the CuO and Cu_2O photocathodes produced $^{15}NH_3$ with a Faradaic efficiency of 17% and 20% at 0.6 V and 0.4 V vs. RHE, respectively. These potentials are significantly more positive than the thermodynamic reduction potential of N_2, which demonstrates how the use of photoexcited electrons in the CuO and Cu_2O photocathodes can reduce the energy input required for NH_3 production. The use of photoexcited electrons in these photocathodes for N_2 reduction, water reduction, and photocorrosion will be discussed.



Scheme 1. Schematic comparison of (a) electrochemical and (b) photoelectrochemical N_2 reduction, illustrating why the use of a photocathode can decrease the overall cell voltage needed to operate the N_2 reduction cell (E_{cell}: voltage required to operate the cell, E_F: Fermi level, CB: conduction band, VB: valence band, CBM: conduction band minimum, η_c: cathodic overpotential, η_a: anodic overpotential).

Managing pH Gradients in Photoelectrochemical Solar Fuel Production

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In studying water splitting with dye-sensitized solar cells, we discovered a system-level problem that arises when the cells are operated near neutral pH. In buffer-based water splitting cells, losses from solution resistance and electrochemically generated pH gradients become substantial over a timescale of hours. This problem can be addressed by using bipolar membrane-based cells in which the cathode and anode operate at low and high pH, respectively. Under these conditions bipolar membranes enable efficient light-driven water splitting. They are also interesting for managing ion transport and pH gradients in other electrochemical energy conversion processes, including CO_2 (photo)electrolysis, fuel cells, and redox flow batteries.

CO_2 electrolyzers and photoelectrolysis cells based on bipolar membranes can operate at high current density and with minimal product crossover. However, their selectivity for CO_2 reduction is poor, especially with gas-fed cathodes. The poor selectivity results from the high acidity of the strong acid side of the bipolar membrane, which faces the cathode of the cell. We have addressed this problem by growing weakly acidic polyelectrolyte layers on the acidic face of bipolar membranes using layer-by-layer (LbL) assembly (Fig. 1). The polyelectrolyte film adds negligibly to the series resistance of the cell, but it alters the local chemical environment of the electrocatalyst where CO_2 reduction takes place. The higher local pH lowers the rate of hydrogen evolution but does not significantly affect the competing process of CO_2 reduction. By labeling selected polyelectrolyte layers with a pH-sensitive ratiometric dye we can measure the pH of individual layers as a function of current density. This technique enables operando pH measurements in LbL films at a resolution of 2-3 nm and reveals a sharp pH gradient across a ~50 nm thick polyelectrolyte layer that is the source of improved selectivity for CO_2 reduction.

pH gradients at electrocatalytic interfaces and in membranes contribute to free energy losses in photoelectrochemical cells, especially for those in which the anode and cathode do not operate at extremes of pH. The LbL assembly of weak acid/weak base polyelectrolytes offers a simple tool for tuning and measuring the pH of the catalyst microenvironment. It is also a potentially useful method for creating bipolar membrane interfaces that do not require a full 830 mV for the autodissociation of water, and for creating films with sharp pK_a gradients that may be interesting media for coupled proton and electron transfer and for light-driven cascade reactions.

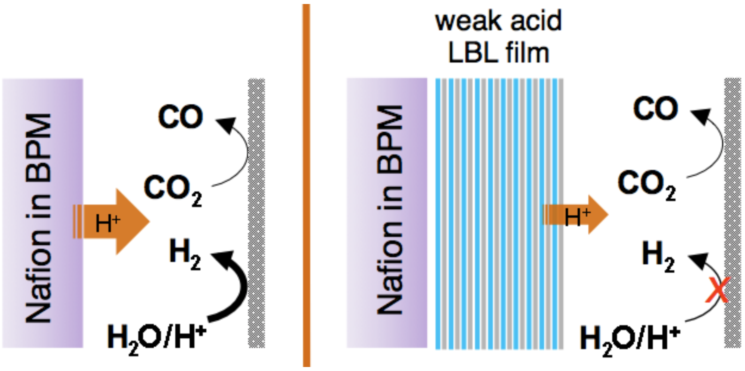

Fig. 1. Layer-by-layer assembly of a weakly acidic cation exchange layer modulates the local pH at the catalyst surface in a bipolar membrane based CO_2 electrolysis cell. Higher local pH improves the conversion efficiency of CO_2 to CO by suppressing the competing hydrogen evolution reaction. (Z. Yan et al., *Nat. Chem.* **13**, 33–40 (2021)).

Nanoscale Mapping of Photoelectrochemical Reactivity by SECM

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The focus of this project is on probing photoelectrochemical reactions at single nanoparticles and nanostructured interfaces by nanoelectrochemical techniques, including scanning electrochemical microscopy (SECM). We developed an experimental setup for photo-SECM measurements on the nanoscale in which a glass-sealed tip simultaneously serves as a nanoelectrode and a light guide and combined it with the new methodology for electrochemical imaging on a TEM finder grid.

Photo-SECM imaging on TEM grids was carried out in the substrate generation/tip collection (SG/TC) mode, where oxygen was produced by water oxidation at the surface of the illuminated TiO_2 nanorod (synthesized in Peng Chen's lab at Cornell University) and reduced at the Pt tip (Fig. 1A). An amorphous carbon film of the TEM finder grid served as a conductive sample support in photo-SECM experiments. A photo-SECM image of two nanorods is shown in Fig. 1B. This approach enabled multi-technique (i.e., SECM/TEM and SECM/AFM) imaging of the same nanorod, suggesting the possibility of correlating photoactivity maps with atomic scale structural and bonding information obtained by TEM.

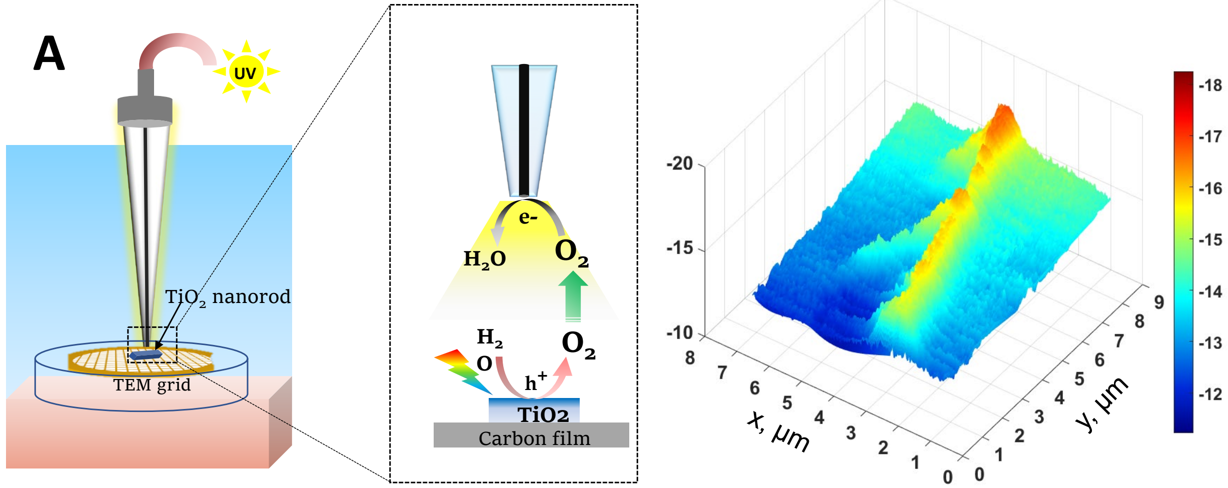

Fig. 1. Photo-SECM imaging on the TEM grid with the through-tip illumination. (A) Schematic representation of the experimental setup used for the SG/TC mode photo-SECM imaging of the oxygen flux generated by a TiO_2 nanorod on the TEM grid. (B) Photo-SECM map of oxygen flux generated under through-tip UV illumination (200 W HgXe lamp) at two adjacent TiO_2 nanorods. The 0.1 M borate buffer solution (pH 8.5) in 0.5 M Na_2SO_4 contained no added redox species except dissolved O_2. The ~100 nm tip was scanned in the x-y plane ~200 nm above the nanorods. The tip and substrate potentials were −1.3 V, and 0.6 V vs. Hg/Hg_2SO_4, respectively.

In the future, we will carry out correlated SECM/TEM imaging of active sites on photocatalyst surfaces. We will also focus on quantitative analysis of photo-SECM data and extraction of localized kinetic information from reactivity maps and current-distance curves.

Toward a Realistic Description of Oxidation at the Semiconductor/Liquid Interfaces

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Our recent experimental studies on oxidation of III-V semiconductors (InP [1] and GaN) by O_2 have been expanded to more complex chemistry, involving water [2, 3]. Such studies aim towards a better understanding and control of physiochemical processes at the photoelectrode/electrolyte interface in photoelectrochemical cells (PEC).

In the case of the H_2O/InP (001) system, we integrated both ambient pressure X-ray photoelectron spectroscopy (APXPS) and high-level first-principles calculations to elucidate the dynamics of interfacial chemistry [2]. Our photoelectron spectroscopy results indicate that in addition to molecular H_2O, OH and H are the only two species found on InP (001) at room temperature (RT). Under elevated temperatures, although the formation of In–O–P is thermodynamically more favorable over In–O–In, the latter can be preferentially generated in a kinetically driven and nonequilibrated environment such as ultrahigh vacuum; however, when InP is exposed to H_2O at both elevated pressures and temperatures, its surface chemistry becomes thermodynamically driven and only In–O–P (or PO_x) oxygen bridges are formed (Fig. 1). Our simulations suggest that In–O–In constitutes a charge carrier (hole) trap that causes photocorrosion in PEC devices. This finding shed light on the fabrication of InP-based photoelectrodes with simultaneously enhanced stability and efficiency [2].

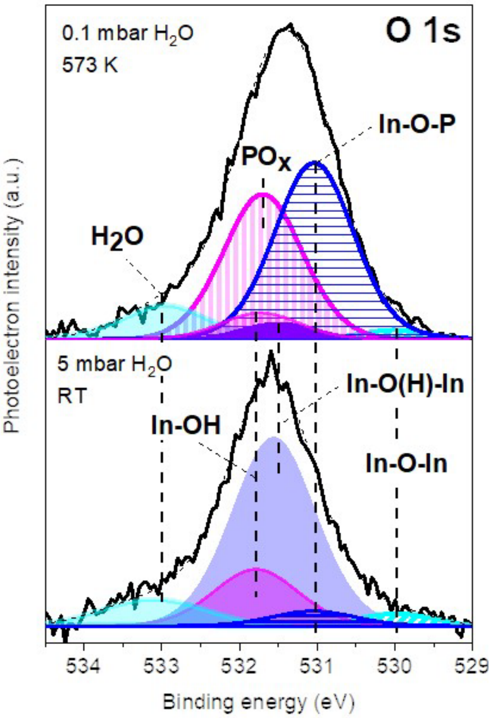

Fig. 1 Fitted O 1s spectra recorded under 5 mbar H_2O at RT and at 573 K in 0.1 mbar H_2O.

[1] X. Zhang, T. Ogitsu, B.C. Wood, T.A. Pham, S. Ptasinska, J. Phys. Chem. C 2019, 123, 30893
[2] X. Zhang, T.A. Pham, T. Ogitsu, B.C. Wood, S. Ptasińska, J. Phys. Chem. C. 2020, 124, 3196-203.
[3] X. Zhang, S. Ptasińska, Appl. Surf. Sci. 2020, 516, 146127.

Investigating Material Properties and Electronic Dynamics of Photovoltaic and Photocatalytic Thin Films *in situ* Using Nuclear Resonance Spectroscopies

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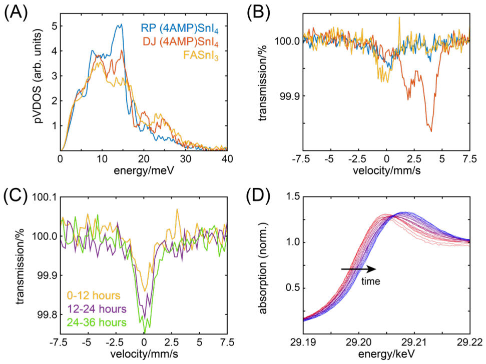
The aim of our research program is to explore novel applications of nuclear resonance techniques for investigating the chemical and physical properties and dynamics of solid-state solar energy conversion materials. We employ a combination of lab-based radioisotope Mössbauer spectroscopy (MS) and synchrotron-based nuclear forward scattering (NFS) and nuclear resonance inelastic X-ray scattering (NRIXS) to characterize photocatalytic and photovoltaic systems.

Optical and X-ray transient absorption characterizations of thin films are complicated by laser-induced heating artifacts. To address this, we are developing a novel solid-state ultrafast technique, time-resolved synchrotron radiation Mössbauer spectroscopy (TRSRM), which will provide an element-specific probe of oxidation and spin state dynamics with exceptional spectral resolution and minimal temperature dependence. As a first step, we aim to measure the ^{151}Eu NFS of a Eu-doped silicate under cw illumination to obtain the quadrupole-split spectrum of the long-lived $^5D_0$ ligand field state. This will be the first-ever MS measurement of a transient electronic excited state, demonstrating proof-of-principle for future time-resolved work. Preliminary steady-state optical and NFS measurements confirm feasibility, and we will perform the measurements in early June.



Tin halide perovskites are excellent candidates for pulsed-laser experiments, where we aim to observe charge carrier dynamics by tracking changes in isomer shift(s). First, we have performed MS and temperature-dependent NRIXS measurements of bulk and oriented 2D perovskites and are currently conducting molecular dynamics simulations to obtain a microscopic description of how low frequency nuclear motions promote charge separation and long-range carrier transport. Intriguingly, the Dion-Jacobson phase exhibits an anomalously high out-of-plane recoil-free fraction, demonstrating that these techniques provide information on motions of the octahedral and organic layers in addition to localized motions of the Sn^{2+} centers. We have also reported real-time measurements of oxidation kinetics in Pb-free perovskites using ^{119}Sn MS and Sn K-edge X-ray absorption spectroscopies (Fig. C-D). These techniques permit isolation of oxidation from hydration and mechanical degradation to guide the development of Pb-free formulations.

Ultimately, we hope to perform ps-resolved MS of hematite, a promising photoanode material for photoelectrocatalytic (PEC) oxygen evolution, using a frequency-domain approach. The temporal resolution of ^{57}Fe NFS is limited by the ^{57}Fe nuclear excited state lifetime (~100 ns), so first we aim to perform NFS on hematite under PEC operating conditions, where transient states persist for µs to ms. We have developed a custom electrochemical cell for *operando* MS and NFS, and we will present steady-state MS obtained at various potentials with and without illumination.

Using Inverted Surface Photovoltage to Measure Space Charge Regions in Nanostructured Solar Fuel Photocatalysts

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Photogenerated charge carrier separation, transport, and recombination are central to the function of devices for the conversion of sunlight into electricity or fuel, but these processes are not yet well understood for micro-heterogeneous photocatalysts (PCs) for the overall water splitting (OWS) reaction. Such photocatalysts differ from more established photovoltaic materials in that they have greater specific surface areas, and consequentially their charge separation properties are more dependent on surface and interfacial states. To gain insight into the charge separating behavior of PCs, this project employs a combination of surface photovoltage spectroscopy (SPS), electrochemistry and photocatalytic measurements. Specific goals are to 1) determine the charge transfer selectivity for various absorber/cocatalyst/substrate configurations, 2) to observe the effect of surface/interface states on charge transfer and trapping, and 3) to assess the role of the space charge region (SCR) and Fermi level pinning on charge separation. Earlier results had suggested that surface photovoltage spectroscopy (SPS) can directly observe the SCR in CdSe quantum dot films. [1] We have now successfully applied the technique to p/n-GaN nanowire films (provided by Zetian Mi and coworkers at U Michigan) [2] and to nanostructured $SrTiO_3$ photocatalysts for OWS. [3] $SrTiO_3$ films of varying thickness were prepared by drop coating the particles from water suspensions onto gold substrates, followed by thermal annealing at 200-500ºC. SPS measurements were performed under vacuum. Films annealed at 400ºC or lower show *normal* photovoltage signals associated with majority carrier diffusion to the gold substrate. Films annealed thermally to 500ºC show *inverted* photovoltages corresponding to charge carrier movement in the SCR at the particle-gold interface. From the inverted photovoltage signal, potential barriers are estimated between 94 and 189 mV and SCR widths between 2.4 and 2.8 µm. These barriers are about ten times smaller than the theory for an ideal $SrTiO_3$/Au Schottky junction, and the observed SCR widths are up to ten times larger. The difference is attributed to trapping of majority carriers in surface states arising from chemisorbed oxygen (Fermi level pinning). Planned work will confirm the SCR with UV and X-ray photoelectron spectroscopy (XPS). The Fermi level pinning hypothesis will be tested with SPS measurements on particle films in the presence of controlled H_2, H_2O, O_2 environments.

References

[1] Zhao, J., B.A. Nail, M.A. Holmes, and F.E. Osterloh, Use of Surface Photovoltage Spectroscopy to Measure Built-in Voltage, Space Charge Layer Width, and Effective Band Gap in CdSe Quantum Dot Films. J. Phys. Chem. Lett., 2016: p. 3335-3340. https://doi.org/10.1021/acs.jpclett.6b01569

[2] Doughty, R.M., F.A. Chowdhury, Z. Mi, and F.E. Osterloh, Surface photovoltage spectroscopy observes junctions and carrier separation in gallium nitride nanowire arrays for overall water-splitting. J. Chem. Phys., 2020. 153(14): p. 144707. https://doi.org/10.1063/5.0021273

[3] Doughty, R.M., B. Hodges, J. Dominguez, R. Han, Z. Zhao, S. Assavachin, and F.E. Osterloh, Fermi Level Pinning Controls Band Bending and Photochemical Charge Separation in Particles of n-SrTiO3, n-SrTiO3:Al, and n-GaAs:Te. J. Phys. Chem. C, 2020. 124(34): p. 18426-18435. https://doi.org/10.1021/acs.jpcc.0c04989

Quantitative Analysis of Voltammetric Responses of Adsorbed Redox Species on Semiconductor Electrodes

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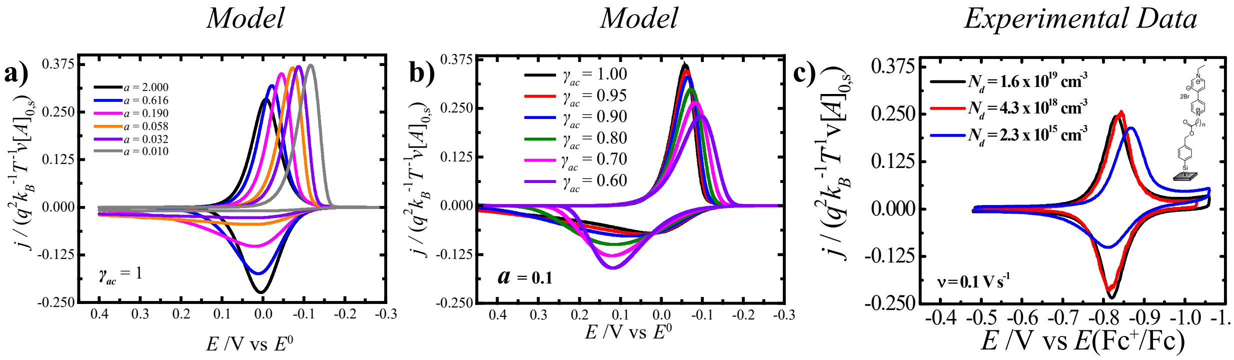

Figure 1. a) Predicted voltammetric responses for an n-type semiconductor electrode coated with a redox monolayer at several different values of the experimental timescale, a, and the fraction of the applied potential dropping in the space charge layer of the semiconductor, γ_{ac}, = 1. b) a) Predicted voltammetric responses for an n-type semiconductor electrode coated with a redox monolayer at several different values of γ_{ac} and $a = 0.1$. c) Experimental voltammetric responses recorded with an n-Si electrode at several different dopant densities and at a constant scan rate.

The transfer of charge between an adsorbed redox species and a semiconductor electrode is explicitly the motif for two of the most researched directions in semiconductor photoelectrochemistry: dye-sensitized solar cells and water-splitting photoelectrochemical systems based on molecular electrocatalysts. In these applications, the operation of the full system hinges critically on specific rates of forward and back charge transfer between the semiconductor and redox species. Common electrochemical measurements have played a comparatively minor part in understanding the details of such charge-transfer reactions. This statement is **bewildering**, as current-potential and current-time data are trivial to obtain and directly report on charge-transfer reactions. More specifically, although quantitative kinetic analyses of redox reactions at metal electrodes have been done for the past half century by the method of Laviron, the ability to glean quantitative rate information from voltammetric responses from a *semiconductor* electrode has not been similarly developed. This presentation details the first description of a compact analytical expression specifically for describing the voltammetry of a **semiconductor** electrode in depletion with an adsorbed redox monolayer as a function of the timescale of the experiment (a). An easily implementable algorithm for predicting voltammetric behaviors for non-ideal semiconductor electrodes, i.e. where the fraction of the applied potential that is dropped specifically in the space-charge layer (γ_{ac}) is ≠ 1, will also be introduced. The model will be discussed in terms of describing experimental results for chemisorbed viologen monolayers on passivated n-Si(111) electrodes, highlighting the ability to estimate the heterogeneous charge transfer rate constant and majority carrier band edge directly by fitting voltammograms by this method. Long term, the presented method will be used to probe heterogeneous charge-transfer reactions at semiconductor electrodes, with the intent of assessing the validity of classical microscopic theories of charge transfer.

Direct Observation of Photoexcited Charge Carrier Dynamics and Electrostatic Fields at Photocatalytic Semiconductor/liquid Interfaces

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We use transient reflectance spectroscopy (TRS) to explore photoexcited charge carrier dynamics and local electrostatic fields at photocatalytic interfaces. Figure 1a shows a schematic diagram of the *pn*-junction formed when a thin protective layer of titanium dioxide (*n*-TiO_2) is deposited on *p*-type gallium phosphide (GaP). Here, the band bending and corresponding built-in electric field ($\mathcal{E}$) is illustrated in the diagram. The photoinduced changes in this built-in electric field can be monitored by the Franz–Keldysh (FKO) oscillation strength plotted in Figure 1b, which shows that the FKO signal amplitude increases under more negative applied potentials from 0 V to -1.5 V. This increase in FKO signal strength represents an increase in the depletion region, built-in field, and band bending that occurs at the semiconductor surface, analogous to a *pn*-junction under reverse-bias. This approach enables us to monitor the free carrier and separated carrier kinetics independently, as plotted in Figure 1c.

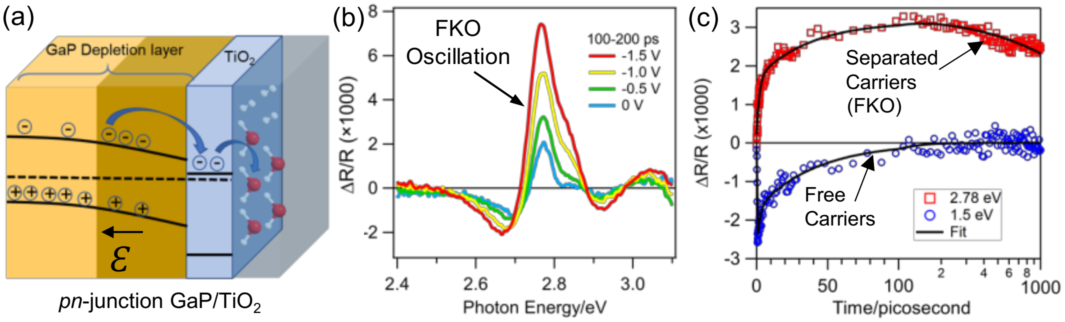

Figure 1. (a) Schematic diagram illustrating the GaP/TiO_2 photoelectrode. (b) Potential-dependent FKO oscillation strength and (b) corresponding free carrier and separated carrier kinetics.

In addition to the electrostatic fields in the solid state system, we also monitored the electrostatic fields in the liquid state at the photocatalytic surface using *in situ* Raman spectroscopy to measure the vibrational Stark shift of various surface-bound species including napthyl nitrile and copper(II) phthalocyanine (CuPc). Figure 2 shows the Raman shift of the C≡N bond in a napthyl nitrile-functionalized silicon surface (in collaboration with Dr. Neale at NREL). A Stark shift of 4.7 cm^{-1} was observed under an applied potential of -1V vs Ag/AgCl, corresponding to an electric field strength of -8MV/cm, according to DFT calculations. Similar Stark fields were observed using CuPc-coupled monolayer graphene electrodes.

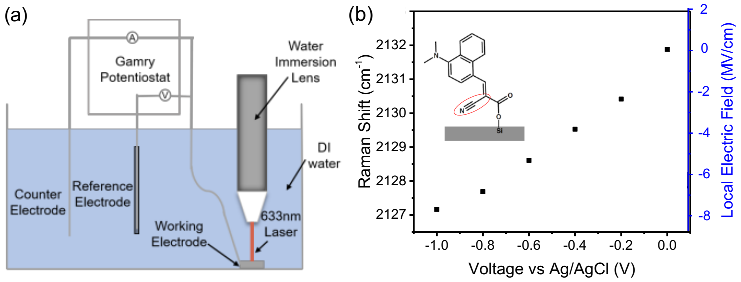

Figure 2. (a) Schematic diagram illustrating our photoelectrochemical measurement setup with *in situ* Raman spectroscopy. (b) Raman shift of the nitrile stretch measured as a function of the applied electrochemical potential.

Nanoscale Properties and Design of Catalyst/Semiconductor Interfaces

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Semiconductor photoelectrodes coupled with electrocatalysts are key components of photoelectrochemical energy conversion and storage systems. The semiconductor/catalyst interface is important because it is responsible for collecting the photo-excited electron-hole pairs generated in the semiconductor and building photovoltage. In this lightning talk, I will report our progress studying nanoscale catalyst contacts to important photoelectrode materials like Si and InP. In classic work by Adam Heller, the excellent performance of appropriately electrodeposited thin Pt catalyst layers on *p*-InP was attributed to work-function shifts associated with H absorption on the Pt. We show that H-absorption is a minor contribution to establishing highly electron-selective Pt contacts on p-InP. Direct measurements of Pt/p-InP nanoscale photochemical interfaces using conductive- and electrochemical-atomic-force-microscopy techniques, coupled with macroscopic dual-working-electrode and surface-chemical characterization, illustrate the key role of so-called "pinch-off" effects in controlling the charge-carrier selectivity. In the case of *p*-InP, it appears that partial surface oxidation generates InO_xP_y with *n*-type character that drives the formation of electron-selective Pt nanocontacts that improve as the size of the contact decreases. These insights and capabilities are being leveraged to understand and design catalyst nanocontacts for more-complex photochemical systems, for example those used in particulate photocatalysts for overall water splitting to produce hydrogen gas.