Proceedings of the

Forty-Third
DOE Solar Photochemistry
P.I. Meeting

Virtual Meeting
June 8-10, 2022

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

FOREWORD

The 43rd 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 8-10, 2022. 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 have again caused the meeting to use a virtual format in 2022. The meeting agenda has been adjusted a bit this year to maximize online interactions. Most sessions will begin with a set of single-slide lightning talks by PIs in Zoom, followed by a GatherTown session at which the same PIs present corresponding posters. New projects will be introduced in several slightly longer presentations.

The meeting this year also features a few invited presentations. Morris Bullock will tell us about the BES Roundtable on Foundational Science for Carbon-Neutral Hydrogen Technologies, which he co-chaired in August 2021. The roundtable goal was to identify research opportunities to enable development of a carbon-neutral, hydrogen-based energy and chemical infrastructure. Two other invited presentations will introduce the Fuels from Sunlight Energy Innovation Hub program awards that received initial funding in 2020. Harry Atwater leads the Liquid Sunlight Alliance (LiSA) that has the mission "To establish the science principles by which durable coupled microenvironments can be co-designed to efficiently and selectively generate liquid fuels from sunlight, water, carbon dioxide, and nitrogen." Jerry Meyer leads the Center for Hybrid Approaches in Solar Energy to Liquid Fuels (CHASE) that seeks "To develop new ways to capture and store the energy of the sun in the high-energy chemical bonds of carbon-based solar fuels."

We would like to express our 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 Linda Severs and her colleagues at the Oak Ridge Institute for Science and Education for their assistance with meeting logistics. Finally, we are grateful to all of the participants in this meeting who have contributed so much to the continued success of the Solar Photochemistry Program.

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

TABLE OF CONTENTS

Abstracts of Oral Presentations

Session I – Opening Session

Session II – PI Flash Talks

Photochemistry with Quantum-Confined and Nanoscale Semiconductors

Charge Transfer Processes in Molecular Chromophores

Mechanisms of Molecular Electrocatalysis

Session III – Presentation about the Hydrogen Roundtable

Session IV – PI Flash Talks

Optical-Vibrational Coupling in Molecular Chromophores

Molecular-Based Photocatalytic Systems

Photocatalysis with Quantum-Confined and Nanoscale Semiconductors

Session V – Hub Presentation

Session VI – PI Flash Talks

Charge Transfer Processes at Photoelectrochemical Interfaces

Dye-Sensitized Photoelectrochemical Systems

Light Harvesting and Charge Separation in Molecular Systems

Session VII – New Project Presentations

Session VIII – PI Flash Talks

Spin Dynamics in Molecular Chromophores

Molecular Photo- and Electocatalysts for Proton or CO_2 Reduction

Understanding Driving Forces in Photocatalysis

Session IX – Hub Presentation

Session X – PI Flash Talks

Organic-Based Protonic and Redox Processes in Photocatalytic Systems

Photocatalysis with Metal Clusters

Photochemistry with Quantum Dot Semiconductors

Charge Dynamics in Molecular Light-Harvesting Systems

Session XI – New Project Presentations

Session XII – PI Flash Talks

Ultrafast Charge Carrier Dynamics in Nanoscale Semiconductors

Characterizing Charge Transfer in Thin Films

Molecularly Inspired Water Oxidation Catalysts

Photoelectrochemical Systems

43rd DOE SOLAR PHOTOCHEMISTRY P.I. MEETING

June 8-10, 2022
Virtual Meeting
All times EDT

PROGRAM

<u>Wednesday, June 8</u>

SESSION I
Opening Session – Zoom

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

11:30 am

SESSION II
PI Flash Talks – Zoom

Photochemistry with Quantum-Confined and Nanoscale Semiconductors

1 Influence of Ligand Structure on Excited State Surface Chemistry of Colloidal Quantum Dots for Photocatalysis
John B. Asbury, Penn State University

2 Functional Ligand Exchanges on PbS QDs
Matthew C. Beard, National Renewable Energy Laboratory

3 Light Harvesting in Semiconductor Quantum Dots
Warren F. Beck, Michigan State University

4 'Spin-Exchange Photochemistry' with Magnetically Doped Quantum Dots
Victor I. Klimov, Los Alamos National Laboratory

5 Charge-Transfer Excitons at 1D and 2D Interfaces
Libai Huang, Purdue University

6 Charge Generation and (De)localization in Nanoscale Semiconductor Heterojunctions
Jeffrey L. Blackburn, National Renewable Energy Laboratory

Charge Transfer Processes in Molecular Chromophores

7 Creating a Spectrochemical Series for Transition Metal-based MLCT Chromophores
James K. McCusker, Michigan State University

8 Synthesis and Photophysics of Next-Generation Cu(I) MLCT Photosensitizers
Felix N. Castellano, North Carolina State University

9 Controlling Charge-Transfer Reactions with Cobalt and Copper Coordination Complexes
Thomas W. Hamann, Michigan State University

Mechanisms of Molecular Electrocatalysis

10 Mechanisms for CO_2 Reduction Modelled with Metal Carbonyl Clusters
Louise A. Berben, University of California Davis

11 Kinetic Barriers to Metal-Based Protonation Influence Proton-Coupled Electron Transfer Reaction Pathways in the Formation of Transition Metal Hydride Complexes
Jillian L. Dempsey, University of North Carolina at Chapel Hill

12 Deciphering the Correlation Between Thermodynamic and Kinetic Hydricities of Transition Metal Hydrides
Mehmed Zahid Ertem, Brookhaven National Laboratory

13 Electrocatalytic, Homogeneous Ammonia Oxidation in Water to Nitrate and Nitrite with a Copper Complex
Gary W. Brudvig, **Robert H. Crabtree**, and **Victor S. Batista**, Yale University

14 Improving and Measuring Water Oxidation Catalyst Viability
Douglas B. Grotjahn and **Diane K. Smith**, San Diego State University

12:20 pm **PI Poster Presentations – GatherTown**
Poster numbers 1–14

1:30 p.m. Break

2:00 pm **SESSION III**
Presentation about the Hydrogen Roundtable – Zoom

BES Roundtable on Foundational Science for Carbon-Neutral Hydrogen Technologies
R. Morris Bullock, Pacific Northwest National Laboratory

2:20 pm

SESSION IV
PI Flash Talks – Zoom

Optical-Vibrational Coupling in Molecular Chromophores

15 Advances in Probing and Steering Excited State Trajectories in Solar Energy Conversion Systems
Lin X. Chen, Karen L. Mulfort, and **Richard D. Schaller**, Argonne National Laboratory
George C. Schatz, Northwestern University
Felix N. Castellano, North Carolina State University
Xiaosong Li, University of Washington

16 Two-Dimensional Electronic Vibrational Spectroscopy of Progressively Large Components of the Photosystem II Antenna System
Graham R. Fleming, Lawrence Berkeley National Laboratory

17 Determination of Vibrational Motions Driving Solar Energy Conversion Processes
Renee R. Frontiera, University of Minnesota

18 Probing the Effects of Electronic-Vibrational Resonance on the Rate of Excited-State Energy Transfer in Bacteriochlorin Dyads
Dewey Holten and **Christine Kirmaier**, Washington University
David F. Bocian, University of California Riverside
Jonathan S. Lindsey, North Carolina State University

Molecular-Based Photocatalytic Systems

19 Mechanistic Investigations of Charge Separated States in Metal Organic Frameworks and their Catalytic Relevance
Amanda J. Morris, Virginia Tech

20 Imine Reversal Mediates Charge Separation and CO_2 Photoreduction in Covalent Organic Frameworks
Jier Huang, Marquette University

21 Single-Atom Metal Oxide Sites as Traps for Charge Separation in the Zirconium-Based Metal–Organic Framework NDC–NU-1000
Joseph T. Hupp, Northwestern University

22 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

23 PCET in Grotthuss-Type Proton Wires – Thermodynamics, Dynamics and Biohybrids
Ana L. Moore and **Thomas A. Moore**, Arizona State University

24 Electron Transfer in Ionic Liquids and Electron-Induced Proton Transfer
Dmitry V. Matyushov, Arizona State University

Photocatalysis with Quantum-Confined and Nanoscale Semiconductors

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

26 Mechanism of Photochemical N_2 Reduction
Paul W. King and **David W. Mulder**, National Renewable Energy Laboratory
Gordana Dukovic, University of Colorado Boulder
John W. Peters, Washington State University
Lance C. Seefeldt, Utah State University

27 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

28 Controlling Optoelectronic Properties of 2D Transition Metal Dichalcogenides
Elisa M. Miller, National Renewable Energy Laboratory

29 Theoretical Investigation into Reductant-Activated Covalent Surface Functionalization of MoS_2 and its Applications in Organic Vapor Sensing
Nathan S. Lewis, California Institute of Technology

3:10 pm **PI Poster Presentations – GatherTown**
Poster numbers 15–29

4:30 pm **Small Group Discussions – GatherTown**

5:00 p.m. Close for the day

Thursday, June 9

11:00 am

SESSION V
Hub Presentation – Zoom

Liquid Sunlight Alliance (LiSA)
Harry A. Atwater, California Institute of Technology

11:30 am

SESSION VI
PI Flash Talks – Zoom

Charge Transfer Processes at Photoelectrochemical Interfaces

30 Understanding and Controlling Charge-Carrier Selectivity at Nanoscale Catalyst/Semiconductor Photochemical Interfaces
Shannon W. Boettcher, University of Oregon

31 Semi-Contactless Measurement of Internal Photovoltage of Solid-Liquid Junctions
Frank E. Osterloh, University of California, Davis

32 Complete Description of the Faradaic and Charging Currents for Redox Adsorbates on Semiconductor Electrodes
Stephen Maldonado, University of Michigan

33 Monitoring Charge Carrier Dynamics and Electrostatic Field Dynamics at Semiconductor-Liquid Interfaces using in situ Spectroscopy
Stephen Cronin, University of Southern California

Dye-Sensitized Photoelectrochemical Systems

34 The Impact of the Bridging Ligand on Interfacial Electron Transfer
Gerald J. Meyer, University of North Carolina at Chapel Hill

35 How Solar-Driven Dye Sensitizer-Catalyst Diads Interact to Drive Water Oxidation
Frances A. Houle, Lawrence Berkeley National Laboratory

36 Solvent and Microenvironment Effects on Photochemical Charge Separation and Charge Recombination at Dye-Sensitized Oxide Semiconductor Interfaces
Thomas E. Mallouk, University of Pennsylvania

37 Functionally Active Linker Design for Photoactive Molecules at Semiconductor Interfaces
Elena Galoppini and **Robert A. Bartynski**, Rutgers University

Light Harvesting and Charge Separation in Molecular Systems

38 Controlling Inter- and Intra-molecular Factors for Long-lived and Directional Charge Separation from Cu(I)bis(phenanthroline) Complexes
Karen L. Mulfort, Argonne National Laboratory

39 Electronic Couplings from Dimer Cations
John R. Miller, Brookhaven National Laboratory

40 Dexter Energy Transfer Pathways
David N. Beratan, Duke University

41 Deciphering Directional Excited-State Charge Transfer Mechanisms Using Ultrafast XFEL Science
Xiaosong Li, University of Washington
Lin X. Chen, **David M. Tiede**, **Karen L. Mulfort**, **Ksenija D. Glusac**, Argonne National Laboratory
Amy Cordones-Hahn, SLAC National Accelerator Laboratory

42 Charge Transfer Acceleration by Aggregate Donor States Described by Generalized Marcus Theory
Gerald F. Manbeck, Brookhaven National Laboratory

12:20 pm **PI Poster Presentations – GatherTown**
Poster numbers 30–42

1:30 p.m. Break

SESSION VII
New Project Presentations – Zoom

2:00 p.m. Optical-Gating of Spin-based Quantum States for QIS
Natia L. Frank, University of Nevada, Reno

2:15 p.m. Photoinduced Ground State Electron Spin Polarization Controlled by Magnetic Exchange Coupling
David A. Shultz and **Martin L. Kirk**, North Carolina State University

2:30 p.m. Direct Harvesting of Bound Triplet Pairs
Matthew Y. Sfeir, City University of New York
Louis M. Campos, Columbia University

2:45 p.m. Strategies for Water Oxidation with Abundant Metals: Catalyst Design, Immobilization on Conducting Substrates, and Sensitizer Integration
Cláudio Verani, Wayne State University

3:00 pm

SESSION VIII
PI Flash Talks – Zoom

Spin Dynamics in Molecular Chromophores

43 Singlet Fission and Spin Dynamics in Dipyridyl Pyrrole Bipentacenes Studied by Time-Resolved EPR Spectroscopy
Oleg G. Poluektov, Argonne National Laboratory

44 Organizing Triplet Forming Molecules at Nanoscale Interfaces
Justin C. Johnson, National Renewable Energy Laboratory

45 Quantifying the Ligand-Induced Triplet Energy Transfer Barrier in a Quantum Dot-Based Upconversion System
Ming Lee Tang, University of Utah

46 Spin Selective Charge and Energy Dynamics in Molecules and at Interfaces
Xiaoyang Zhu and **Colin Nuckolls**, Columbia University

47 Effects of Chromophore Packing on Singlet Fission Rate
Josef Michl, University of Colorado Boulder

Molecular Photo- and Electocatalysts for Proton or CO_2 Reduction

48 Dirhodium(II,II) Complexes for Photo- and Electrocatalytic H_2 Production
Claudia Turro, The Ohio State University

49 Photohydrides: Mechanism-Guided Development of Molecular Photoelectrocatalysts
Alexander J. M. Miller, University of North Carolina at Chapel Hill

50 Roles of Triethanolamine in the Photocatalytic Reduction of CO_2 to Formate by Ruthenium Complexes in Organic Solvents
David C. Grills, Brookhaven National Laboratory

51 Photochemistry and Electrochemistry of a Binuclear Fe(III) Fused Porphyrin
Gary F. Moore, Arizona State University

52 Selective and Durable Catalysts for Photochemical CO_2 Reduction to CO and Formate
Javier J. Concepcion, Brookhaven National Laboratory

53 Progress Towards Low Overpotential Reversible Aqueous CO_2/HCO_2^- Electrocatalysis and Activating Formate for > 2 e^- Reduction in a Cascade Catalytic Scheme
Jenny Y. Yang, University of California, Irvine

Understanding Driving Forces in Photocatalysis

54 Particle Size Effects on Electron Transfer and Catalysis at Metal/Semiconductor Interfaces
Tianquan (Tim) Lian, Emory University

55 Atomistic Characterization of Physical and Chemical Characteristics of Metal/Semiconductor Interfaces on Functioning Photocatalysts
Suljo Linic, University of Michigan

56 Photo-SECM of Single Semiconductor Particles
Michael V. Mirkin, Queens College-City University of New York (CUNY)

3:50 pm **PI Poster Presentations – GatherTown**
Poster numbers 43–56

5:00 p.m. Close for the day

Friday, June 10

11:00 am **SESSION IX**
Hub Presentation – Zoom

Center for Hybrid Approaches in Solar Energy to Liquid Fuels (CHASE)
Gerald J. Meyer, University of North Carolina at Chapel Hill

11:30 am

SESSION X
PI Flash Talks – Zoom

Organic-Based Protonic and Redox Processes in Photocatalytic Systems

57 Detailed-Balance Efficiency Limits for Protonic Energy Conversion by Aqueous Photoacids
Shane Ardo, University of California Irvine

58 The Redox Potential of O_2 in the Nonpolar Environment of Molecular Films
Matthew Bird, Brookhaven National Laboratory

59 Controlling Interfacial Charge Separation Energetics and Kinetics: Strong Photoinduced Organic Oxidants for Exploring Marcus Theory at TiO_2 and Driving Water Oxidation
Jared H. Delcamp, University of Mississippi

60 Redox Properties of Strongly Oxidizing Radicals in Organic Solvents Probed by Pulse Radiolysis
Dmitry E. Polyansky, Brookhaven National Laboratory

Photocatalysis with Metal Clusters

61 Electronic and Nuclear Structural Characterization of Catalytically and Photocatalytically-active Transition Metal Complexes by Static and Transient X-ray Absorption Spectroscopy
Lin X. Chen, Argonne National Laboratory

62 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

63 Sequential Surface Synthesis for Operando X-ray Analysis and Few-Atom Cluster Synthesis
Alex B. F. Martinson, Argonne National Laboratory

Photochemistry with Quantum Dot Semiconductors

64 Photoinduced Electron Transfer in $AgInS_2$ and $AgInS_2$-CdS Nanocrystals
Prashant Kamat, Notre Dame Radiation Laboratory

65 Kinetically Stable Semiconductor Nanocrystals for Solar Photoconversion
Nathan R. Neale, National Renewable Energy Laboratory

66 High Quantum Yield Sensitization of Single Crystal TiO_2 Electrodes with $CsPbBr_3$ Nanocrystals
Bruce A. Parkinson, University of Wyoming

Charge Dynamics in Molecular Light-Harvesting Systems

67 Regulating Singlet-Triplet Energy Gaps through Substituent-Driven Modulation of the Exchange and Coulomb Interactions
Michael J. Therien, Duke University

68 Sensitizers for Solar Fuels Production: (carbene)M(amide) Complexes (M = Cu, Ag, Au)
Mark Thompson and **Stephen Bradforth**, University of Southern California

69 Accelerating Symmetry-breaking Charge Separation in a Perylenediimide Trimer through a Vibronically Coherent Dimer Intermediate
Michael R. Wasielewski, Northwestern University

70 Leveraging Entropy for Solar Photochemistry
Gregory D. Scholes, Princeton University

12:20 pm **PI Poster Presentations – GatherTown**
Poster numbers 57–70

1:30 p.m. Break

SESSION XI
New Project Presentations – Zoom

2:00 p.m. From Discrete Molecular Catalysts to Multidimensional Architectures: Effects of Charge Delocalization, Electronic Coupling, and Intramolecular Electrostatics on Electrocatalysis
Charles C. L. McCrory, University of Michigan

2:15 p.m. Understanding the Multiple Concurring Redox Processes at Semiconductor Photocatalysts
Shu Hu, Yale University

2:30 p.m. Cathodic Corrosion Mechanisms for p-Type III-V Semiconductor Photoelectrodes
Nathan S. Lewis, California Institute of Technology

2:45 pm

SESSION XII
PI Flash Talks – Zoom

Ultrafast Charge Carrier Dynamics in Nanoscale Semiconductors

71 Slow Cooling of Hot Excitons in Transition-Metal Dichalcogenides by Ultrastrong Coupling to Plasmon Polaritons
Jao van de Lagemaat, National Renewable Energy Laboratory

72 Transient X-rays and XUV Reveal Element- and Carrier-Specific Semiconductor Photophysics
Josh Vura-Weis, University of Illinois at Urbana-Champaign

73 Type-I Hot-carrier Extraction in Monolayer MoS_2 Photoelectrodes
Justin B. Sambur, Colorado State University

74 Ab Initio Quantum Dynamics of Charge Carriers in Advanced Solar Materials
Oleg Prezhdo, University of Southern California

Characterizing Charge Transfer in Thin Films

75 Molecular Regulation of Charge Transfer at Organic Semiconductor Electrodes
Erin L. Ratcliff, University of Arizona

76 Short and Long-range Electron Transfer Compete to Determine Free-charge Yield in Organic Semiconductors
Garry Rumbles, National Renewable Energy Laboratory

77 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

Molecularly Inspired Water Oxidation Catalysts

78 Mixed-Metal Oxide Energy Conversion Catalysts for Integration with Photoabsorbers
Daniel G. Nocera, Harvard University

79 Finding Connections Between Light-Activated Excited-States and Electrochemistry for Amorphous Cobalt Oxide Water-Splitting Catalysts
David M. Tiede, Argonne National Laboratory

80 Probing Water Oxidation Mechanisms on Catalysts with Atomically Defined Active Centers
Dunwei Wang and **Matthias Waegele**, Boston College

Photoelectrochemical Systems

81 Enhancing Photostability of Cu_2O Using Buffer and Protection Layers Prepared by Non-Atomic Layer Deposition Methods
Kyoung-Shin Choi, University of Wisconsin

82 Copper Bismuthate Photonic Glass Photoelectrodes for Solar-Driven, Photoelectrochemical Glycerol-to-Hydrogen Evolution
Rob Coridan, University of Arkansas

83 Re-Evaluating Routes of Oxidation of III-V Semiconductor Surfaces
Sylwia Ptasinska, Notre Dame Radiation Laboratory

84 Energy Materials Chemistry Integrating Theory, Experiment and Data Science
John M. Gregoire, California Institute of Technology
Carla P. Gomes, Cornell University
Jeffrey B. Neaton, Lawrence Berkeley National Laboratory

3:35 pm **PI Poster Presentations – GatherTown**
Poster numbers 71–84

4:45 p.m. BES Closing Remarks

5:00 p.m. Adjourn

Influence of Ligand Structure on Excited State Surface Chemistry of Colloidal Quantum Dots for Photocatalysis

Eric R. Kennehan, Kyle T. Munson, Grayson S. Doucette, Ashley R. Marshall, Matthew C. Beard, John B. Asbury

Department of Chemistry
The Pennsylvania State University
University Park, PA 16802

The ligand-nanocrystal boundaries of colloidal quantum dots (QDs) mediate the primary energy and electron transfer processes that underpin photochemical and photocatalytic transformations at their surfaces. We used mid-infrared transient absorption spectroscopy to reveal the influence that ligand structure and bonding to nanocrystal surfaces have on changes of the excited state surface chemistry of this boundary in PbS QDs and the corresponding impact on charge transfer processes between nanocrystals. We demonstrated that oleate ligands undergo marked changes in their bonding to surfaces in the excitonic excited states of the nanocrystals due to an increase of surface electron density, causing oleate passivated PbS surfaces to undergo significant structural changes following photoexcitation. A shift was observed from stronger chelating and bridging to weaker monodentate bonding geometries in the excited states of the QDs. These changes in excited state surface chemistry can impact the surface mobility of the ligands and the ability of redox shuttles to approach the nanocrystal surfaces to undergo charge transfer in photocatalytic reactions.

In contrast, markedly different transient vibrational features were observed in mercaptoproprionic acid (MPA) passivated PbS QD films that result from charge transfer between neighboring nanocrystals and localization of holes at the nanocrystal surfaces near MPA ligands. The transient vibrational spectra represented in **Figure 1** (left) highlight the changes in vibrational features of carboxylate groups of MPA ligands following optical excitation of the QD films. The transient spectra reveal a uniform 25 cm^{-1} shift in frequency of the carboxylate vibrational modes that results from changes in surface hole density caused by interactions with surface bonded thiol groups of MPA ligands **Figure 1** (right).

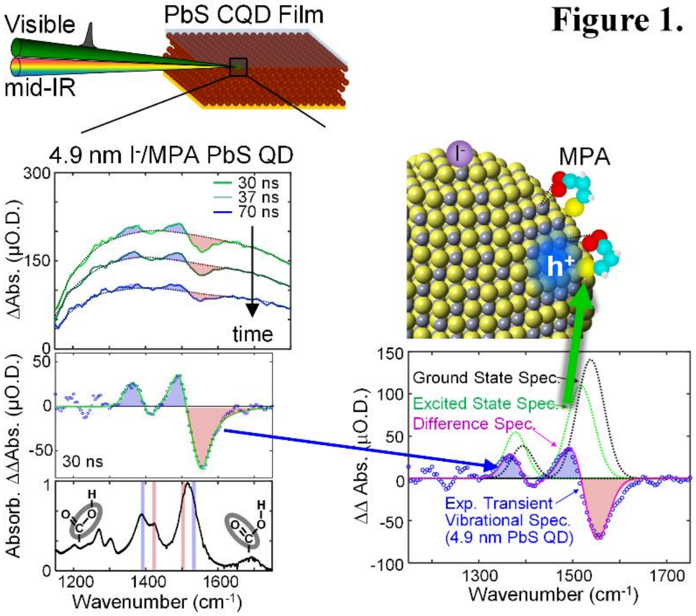


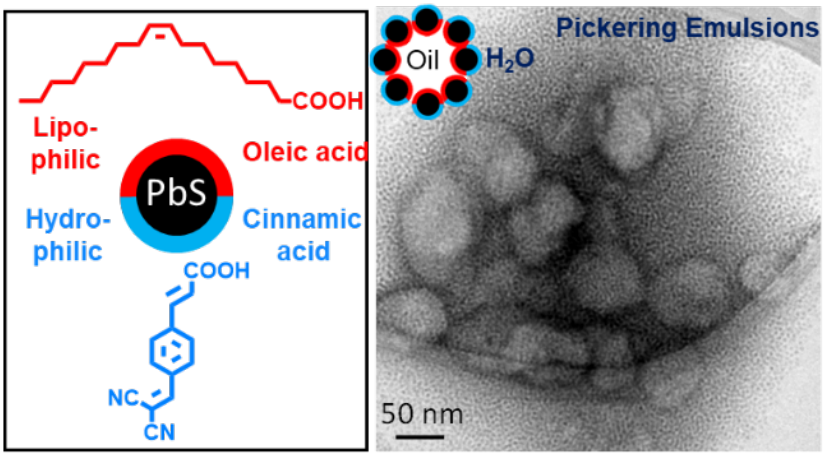
Figure 1.

The ability to distinguish the influence that excitonic excited states versus charge transfer and hole localization have on the surface chemistry of the ligand-nanocrystal boundary lays the groundwork for exploration of how this boundary can be understood and controlled for the design of nanocrystalline materials tailored for specific applications in solar energy harvesting and photocatalytic reactions.

Functional Ligand Exchanges on PbS QDs

Zhiyuan Huang, Marissa Martinez, Jeffrey Blackburn, Justin Johnson, Matthew C. Beard
Materials, Chemistry, and Computational Sciences
National Renewable Energy Laboratory
Golden, CO, 80401

Colloidal semiconductor nanocrystals, specifically quantum dots (QDs), are of interest to solar photochemistry due to their highly tunable optical and electronic properties. Here we discuss our efforts in controlling the optical and electrical properties of QDs and their assemblies using various ligand chemistries. By taking advantage of ligand-ligand coupling on the QD surface we can construct Janus-ligand shell systems. Which are ligand shells where one half the QD is covered in one type of ligand and the other half with a different ligand. Janus nanoparticles (JNPs) are nanostructures that have an asymmetric distribution of one of its compositions but yet still retains its physically symmetric shape and have been intensely studied for applications ranging from nano-motors with controlled movement, catalysis and electrochemical applications, to drug delivery, biosensing and cancer therapy. But seldom have Janus-ligand shells been applied to semiconductor nanocrystals in the size regime below 10 nm. We show that such asymmetric ligand-shells can be used to direct the assembly of QDs in arrays and demonstrate that control through the fabrication of artificial pyroelectric films. We also demonstrate that they can form Pickering emulsions in solution, where the QDs self-assemble at the interface of water and dichloromethane and show that such emulsions can enhance the QDs photoactivity. Finally, we are exploring photoactive ligands that inject carriers with excess energy into the conduction band of PbS QDs and then undergo multiple exciton generation (MEG). We find an enhancement in MEG when the ligand is photoexcited and transfers and electron into the QDs.



Light Harvesting in Semiconductor Quantum Dots

PI: Warren F. Beck, Department of Chemistry, Michigan State University,
East Lansing, Michigan 48824 USA

co-PI: Benjamin G. Levine, Department of Chemistry and Institute for Advanced Computational Science, Stony Brook University, New York 11794 USA

co-PI: P. Gregory Van Patten, Department of Chemistry, Middle Tennessee State University, Murfreesboro, Tennessee 37132 USA

co-PI: Mengliang Zhang, Department of Chemistry, Middle Tennessee State University, Murfreesboro, Tennessee 37132 USA

In this project, we are testing the hypothesis that the spectroscopy and dynamics of semiconductor quantum dots (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 QD core and surface capping ligands, respectively, accounts for the absorption and photoluminescence properties. Our current results favor a many-electron, molecular theory for the electronic structure of QDs where the vibrations of the organic ligands serve as branching modes in a coherent nonadiabatic nonradiative decay mechanism. An important implication 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.

The Beck group has applied broadband 2DES spectroscopy with 6–7-fs mid-visible excitation pulses and 3DES oscillation maps to characterize vibronic coherences that accompany hot-carrier cooling (X3–X1) and luminescence (X1–PL) relaxation dynamics in QDs with hexadecylamine[1] or oleate ligands.

The Levine group has computed conical intersections between excited potential energy surfaces responsible for hot carrier cooling in amine liganded CdSe QDs and identified vibrational modes that participate in cooling. We are currently identifying intersections responsible for cooling in a series of dots with different ligands to determine how ligand vibrational motions and electronic structure impact the rate of cooling.

The Van Patten and Zhang group has developed a novel and reliable thermal desorption DART-MS method to confidently identify organic ligands and possible residues on QDs.[2] We are currently extending our methods to prepare soluble CdSe QDs capped exclusively by a thiol containing an electronically-active functionality with a distinct vibrational spectrum (2-phenylethane thiol). We are also developing quantitative strategies to permit precise determination of the amount of ligands on QD surfaces.

(1) Tilluck, R. W.; Mohan T M, N.; Hetherington, C. V.; Leslie, C. H.; Sil, S.; Frazier, J.; Zhang, M.; Levine, B. G.; Van Patten, P. G.; Beck, W. F. Vibronic Excitons and Conical Intersections in Semiconductor Quantum Dots. *J. Phys. Chem. Lett.* **2021**, *12*, 9677–9683, DOI: 10.1021/acs.jpclett.1c02630.

(2) Frazier, J.; Cavey, K.; Coil, S.; Hamo, H.; Zhang, M.; Van Patten, P. G. Rapid and Sensitive Identification and Discrimination of Bound/Unbound Ligands on Colloidal Nanocrystals via Direct Analysis in Real-Time Mass Spectrometry. *Langmuir* **2021**, *37*, 14703–14712, DOI: 10.1021/acs.langmuir.1c02548.

‘Spin-Exchange Photochemistry’ with Magnetically Doped Quantum Dots

Victor I. Klimov

Chemistry Division, Los Alamos National Laboratory

Los Alamos, New Mexico 87545

Materials displaying electron photoemission under visible-light excitation are of great interest for applications in photochemistry, photocathodes, advanced electron beam sources, and electron microscopy. We demonstrate that using core/shell CdSe/CdS colloidal quantum dots (CQDs) heavily doped with manganese (Mn) [1], we can realize highly efficient electron photoemission under excitation with visible-light pulses. This effect is enabled by extremely fast (<300 femtoseconds) spin-exchange Auger energy transfer from excited Mn ions to an intrinsic CQD exciton [2]. Since the rate of this process outpaces that of intra-band cooling, the high-energy ‘hot’ electron produced by the first Auger-excitation step can be efficiently promoted further into the external ‘vacuum’ state via one more Mn-to-CQD energy-transfer step (**Figure 1a**).

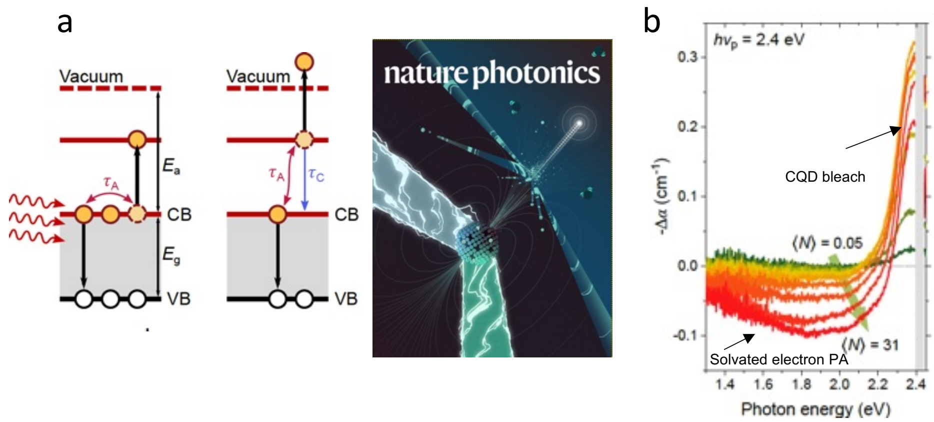


Figure 1. a, Electron ejection from the CQD due to two-step Auger ionization (left) and its artistic representation (right). In our Mn-doped CQDs, the band-edge transition is resonant with the d-d transition of the Mn-ion. As a result, photoexcited excitons circulate between the intrinsic QD and Mn states. **b,** Water-based Mn-doped CdSe/CdS CQDs excited with 2.4 eV photons exhibit a photoinduced absorption (PA) feature at ~1.8 eV due to solvated electrons produced via two-step spin-exchange photoemission (panel **a**, left)

This CQD ionization pathway exploits exceptionally large up-hill energy gain rates associated with the spin-exchange Auger process (>10 eV ps^{-1}) and leads to highly efficient photoemission due to single- and two-step Auger ionization [3]. Using the latter process, we achieve high-yield production of solvated electrons with more than 3% internal quantum efficiency per absorbed photon (**Figure 1b**). Importantly, this effect is realized using visible-range 2.4-eV photons. It persists down to photon energies of ~2 eV, implying that it can make use of *ca*. 40% of photons from the solar spectrum. This makes it of considerable utility for realizing visible-light-driven ‘*spin-exchange photochemistry*’ such as photoreduction due to spin-exchange photoemission.

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Charge-Transfer Excitons at 1D and 2D Interfaces

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Overview: The overarching goal of this project is to understand charge transfer and energy transport at the interfaces of low-dimensional excitonic nanostructures. Here, we present our recent results on the transport of charge-transfer (CT) exciton at the interfaces of two-dimensional (2D) transition metal dichalcogenides (TMDCs) as well as one-dimensional (1D) single walled-carbon nanotubes imaged by ultrafast microscopy. These results demonstrate rapid (ps) charge transfer and long-range transport at these interfaces, suggesting potential applications in solar energy conversion.

Interfacial 1D exciton dynamics and transport We have recently investigated the transport of 1D interfacial CT excitons at atomically precise lateral heterojunctions of WSe_2- $WS_{1.16}Se_{0.84}$.[1] As shown in **Figure 1a**, electrons and holes were found to be spatially separated in $WS_{1.16}Se_{0.84}$ and WSe_2 parts. The charge transfer exciton is the ground state of the lateral heterostructure and the interface can be viewed as an ultrathin excitonic "high way". Significantly slower carrier recombination was observed at the interface, supporting the spatial indirect nature of interfacial CT excitons. We employed ultrafast microscopy with ~ 200 fs temporal resolution to image the transport of different exciton phases. These measurements visualized long-range exciton transport and extremely rapid expansion of a highly non-equilibrium electron-hole (e-h) plasma phase with a Fermi velocity up to 3.2×10^6 cm s^{-1} at high exciton density (**Figure 1b**).

Charge transport at MoS_2-SWNT interfaces We have carried out measurements on carrier transport in MoS_2-SWNT heterostructures using transient absorption microscopy (**Figure 1c**).[2] Our results showed that carrier transport in the heterostructures is highly time-dependent; transport is very rapid initially with a diffusion constant up to 7 cm^2s^{-1} but slows down on the timescale of ~ 200 ps (**Figure 1c**), despite that the charge-separated states have lifetimes as long as µs. The time-dependent behavior with initial faster transport could suggest a repulsive interaction between bound CT excitons. Because the dielectric screening is low for both TMDC and SWNT, we hypothesize that bound CT instead of free carriers are formed initially at the interfaces. In such a case, interfacial CT states have their permanent dipole moments aligned along the 1D interface. As a result, there are expected to be strong repulsive interactions between the CT excitons.

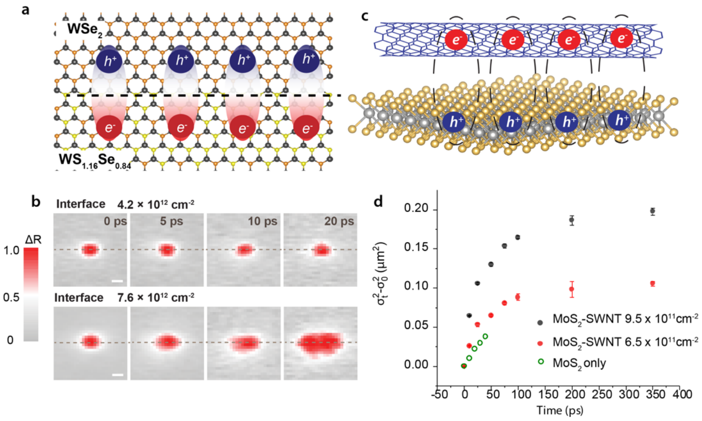

Figure 1. (a) Charge-transfer (CT) excitons at 2D and 1D interfaces. (a) CT excitons at atomically precise lateral heterojunctions of WSe_2-$WS_{1.16}Se_{0.84}$. (b) Exciton-density dependent transport of the CT exciton resulting from exciton-exciton interactions. (c) CT excitons at MoS_2-SWNT interfaces. (d) Time- and density-dependent exciton transport of CT excitons showing long-range transport due to repulsive interactions.

References: 1. L. Yuan et al., Submitted (2022). 2. D. Blach et al., in preparation (2022).

Charge Generation and (De)localization in Nanoscale Semiconductor Heterojunctions

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Excitonic solar cells and some envisioned solar fuels strategies rely upon the efficient conversion of bound electron-hole pairs (excitons) into free charge carriers across a donor/acceptor interface. The features and mechanisms of nanoscale semiconductor heterojunctions giving rise to long-lived free charge carriers are not fully understood, so our group focuses on using time-resolved spectroscopy to help fill these knowledge gaps. Here I highlight some recent advances in our understanding of the charge generation and recombination processes in model donor/acceptor heterojunctions of nanoscale excitonic semiconductors.

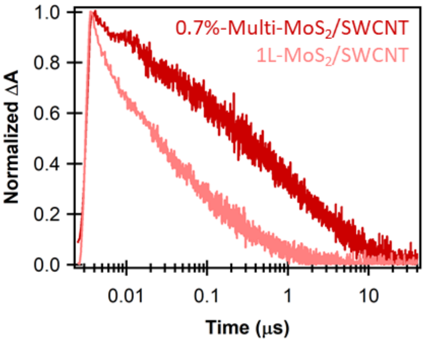

Figure 1. Longer lifetime of charges for SWCNT/MoS$_2$ heterojunction where the MoS$_2$ contains multi-layers.

In one study, we employ a combined pump–probe ultrafast transient absorption (TA) spectroscopy and time-resolved microwave conductivity (TRMC) study on a suite of model excitonic heterojunctions consisting of monochiral semiconducting single-walled carbon nanotube (s-SWCNT) electron donors and small-molecule electron acceptors. These two techniques are commonly employed to track charge carrier dynamics in a variety of systems, but seldom combined. We find a quantitative match for the dynamics measured by each technique over the 0.5 microsecond time scale, conclusively demonstrating that photoinduced charge carriers separated across these heterojunctions do not form bound charge transfer states, but instead form free/mobile charge carriers.[1] We also explore heterojunctions between monochiral s-SWCNT networks and the prototypical layered 2D semiconductor MoS$_2$. Specifically, we probe the role of monolayer-multilayer homojunctions within the MoS$_2$ in extending carrier lifetimes while spatially directing charges to multilayer sites. We find that a small fraction of multilayer sites (<1% of the film's total area) results in a five-fold increase in carrier lifetimes, with charges in the s-SWCNTs persisting past 10 μs, and a doubling of the charge separation yield.[2] Interestingly, TRMC measurements suggest that an appreciable density of free charge carriers persist beyond the millisecond time scale in the MoS$_2$ multilayers, even after carriers in the s-SWCNT layer have recombined. This result is consistent with another recent study where we found persistent photoconductivity lasting up to several days for MoS$_2$/WS$_2$ heterojunctions, where the long-lived carriers were specifically relegated to the multilayer MoS$_2$ domains.[3] Our studies suggest that even very small changes to the 2D layer number and density within such heterojunctions can lead to dramatic changes in the exciton dissociation yield and free charge carrier lifetimes.

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Creating a Spectrochemical Series for Transition Metal-based MLCT Chromophores

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In recent years, there has been renewed interest in the photophysics of first-row transition metal-based charge-transfer complexes. Based in part on our DOE-supported work in this area, it is now well-established that the inversion in the relative energies of charge-transfer versus metal-centered ligand-field (i.e., “d-d”) excited states in first-row complexes as compared to their second- and third-row congeners undercuts efforts to leverage such compounds for photo-induced electron transfer chemistry due to ultrafast (~100 fs) deactivation of CT states to lower energy ligand-field excited states; ligand-field states are not characterized by charge separation and therefore have significantly less propensity toward electron transfer chemistry. Circumventing this problem has therefore become an important objective for a growing number of research groups in this expanding area of physical-inorganic chemistry.

One research thread that holds considerable promise is the creation of ligands that present ligand-field strengths sufficient to destabilize d-d excited states and position charge-transfer states lowest in the compound’s excited-state energy profile. A significant impediment to the rapid development of such ligands is the inability to experimentally assess the energies of these ligand-field states. In the case of Fe(II), for example, the molar absorptivity of the main MLCT band in the visible is on the order of 10,000 M^{-1} cm^{-1} - exactly what one wants from the perspective of light capture - but its large oscillator strength simultaneously prevents an evaluation of the ligand-field strength associated with 2,2'-bipyridine because the (much weaker) d-d transitions that inform on ligand-field strength are buried under the MLCT envelope.

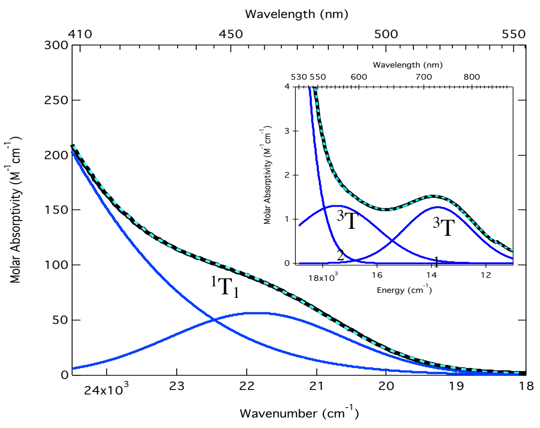

Figure 1. Electronic absorption spectrum of [Co(bpy)$_3$](PF$_6$)$_3$ in CH$_3$CN solution. The inset shows data collected at high concentration in a 10-cm pathlength cell, revealing spin-forbidden d-d absorptions.

We have developed an approach to overcome this challenge through the synthesis and characterization of Co(III) polypyridyl complexes. Co(III) is isoelectronic with Fe(II) so therefore possesses all of the same ligand-field excited states, but the change in character of the charge-transfer band from MLCT in the case of Fe(II) to LMCT for Co(III) contributes to a dramatic blue-shift of this absorption feature into the near-ultraviolet: this allows the lower intensity d-d bands in the visible region of the spectrum to be revealed (Figure 1). We can now quantify not only ligand field-state energetics in the Co(III) complexes, but also in the corresponding Fe(II) complexes, as well, through a calibration factor that we were able to discern from a comparative analysis of several Fe(II) complexes for which certain optical transitions could be observed. We believe this method will therefore prove useful in the development of new ligand systems to expand the photofunctionality of first-row chromophores.

Synthesis and photophysics of next-generation Cu(I) MLCT photosensitizers

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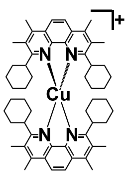

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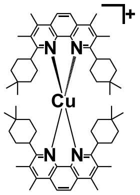

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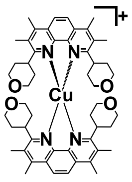

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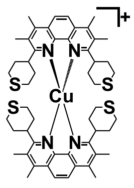

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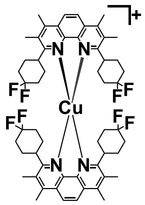

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A series of five Cu(I) *bis*(phenanthroline) metal-to-ligand charge transfer (MLCT) photosensitizers featuring 2,9-cyclohexyl subunits flanked by 3,8-methyl steric supports have been prepared. Synthetic design, in addition to electrochemical and both static and dynamic photophysical characteristics of all 5 chromophores are detailed. Figure 1 presents the UV-Vis, static photoluminescence (PL) spectra, and PL intensity decays of **1-5**. The ground and excited state properties of **1** and **2** echo each other. The incorporation of heteroatoms into the cyclohexyl platform in **3-5** resulted in an MLCT excited state lifetime extension beyond that of any other Cu(I) *bis*(diimine) adhering to strictly 2,9-hydrocarbon architecture, Table 1. The lifetime extension is accompanied by systematic hypsochromic shifts and decreases in k_{nr}, rationalized by the energy gap law, Table 1. Cyclic voltammograms in acetonitrile indicate systematic variation of the metal-based one-electron oxidation and the first ligand-based one-electron reduction because of heteroatom inclusion in the 2,9-substituents, Table 1. Ultrafast transient absorption spectroscopy in deaerated dichloromethane revealed the ^{1}MLCT-^{3}MLCT intersystem crossing time constants. In summary, heteroatom 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.

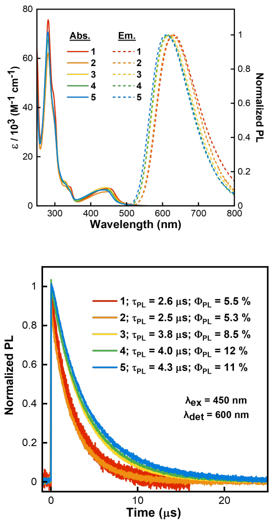

Figure 1. UV-Vis absorption and PL spectra (top) and the PL intensity decays (bottom) of **1-5** measured in degassed CH_2Cl_2 at RT.

Table 1. Summary of the Photophysical and Electrochemical Properties of **1-5**.

Molecule	τ (µs)^a	λ (nm)^a	Φ_{PL} (%)^a	k_r ($\times 10^4$ s^{-1})^a	k_{nr} ($\times 10^4$ s^{-1})^a	E_{ox} (V)^b	E_{red} (V)^b	E^*_{ox} (V)^b
1	2.6	631	5.5	2.1	36	0.43	-2.38 -2.59	-1.77
2	2.5	629	5.3	2.1	38	0.46	-2.40 -2.63	-1.73
3	3.8	618	8.5	2.2	21	0.55	-2.29 -2.52	-1.68
4	4.0	616	12	2.8	22	0.59	-2.28 -2.48	-1.64
5	4.3	612	11	2.4	21	0.63	-2.24 -2.45	-1.62

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

Controlling Charge-Transfer Reactions with Cobalt and Copper Coordination Complexes

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All photochemical conversion systems involve fundamental processes of light absorption, charge separation and charge collection. Dye-sensitized solar cells (DSSCs) are an excellent platform to demonstrate the subtle interplay of various electron-transfer reactions that give rise to charge separation and collection following light absorption by molecular chromophores. This talk will highlight our recent efforts to design first-row transition metal coordination complexes to control the kinetics of such electron-transfer reactions in the context of DSSCs.

The spin state of Co redox couples can have a dramatic effect on the inner-sphere reorganization energy and thus electron-transfer kinetics. For example, the self-exchange rate constants of low-spin Co(II) to low-spin Co(III) complexes can be roughly 4 orders of magnitude faster than high-spin Co(II) to low-spin Co(III) octahedral complexes. In order to exploit this phenomenon, 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 data on these new redox couples employed in DSSCs.

Cu-based redox shuttles coordinated with bidentate pyridyl ligands have recently been shown to perform remarkably well as redox shuttles in DSSCs. We have shown that such bidentate ligands are susceptible to ligand exchange with exogeneous Lewis bases such as 4-tert-butylpyridine (TBP) that are added to enhance cell performance. We have synthesized a new Cu complex featuring the hexadentate ligand bpyPY4 (6,6'-bis(1,1-di(pyridine-2-yl)ethyl)-2,2'-bipyridine) to facilitate efficient electron-transfer kinetics and achieve high stability via the chelate effect. Cyclic voltammetry, UV-visible and NMR spectroscopy indicate that non-coordinated pyridyl donors block binding of TBP. The Cu system, [Cu(bpyPY4)]2+/+, where exhibits a dynamic coordination environment around the metal center as evidenced by X-ray crystallography and variable-temperature 1H NMR studies. The [CubpyPY4)]2+/+ complex exhibits remarkably similar kinetics as [CoPY5Im]3+/2+, and general conclusions from this observation will be discussed.

Mechanisms for CO_2 Reduction Modelled with Metal Carbonyl Clusters

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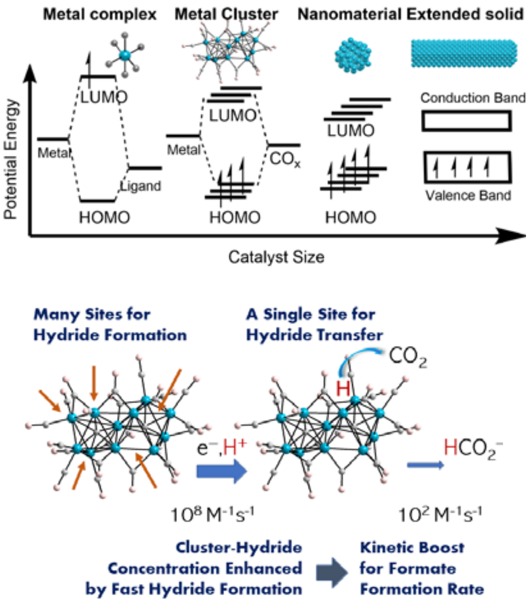
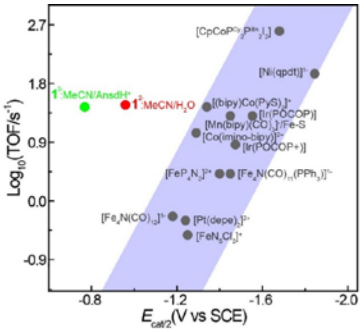
The long-term goal of this project is to understand and control the elementary chemical bond-making and -breaking steps in photocatalytic reactions that involve hydride transfer (HT) to substrates. This is a mechanism-driven approach to improve photocatalyst performance. The nanoscale clusters used as model systems are large enough to possess properties like those of nanomaterial and heterogeneous extended solid photocatalysts, including having many surface sites for chemical reactions and exhibiting delocalized electronic structures, as shown at right. At the same time, these nanoscale metal clusters are molecular with precisely known structures, and they can be characterized using the powerful tools of molecular chemistry and dark electrochemistry.



(**top**) Nanoscale metal clusters enable use of molecular characterization tools to probe elementary chemical steps in photocatalysis. (**bottom**) Independent control and enhancement of hydride formation (k_1) and hydride transfer (k_2) rate.

Secondary coordination sphere (SCS) proton relays enhance overall H_2 evolution rates by orders of magnitude: all PT steps get faster and this is not useful for C-H bond formation with CO_2. We demonstrated 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 fast formation of the hydride intermediate $[H\text{-}Co_{11}C_2(CO)_{23}]^{3-}$, provides a kinetic effect resulting in an anodic shift in reduction potential that lowers the overpotential for hydride transfer down to 10 mV. The rate for hydride transfer to CO_2 is 100 $M^{-1}s^{-1}$ which is faster than other known catalysts that operate at higher overpotentials.

And this fast rate for formate formation from CO_2 arise again from the fast PT reactivity to afford the intermediate hydride. The comparison against other known catalysts can be seen in the plot at right.



Comparison with reported catalysts highlights the low overpotential for C-H bond formation with CO_2.

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; ii) elucidation of the role of a hydrophobic microenvironment on the transport of charged and uncharged substrates; and iii) probing potential-pKa relationships for large cobalt clusters to design multi-electron and -proton processes for solar fuels chemistry.

Kinetic Barriers to Metal-based Protonation Influence Proton-coupled Electron Transfer Reaction Pathways in the Formation of Transition Metal Hydride Complexes

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The elementary proton-coupled electron transfer (PCET) processes underpinning fuel-production reactions can proceed via stepwise or concerted reaction pathways. Concerted proton-coupled electron transfer (CPET) routes circumvent the high energy, charged intermediates associated with stepwise pathways, and are therefore hypothesized to lead to more efficient, durable, and selective energy conversion processes. The design principles needed to direct catalysts through concerted PCET routes are currently unknown, and our work seeks to fill this gap in knowledge by identifying the parameters that influence reactivity patterns.

Mechanistic studies of several H_2-evolving catalysts in our lab show that PCET reactions to form metal hydride intermediates almost exclusively proceed via a stepwise electron transfer–proton transfers, with rate-limiting proton transfer.[1–5] In several examples, a thermodynamically unfavorable ligand protonation is kinetically favored over direct metal protonation, followed by tautomerization to form the stable hydride product.[2,6,7] This finding suggests an intrinsic barrier to direct metal protonation. We hypothesize such a kinetic barrier inhibits access to a CPET process.

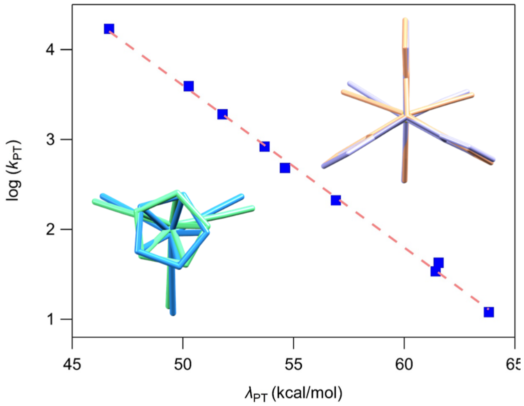

Figure 1. For 9 separate complexes, a clear correlation is observed between proton transfer rate constant and reorganization energy for the proton transfer reaction $ML_n^- + HA \rightarrow HML_n + A^-$. (Inset) structural differences between ML_n^- and HML_n visualized for two of these complexes.

Minimizing reorganization energy accompanying the proton transfer component is predicted to lower the barrier to proton transfer and enhance the kinetics of hydride formation. For a range of transition metal complexes that form stable hydride species, we show a strong correlation between rate constants for the isolated proton transfer step and reorganization energy. This trend encompasses a range of ligand motifs and transition metal centers. Mechanistic studies are underway to map the reaction mechanisms of the PCET reactions that form these metal hydride species in order to examine the role of reorganization energy in dictating accessible reaction routes.

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Deciphering the Correlation Between Thermodynamic and Kinetic Hydricities of Transition Metal Hydrides

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Transition metal hydrides are essential intermediates in a wide range of catalytic reactions including those relevant to energy storage applications such as the reversible hydrogenation and dehydrogenation of CO_2 to formic acid or methanol. In many of these reactions, hydride transfer is the rate limiting step, thus an increased fundamental understanding of hydride transfer with transition metals as either the hydride donor or acceptor is critical for the rational design of efficient catalysts. The ability of a transition metal hydride to donate a hydride can be depicted by **(i)** thermodynamic hydricity (Fig. 1a), defined as the free energy required to release a free hydride ion, H^-, from a species in solution (ΔG^{o}_{H-}) and by **(ii)** kinetic hydricity (Fig. 1b) which is related to the free energy of activation ($\Delta G^{\ddagger}_{H-}$) and provides information on the rate of hydride transfer.

In this contribution, I will present our computational modeling studies on the correlation between thermodynamic and kinetic hydricities of **(i)** a series of pentamethylcyclopentadienyl iridium(III) complexes with $[Cp^*Ir(L)(H)]^q$ general formula ($q = -1, 0, 1$ depending on the ligand charge by deprotonation or protonation events) towards CO_2 (Fig. 1c) and **(ii)** similar correlations for hydride transfer from $Re(^{R}bpy)(CO)_3H$ (bpy = 4,4'-R-2,2'-bipyridine; R = OMe, ^{t}Bu, Me, H, Br, COOMe, CF_3) to CO_2 and different cationic N-heterocycles. Our results show that in general, the rate of hydride transfer increases as the thermodynamic driving force for the reaction increases but even slight perturbations in the steric properties result in large deviations in the predicted rate of hydride transfer based on thermodynamic driving forces. This indicates that thermodynamic considerations alone cannot be used to predict the rate of hydride transfer, which has implications for catalyst design.

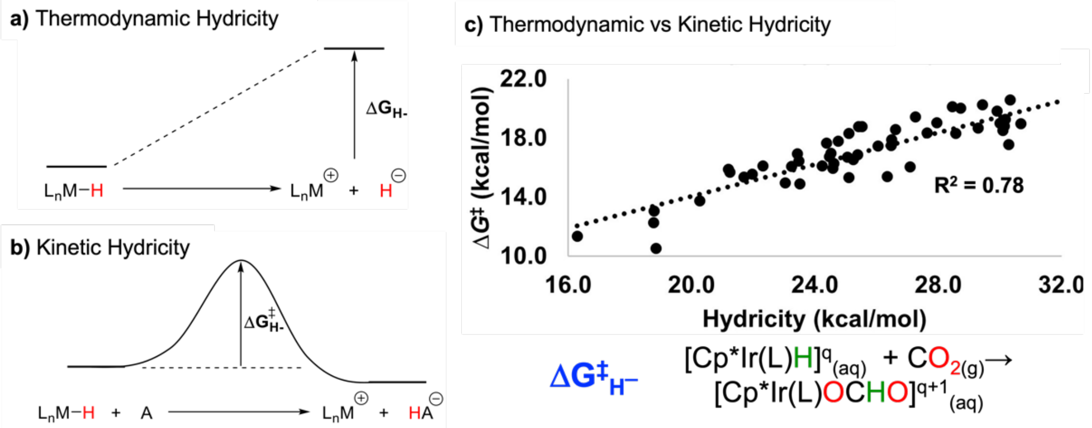

Figure 1. Schematic representations of **(a)** Thermodynamic hydricity and **(b)** Kinetic hydricity, and **(c)** correlation between computed thermodynamic and kinetic hydricities for CO_2 additon to $[Cp^*Ir(L)(H)]^q$.

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

Electrocatalytic, Homogeneous Ammonia Oxidation in Water to Nitrate and Nitrite with a Copper Complex

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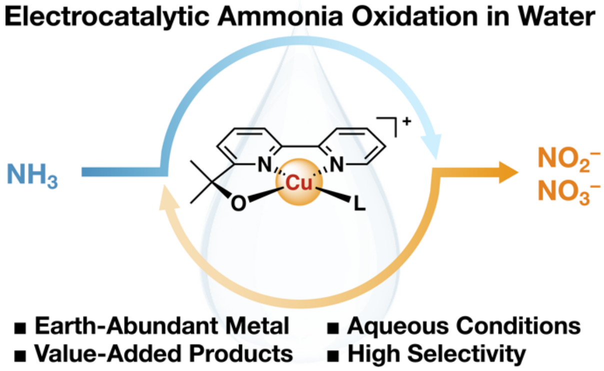
Electrocatalytic ammonia oxidation at room temperature and pressure allows energy-economical and environmentally-friendly production of nitrites and nitrates. Few molecular catalysts, however, have been developed for this six- or eight-electron oxidation process. We now report $[Cu(bipyalk)]^+$ (bipyalkH = 2-[(2,2'-bipyridin)-6-yl]propan-2-ol), a homogenous electrocatalyst that realizes the oxidation of ammonia to nitrate and nitrite in water at 94% faradaic efficiency. The nitrite and nitrate produced were quantitatively detected using the Greiss colorimetric method. The catalyst exhibits high selectivity against water oxidation in aqueous media, as $[Cu(bipyalk)]^+$ is not competent for water oxidation. Based on initial mechanistic and computational studies, we propose monometallic catalysis and a nucleophilic attack mechanism for N–O bond formation. This work suggests that other catalysts, although unsuccessful for water oxidation, might nonetheless be useful for ammonia oxidation.



Improving and measuring water oxidation catalyst viability

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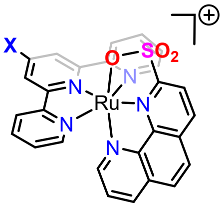
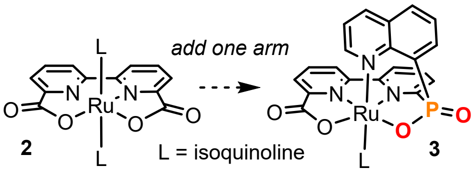
Our overall goals are to (1) slow the rate of water oxidation electrocatalyst (WOEC) degradation, (2) enable molecular WOEC activity in acid, and (3) create and refine new methods for characterizing WOEC stability. We have made progress in all three areas. Our labs published a paper in early 2021 disclosing the profound benefits of including a sulfonate functional group in the active site of a water oxidation catalyst (**1a**), improving initial rates in Ce(IV)-driven reactions by 300x, and in electrocatalytic reactions in 0.1 M nitric acid by >40x. Here we report added improvements when an electron-releasing OEt group (**1b**) is positioned opposite the metal center on a pyridine ring, with movement of the 2/3 couple and onset potential to less positive values. Initial rates in Ce(IV)-driven reactions increase by 30x, and in electrocatalytic reactions in pH 7 phosphate buffer by 3x relative to those for **1a**. Derivatives **1c** and **1d** are still being studied. In addition, using an NNN ligand that bears two benzimidazolyl rings on a central pyridine lowers the potentials further, but with lower currents and stabilities.



1a **X** = H (published 2021)
1b **X** = OEt
1c **X** = CF_3
1d **X** = NO_2

Great improvements in WOEC stability were seen in comparing pentadentate-ligand catalyst **3** to **2**. Bulk electrolysis in pH 7 phosphate for 15 h using a ~2 cm^2 BDD electrode showed that **3** remains soluble whereas **2** mostly decomposes. The current for **2** at the end of 15 h was shown to be from solids deposited on the electrode. Faradaic efficiency for **3** driven at 1.43 V vs Ag/AgCl was >98%, and the ~50x greater reactivity of **3** vs **2** (k_{H_2O}) is ascribed to the carboxylate decoordinating and acting as internal base (DFT).



Meyer group data:
k_{H2O} = 6 s^{-1}
k_{cat} = k_{H2O} + [B]k_B

our data:
k_{H2O} = 300 s^{-1}
k_B = 6800 s^{-1} M^{-1}

Our bulk electrolysis / gas analyzer system has now been thoroughly tested, and can quantitatively measure the headspace gas of electrocatalytic water oxidation in a closed environment, with a CO_2 detection limit of 5 ppm vs typical O_2 levels after 100 TON of 50,000 to 150,000 ppm. The system allows for the benchmarking of multiple WOEC under various realistic electrocatalytic conditions.

Electrochemical simulations of WOEC have been run to explore the lack of pure kinetic, s-shaped curves during catalysis. The CVs of many WOEC display catalytic current profiles that suggest either the depletion of water or catalyst and lack diffusion limited current necessary for proper kinetic analysis. Our goal is to complement existing methods for analyzing CV data such as foot-of-the-wave analysis. Our new simulation program has a very user-friendly interface that allows one to gradually change a parameter to gauge the effects of that parameter on the voltammogram.

Progress in synthesis and evaluation of other sulfonate-bearing WOEC will be reported, along studies to determine the roles of the sulfonate, including the possibility that it is acting through electrostatic effects.

Advances in Probing and Steering Excited State Trajectories in Solar Energy Conversion Systems

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The project aims at understanding light-matter interactions across various solar energy conversion systems on the time scale of electron and nuclear motions. We hypothesize that light excitation launches coherent electronic and atomic motions that correlate in phase and these motions potentially lead to transition states that can be steered and controlled in photoinduced electron/energy transfer processes. The program thrusts are: A) the search for key vibrational coordinates in the excited state in photoinduced energy and electron transfer processes; B) the control of photoinduced electron transfer coherently with vibrational excitation in transition metal donor-bridge-acceptor systems and C) to investigate coherent coupling of surface bound molecular chromophores with plasmonic oscillations in metallic nanoparticles. Our collaborative team seeks 1) to achieve rational design of intrinsic structural factors that could control the coherent electronic and vibronic motions; 2) to execute ultrafast optical spectroscopic and X-ray structural characterization of excited state pathways to uncover the coherent electronic and nuclear motions; and 3) to develop advanced quantum dynamics and molecular dynamics calculations including excited state potential energy surfaces and trajectories, as well as spectral responses in valence and inner shell electronic transitions.

Significant achievements realized over the past year include 1) the observation of key vibrational modes in Pt(II) dimers directed along excited state trajectories on potential energy surfaces measured in real time to quantify Pt-Pt bond stretching and ligand twisting amplitudes and dynamics; 2) the influence of ligand structure on the excited state energetics and coherent vibrational wavepacket motions in modulating dual ISC pathways; 3) probing the influence of coherent wavepacket motions in electron donor-acceptor supramolecular systems; 4) revealing the interplay between plasmons and interband transitions in single gold bipyramids through photoluminescence excitation pattern imaging; 5) using electronic structure calculations to understand pressure effects on the photoluminescence of gold nanoclusters, and to identify features leading to high photoluminescence quantum yields.

Our future research includes 1) searching for key coherent vibrational coordinates in photoinduced electron transfer and bond breaking processes; 2) control photoinduced electron transfer coherently with vibrational excitation in donor-bridge-acceptor systems by modulating electronic coupling between the donor and acceptor, 3) investigating coherent coupling of surface bound molecular chromophores with plasmonic oscillations in metallic nanoparticles and nanoclusters; and 4) develop a broken symmetry DFT method to determine electron configurations of atoms in a Co_4 cluster, and from this the effect of vibrational excitation on electron transfer water oxidation catalysis; 5) Develop density functional methods to characterize gold bipyramid interactions with adsorbed molecules.

Two-Dimensional Electronic Vibrational Spectroscopy of Progressively Large Components of the Photosystem II Antenna System

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The pigment-protein complexes utilized by plant and algae photosystem II to collect and focus excitation energy on the site of the water splitting reaction provide substantial challenges for optical spectroscopies such as two-dimensional electronic spectroscopy because of the highly congested optical spectra. There are some specific advantages of two-dimensional electronic vibrational (2DEV) spectroscopy for study of the ultrafast dynamics of these systems. In particular, the combination of excitonic splitting giving rise to a manifold of electronic energy levels combined with the sensitivity of vibrational frequencies to local protein environment, enable spectral resolution along both excitation (visible) and detection (infrared) axes, a key aspect of 2DEV spectroscopy [1]. In the poster we describe 2DEV data for the PSII reaction center, the core complex of PSII, containing CP43 and CP47, and a complex in which CP26, and CP29 (the minor complexes) are also present. We provide clear evidence for the initial charge separation step in PSII being ($\mathrm{Chl_{D1}Pheo}$) → $\mathrm{Chl_{D1}^{+}Pheo^{-}}$, followed by hole transfer from $\mathrm{Chl_{D1}}$+ to $(\mathrm{P_{D1}P_{D2}})^{+}$ [2]. For the larger systems we describe energy flow pathways into the reaction center.

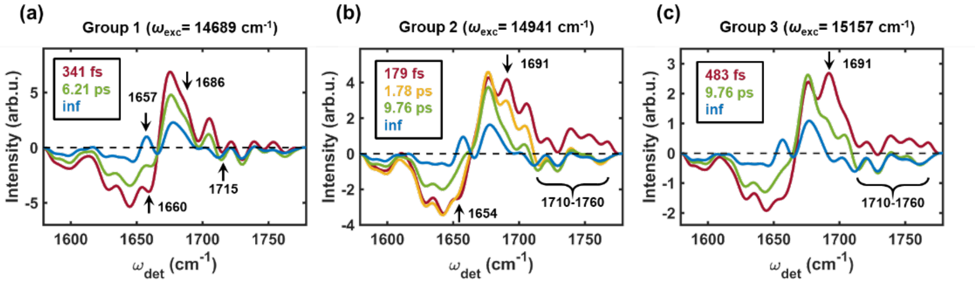

Figure 1. Different excitation frequencies give rise to different dynamical pathways in PSII.

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Determination of Vibrational Motions Driving Solar Energy Conversion Processes

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The goal of our DOE-sponsored research is to identify vibrational and vibronic coordinates responsible for facilitating fast and efficient solar energy conversion. We make extensive use of femtosecond stimulated Raman spectroscopy (FSRS) in order to track structural changes as a function of time. With DOE CAREER support, we have extended the FSRS system to examination of solid state systems, including microscopic molecular crystals.

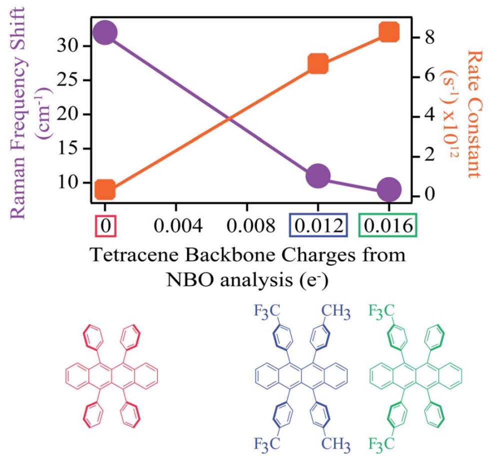

Figure 1. **FSRS-guided synthetic design of singlet fission chromophores**. Using insights from our FSRS studies on rubrene (red molecule), we hypothesized that a reduction in electron density in the tetracene core would facilitate singlet fission. Newly synthesized derivatives (blue and green molecules) proved this hypothesis, correlating both the degree of structural rearrangement and the triplet separation rate constant with the tetracene electron density. ***Chem. Sci.***, 2021,**12**, 13825-13835

A portion of our studies have focused on understanding and optimizing singlet fission processes. In our latest work, we use insights gained from FSRS to guide the design of molecular modifications for improved rates and yields of singlet fission. This work builds off of our 2018 paper which used FSRS to track singlet fission in crystalline rubrene. In that work, we found that triplet separation involves a loss of electron density in the tetracene core. With those spectroscopic insights in hand, we hypothesized that rubrene derivatives which have electron withdrawing substituents on the outer rings would more readily undergo triplet separation. In collaboration with synthetic chemist Christopher Douglas, we made a series of rubrene derivatives which had reduced electron density on the tetracene portion (Figure 1). Using only those with orthorhombic packing, we then used FSRS to monitor the rate of singlet fission as well structural changes occurring during the triplet separation process. Impressively, we found that the optimized derivatives lost significantly less energy to structural reorganization, and experienced nearly an order of magnitude improvement in singlet fission yields. Overall, this work points to the value of spectroscopy-guided synthesis, showing that time-resolved Raman measurements can clearly identify structural changes which improve the photochemical reactivity.

Additional recent DOE-funded work in our group has included the vibrational contributions mediating transitions between chiral and achiral excitons (JPCC 2021), identification of vibrations driving exciton transport (JPCL 2020), as well as the development of a new method which uses coherent control methods to screen functional from spectator vibronic coherences (JPCL 2020).

Probing the Effects of Electronic-Vibrational Resonance on the Rate of Excited-State Energy Transfer in Bacteriochlorin Dyads

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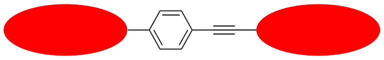
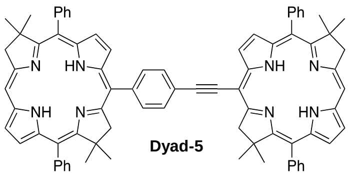
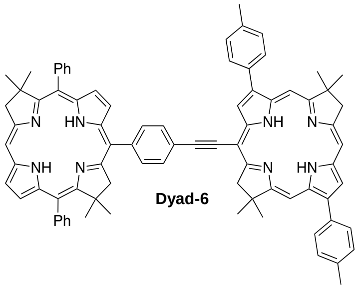
Questions of fundamental importance have been raised in the recent years concerning the extent to which energy (and electron) transfer processes in photosynthetic systems may be enhanced by electronic-vibrational coherent phenomena. Attempts to address such phenomena in the natural systems are often confounded by the inherent complexity wherein large numbers of chromophores are present encompassing diverse 3-dimensional arrangements. Such systems remain largely unmalleable at least with the molecular specificity required for incisive probing. Therefore, we have synthesized and characterized a set of nine bacteriochlorin dyads that employ a phenylethyne linker. A generic structure and three such dyads that utilize the same energy donor (connected to the phenyl of the linker) are shown at the right. A key feature is the tuning of the position of the $S_0 \rightarrow S_1$ absorption band, and the associated $S_1 \rightarrow S_0$ fluorescence band, of the respective donors and acceptors (below left). The donor-acceptor excited-state energy difference has been stepped in relatively small increments from ~180 cm^{-1} (**Dyad-1**) to ~1100 cm^{-1} (**Dyad-9**) by modifying substituents on the bacteriochlorin units. The fine-tuning of the energy gap affords a high probability of hitting a resonance, $\Delta E_{\text{electronic}} = E_{\text{vibration}}$, at which the rate could be potentially enhanced by coherence.

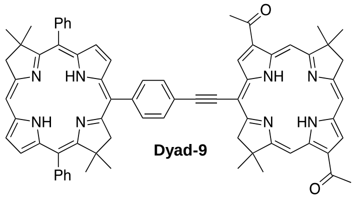




Dyad-5

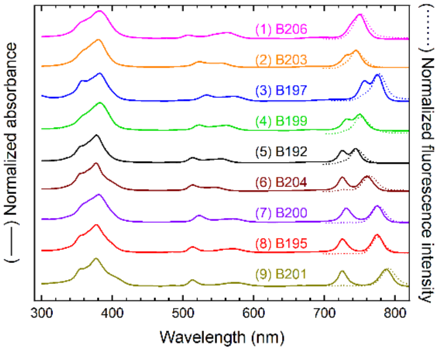


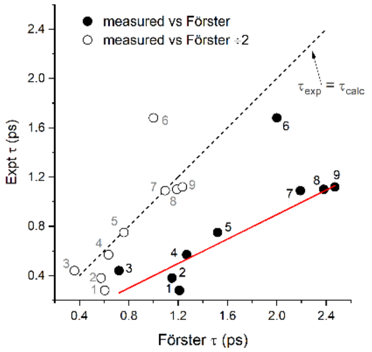
Dyad-6



Dyad-9

Ultrafast excited-state energy transfer is observed in the dyads, with rate constants of (0.3 ps)$^{-1}$ to (1.7 ps)$^{-1}$. The difference in rate among dyads is consistent with prediction using Förster theory within a factor of two (solid symbols, figure at the right). In fact, for most dyads there is a match between measured and calculated rates if the Förster rates are increased by a factor of two, which may reflect limitations of the dipole-dipole approximation at the distances involved (open symbols, figure at the right). Thus, if electronic-vibrational coherences occur in these dyads, the impact on the energy transfer rate is minimal.





Mechanistic Investigations of Charge Separated States in Metal Organic Frameworks and their Catalytic Relevance

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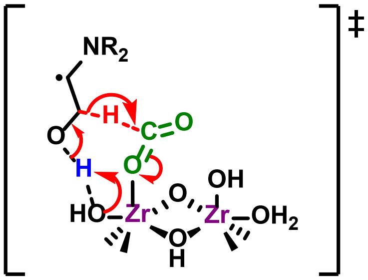
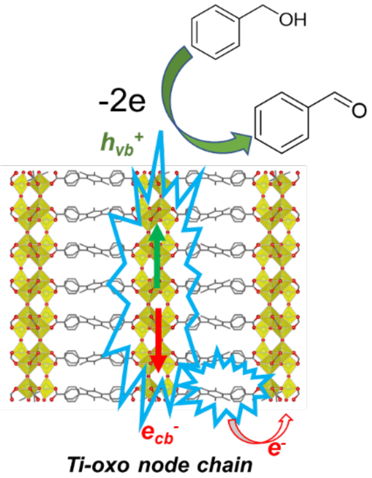
Photoactive metal organic frameworks (MOFs) have been employed in a wide range of chemistries, including water oxidation, carbon dioxide reduction, and proton reduction. In many of the putative mechanisms reported, the critical step is the formation of a charge separated state between a photoactive linker and a structural node. In this flash talk, we determine the role of charge separated states in two classes of MOFs – one that features a Ti-oxo chains, and one based on Zr-oxo clusters. We employ steady-state absorption spectroscopy, photoluminescence spectroscopy, electron paramagnetic resonance spectroscopy, and transient absorption spectroscopy (nano- and femto-second) to determine the relevant excited states.



First, the work uncovers a new role for triethanolamine (TEOA) on the mechanism of photochemical CO_2 reduction by the Zr-based porphyrinic framework, PCN-222. Linked together by the photosensitizer tetrakis(carboxyphenyl)porphine (TCPP), the Zr-oxide nodes of PCN-222 putatively serve as the catalytically active sites for reducing CO_2 to formate at enhanced yields compared to TCPP and TEOA in solution. Prior research attributes the enhanced visible-light photocatalytic activity in PCN-222 to electron injection into the Zr-node, with TEOA quenching a radical cation formed on TCPP. Yet, the Zr-oxide clusters behave like bulk ZrO_2, and electron injection from the TCPP LUMO into the Zr-node conduction band is too energetically uphill to be feasible. From our experimental and computational measurements, we provide a plausible mechanism that CO_2 reduction by PCN-222 arises from the presence of TEOA radicals actively reducing CO_2 bound to open-metal sites, rather than from a reduced Zr^{3+} species resulting from electron injection into the node. The research highlights the potential pitfalls associated with using SEDs in MOF-based photocatalysis and beyond, as they may aid the catalytic cycle in more ways than intended.



Second, we determine the role of co-excitation – node and linker – on catalytic oxidation and reduction by a series of Ti-MOFs. The MOF features Ti-oxo chains bridged by dimethyl-terphenyl linkers and exhibits absorption at wavelengths < 400 nm with linker absorption features < 310 nm. MOF excitation with 355 nm light results in pure Ti-oxo chain photochemistry like Ti-clusters and TiO_2, whereas excitation with 280 nm (ns) or 267 nm (fs) results in both direct Ti-oxo photochemistry and ligand photoexcitation. There is evidence for the radical cation of the linker, resulting from a putative electron or hole transfer to the node. The lifetime of the charge-separated state is short in comparison to the generation of trapped electrons-holes on the titanium clusters (2 μs vs. 20 μs).

Imine Reversal Mediates Charge Separation and CO_2 Photoreduction in Covalent Organic Frameworks

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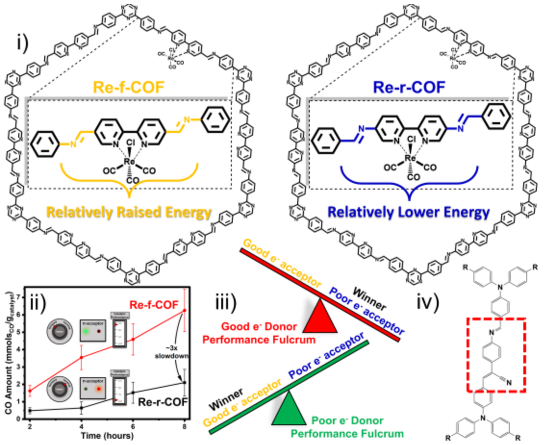
Working towards economical solar-driven CO_2 photoreduction for greenhouse remediation necessitates replacement of expensive reaction components like the sacrificial electron donor triethanolamine (TEOA) with ones that are abundant and easily accessible like water (H_2O). TEOA works very well alongside a Re molecular catalyst (MC) embedded into covalent organic framework (Re-COF) because its reduction potential allows facile electron donation to Re MC, and its oxidized form is advantageously stable. Therefore, while replacing TEOA is highly desirable it is not easily accomplished. One step we have taken towards TEOA replacement is to precisely alter the oxidation and reduction potentials of Re-COF by a straightforward, yet subtle reversal of the imine bond used to link COF monomers together. Our hope is that this bond can serve as a crucial tool to make H_2O a potentially suitable electron donor which could eventually make solar-driven CO_2 photoreduction economically feasible.

In this presentation, I will share some of our latest findings about fundamentals we've uncovered regarding how imine reversal mediates charge separation (CS) in Re-COF, and how mediated CS deleteriously affects CO_2 photoreduction. Diving into the electronic and energetic effects at the heart of this mediation phenomenon reveals that imine reversal from Re-COF with forward imine (Re-f-COF) to Re-COF with reverse imine (Re-r-COF) widens the energy gap between Re MC and COF, leading to lower affinity between the two. Lowered affinity in Re-r-COF manifests as poor π-electron accepting abilities of the bipyridine embedding site which is observed by XAFS and FTIR. Another result of the lowered affinity in Re-r-COF is rapid charge recombination in Re-r-COF compared to the long-lived CS state in Re-f-COF. Altogether, imine reversal in Re-r-COF hinders CO_2 photoreduction performance, but the essential insight we take from this work can guide the design of COF in the future. Finally, I will present future directions of our work and how we plan to take inspiration from our recent publication to exploit CS mediation to increase the efficiency of a newly designed Re-COF and the nuances we expect to encounter in the relationship between CS mediation and donor/acceptor architecture. We will also attempt to introduce asymmetric monomers into the COF structure, thereby opening sites with distinct redox potentials where one may be suitable towards water oxidation, and the other towards CO_2 reduction.



Figures i) Diagram showing Re-f-COF and Re-r-COF and the general principle behind the difference in their catalytic performance. ii) Catalytic performance of Re-f-COF vs Re-r-COF. iii) Scheme showing the general principle behind the future direction for Re-COF. iv) Design scheme for incorporating asymmetric monomer into COF.

Single-Atom Metal Oxide Sites as Traps for Charge Separation in the Zirconium-Based Metal–Organic Framework NDC–NU-1000

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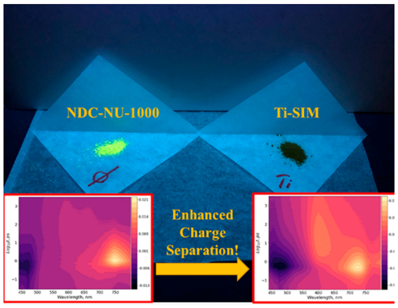
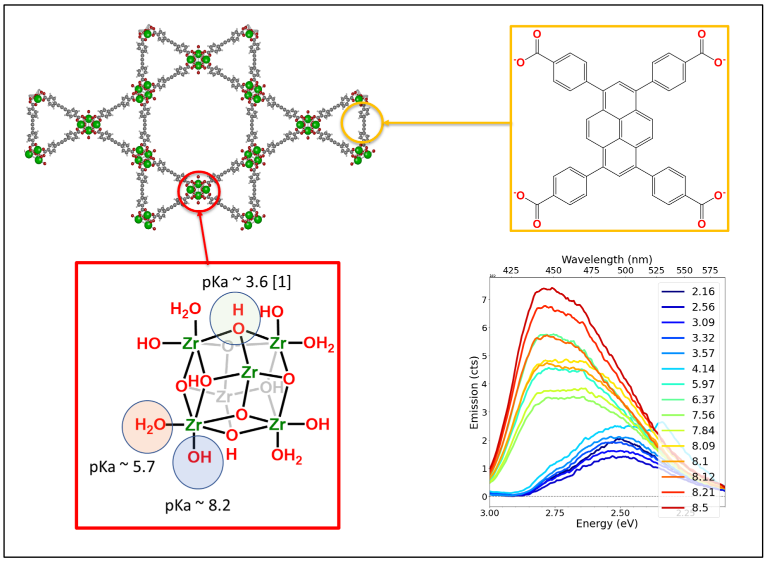
Solvothermal installation in metal–organic frameworks (MOFs) can be used to mount single-metal-atom catalytic species at chemically reactive sites on hexa-Zr(IV)–oxy nodes in nanoscale crystallites of the MOF NDC–NU-1000 in a self-limiting fashion. Upon photoexcitation of the pyrene-based chromophores of the parent framework, charge transfer may occur between the chromophores and the installed heterometal sites. Extended X-ray absorption fine structure studies revealed the single-atom nature of the installed species. We used a combination of steady-state and ultrafast optical spectroscopy to uncover evidence of a charge-separated (CS) state arising in each metalated samples. The relevant dynamics were characterized with transient photoluminescence and femtosecond transient absorption spectroscopy. We find that a titanium-oxy single-metal-atom site gives rise to the longest-lived CS species. This study provides guidance in designing MOF-based catalytic systems for photocatalysis and solar fuel production.



Kramer*, et al.*, *Energy & Fuels*, **2021**, *35*, 19085-19091

Our next steps, aimed at understanding *proton-coupled*-electron transfer, with MOF-immobilized single-metal-atoms as acceptors, yielded, via acceptor-free control experiments, unexpected results that unveil extraordinary photophysical complexity for the framework itself. Briefly, the character of the emissive photo-excited state displays high sensitivity to the extent of protonation of nominally electronically inert MOF nodes, as well as striking H/D isotope effects. Collaborative computational work with our NU colleague, Prof. Roel Tempelaar, implicates previously unrecognized hole-transfer phenomena in both the local photophysics and in the rapid exciton-transport behavior that renders the framework effective as an antenna. The importance of this work may be in helping us understand how to make the leap from antenna-like light-harvesting systems involving ~300 chromophoric MOF linkers to ones involving a few thousand chromophoric linkers. A poster presentation will extend to photocatalysis.



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

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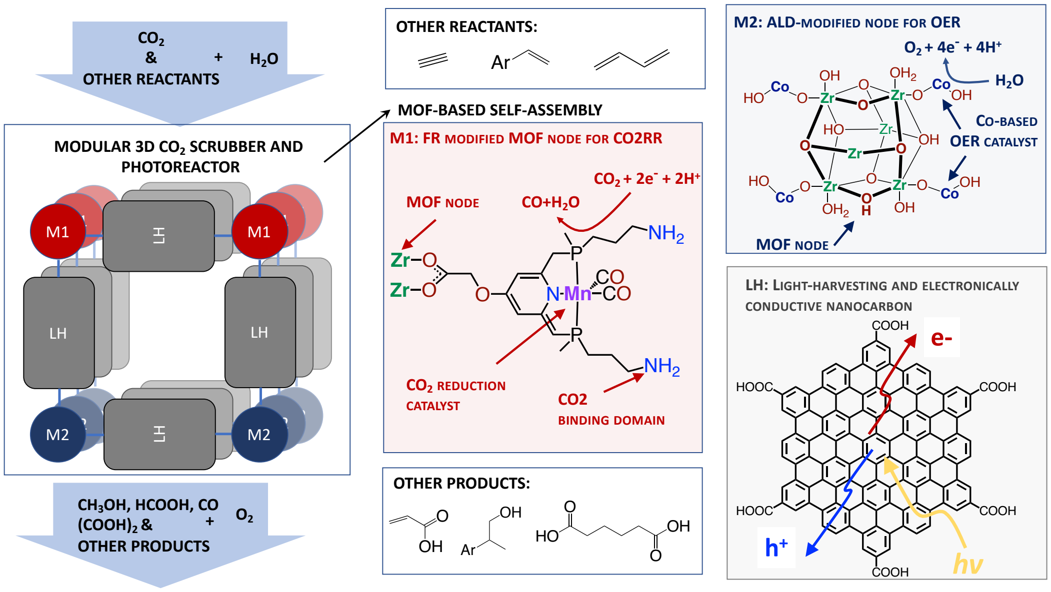
Carbon dioxide is an abundant and inexpensive reagent that, if captured from the air, can serve as a source of value-added chemicals. However, efficient approaches toward direct-air capture (DAC) of CO_2 rely on the formation of strong chemical bonds with the capturing reagent, which require prohibitively 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 formate ion or methanol, using visible light as an energy input.



Here, we report our recent findings on photo-reactive CO_2 capture: (i) the mechanism of photochemical CO_2 reduction by metal-organic frameworks (MOFs) composed of Zr-nodes and nanocarbon ligands was investigated using a combination of spectroscopic and computational studies. Our results reveal the role of biexcitons in the photochemical reduction of catalytic Zr-nodes; (ii) A novel approach to reactive CO_2 capture has been explored: the insertion of CO_2 into metal-hydride bonds to generate formate adducts. Using a MOF material modified with Ru- and Co-based hydrides, we investigate the efficiency of such reactive CO_2 capture; (iii) novel Co-based electrocatalysts for reduction of CO_2 and carbamates have been discovered and the effect of the secondary coordination sphere on the catalytic activity and product selectivity are being explored. (iv) Combined CO_2 capture and thermal hydrogenation has been explored using catalysts composed of amine-based capture groups and transition-metal based hydrogenation catalysts. The product selectivity and efficiency are affected by the presence of the capturing groups.

PCET in Grotthuss-Type Proton Wires – Thermodynamics, Dynamics and Biohybrids

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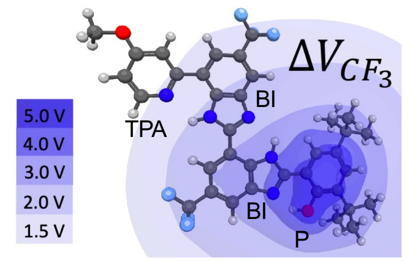
Oxidation of the phenol (P) in the construct shown in the Figure drives a multi proton-coupled electron transfer (MPCET) process whereby protons translocate between P and the terminal proton acceptor (TPA) by a Grotthuss-type mechanism along a hydrogen-bonded network of concatenated benzimidazoles (BIs). Unfortunately, E_{mid} of P decreases 60 mV per BI, jeopardizing its role in water oxidation.[1] But, because the BIs are non-innocent participants in MPCET,[2,3] E_{mid} of P can be increased by substituting the BIs with electron-withdrawing groups (EWGs) such as CF_3, reducing the drop to 20 mV per substituted BI. Theory indicates the molecular electrostatic potential (MEP) induced by the electrochemical oxidation is centered around P and includes the TPA (see Figure). The difference in MEPSs between the unsubstituted and substituted proton wires provides insight into how the CF_3 groups alter the induced electric field responsible for the MPCET.



Change in the molecular electrostatic potential upon oxidation of the phenol

Using two-dimensional electronic-vibrational spectroscopy and a high potential porphyrin linked to a BIP having a pyridine derivative TPA, we explored the dynamics of photoinduced one-electron, two-proton transfer processes. We found that following porphyrin excitation, proton arrival on the TPA and electron arrival on the porphyrin are concerted to within 24 femtoseconds. The analysis revealed a low-frequency mode that strongly couples nuclear and electronic degrees of freedom.[4]

Initiating our study of model PCET in protein environments, a hybrid construct consisting of a four-helix bundle enclosing a Mn-porphyrin (MnIII-Por) docked to a high potential bacterial reaction center (BRC) was assembled. Exciting the BRC at 865 nm reversibly reduces MnIII-Por to MnII-Por, demonstrating that the BRC communicates in a redox process with the Mn-porphyrin.[5] This is an unexpected but promising result; it foretells hybrid artificial photosynthetic constructs in which energy-conserving processes could be reengineered and optimized.

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. Sci.* **2020**, *11*, 3820-3828.
3. Odella, E., *et al.*, "Multi PCET in symmetrically substituted benzimidazoles." *Chem. Sci.* **2021**, *12*, 12667-12675.
4. *Manuscript under revision.*
5. *Manuscript in preparation.*

Electron Transfer in Ionic Liquids and Electron-Induced Proton Transfer

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Experiments to measure charge-transfer optical bands in room-temperature ionic liquids (ILs) were performed and used to extract reorganization energy of electron transfer [1]. Remarkably, the reorganization energies in ILs are close to those in cyclohexane. This result runs against common wisdom in the field since conducting ILs, characterized by an infinite static dielectric constant, and nonpolar cyclohexane fall to the opposite ends of the polarity scale based on their dielectric constants. Theoretical calculations employing structure factors of ILs from molecular dynamics simulations support low values of the reorganization energy. Standard dielectric arguments do not apply to solvation in ILs and nonergodic reorganization energies are required for a quantitative analysis.

We have developed a new mechanism for activationless proton transfer induced by an electron transfer reaction [2]. Long-range electron transfer produces a highly nonequilibrium medium polarization that can drive proton transfer in the course of thermalization dynamically altering the Coulomb electron-proton screening. The cross electron-proton reorganization energy was defined as the main energetic parameter of the theory. It exceeds in magnitude the proton-transfer reorganization energy roughly by the ratio of the electron-transfer to proton-transfer distance. This parameter can be either positive or negative and is related to the difference in pKa values in two electron-transfer states. Nonequilibrium medium configuration promoting proton transfer can be induced by either thermal or photoinduced charge transfer.

[1] G. Kodis, M. Ertem, M. Newton[1], and D. V. Matyushov, Reorganization energy of electron transfer in ionic liquids, J. Phys. Chem. Lett. **13** (2022) 3297.

[2] D. V. Matyushov and M. Newton, Electron-induced proton transfer, J. Phys. Chem. B **125** (2021) 12264.

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.

We have been keenly interested in improving proton reduction yields by accelerating hole transfer from QDs, which is a major fundamental obstacle. Rapid hole transfer has typically required the *ex situ* functionalization of hole acceptors with groups that can coordinate to the surface of the QD. In addition to being synthetically limiting, this strategy also necessitates a competitive binding equilibrium between the hole acceptor and native, solubilizing ligands on the nanocrystal. Recently, we have been exploring how polyoxovanadate (POV)-alkoxide clusters can act as redox mediators to remove photogenerated holes from CdSe QDs. In particular, we discovered that incorporation of oxygen-vacancies in polyoxovanadate-alkoxide clusters drastically improves hole transfer efficiency by enabling surface coordination of the metal oxide assembly to the QD. Remarkably, we found that the oxygen deficient cluster quenches the fluorescence of the QDs at near-unity efficiency; upon addition of 0.5 equivalents of cluster the photoluminescence intensity is reduced by 49%, indicating that nearly every added cluster quenches a corresponding QD (Figure 1). Investigating the reactivity of oxygen-deficient clusters with phosphonate-capped QDs reveals irreversible complexation of the POV-alkoxide with a ligand at the nanocrystal surface, while sterically preventing access to the oxygen vacancy site prevented complexation (Figure 1, blue curve). These findings reveal a new method of facilitating QD-hole acceptor association that bypasses the restrictions of exchange interactions.

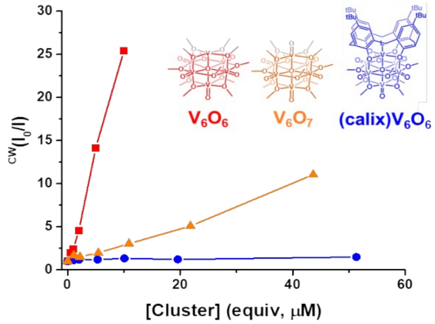

Figure 1: Stern-Volmer plots for $V_6O_6^{-1}$ (red), $V_6O_7^{-1}$ (orange), and (calix)$V_6O_6^{-1}$ (blue) polyoxovanadate-alkoxide clusters.

We also characterized two new systems using cobalt porphyrin-based semisynthetic and synthetic biomolecular catalysts for light-driven hydrogen evolution. We found overall excellent activity, even when using organic dyes as photosensitizers, and determined that the lifetime of these systems is limited by the molecular photosensitizer rather than the catalysts. These results provide fundamental insights into how charge transfer mechanisms and catalyst properties impact photocatalytic system activity and longevity and suggest that pairing these robust and active catalysts with QDs may yield long-lasting systems for light-driven hydrogen production. Accordingly, we observe long-lived (> 1 week) H_2 production when pairing CdSe QDs with the biocatalysts, but with system activity dependent on QD capping ligand in a way that points to the importance of electrostatic interactions in the catalyst-QD interaction.

Mechanism of Photochemical N_2 Reduction

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This research program focuses on the mechanism of photochemical dinitrogen (N_2) reduction to ammonia (NH_3) in a nanocrystal-nitrogenase complex (Figure 1). Activation and reduction of dinitrogen is one of the most energy demanding and difficult chemical reactions. The enzyme nitrogenase catalyzes the reaction by coupling ATP hydrolysis by the Fe protein to drive the sequential delivery of electrons to the catalytic MoFe protein. Nanocrystalline materials are used to photochemically activate electron transfer directly to MoFe protein, circumventing the requirement for ATP-dependent electron transfer by the nitrogenase Fe protein.

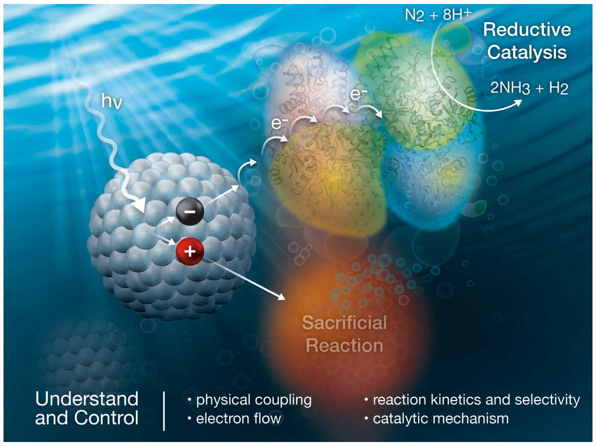

Figure 1. CdS quantum dot (sphere) nitrogenase MoFe protein (blue-green) complex. Photon absorption by QD generates a photoexcited electron-hole pair, electron transfer to MoFe protein catalyzes reduction of N_2 to NH_3 and H_2.

Tunable light-harvesting and photochemical properties of nanocrystals allow the analysis of how nitrogenase couples electrons to N_2 reduction chemistry at the catalytic site. The binding and molecular interactions between nanocrystals and MoFe protein and selective design of binding sites is enabling an understanding of how molecular assembly and binding orientations, along with relative positions of the catalytic metal clusters and nanocrystals control interfacial electron transfer. Light initiated electron transfer into nitrogenase and overcoming the need for Fe protein dependent catalysis has a profound impact for the study of the mechanism of nitrogenase catalyzed N_2 reduction and supports synchronous control of catalysis. This ability overcomes technical barriers of enabling the population of reaction intermediates, previously inaccessible, providing new insights into unresolved aspects of the chemical mechanism. The outcome addresses understanding of nanocrystal photocatalysis, determinants of interfacial electron transfer, and the mechanism of nitrogenase catalyzed N_2 reduction in a framework where alternative energy production can be realized.

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2. Badalyan, A., et al. 2022. “Tailoring Electron Transfer Pathway for Photocatalytic N_2-to-NH_3 Reduction in a CdS Quantum Dots-Nitrogenase System.” *Sustain. Ener. Fuels*. DOI: 10.1039/d2se00148a.

Design of CdS Quantum Dot (QD) Ligand Shell Promotes the Photo-oxidation Step for the Methane-to-Methanol Conversion in Water

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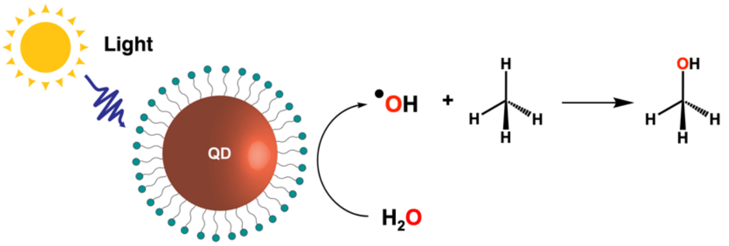
Methane (CH_4) is the principal component of natural gas, and it is responsible for 20% of anthropogenic global warming. CH_4 is stubbornly inert such that its transformations are hard to control. Under conditions where the reaction of CH_4 is fast enough to be of interest (typically > 700 °C), the formation of CO_2 is so favorable ($\Delta H° \sim -800$ kJ mol^{-1}) that the production of useful chemicals, such as methanol, is not economically feasible. In contrast to conventional industrial methane transformation processes, which rely on high temperatures, we propose to perform this reaction at room-temperature by accessing the electronic excited states of the reagents with photons using metal-chalcogenide CdS quantum dot (QD) photocatalysts. Direct photoexcitation or photoionization of CH_4 using QD photocatalysts to achieve H-atom abstraction is not possible – the first electronic absorption band is <140 nm, and photoionization requires 98 nm light. We aim, instead, to indirectly photoactivate methane by using CdS QDs to photo-oxidize water to produce hydroxide radicals, which are capable of performing H-atom abstraction from CH_4.



The oxidation of water to form hydroxyl radicals is energetically demanding – $E^0(H_2O/OH\cdot) = +2.31$ V vs. NHE at pH 7 – but can be accomplished using CdS QDs ($E^0(QD/QD^+) = +2.2 - 2.5$ V vs. NHE) in aqueous solutions. Modification of the QD ligand shell enables us to tune the reaction medium and the affinity for substrates. Exchanging the native hydrophobic ligands of the QDs with hydrophilic ligands enables aqueous solubility, but these hydrophilic ligands must also provide colloidal stability (for at least the duration of illumination) and prevent agglomeration. Conventional methods of achieving water-solubility with QDs relies on the use of tight-binding, hydrophilic thiolate ligands. While thiolate ligands provide excellent colloidal stability, they are also known to introduce mid band-gap trap states for photogenerated holes, impeding the mobility of these charge carriers. Consequently, it is necessary to move to thiolate-free, weak-to-intermediate binding ligands for aqueous QD catalysis. Previous work in our group has demonstrated the utility of sulfur-free weak-to-intermediate binding ligands, such as phosphonopropionic acid and aminoethyl phosphonic acid for aqueous solubilization of metal-chalcogenide QDs. Here, we demonstrate that these ligands enhance the photo-oxidation of water to form hydroxyl radicals. In general, designing a system to perform water oxidation for the generation of hydroxyl radicals, which are potent oxidizing species, must consider a trade-off between long-term colloidal stability and charge carrier mobility in aqueous solutions.

Controlling Optoelectronic Properties of 2D Transition Metal Dichalcogenides

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Transition metal dichalcogenides (TMDCs) are an important class of materials because they can be reduced to two dimensional (2D), where their quantum confined properties are easily manipulated for various applications, such as catalysis, sensors, photovoltaics, and batteries. Here, we present on two different monolayer TMDCs: molybdenum disulfide (MoS_2) and tungsten disulfide (WS_2). For the monolayer MoS_2, our results provide a simple surface functionalization technique that will allow these monolayers to be incorporated into air-exposed devices. 2D MoS_2 can be converted between the semiconducting (2H) and metallic/semi-metallic (1T/1T') phases or heavily n-type doped 2H phase with ion intercalation, strain, or excess negative charge. Using *n*-butyl lithium (BuLi) immersion treatments, we achieve 2H MoS_2 monolayers that are heavily n-type doped with shorter immersion times or conversion to the 1T/1T' phase with longer immersion times; however, these doped/converted monolayers are not stable in air. To overcome this issue, we use BuLi treatments plus surface functionalization p-$(CH_3CH_2)_2NPh$-MoS_2 (Et_2N-MoS_2)—to maintain heavily n-type doped 2H phase or the 1T/1T' phase, which is preserved for over two weeks.

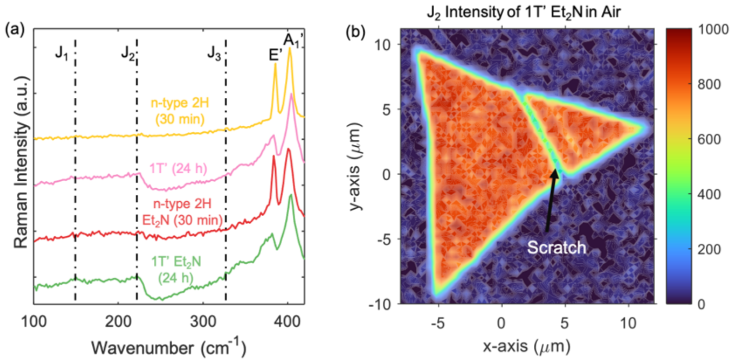

Figure 1. (a) Raman spectra of MoS_2 monolayers immersed for different times in n-butyl lithium. (b) Raman mapping of the J_2 mode (~225 cm^{-1}) intensity extracted from 1T' Et_2N MoS_2 measured in air. Ref 1.

In another study, monolayer WS_2 optoelectronic properties are influenced by surface photoreactions.[2] By performing control experiments, where the pristine WS_2 is exposed to N_2 only, dry air (O_2 rich), and humidified N_2 (H_2O rich), we can probe the changes in optoelectronic properties and specifically WS_2 photoluminescence (PL) and photoconductivity. In our studies, O_2 + illumination yields a WS_2 photoluminescence (PL) increase and red shift that is due to increased trion (X^-) emission, whereas H_2O + illumination results in an overall PL increase that is dominated by exciton (X^0) emission. The WS_2 photoconductance is anti-correlated with the PL intensity; and, in a O_2 or H_2O vapor environment, WS_2 photoconductance decreases. By analyzing the photoluminescence (PL) in these different environments, we demonstrated a contactless, relative humidity sensor using WS_2 monolayers.

[1] *2D Mater.* **9,** 015033 (2022) **DOI**:10.1088/2053-1583/ac3f44
[2] *Nanoscale* **12**, 8344 (2020) **DOI**: 10.1039/c9nr09326e

Theoretical Investigation into Reductant-Activated Covalent Surface Functionalization of MoS_2 and its Applications in Organic Vapor Sensing

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Reductant-activated surface functionalization has enabled enhanced methylation of chemically exfoliated MoS_2 (*ce*MoS_2) by introducing excess negative charge to facilitate nucleophilic attack toward methyl halides (Figure 1a). Using one-electron donors, methylation of *ce*MoS_2 results in a two-fold increase in coverage per MoS_2 relative to the reaction in the absence of reductant, from ~40% to ~70% coverage per MoS_2. Using Grand Canonical Quantum Mechanics (GC-QM), we have elucidated several factors governing reductant-activated surface functionalization that can explain this coverage limitation at 70% even with the use of stronger reductants. Theoretical calculations demonstrated that the free energy (ΔG) and free energy barrier ($\Delta G^{\ddagger}$) increased as the electrochemical potential became more reducing and that these energies were less favorable for methylation at half of the sulfurs with shorter Mo–S bonds "high-S" compared to functionalization at other sulfur sites "low-S" at constant potential. Additionally, ΔG was generally more favorable for methylation of sulfur sites with no adjacent methyl groups compared to sites with 1 or more adjacent groups. Random surface functionalization simulations based on these observations predicted that methylation at low-S sites with no adjacent groups resulted in coverages of ~44% per MoS_2, while functionalization at sulfur sites with no more than one adjacent group at the time of reaction resulted in coverages of 75% per MoS_2, showing good agreement with experiment data.

We have applied this reductant-activated surface modification method to generate covalently functionalized MoS_2 chemiresistors that enable organic vapor sensing with high sensitivity for polar and non-polar volatile organic compounds (VOCs). These sensors were an order of magnitude more sensitive than similar devices based on carbon black or metal nanoparticles, with sensitivity (S_R) values above 10 for most analytes. A dependance of S_R on the Hammett parameters of functional groups was observed, indicating that electronic effects, rather than polarity, dominated sensor-analyte interactions (Figure 1b). Functionalized sensors exhibited good stability, retaining 70% of initial responsiveness after 72 and 100 h analyte exposures.

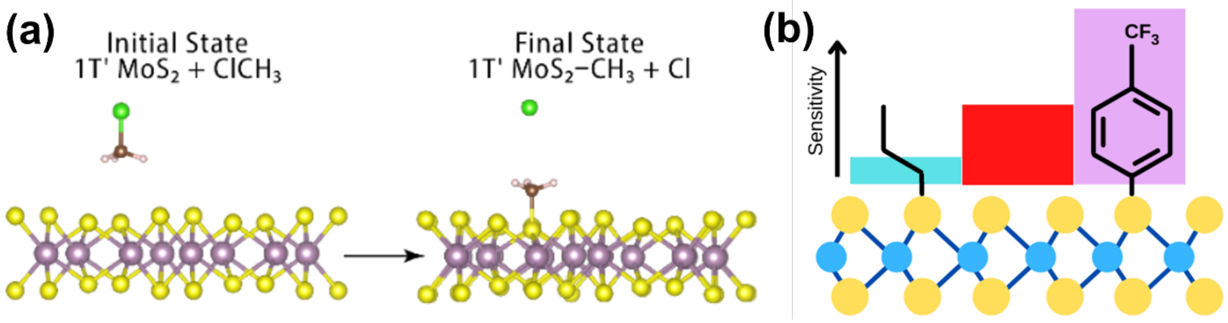

Figure 1. (a) Reaction scheme for the *ce*MoS_2 methylation reaction investigated using GC-QM (green = Cl, purple = Mo, brown = C, white = H, yellow = S). (b) Sensitivity toward for VOCs was a correlated with the functional group used to derivatize the MoS_2 surface.

Liquid Sunlight Alliance (LiSA)

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The Liquid Sunlight Alliance (LiSA) is working to establish the science principles by which assemblies of microenvironments can directly generate liquid fuels from sunlight, water, carbon dioxide and nitrogen. LiSA is addressing the liquid solar fuels challenges of performance and durability by developing the science needed to create microenvironments and assemble them into solar fuels systems. This requires understanding and control of the complex interplay of sequential or coupled transfers of multiple photons, electrons, protons, and reactants. This approach enables the coupling of microenvironments to achieve more complex products by CO_2 reduction (CO_2R) via creating, for example, gradients in CO_2 concentration and pH from the fluxes of protons, electrons, reactants, and intermediates, thereby setting up sequential catalytic steps and tailoring the chemical landscape for each step. The coupling of microenvironments raises intriguing scientific questions both about microenvironment design itself and the interactions and compatibilities required to create, assemble, and couple systems of microenvironments.

In its second year of operation, LiSA is completing Phase I of its three project phases, which has focused on design of components and microenvironments, and on science advances that facilitate coupling in tandem or cascade reactions to enable multicarbon product generation from CO_2.

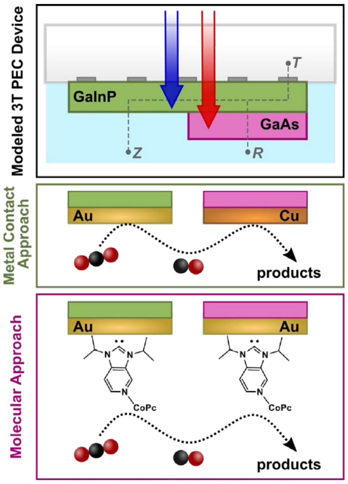

Figure 1. *Schematic 3 terminal tandem photoelectrode for CO_2R cascades. Top: schematic of contacts (T,R,Z). Middle: metal solution contacts; Bottom: molecular catalysts.*

In the first phase, LiSA researchers have laid the foundation for photo-driven systems and microenvironment designs. The scientific strategy includes developing systems and microenvironment concepts for effective tandem photocatalysis, including techniques for independently controlling current and potential at the electrode, as depicted in Fig. 1. Several applications of organic (photo)electrode coatings have been evaluated for their ability to steer selectivity and modify the reactivity of multielement catalysts. To characterize local water ion availability for CO_2 reduction, the team has examined water dissociation in the electrolyte, key to providing protons for the reduction reaction, and has developed techniques for monitoring pH in the catalytic microenvironment.

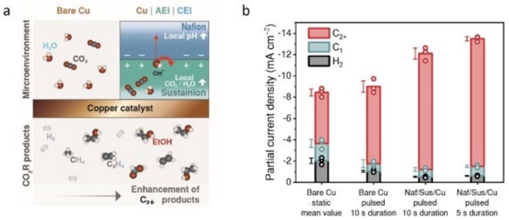

***Figure 2**. (a) Schematic illustration of tailored microenvironments near Cu CO2RR catalyst using bilayer ionomer coatings. (b) product distributions using bilayer ionomer coatings under static and*

During CO_2RR, a homogeneous buffering reaction ($HCO_3^- \leftrightarrow CO_2 + OH^-$) occurring in the microenvironment near a Cu catalyst limits CO_2RR activity at high local pH, and the C_{2+} selectivity at low local pH. To achieve both high local pH and local CO_2 concentrations, by altering the microenvironment near the Cu surface by coating it with thin films (~ 30 nm) of cation- and anion-exchange ionomer (Nafion and Sustainion), this increases both the activity and selectivity for CO_2 conversion to C_{2+} products (Figure 2). This effect results because the inner Sustainion layer has a local ratio of CO_2/H_2O that is 58 times higher than that in the aqueous electrolyte and a high local pH resulting from Donnan exclusion of OH^- by the outer Nafion layer.

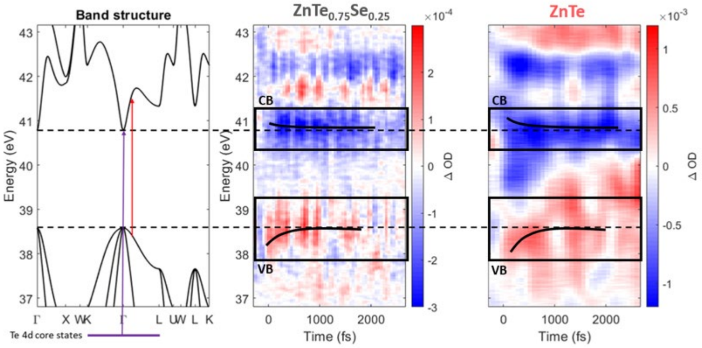

***Figure 3** (left) Band structure of ZnTe. Transient reflectivity spectra at the Te N4,5 absorption edge after photoexcitation with 400 nm pulses for (center) ZnTe0.75Se0.25 and (right) ZnTe thin films.*

In the first phase, LiSA has also focused on understanding carrier dynamics within photocatalysts and across interfaces in their assembled systems, using multiple methods. LiSA-derived new materials such as $CuFeO_2$, ZnTe and $ZnTe_{0.75}Se_{0.25}$ thin films have been characterized for sub-picosecond carrier dynamics at their surface followed by ps carrier thermalization.

Sub-picosecond nonequilibrium electron and hole cooling has been measured in ZnTe thin films (Fig. 3) These measurements of ZnTe were extended to $ZnTe_xSe_{1-x}$ alloys to determine the effects of anionic substitution for II-VI semiconductors on carrier thermalization and recombination dynamics. The experiment probed the surface dynamics of the sample by using reflection sample geometry. The measurements feature femtosecond carrier excitation and thermalization, followed by picosecond carrier decay, related to carrier diffusion or surface recombination. Acoustic phonon oscillations are observed at higher photoexcited carrier densities. These measurements on II-VI semiconductors will form the foundation for future studies of junctions between photoabsorbers and co-catalysts (Au or Pt), where element-specific measurements can reveal interfacial transfer of electrons and/or holes in addition to changes in hot carrier thermalization.

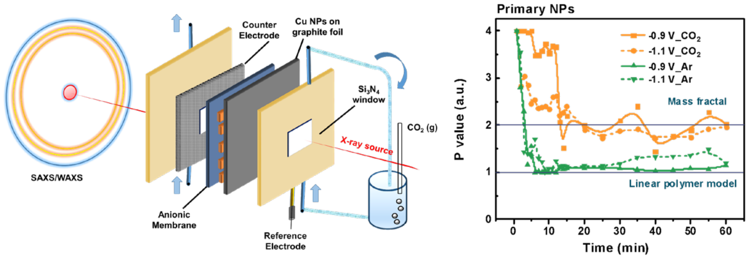

***Figure 4.** Left: Electrochemical cell design for in situ SAXS measurements. Right: Aggregation of Cu nanoparticles under different applied potentials and with CO_2 versus Ar gas sparges. Growth mechanisms and aggregate structures depend greatly on reaction conditions.*

LiSA is working to establish a scientific approach to understanding component durability, with studies aimed at investigating nanoparticle dynamics during electrocatalysis, as well as developing a fundamental understanding of catalyst corrosion. Recent evidence shows that Cu-based CO_2 reduction catalysts undergo significant structural and morphological transformations during operation, which limits durability. By characterizing Cu nanoparticle CO_2 reduction catalysts using *in situ* small angle X-ray scattering (SAXS), one can track size and shape distributions with a time resolution of seconds (Fig. 4). A custom electrochemical cell for SAXS measurements was developed and used to collect data on Cu nanoparticles under different applied potentials during CO_2 reduction, as well as control measurements with Ar gas in place of CO_2. Aggregation behavior that depends strongly on the applied potential is observed.

Understanding and Controlling Charge-Carrier Selectivity at Nanoscale Catalyst/Semiconductor Photochemical Interfaces

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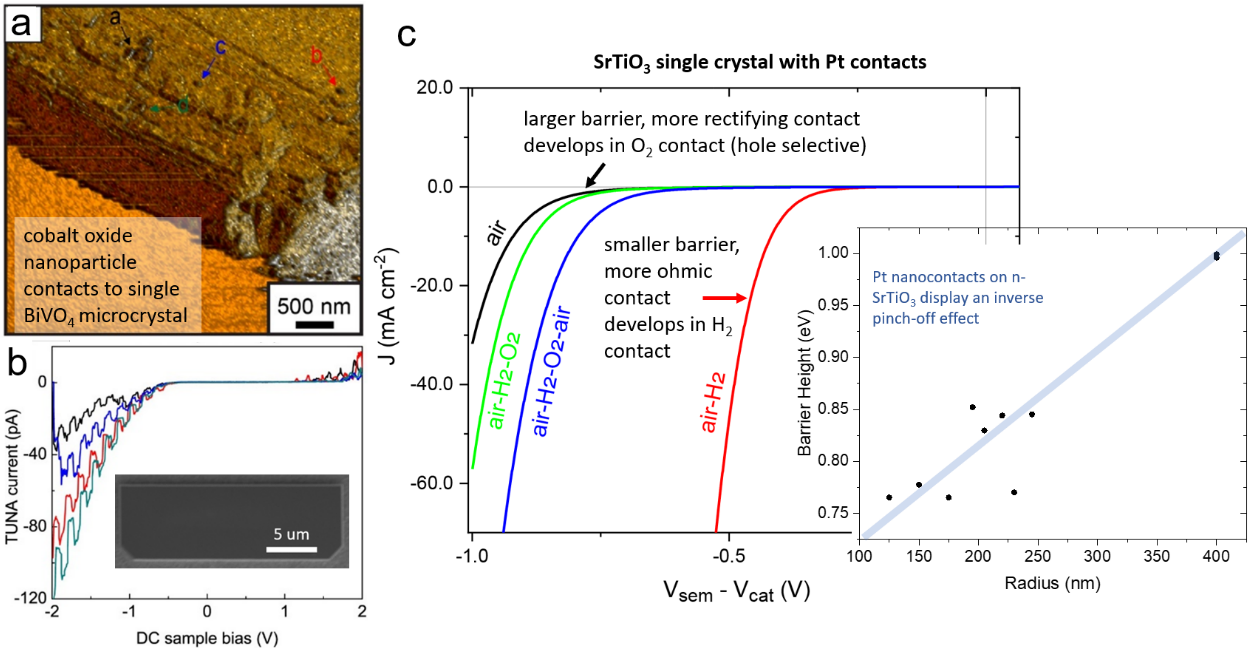
Nanoscale catalyst/semiconductor interfaces are key functional elements in architectures for photoelectrochemical energy conversion and storage. Electrocatalyst nanoparticles, like Pt or CoO_x, are often sparsely deposited onto light-absorbing semiconductor electrodes, or specific facets of particulate systems, so that they selectively collect either electrons or holes, drive fuel-forming reactions (with low free-energy loss), and (ideally) minimally block light. The properties of the resulting semiconductor/catalyst nano-junctions are heterogeneous and vary based on surface chemistry, deposition route, particle size, and/or during operation. These complex nanoscale catalyst/semiconductor interfaces are difficult to characterize electrically, especially under relevant photoelectrochemical conditions. In this presentation, I will report our progress studying nanoscale catalyst contacts to important oxide photoelectrode materials including benchmark $SrTiO_3$ single crystals which show both dynamic and size-dependent contact behavior, and well-defined microcrystals of $BiVO_4$. I will also introduce a new approach to measure charge-carrier selectivity and photovoltage generation using photoelectron spectroscopy without the use of electric connection to semiconductor, oxidation catalyst, or reduction catalyst, which is therefore of use in understanding, and hence controlling performance of, particulate "overall-water-splitting" photocatalyst systems.



Semi-Contactless Measurement of Internal Photovoltage of Solid-Liquid Junctions

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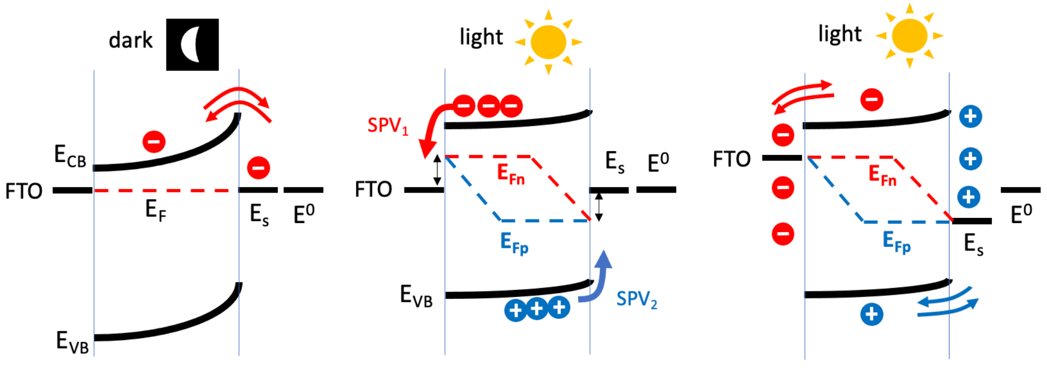
The efficiency of photoelectrochemical systems for the conversion of solar energy into fuel depends on the photovoltage of the underlying solid-liquid junctions. While electrochemical measurements can provide the potential of the majority carriers at the semiconductor back-contact, the internal photovoltage (the quasi-Fermi level splitting) and the electrochemical potential of the minority carriers are difficult to determine experimentally, due to the lack of a direct electrical connection at the front semiconductor/electrolyte interface. Here we show that the internal photovoltage of a solid-liquid junction can be observed in a semi-contactless way with surface photovoltage spectroscopy (SPS). For the measurements, thin semiconductor films ($BiVO_4$ and $CuGaSe_2$ thin films on conductive substrates) or wafers (n-GaP or p-GaP) are electrically grounded, immersed in aqueous electrolyte, covered with a glass cover, and placed underneath a vibrating Kelvin probe. Under these conditions, the observed contact potential difference change ($\Delta CPD = SPV_1 + SPV_2$) under illumination (the surface photovoltage) directly corresponds to the internal photovoltage of the junction (see Figure below). We find that measured photovoltages depend on the semiconductor, the semiconductor back contact (gold/Mo/FTO), the light intensity, and the electrochemical properties of the redox couples (sulfite, tri-iodide/iodide, hexacyanoferrate(II/III), sulfur/sulfide, methylviologen, O_2/H_2O_2). For fast redox couples, ΔCPD values agree well with external photovoltage values (V_{OC} from photoelectrochemistry and open circuit measurements), but for slow redox couples, the ΔCPD signal is often larger than V_{OC}, due to the presence of kinetic overpotentials. In some systems, a correlation between band bending and the ΔCPD signal is seen, while in others the ΔCPD signal and the minority potentials are pinned by surface states. The implications of these findings on the understanding and optimization of solar fuel photoelectrodes will be discussed.



at equilibrium (dark) before equilibrium (light) at equilibrium (light)

Energy diagram showing band edges, electrochemical potentials (E^0 of solution, E_S of surface), and Fermi levels (E_F, E_{Fn}, E_{Fp}) of n-semiconductor liquid junction in the dark and under illumination. The ΔCPD signal is generated by majority and minority carrier transfer under illumination: $SPV_1 = E_{Fn} - E_S$; $SPV_2 = E_S - E_{Fp}$, $\Delta CPD = SPV_1 + SPV_2 = E_{Fn} - E_{Fp}$

Complete Description of the Faradaic and Charging Currents for Redox Adsorbates on Semiconductor Electrodes

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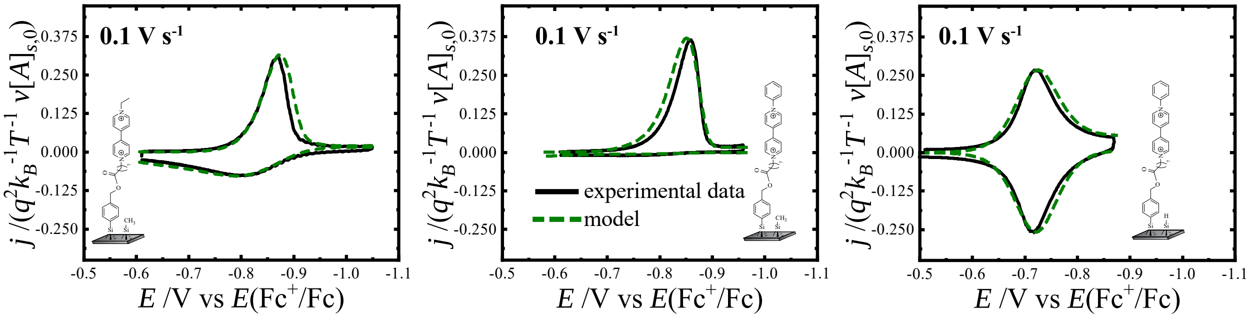

Figure 1. Comparison between (solid black line) experimental and (dashed green line) simulated voltammetric responses for chemisorbed, asymmetric viologens tethered on n-Si(111) electrodes immersed in methanolic 0.1 M $LiClO_4$. All data are normalized by the total adsorbate coverage and scan rate. The asymmetric viologens were attached through an alkyl chain ($n = 7$) terminated with a carboxylic acid that was connected to a surface-grafted benzyl alcohol via an ester-bond linkage. The terminal R group from each asymmetric viologen is shown in the corresponding inset. All data correspond to a scan rate of 0.1 V s^{-1} and the absence of illumination.

The electrochemical transfer of charge between adsorbed molecules and semiconductor electrodes is central to the operation of dye-sensitized solar cells and molecular electrocatalysts in fuel-forming photoelectrochemical systems. Cyclic voltammetry is inarguably the most widely-used electroanalytical method to probe redox adsorbates, but voltammetric charge-transfer rate measurements between molecular adsorbates and semiconductors are rarely, if ever, performed.

We recently developed a 3 layer model to describe charge-transfer reactions of redox adsorbates on semiconductor electrodes. This physical model features a set of analytical expressions that describe the voltammetric responses at any experimental condition, i.e. reversible, quasi-reversible, or irreversible charge-transfer kinetics. In this presentation, we present experimental data using chemisorbed viologens that test this model. Si is a natural choice since there is over 5 decades of documentation on, development of, and refinement in the wet chemistry of Si surfaces. Viologens are separately ideal test molecular adsorbates since they are canonical $1e^-$ outer-sphere redox probes; their standard potentials are easily adjusted over a large range; and their rates of heterogeneous charge transfer with Si when dissolved in solution is well-documented. The reduction of adsorbed viologen dications also has the practical advantage that negative biases naturally protect against Si oxidation, which could further complicate data analysis.

Figure 1 illustrates representative data that will be discussed. In Figure 1, the voltammetric responses as a function of asymmetric viologen type (R = ethyl vs phenyl) and as a function of surface termination (-H vs $-CH_3$) are shown. In each case, the voltammetric shape of the corresponding viologen and surface types are accurately described by the analytical model. These fits do not include any adjustable parameters (i.e. ideality factors) and instead only include physically measureable constants that describe the semiconductor, surface, and electrolyte.

Monitoring Charge Carrier Dynamics and Electrostatic Field Dynamics at Semiconductor-Liquid Interfaces using *in situ* Spectroscopy

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TiO_2-protected semiconductor photoelectrodes show enhanced stability and performance for solar fuels generation, although the mechanism for the performance enhancement remains unclear due to a lack of understanding of the microscopic interfacial field and its effects. Here, we directly probe the interfacial fields at *p*-GaP electrodes protected by *n*-TiO_2 and its effect on charge carriers by transient reflectance spectroscopy. Increasing the TiO_2 layer thickness from 0 to 35 nm increases the field in the GaP depletion region, enhancing the rate and efficiency of interfacial electron transfer from the GaP to TiO_2 on the ps time scale as well as retarding interfacial recombination on the microsecond time scale. This study demonstrates a general method for providing a microscopic view of the photogenerated charge carrier's pathway and loss mechanisms from the bulk of the electrode to the long-lived separated charge at the interface that ultimately drives the photoelectrochemical reactions. (Nano Letters, 21, 8017-8024 (2021))

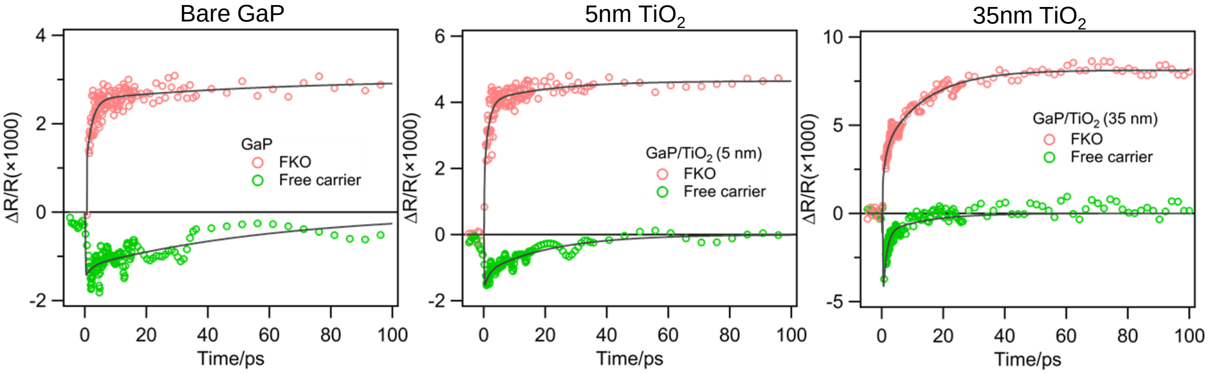

Figure 1. Transient reflection spectra and kinetics of GaP/TiO_2.

In addition to probing electric fields within the solid-state system, we have developed spectroscopic techniques for probing surface reporter molecules in solution at the semiconductor liquid interface. We will present the novel use of surface enhanced Raman scattering (SERS) spectroscopy to detect charge transfer in ferrocene/ferrocenium (Fc/Fc^+) bound to an active electrode under electrochemical working conditions. Here, we utilize ferrocene molecules bonded to Au nanoisland films, which are strongly plasmon resonant and, hence, SERS-active. The electrochemistry of the surface-tethered ferrocene produces Fc/Fc^+ couple voltammograms exhibiting charge transfer above 0.4V vs. Ag/AgCl. In addition, we monitor the charge state oxidation of ferrocenium using *in situ* micro-Raman spectroscopy with a water immersion lens. Upon charge transfer, we observe substantial changes in the Raman intensity and vibrational frequency of the $(C\text{-}H)_{cp}$ in-plane bending mode around 1072cm^{-1} and the C_P-breathing mode around 1104 cm^{-1} of both the neutral ferrocene (Fc) and radical cation ferrocenium ($Fc^{+\cdot}$), which provide direct spectroscopic evidence of charge transfer occurring during the electrochemical process. In particular, the Fc^+ state is characterized by the disappearance of the C_p-breathing mode (1104 cm^{-1} peak) and a 11-fold increase in the $(C\text{-}H)_{cp}$ in-plane bending mode around 1072 cm^{-1}.

The Impact of the Bridging Ligand on Interfacial Electron Transfer

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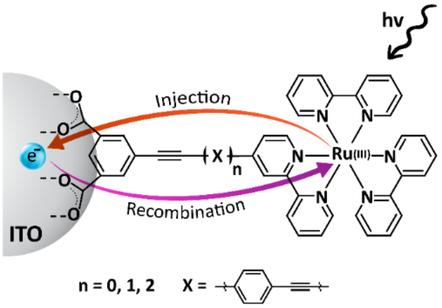
Light initiated electron transfer across the interface between a solid-state material and a molecular acceptor is of central importance to the development of solar energy conversion technologies. For example, semi-conducting metal oxide materials like TiO_2 have been sensitized to visible light with molecular dyes for applications in regenerative and photoelectrosynthetic solar cells.[1] In these applications, a molecular dye or sensitizer, S, absorbs a photon to generate an excited state that transfers an electron to the semiconductor. Ideally, the interfacial charge separated state product undergo subsequent electron transfer reactions to general electrical power or chemical fuels. A kinetically competitive unwanted reaction is recombination of the injected electron with the oxidized sensitizer to yield ground-state products. A successful strategy for inhibiting recombination is to place bridge units between the sensitizer and the surface anchoring groups.[2] Slower recombination with increased distance was often evident; in one particular conjugation of aromatic bridge units was found to change the mechanism from adiabatic to non-adiabatic interfacial electron transfer.[3] However in general, extraction of the fundamental Marcus parameters necessary to model and predict the kinetic behavior were hampered by uncertainties in the energetic position of the conduction band and/or $Ti^{IV/III}$ trap states. In this lightning talk, a kinetic study of three rigid-rod sensitizers linked to the *conductive* oxide tin-doped indium oxide (ITO) will be presented.



The conductive nature of ITO enables the Gibbs free energy change, $-\Delta G°$, for electron transfer to be systematically tuned. Hence, following pulsed laser excitation, the kinetic rate constants for electron transfer from ITO to the rigid-rods was quantified as shown schematically. Marcus-Gerischer theoretical analysis allowed the reorganization energy, λ, and the electronic coupling matrix element, H_{ab}, to be quantified. In rough accordance with dielectric continuum theory, λ was found to increase from 0.61 to 0.80 eV as the number of bridge units was increased. In contrast, H_{ab} decreased markedly with distance from 0.54 to 0.11 cm^{-1} consistent with non-adiabatic electron transfers. Comparative analysis with previous reports indicates that the phenylene ethynylene bridge did not increase H_{ab} relative to bridge units with sp^3 hybridized carbon atoms.[4] The implications for solar energy conversion will be discussed.

[1] **Dye-Sensitized Solar Cells Strike Back**. Munoz-Garcia, A.; Benesperi, I.; Boschloo, G.; Concepcion, J.; Delcamp, J.; Gibson, E.; Meyer, G.J; Pavone, M.; Pettersson, H.; Hagfeldt, A.; Freitag, M. *Chem. Soc. Rev.* **2021**, *50,* 12450-12550.

[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*, 16099-16116.

[3] **Entropic Barriers Determine Adiabatic Electron Transfer Equilibria**. Piechota, E.J.; Sampaio, R.N.; Troian-Gautier, L.; Maurer, A.B.; Berlinguette, C.P.; Meyer, G.J. *J. Phys. Chem. C* **2019**, *123*, 3416–3425.

[4] **Reorganization Energies for Interfacial Electron Transfer Across Phenylene Ethynylene Rigid-rod Bridges.** Heidari, M.; Loague, Q.; Bangle, R.E.; Galoppini, E.; Meyer, G.J. *submitted.*

How Solar-Driven Dye Sensitizer-Catalyst Diads Interact to Drive Water Oxidation

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Dyes and molecular catalysts can be directly coupled into diads, providing a single structure that can use sunlight to drive water oxidation catalysis. While the mechanisms for the two components of the diads have been extensively studied, little is known about how their photophysical and chemical processes work together. The degree of coordination between the dye and the catalyst in time determines the overall water oxidation system's efficiency, so understanding what influences this coordination provides insights to strategies to improve this class of systems. In this study we examine the details of the photophysics and photochemistry in natural sunlight of a TiO_2-supported diad system, RuP2 dye coupled to a Ru(bpy-tpy) catalyst using stochastic kinetics simulations. The kinetic model spans all processes from the fs-scale (charge injection) to hour-scale (up to the diurnal sunlight cycle) in a single simulation. The fastest processes are charge injection by RuP2, whose rate coefficient we have been recently determined to be $2x10^{-12}$ s^{-1} from both singlet and triplet states. The accepted kinetics for water oxidation by this catalyst from the literature are used for the chemical scheme. Catalysis follows a sequence of 4 stages, each initiated by a dye charge injection event followed by charge transfer from the catalyst to the dye. Stage 1 is purely charge transfer. Stages 2-4 involve thermal (non-photo-driven) catalytic reactions and are much slower. We investigated both large ensembles of diads over 40 minutes to get insights to how these very different timescales are coupled on average, and single diads for 24 hours to investigate the stochastics of their coupling.

The simulation results for both ensembles of diads and single diads show that progress through the water oxidation catalytic cycle is not controlled by the relatively low flux of solar irradiation or by charge or excitation losses. Instead, it is gated by a buildup of intermediates whose chemical reactions are not accelerated by photoexcitations. The stochastics of these thermal reactions, illustrated for a single diad in Figure 1, govern the level of coordination between the dye and the catalyst. Stage 1 reflects purely solar stochastics, while the other stages are controlled by chemical stochastics. This suggests that catalytic efficiency can be improved by providing a means for light to drive all steps, where progress through the chemistry would be governed by random absorption of solar photons alone.

Work in progress aims to deepen understanding of the dye excitations themselves, including excited state mixing (M. Head-Gordon, UC Berkeley) and photonic effects in nanoparticulate photoelectrodes (R. Coridan, U Arkansas).

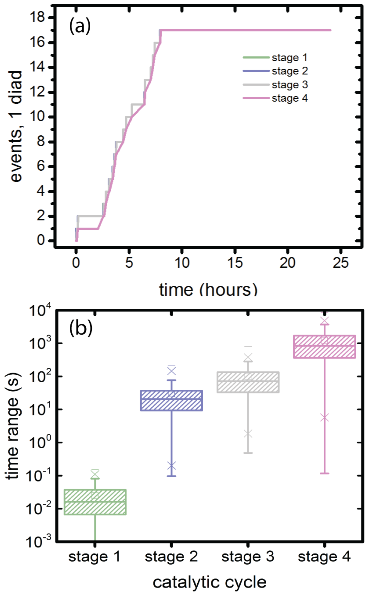

Figure 1. Progression of a single diad through the 4 catalytic stages during 8 hours of illumination followed by 12 hours in the dark. (a) the number of times the diad reaches each stage (typical trace); (b) distribution of times a diad takes to complete each stage (all data, 404 runs).

Solvent and Microenvironment Effects on Photochemical Charge Separation and Charge Recombination at Dye-Sensitized Oxide Semiconductor Interfaces

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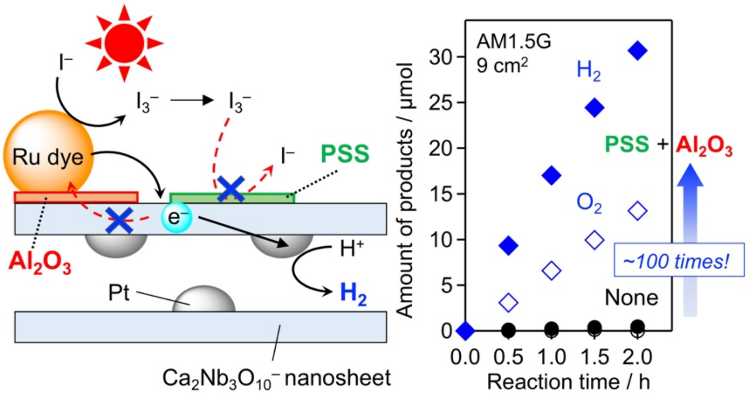
Dye-sensitized oxide semiconductors, which have been well studied in the context of dye-sensitized solar cells, are of current interest for use in photoelectrochemical and photocatalytic water splitting systems. Dye-sensitized TiO_2 and SnO_2/TiO_2 core-shell electrodes can be functionalized with water oxidation catalysts to make oxygen-evolving photoanodes. There is a narrow window of pH in which phosphonate-terminated ruthenium polypyridyl dyes adsorb to the TiO_2 surface and drive water oxidation in competition with back electron transfer. With the optimal core-shell and catalyst architectures, the most significant loss mechanism in this system is the low quantum efficiency (~30-40%) of light-driven charge injection. This is surprising, given that non-aqueous dye cells have upwards of 90% charge injection efficiency. Possible reasons for this striking difference include the larger solvent reorganization energy of water and solvent- or adsorbate-induced changes in the semiconductor flat band potential. We have used ultrafast terahertz spectroscopy and nanosecond transient absorption spectroscopy to measure the rates of excited state electron transfer and charge recombination in acetonitrile-water mixed solvent systems. The kinetics of charge injection are multiphasic, with contributions from both the singlet and triplet MLCT excited states of the dyes. At pH 4.5, where the dye molecules are stably adsorbed, the charge injection yield is substantially higher in mixed solvents. We are now synthesizing oligomeric dye molecules that will enable us to extend these studies to near neutral pH where the most efficient water splitting photoanodes have been reported.

Dye-sensitized metal oxides such as the layer perovskite $HCa_2Nb_3O_{10}$ can also function as the hydrogen evolving photosystem of water-splitting Z-schemes. Pt nanoparticles are deposited exclusively in the interlayer galleries of $HCa_2Nb_3O_{10}$. There they catalyze the hydrogen evolution reaction but not the recombination reaction between hydrogen and triiodide, which is the hole relay to WO_3-based oxygen-evolving particles. Triiodide is excluded from the interlayer galleries by the negative charge on the nanosheets. At the hydrogen-evolving particles the dominant charge recombination pathway is scavenging of conduction band electrons by triiodide. Adsorption of a negatively charged polyelectrolyte (PSS = polystyrene sulfonate) dramatically slows charge recombination and thus increases the hydrogen/oxygen yield by excluding triiodide ions from the oxide semiconductor surface. We are now experimenting with polycation modification of the oxygen-evolving half of the system to control access of iodide to that surface.



Functionally Active Linker Design for Photoactive Molecules at Semiconductor Interfaces

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Robert A. Bartynski, Sylvie Rangan, Jonathan Viereck
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Our research program focuses on the design of "functionally active" linkers with three types of intrinsic properties that can be used to influence interfacial photochemical reaction pathways of organic chromophores bound to oxide semiconductors. The linkers feature a) dual linker units, b) molecular dipoles, and c) stimulus (IR)-gated bridges, as shown in Fig.1. Taken together the first two cases demonstrate that advanced linker design enable the manipulation of charge transfer rates, tuning electronic coupling, and producing predictable shifts of energy levels. **a)** We developed dual likers to control photoinduced charge transfer pathways between perylene and a metal oxide, focusing on saturation and conformational effects as well as the number of linkers (one vs two) and their substitution position (*ortho* vs *peri*);[1] Recent results indicate that the influence of the substitution position on interfacial electron transfer was much smaller than what was predicted based on the difference in the static electronic structure, whereas restricted conformations of dual linkers had a significant effect on injection rates. Current work is focusing on electron recombination effects. **b)** We recently demonstrated that it is possible to predictably shift the energy alignment at the C_{60}/TiO_2 interface using C_{60} deposited onto a monolayer of a helical peptide with a large (18.6 D) and highly oriented molecular dipole. The C_{60} HOMO was shifted 600 meV below that measured in the absence of the dipole later;[2] This is the most versatile approach, compared to those reported before (covalent link, mixed layer approach). **c)** Finally, we will report our progress in an exploratory direction involving IR-active linkers, where charge transfer can be modulated by excitation with infrared radiation. We recently synthesized the first model system (Pyrene-carborane-*N,N*-dimethylaniline),[3] which is currently being studied by the Rubtsov group at Tulane. Probing in the visible (400 nm pump) shows spectral changes which are consistent with electron transfer process: the initial spectrum does change significantly with a characteristic time of ca. 350 ps. The 400-pump/mid-IR probe experiments are in progress, and will be presented in the lightning talk.

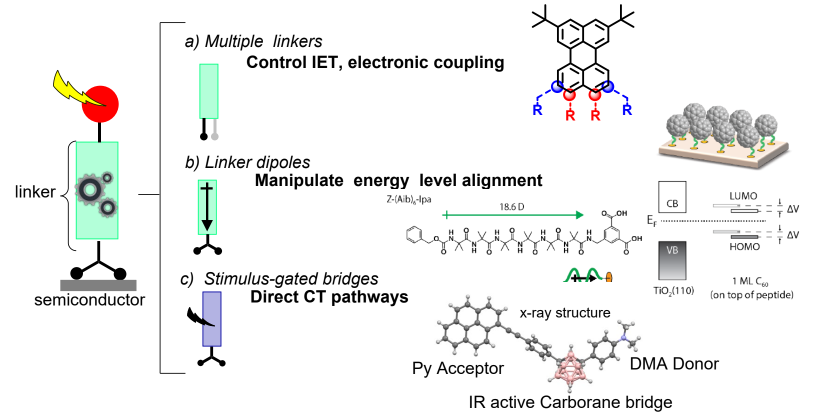

Figure 1. Schematic representation of three types of functionally active bridges developed in the program.

References: **(1)** *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)** *Energy alignment manipulation at the C60/TiO2(110) interface using a blanket molecular dipole approach* Rangan, S.; Viereck, J.; Lloyd, K.; Galoppini, E.; Bartynski, R.A. *Surface Science* **2022**, submitted, in revision. **(3)** manuscript in preparation.

Controlling Inter- and Intra-molecular Factors for Long-lived and Directional Charge Separation from Cu(I)bis(phenanthroline) Complexes

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This poster will describe our group's recent work toward understanding how to manipulate inter- and intramolecular factors to facilitate directional electron transfer and long-lived charge-separated states from heteroleptic Cu(I)bis(phenanthroline) (CuHETPHEN) complexes. To investigate intermolecular interactions between chromophores and electron acceptors, we have synthesized a CuHETPHEN complex with negatively charged sulfonate groups (Cu-SO_3) which promote solubility in water, and present a site for interaction with the positively charged electron acceptor methyl viologen (MV) (Figure 1). The metal-to-ligand charge-transfer (MLCT) lifetime of Cu-SO_3 in water follows a biexponential decay, with τ_{MLCT1} = 10 ns and τ_{MLCT2} = 77 ns, suggesting that the amphiphilic nature of Cu-SO_3 gives rise to two different aqueous microenvironments. On addition of MV to Cu-SO_3 in water, we clearly observe photoinduced electron transfer (PET) by formation of singly reduced MV with near unity quantum yield (Φ_{ET} = 98%) and a long-lived charge separated state that persists for 3 μs, and no PET to MV is observed with the unsulfonated CuHETPHEN analog. We anticipate leveraging this dynamic assembly approach to investigate PET and charge accumulation from earth-abundant CuHETPHEN chromophores to molecular catalysts for H_2 evolution.

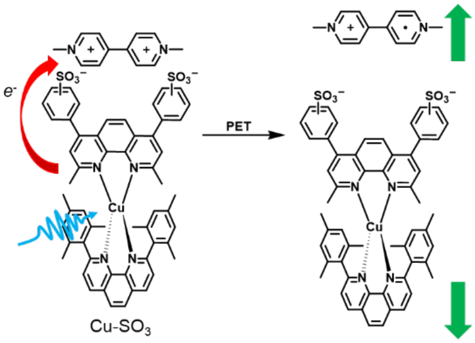

Figure 1. Dynamic, electrostatically-enabled assembly of Cu-SO_3 and MV leading to efficient PET and long-lived charge separation.

The asymmetric coordination environment of CuHETPHEN complexes presents an opportunity to understand *intra*molecular, directional MLCT and how this can be used to create efficient electron-transfer pathways. We have evaluated the ultrafast kinetics of a new series of CuHETPHEN and found that their MLCT lifetime is highly dependent on the Hammett parameter of the 4,7-phenanthroline substitution, but the trend is dependent on coordinating vs. non-coordinating solvent (Figure 2). Cyclic voltammetry and DFT calculations confirm that the LUMO moves from the mesityl-substituted blocking ligand to the 4,7-phen ligand when electron-withdrawing substituents are present. This work provides the foundational knowledge for how both ligand electronic structure and solvent interactions impact CuHETPHEN excited-state dynamics.

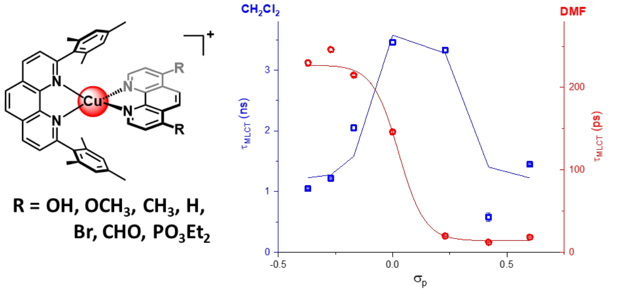

Figure 2. Left: chemical structure of CuHETPHEN with electron-donating and –withdrawing substitution; right: MLCT lifetime as a function of the Hammett parameter in CH_2Cl_2 and DMF.

Electronic Couplings from Dimer Cations

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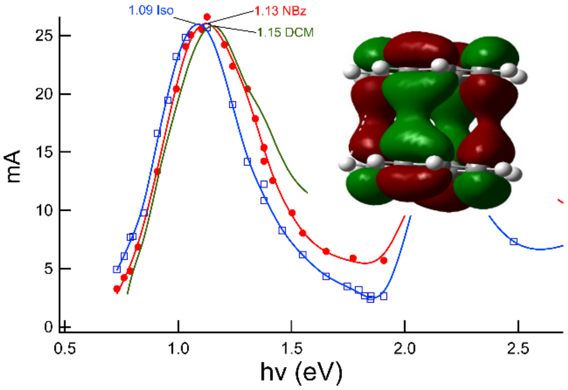
[2] Chemistry, University of Connecticut

Radical cations often dimerize with one neutral molecule as in this example for naphthalene:

$$\mathrm{Nap}^{\cdot +} + \mathrm{Nap} \rightleftharpoons \mathrm{Nap}_2{}^{\cdot +}$$

The dimers are bound together by intermolecular electronic couplings also known as two-center, one-electron exchange matrix elements, H_{da}, that give rise to new spectroscopic transitions. For symmetric dimers like $\mathrm{Nap}_2{}^{\cdot +}$ the observed transitions occur at $2H_{da}$ if the charge is delocalized equally over both Nap units, but the band peaks instead at the reorganization energy λ if $\lambda > 2H_{da}$. Robin and Day(1) described these as charge-delocalized (class III) and charge-localized (class II). Our recent results(2) led to the conclusion that smaller electronic couplings support use of the Marcus inverted region to prevent highly-exoergic back reactions in light-driven energy storage. Thus understanding of H_{da} and its possible measurement in dimer cations is important.

But how can we know if a particular dimer is delocalized: is observed transition is at $2H_{da}$ or at λ? For charge-localized dimers λ includes a contributions from both internal and solvent reorganization energies. The solvent reorganization energy varies with polarity. The figure shows pulse radiolysis experiments that produce $\mathrm{Nap}_2{}^{\cdot +}$ in highly-polar nitrobenzene (NBz), moderately polar dichloromethane (DCM) and nonpolar isooctane (Iso). The energy of the dimer band is almost invariant with solvent polarity identifying the dimer as delocalized, class III in agreement with the DFT result in the inset that finds the hole to be delocalized. Pulse radiolysis is unique in its ability to produce radical ions even in completely nonpolar media and thus to determine H_{da}. The poster will present dimer ions of molecules having different sizes to examine one factor controlling H_{da}.



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Dexter Energy Transfer Pathways

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Triplet exciton transfer in molecular and nanostructured assemblies, especially across molecule-nanoparticle interfaces, is a critical process that limits the efficiency of solar-energy conversion processes associated with exciton fission and fusion reactions. This project develops and applies theoretical approaches to understand and to control the flow of triplet excitation energy through Dexter energy transport (DET) mechanisms.

Recent results: **(1)** We studied the possible origins of ultrasoft distance dependent DET between organic chromophores and core-shell CdSe/CdS quantum dots. Recent experiments by Lian et al. indicate that the DET coupling decays much more slowly as a function of distance than is predicted from the distance dependence of electron and hole transfer in the same structures, thus challenging the expectation that DET is well approximated as the coherent sequential transfer of an electron and a hole. Using the effective mass approximation, we evaluated contributions to the distance dependent DET coupling from charge transfer and triplet bridge exciton mediation mechanisms. Our preliminary analysis finds that bridge localized exciton mediation may be responsible for the soft DET distance dependence, which arises from a large donor-acceptor wave function overlap and a large bridge exciton density of states. **(2)** We established structure-function relationships for molecular structures that enable very long distance ballistic DET. These relationships assist with the design of polymers that should have large inter-monomer DET couplings and low dynamic and structural disorder. One of the proposed structures (Fig. 1) is predicted to enable coherent DET over extreme distances.

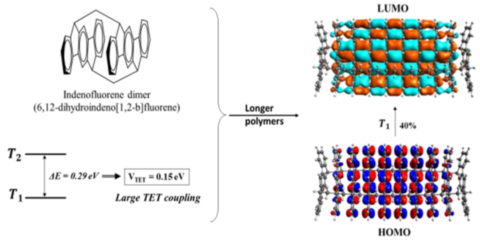

Fig. 1 Indenofluorene polymer. A strong monomer-to-monomer DET coupling and a rigid geometry creates extended delocalized triplet excitons, even at room temperature.

Future Plans: **Manipulating DET in Optical Cavities**: Exciton-polariton states enable the manipulation of energy transfer mechanisms. We are exploring the use of cavities to modulate DET in donor-acceptor assemblies. Earlier theoretical studies of electron transfer (ET) reactions in cavities found that the coupling pathways can be manipulated in the cavity. Since DET is described as coupled electron and hole transfer, we are generalizing our earlier theoretical analysis to describe DET pathway interferences within cavities. We expect that the cavity interactions will significantly enhance the conventional nanometer scale DET couplings. The large electronic density of states in nanostructures may produce different interference mechanisms compared to those found in organic DET chromophores when the nanostructures are studied in optical cavities.

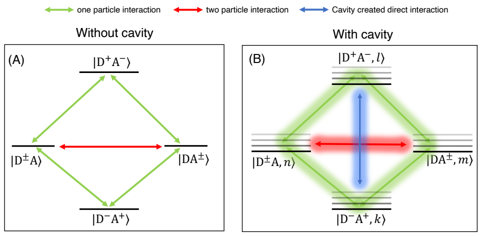

Fig. 2 (A) Energy landscape for DET. (B) Light-matter hybrid states, where *n, l, m*, and *k* indicate the photon numbers in the corresponding hybrid states. The green and red arrows represent the one- and two-particle interactions in the cavity. The blue arrow indicates cavity-created interactions between the $|D^+A^-\rangle$ and $|D^-A^+\rangle$ states.

Deciphering Directional Excited-State Charge Transfer Mechanisms Using Ultrafast XFEL Science

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[3]Stanford PULSE Institute, SLAC National Accelerator Laboratory

This program aims to correlate the very earliest electronic and structural dynamics following photoexcitation with longer timescale events in transition metal complexes and their hybrid heterogeneous assemblies relevant to solar energy conversion. We hypothesize that mapping the response of excited state trajectories to molecular structures and ground state energetics will provide us with a clear path to effectively utilize the earliest excited state energetics to drive specific photochemical outcomes. This will be achieved by leveraging the femtosecond time resolution and elemental specificity of the XFEL capabilities at LCLS and LCLS-II to investigate the photoinduced excited state trajectories of photo- and redox-active transition metal complexes along their potential energy surfaces. The cohesive team brings together expertise in multiple time-resolved laser and X-ray spectroscopy/scattering techniques with targeted molecular synthesis and computational modeling of inner-shell and valence excited state dynamics.

In this research program, we detect ultrafast excited state pathways with two thrusts: 1) homogeneous supramolecular assemblies of transition metal complexes and 2) in immobilized transition metal complexes on inorganic and organic semiconductor surfaces. The theoretical calculation results on X-ray spectroscopic feature for excited and transient states are closely correlated with experimental results to gain new insights in light energy conversion in these systems.

Using ultrafast impulse stimulated Raman spectroscopy and X-ray solution scattering, cooperative vibrational modes and their phase correlation in the excited state building block $Cu(I)(phen)_2I_4$ have been quantified from which a dynamic intersystem crossing and Jahn Teller distortion can be descripted with future promises of new design rules to optimize photoinduced electron transfer. Excited state structural dynamics of a bimetallic transition metal supermolecule of Cu and Os centers linked with a conjugated bridge have been investigated by X-ray transient absorption measurement at the Cu K-edge and Os L3-edge using an XFEL source. The results have demonstrated in-phase electron density oscillations between the two metal centers mediated by delocalized vibrations of the bridging ligand, opening opportunities to ligand design for modulating unidirectional, long distance, and inter-metal center charge transfer. Using N K-edge absorption spectroscopy we have identified unique spectral features of the excited state donor and acceptor orbitals on the photosensitizer ligands and bridging ligand, respectively. We will take advantage of this spatial sensitivity to identify the real-time charge transfer dynamics across the bridging ligand between a Ru photosensitizer and Pt catalyst in upcoming LCLS experiments. Studies were also carried out on electronic and nuclear coordinate dynamics following charge transfer excitation in metal-oxo clusters. These include the molecular cobalt cubane and amorphous cobalt oxide thin file water-splitting catalysts that share a common cobaltate core and oxo-ligand to metal (LMCT), metal-to-metal (MMCT) charge transfer and d-d transitions. To explore the capabilities of using high X-ray photon energy for pair distribution function (PDF) measurements at XFEL facilities (e.g., LCLS-HE), we benchmarked the solution phase structure of five bridged bimetallic complexes with 0.26 Å spatial resolution, and using DFT calculations identified substantial conformational differences from the solid state single crystal structure. We also designed interfacial charge transfer systems with carbon quantum dots incorporating redox transition metal centers to either accept or donate electron density to the catalytic site for photocatalytic reactions. , the detailed structural dynamics of these systems have been planned for the future XFEL.

Charge Transfer Acceleration by Aggregate Donor States Described by Generalized Marcus Theory

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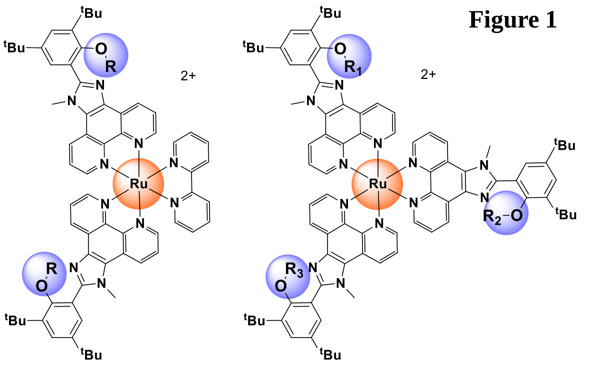
The rate of charge transfer between discrete donor-acceptor (D/A) pairs is well-modeled by semi-classical electron transfer theory; however, there are cases in which electronic delocalization among multiple donors or acceptors may occur. Generalized Marcus theory (gMT) was recently proposed to account for inter-donor or inter-acceptor delocalization in aggregated states and significant effects on rates were predicted to occur by supertransfer or nuclear factor tuning.[1] The present study tests and verifies predictions of gMT using a series of $[Ru(L)_n(OH)_{3-n}]^{2+}$ donor-acceptor complexes containing 1, 2, or 3 identical, covalently bound, and geometrically-fixed phenolic electron donors linked to Ru through phenanthroline bridges (OH = 2,4-di-tert-butyl-6-(1-methyl-1H-imidazo[4,5-f][1,10]phenanthrolin-2-yl)phenol), Figure 1. Upon flash photolysis and oxidative quenching by methyl viologen, the transient Ru(III) oxidizes an appended phenol. The intramolecular charge transfer rate was accelerated by 3.2-fold and 6-fold as the number of donors was sequentially increased from 1 to 2 and 3, respectively. This acceleration occurred without a change in driving force and is attributed to the effects of gMT: larger electronic coupling (H_{DA}) and decreased reorganization energy (λ_{DA}) which lowers the activation barrier. Due to strong D/A coupling, there is also acceleration related to the increased adiabaticity parameter. The final phenoxyl radical state is localized, and therefore the recombination reaction with the viologen radical is *not* accelerated. In practice, our results suggest possible differential control of charge separation/recombination rates by using aggregate electronic states and represent an important strategy in the productive utilization of photoinduced charge separated states.

Figure 1



Ru(bpy)(OH)$_2$ R = H
Ru(bpy)(OMe)$_2$ R = CH$_3$

Ru(OMe)$_2$(OH) R$_1$ = H; R$_2$ = CH$_3$; R$_3$ = CH$_3$
Ru(OMe)(OH)$_2$ R$_1$ = H; R$_2$ = H; R$_3$ = CH$_3$
Ru(OH)$_3$ R$_1$ = H; R$_2$ = H; R$_3$ = H
Ru(OMe)$_3$ R$_1$ = CH$_3$; R$_2$ = CH$_3$; R$_3$ = CH$_3$

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1. Taylor, N. B.; Kassal, I. Generalised Marcus theory for multi-molecular delocalised charge transfer. *Chem. Sci.* **2018**, 9, 2942-2951.

Optical-Gating of Spin-based Quantum States for QIS

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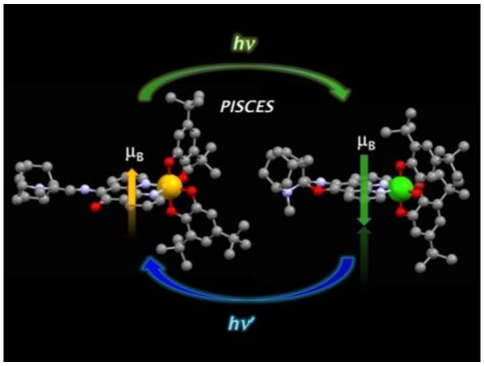
Abstract. *The goal of the proposed research is to utilize optically-gated spin qubits developed in our lab to optimize coherence times and sensitivity for quantum computing and quantum sensing technologies.* Quantum computing, communications and quantum sensors all rely on the fundamental unit of a qubit. The coherent transduction of information from one modality to another, such as light to electron or spin-based quanta at the single-particle, single molecule or quantum level, is at the core of quantum measurement and information processing. The most critical challenge currently facing development of spin-based qubits is the control of decoherence times, T_1 and T_2. While nuclear spins typically exhibit slower spin relaxation processes due to a greater insensitivity to the environment (bath), this insensitivity to the bath also leads to challenges in the control of nuclear spin states by external stimuli for qubit initialization. The decoherence times, T_1 and T_2 of electron-spin based qubits on the other hand are extremely short due to coupling to bath through electron nuclear interactions (hyperfine coupling), dipolar coupling, and coupling to the bath. Ultimately, qubits will need both slow relaxation and the ability for external control by external stimuli in order to switch between various entangled states. ***The strategy employed here is to utilize ligand control (stimuli sensitivity) of nuclear spin states (long decoherence times) in electronically bistable metal complexes.***



In molecular systems, the optical manipulation of spin quantum states provides an important strategy for quantum control/gating with both temporal and spatial resolution. We have recently reported the generation of photoinduced spin states with unusually long lifetimes (s) in the thin film state at T > 300 K. Light modulation of a photochromic ligand bound to a cobalt complex induces changes in the electronic and spin state at the metal center with a high magnetic transition temperature ($T_{1/2} \sim 325$ K) through a Photoisomerization-Induced Spin–Charge Excited State (PISCES) process. The advantages of the PISCES strategy for development of optically gated spin qubits are (i) optical modulation of spin-state that originates at the single molecule level, giving rise to an externally addressable spin-based qubit, and (ii) ability to undergo switching in the thin film state allowing incorporation into 2D arrays. This research project described herein probes the fundamental basis of the structural and electronic parameters that govern the PISCES process in photochrome-driven spin-based qubits with the goal of developing a generalized strategy for quantum-based switching, memory and sensor applications. The proposed research in optical gating of spin-based qubits at the single molecule level will develop approaches for light-to-electron transduction in 2D arrays and a "read-out" through magnetic-optical effects (polarized light). The results of the proposed studies will advance our understanding of the scaling of coherence lengths and times with system size and complexity through the generation of well-defined 2D arrays of single molecule spin-based qubits that can be initiated at the single molecule level by light.

Photoinduced Ground State Electron Spin Polarization Controlled by Magnetic Exchange Coupling

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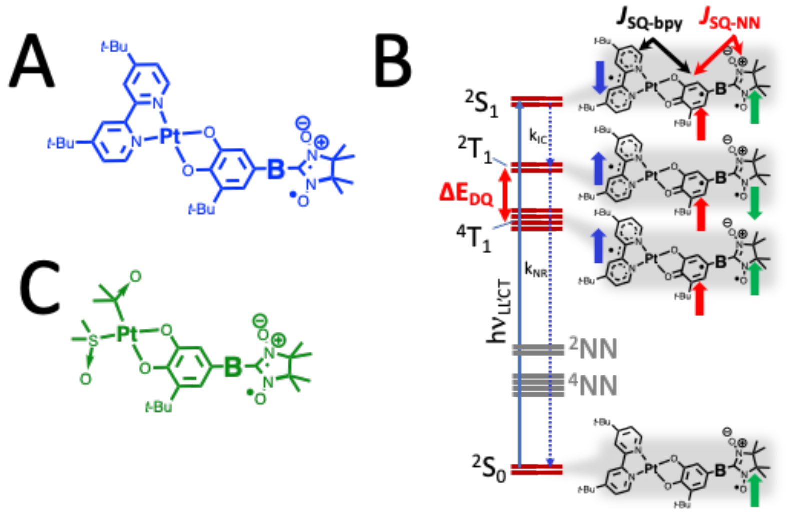

Figure 1. **A:** Structure of radical-appended LL'CT complexes. **B:** Jablonski diagram and drawings of ground-state and 3-spin LL'CT excited state manifold. **C:** Structure of control complexes that contain NN radical, but lack LL'CT chromophore.

This project (DE-SC0020199, "Optical Generation and Manipulation of Spin Qubits") focuses on initiating and controlling molecular electron spin polarization (ESP) using visible light. The research advances our understanding of how photogenerated quantum (spin) bits (qubits) can be used to develop large ground-state ESPs on an ultrafast timescale. Our long-term goal is to develop novel molecular systems that can be optically initiated to enable magnetic exchange-mediated multi-qubit entanglement, and by virtue of designed short-lived excited states, facilitate large spin qubit polarizations in recovered ground states. This will allow us to develop spatial and temporal control of both individual and coupled spin qubits with spin polarization lifetimes that are markedly longer than the photoinitiation process. Here, we demonstrate a dependence of ground-state ESP on excited state magnetic exchange couplings, specifically the pairwise exchange coupling between photogenerated, spin-½ semiquinone (SQ) and a covalently attached, spin-½ radical, nitronylnitroxide (NN).

Our (bpy)Pt(CAT-B-NN) chromophores (Fig. 1A) possess low-energy ligand-to-ligand charge transfer (LL'CT) states with a variety of bridges that link the pendant NN radical to the catecholate (CAT). LL'CT excitation at ~570 nm results in near quantitative CAT → bpy CT and creation of a 3-spin LL'CT excited state, $^2S_1$ (Fig. 1B). Following internal conversion to $^1T_1$, transitions amongst m_s-levels of $^1T_1$ and, *e.g.* $^4T_1$ excited states result in spin polarization of the $^2T_1$ state which is subsequently transferred to the $^2S_0$ ground state upon charge recombination. The sign and magnitude of the ground state ESP is a function of the molecular bridge, which determines $J_{SQ\text{-}NN}$, and is absent in complexes containing the radical, but lacking the LL'CT chromophore (Fig. 1C).

Direct Harvesting of Bound Triplet Pairs

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Singlet fission is commonly defined as the generation of two triplet excitons from a single absorbed photon. However, ambiguities within this definition arise due to the complexity and interconversion between the various triplet pair states that exist in SF chromophores. To clarify this process, singlet fission is frequently depicted as sequential two-step conversion in which a singlet exciton decays into a bound biexciton (triplet pair) state which dissociates into two "free" triplet excitons. However, this model is limited in that it discounts the potential for direct harvesting from the coupled biexciton state.

Our project is developing new paradigms for *integrated* multielectron photochemical systems based on direct triplet pair harvesting from *intramolecular* singlet fission (iSF) compounds. Our goal is to develop next-generation molecular frameworks that activate *multielectron chemical transformations near the multiexciton generation site*, avoiding loss-prone transport processes. This approach is only possible using a strategy that integrates SF chromophores with *active chemical bridges*. The bridge serves a dual role in mediating the electronic and spin coupling between SF chromophores to optimize multiexcitons for energy harvesting and acting as a substrate to turn triplet pairs into chemical potential.

We present preliminary results which demonstrate that individual triplet excitons can be extracted directly from a bound biexciton pair, prior to triplet pair dissociation. We investigate this process using intramolecular singlet fission compounds that exhibit unique spectral and kinetic signatures, which can be used to quantify biexciton harvesting yields. We achieve an internal quantum efficiency greater than 50%, a value that is only limited by the solubility of the studied compounds. Furthermore, the harvesting process is not dependent on the net multiplicity of the triplet pair state. These suggest that triplet pairs are capable of being used for chemical or electrical work, and that an explicit dissociation step is not a requirement for singlet fission.

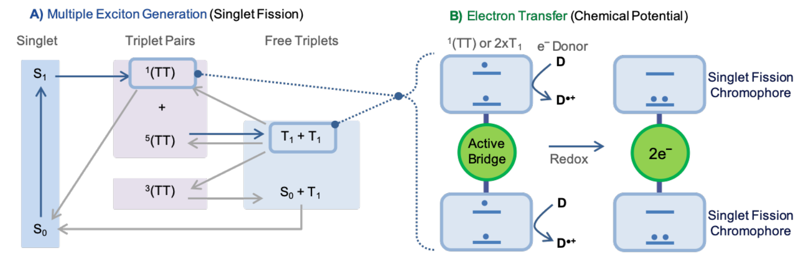

Figure 1. A) Singlet fission converts one photon to a triplet pair, which can be harvested directly or after dephasing into two free triplet excitons. We propose new chemical means to provide the requisite control. **B)** We are developing chemical systems to convert a triplet pair into chemical potential through the use of redox-active bridges.

We will also briefly introduce other ongoing projects supporting this effort, including the use of quantum interference principles to control the nature and lifetime of triplet pair states and the development of photochemically active chemical bridges containing organometallic redox centers.

Strategies for Water Oxidation with Abundant Metals: Catalyst Design, Immobilization on Conducting Substrates, and Sensitizer Integration

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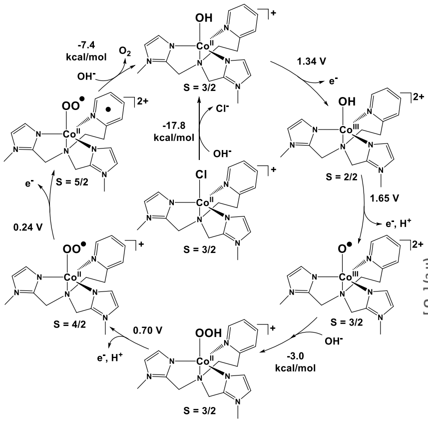
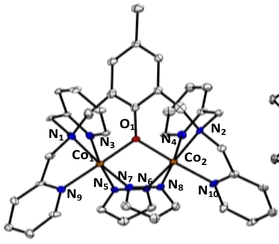
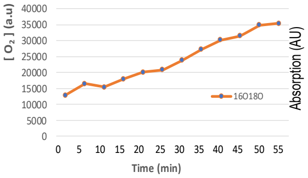
A comprehensive effort is under development at Wayne State University aiming at the development of strategies for water oxidation with abundant metals such as cobalt, iron, and manganese. The proposed research aims to investigate and address persistent bottlenecks to the development of 3d-based catalysts, thus in harmony with core values of the Solar Photochemistry program. The development of sustainable and robust molecular catalysts that promote and withstand water oxidation will require metal/ligand structural and electronic cooperativity, immobilization onto solid and conductive substrates, and close connectivity to sensitizers. Specific goals include (i) establishing the oxidizing activity and mechanisms of new molecular catalysts, (ii) enhancing the stability of catalysts by immobilization via anchoring of modified ligands onto conductive substrates, and (iii) designing integrated heterometallic photosensitizer/catalyst systems for photoinduced water oxidation.

$[L^1Co\,Cl]^+$ (**1**)

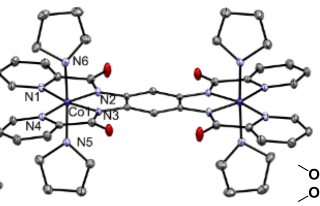


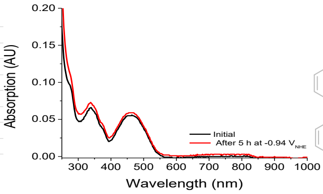
$[L^2Co_2(\mu\text{-}Pz)_2]^{3+}$ (**2**)





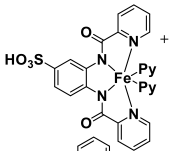
$[L^3Co_2(Pyr)_4]^{2+}$ (**3**)



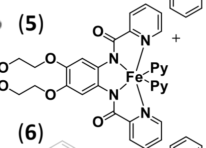


Fe-amido complexes

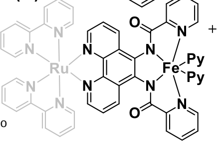
(**4**)



(**5**)



(**6**)



To date we have addressed goal (i) with a new tripodal pyridine/imidazole system $[L^1Co^{II}Cl]^+$ (**1**) capable of generating O_2 with TON 103 at pH 11, *via* formation of nominal Co^{IV}=O and Co^{III}-OOH species that invoke electron delocalization over the ligands. We are currently wrapping up a study with $[L^2Co^{III}_2(\mu\text{-}Pz)_2]^{3+}$(**2**) in which we verify O_2 generation through oxygen transfer from the oxidizer oxone using O^{16}-O^{18} mass spectrometry. We also incorporated a sulfonate to the Fe^{III} amido (**4**) system to improve water solubility. System $[L^3Co_2(Pyr)_4]^{2+}$ (**3**) has been tested as a reasonable catalyst in water with TOF 60/min, ergo a trifold increase over the equivalent monometallic species. The post-catalytic analyses support molecular activity for oxidation via UV-visible spectroscopy and XPS analyses are ongoing. The systems will soon be transferred onto carbon black for immobilization studies proposed in goal (ii) along with species **5.** Finally, we have obtained the ligand shown in system **6**. This species is relevant for goal (iii) when attached to a ruthenium photosensitizer, and the initial synthesis of its Fe^{III} species seems successful.

Singlet Fission and Spin Dynamics in Dipyridyl Pyrrole Bipentacenes Studied by Time-Resolved EPR Spectroscopy

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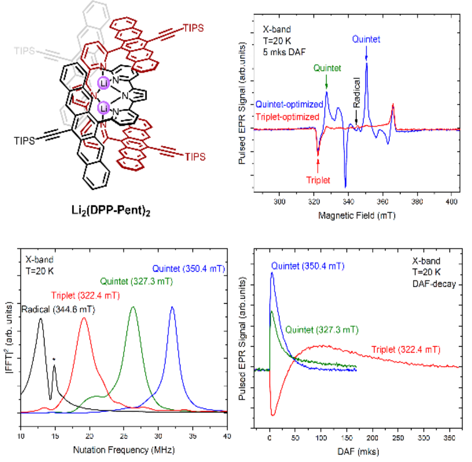
The ultimate goal of our solar energy conversion research is to resolve fundamental mechanisms of photochemical energy conversion and, as a long term aim, devise integrated systems that can capture, convert, and store solar energy. Photovoltaic system based on organic donor-acceptor materials, OPV, are highly capable man-made devices for direct solar energy utilization. These technologies could potentially provide sufficient energy to satisfy the global energy demands in the near future. One of the limitations of OPVs is relatively low conversion efficiency. At present the level is 18% and still well below the theoretical Shockley-Queisser limit (33-34%) of the efficiency in single-junction solar cells.

One promising pathway to improve the efficiency of photovoltaic cells is an implementation of multiple exciton generation, MEG, the process which allows to create multiple charge separated states from absorption of a single photon. One type of the MEG is singlet fission, SF, which can be observed in some organic materials. For SF to occur, one organic molecule is excited from its ground state, S_0, to singlet excited state, S_1, and interacts with a neighboring molecule in ground state, S_0. This interaction creates a correlated triplet pair in singlet state ^{1}(TT), which can be converted by coherent spin-mixing to the quintet state ^{5}(TT), followed by decay to two independent triplets. While this process was first reported in molecular crystals more than 50 years ago, recent interests is related to the possible application of this phenomenon to the novel technologies with tailored SF materials.

The main question that should be answered is how to improve generation of the correlated triplet pair and, therefore, the efficiency of SF. Recently, photophysical properties of the novel bipentacene dipyridyl pyrrole and its Li- and K-coordinated derivatives with high SF efficiency were reported. While optical TA spectroscopy is a powerful technique to unravel photophysics and kinetics of SF, it cannot separate strongly and weakly coupled triplet pairs and reveal the spin dynamics of the spin-correlated states.

Here we report a time-resolved EPR study of these three complexes which allows to unravel the spin dynamics and quantify the relative efficiency of SF processes in these materials. The analysis of the EPR data demonstrates the importance of designing and controlling the structures of supramolecular assemblies for improved singlet fission performance.



Structure of Li_2(DPP-Pent)$_2$ dimer (top left), which demonstrates the highest SF efficiency. Rubi nutations (bottom left) recorded at the canonical components of the pulsed EPR spectra (top right) allows for precise description of spin dynamics (bottom right).

Organizing Triplet Forming Molecules at Nanoscale Interfaces

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Molecules that readily form triplet state populations after photoexcitation have a distinct role in downconversion, upconversion, and other energy transfer schemes. Nanoscale semiconductors can often serve as convenient partners in these schemes through endowing the hybrid architecture with favorable properties, such as a strong absorptive or emissive component. Arranging molecules in a rational way at nanostructured interfaces requires a balance between forces known to drive molecular aggregation (i.e., van der Waals or hydrogen bonding) and covalent binding to a semiconductor layer. This interplay leads to challenges and opportunities to realize functional molecular aggregates that participate in interfacial energy or charge transfer processes.

I will present several manifestations of this general notion for dye-sensitized nanostructured oxides and ligand-exchanged quantum dots. For anthradithiophene dyes bound to oxide interfaces, triplets born through singlet fission are shown to undergo dissociation at the oxide acceptor interface on a ns timescale, far slower than their singlet counterparts. The role of triplet localization is highlighted as a hindrance to ultrafast transfer, supported by related measurements in all-molecular donor-acceptor systems. For semiconductor quantum dots, excitons traverse the quantum dot-ligand interface rather slowly, forming triplets in nanoseconds, sometimes mediated by charge transfer. To understand the mechanism, we alter the tetracene-based ligand binding geometry and the degree of ligand aggregation, characterizing the bound-free ligand equilibrium as it relates to inter-ligand hydrogen bonding. The types of aggregates that form in either mono- or diacid functionalized ligands at various concentrations in solution can be characterized by ^{1}H-NMR and UV-VIS absorption and connected to their ability to undergo ligand exchange. The packing motifs of quantum dots in arrays revealed by x-ray scattering also report on ligand structure at the surface. As structures and their chemical behavior are revealed, the associated excited state dynamics of photoexcited aggregates can be leveraged for specific roles in photocatalysis schemes.

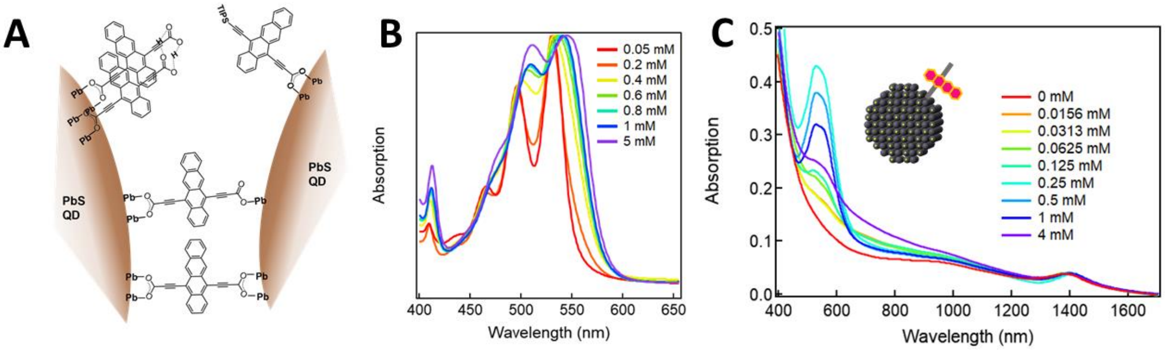

Figure 1. A, Possible binding motifs for mono- and diacid tetracene. B. UV-VIS absorption vs. ligand concentration in solution for the diacid. C, Ligand-exchanged quantum dot absorption vs. solution concentration, showing nonmonotonic behavior.

Quantifying the Ligand-Induced Triplet Energy Transfer Barrier in a Quantum Dot-Based Upconversion System

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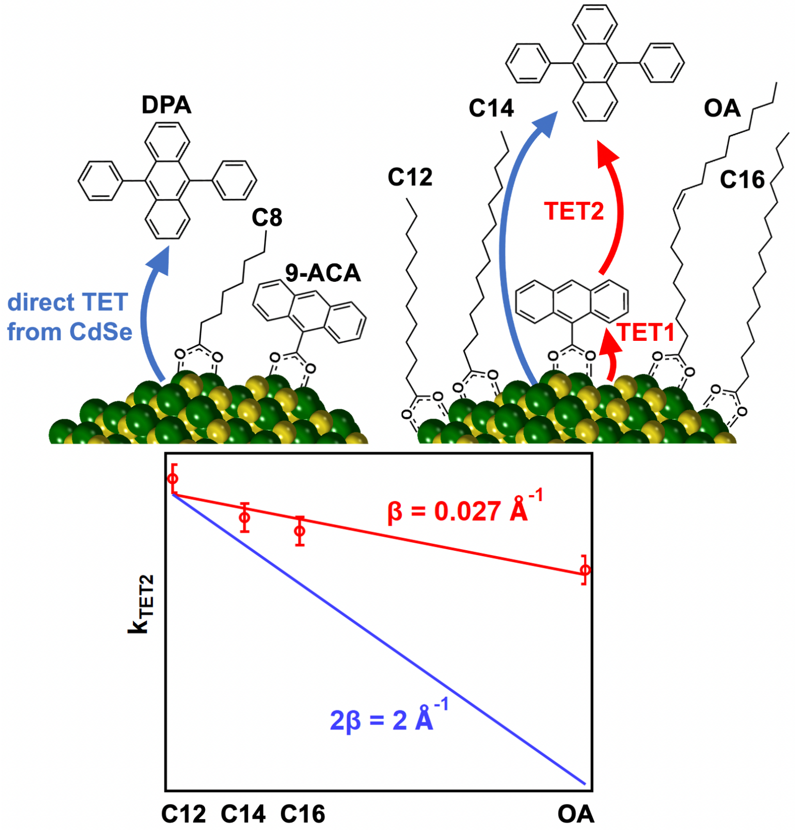

During photon upconversion, quantum dots (QDs) transfer energy to molecules in solution through a long ligand shell. This insulating ligand shell imparts colloidal stability at the expense of efficient photosensitization. For the first time, we quantify the barrier these aliphatic ligands pose triplet enregy transfer in solution. Using transient absorption spectroscopy, we experimentally measure a small damping coefficient of 0.027 Å^{-1} for ligand exceeding 10 carbons in length. The dynamic nature of ligands in solution lowers the barrier to charge or energy transfer compared to organic thin films. In addition, we show that surface ligands shorter than 8 carbons in length allow direct energy transfer from the QD, bypassing the need for a transmitter ligand mediating energy transfer, leading to a 6.9% upconversion quantum yield compared to 0.01% for ligands with 18 carbons. This experimentally derived insight will enable the design of efficient QD-based photosensitizers for catalysis and energy conversion.

DOE Solar Photochemistry Sponsored Publication 2022

T. Miyashita, P. Jaimes, T. Lian, **M. L. Tang**, Z. Xu, "Quantifying the Ligand-Induced Triplet Energy Transfer Barrier in a Quantum Dot-Based Upconversion System", *J. Phys. Chem. Lett.,* 13, 3002, **2022**. (selected for supplementary journal cover)

Spin Selective Charge and Energy Dynamics in Molecules and at Interfaces

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This research program aims to explore molecular strategies for spin-selective tuning of excited electronic states, including singlet and triplet states. Such spin-selective tuning of energetics may allow the control of charge and energy transfer. During the current funding period, the PIs have accomplished the following: 1) continuing effort in using molecular contortion to enable singlet fission; and 2) new efforts in exploring spin-selective interfacial charge transfer.

Singlet fission occurs only in a limited number of molecules and expanding the molecular toolbox is necessary for progress. These molecules must be environmentally robust and stable, show high singlet fission yields, and possess sufficiently high triplet energy for applications. Previously, the PIs have posited a design strategy of molecular contortion to tune the singlet and triplet energetics and demonstrated this approach for perylene diimide (PDI). While PDI is known to undergo endoergic singlet fission in solid films with low rates, contortion of PDI enables isoenergetic singlet fission with rates increased by two-to-three orders of magnitude. Here the PIs apply the molecular contortion strategy to tune singlet and triplet energies and successfully turn on singlet fission in thin films of contorted perylene. Perylene is a prototypical molecular chromophore, which does not undergo singlet fission in its planar form. The tuning of the energetics that control singlet fission through molecular contortion can be applied to a large repertoire of established molecular chromophores.

The spin selective dynamics in not only central to singlet fission, but also key to important interfacial charge transfer reactions. The best-known examples are interfacial processes of molecular oxygen, which in its ground state is a spin triplet. Both oxygen reduction and oxygen evolution reactions (ORR & OER) involve the conversion between singlet and triplet molecular species. The fundamental requirement of spin angular momentum conservation thus may serve as a rection barrier or mechanism of control. Recent studies have indeed suggested the enhancement of such reactions by spin alignment either with ferromagnetic materials or in the presence of an external magnetic field. The PIs have embarked on a new approach to systematically probe spin selectivity in interfacial charge transfer reactions involving singlet-triplet conversion. Specifically, the PIs are exploring the use of a novel source of highly spin-polarized electrons from photo-excited two-dimensional semiconductors, transition metal dichalcogenide (TMDC) monolayers or heterobilayers, where the unique spin-valley locking allows the photogeneration of highly spin polarized electrons. The nanometer thickness of these spin-polarized electron source minimizes depolarization due to scattering and the non-magnetic nature eliminates complications due to interfacial magnetic polarization. In the model system of $MoSe_2/WSe_2$ heterobilayer under circularly polarized optical excitation, transient Faraday rotation revealed long-lived spin polarized e-h separation for as long as ~100 ps. Experiments on photo-induced transfer spin-polarized electron from TMDCs to molecular electron acceptors, including PDI oligomers, are underway.

Effects of Chromophore Packing on Singlet Fission Rate

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Advances in the search for a practical singlet fission material come from (i) choosing a better chromophore, (ii) packing chromophores better in the solid state, and (iii) better conversion of triplet excitons into better harvested charge carriers. We have worked on the first two of these tasks and have chosen advances in understanding the effects of chromophore packing for this year's presentation. We have prepared a dozen fluorinated derivatives of 1,3-diphenylisobenzofuran, obtained their single crystal X-ray structures, and determined their singlet fission (k_{SF}) and excimer formation (k_{EXC}) rate constants along with other photophysical properties in thin solid layers. The molecular properties of all these compounds are similar but their crystal packing varies widely. Most of them undergo singlet fission whereas excitation in others is trapped in excimers. The trend in rate constants k_{SF} agreed qualitatively with results of calculations by our previously developed simplified version of the frontier orbital model for a molecular pair. We shall point out the main shortcoming of the theoretical procedure for the evaluation of k_{SF} and describe how we are currently attempting to overcome it. We are also adding another dozen of fluorinated 1,3-diphenylisobenzofurans to make our test compound and rate constant collection more robust, and developing a simple procedure for a predictive estimation of the rate constants k_{EXC} for the main competing decay channel, needed for the prediction of triplet yields.

Dirhodium(II,II) Complexes for Photo- and Electrocatalytic H_2 Production

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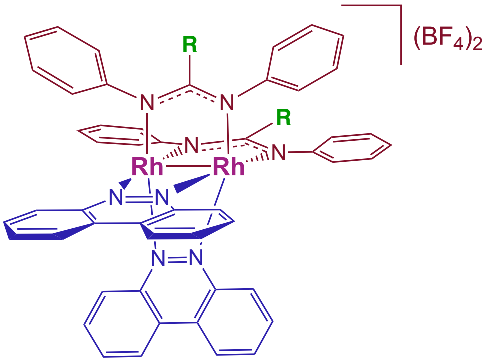
It is predicted that the current rate of population growth and increasing need for fuels will result in more than double the global energy demand from the year 2020 to 2050.[1] This surge in energy requirement demands schemes that store the intermittent energy of sunlight in a stable and deliverable manner, such as its transformation into the chemical bonds in carbon-free molecules. We have developed dirhodium(II,II) complexes that are air-stable, robust, single-molecule photocatalysts with broad absorption from the UV to the near-IR for the reduction of protons to H_2. The Rh_2(II,II) compounds operate with low-energy light, 650 – 735 nm, as well as higher energy photons in the UV and visible ranges, featuring TONs > 200 (λ_{irr} = 670 nm, 24 h).[2–3] The molecular structures of two of our leading compounds are shown in Figure 1, *cis*-$[Rh_2(DPhF)_2(bncn)_2]^{2+}$ (**1**; $DPhF^-$ = *N,N′*-diphenylformamidinate, bncn = benzo[*c*]cinnoline) and *cis*-$[Rh_2(DPhB)_2(bncn)_2]^{2+}$ (**2**; $DPhB^-$ = *N,N′*-diphenylbenzamidinate).[2,3] In **1**, excitation of the $Rh_2(\delta^*)$/DPhF(nb) → bncn(π^*) metal/ligand-to-ligand charge transfer (ML-LCT) transition (λ_{abs} = 624 nm, ε = 8600 $M^{-1}cm^{-1}$) results in the population of the ^{3}ML-LCT state with τ = 19 ns in CH_3CN. The ^{3}ML-LCT lifetime of **2** is longer, 33 ns in CH_3CN.

Understanding the mechanism of photocatalytic H_2 evolution in these systems is of interest not only to further improve them, but also to develop the principles that permit this reactivity to be applied to the creation of new compounds from abundant elements. The photo- and electro-catalytic H_2 evolution by **1** arises from the doubly-reduced complex, $[\mathbf{1}]^{2-}$, produced following two sequential light absorption and charge transfer steps. Chemically- and electrochemically-generated $[\mathbf{1}]^{2-}$ reacts with strong acids to generate H_2, but the singly-reduced complex, $[\mathbf{1}]^{-}$ is unreactive in acidic conditions. Relevant excited state and redox properties of the Rh_2(II,II) photocatalysts, along with mechanistic insights obtained from electrocatalysis and other methods, will be presented.



1 R = –H

2 R = –Ph

Figure 1. Molecular structures of **1** and **2**.

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Designing Ligands for Light-Driven Reactions of Metal Hydrides

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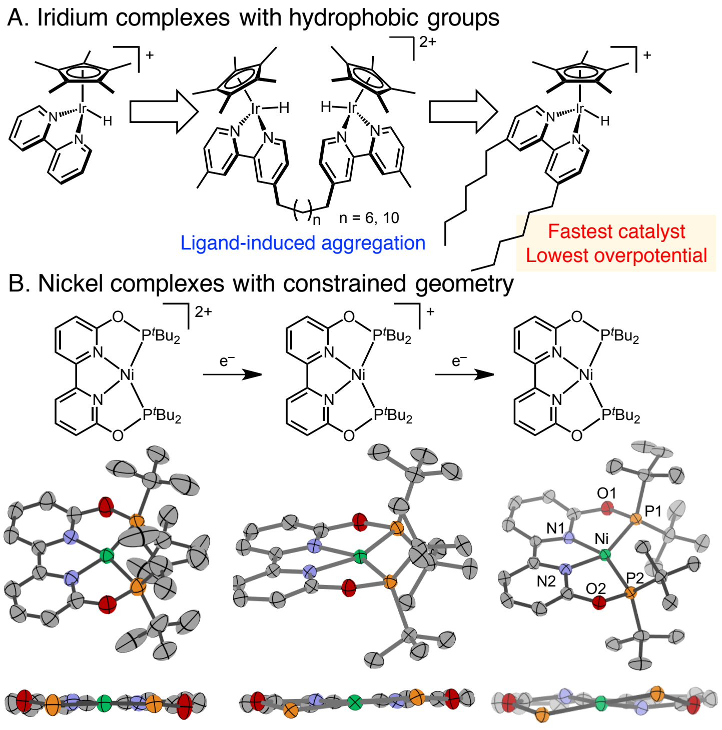
Metal hydride complexes that utilize visible light to drive fuel-forming chemical reactions are promising catalysts for fuel synthesis.[1] One potential advantage of a single molecule capable of both harvesting light and forming strong chemical bonds is that the supporting ligands can be tuned to control the photophysical properties and reactivity. Two examples where ligand modification has helped address challenges in molecular photoelectrocatalysis will be presented.

Iridium complexes such as [Cp*Ir(bpy)H]$^+$ are capable of efficient light-driven H_2 evolution via a mechanism involving bimolecular excited state electron transfer and H–H coupling of two Ir–H units.[2] The interaction of two Ir complexes led us to prepare binucleating ligands that could hold the two metal hydrides in proximity. Initial experiments showed promising enhancement in photoelectrocatalytic activity, but concentration dependence studies implied a more complicated mechanism. A key role was identified for aggregation driven by hydrophobic groups on the organometallic complexes. Recognizing the power of ligand-induced aggregation enabled new monometallic designs that harness noncovalent interactions to bring catalysts into proximity and achieve faster rates at lower overpotential.



Nickel bis(diphosphine) hydride complexes were recently found to be promising 3d transition metal photoelectrocatalysts.[3] Unlike the Ir system, the Ni hydride complexes undergo unimolecular excited state reactions attributed to Ni–H homolysis. To improve the light absorption cross section of these complexes and anodically shift their reduction potentials, diphosphino-bipyridine analogues have been explored. An isostructural series of nickel complexes spanning three charge states was prepared, providing a foundation for understanding electrochemical and photochemical reactivity.

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Roles of Triethanolamine in the Photocatalytic Reduction of CO_2 to Formate by Ruthenium Complexes in Organic Solvents

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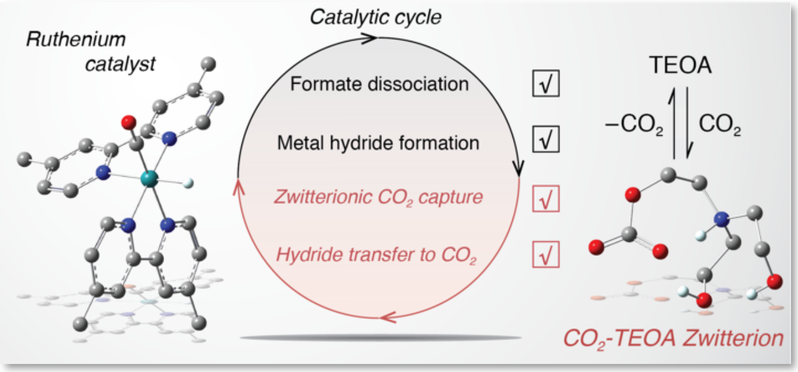
Triethanolamine (TEOA) is commonly employed in mechanistic studies of photocatalytic CO_2 reduction reactions in organic solvents, either as a sacrificial electron donor or as a Brønsted base to ensure the irreversibility of another, more potent, electron donor, by rapid deprotonation of the oxidized donor. However, much of the published research ignores the possibility of secondary roles of TEOA in proposed catalytic mechanisms. Here, we have investigated a series of 4,4′-dimethyl-2,2'-bipyridyl ruthenium(II) complexes with carbonyl ligands using a combination of electrochemical and spectroscopic methods with infrared detection to map out the catalytic pathways and provide structural information on reaction intermediates in the photochemical reduction of CO_2 to formate in acetonitrile (CH_3CN).[1]



An unsaturated, five-coordinate intermediate was characterized, and the hydride transfer step to CO_2 from a singly-reduced metal hydride complex was observed with kinetic resolution. While TEOA was expected to act as a proton acceptor to ensure the sacrificial behavior of the electron donor, 1,3-dimethyl-2-phenyl-2,3-dihydro-1*H*-benzo[*d*]imidazole (BIH), time-resolved infrared (TRIR) measurements revealed that, in contrast to previous expectations, about 90% of the photogenerated one-electron reduced complexes undergo unproductive back electron-transfer in CH_3CN. Furthermore, we found that TEOA partakes in critical supporting reactions, including the zwitterionic capture of CO_2, and assistance in metal-hydride formation and formate product dissociation. TEOA also provides an alternative mechanism in which the hydride is transferred to CO_2 to form the bound formato complex, with a 10^6 rate enhancement compared to in the absence of TEOA. More recently, we have extended this work to *N*,*N*-dimethylformamide (DMF), a solvent that is more commonly employed for photocatalytic CO_2 reduction. The results in DMF are quite different to in CH_3CN. For example, TEOA is a stronger base in DMF, resulting in efficient deprotonation of oxidized BIH and the elimination of back electron-transfer. The reactions of the reduced catalytic intermediates in DMF have been probed by TRIR, including hydride transfer to CO_2. Collectively, our data provide an overview on transient intermediates of Ru(II) carbonyl complexes, and emphasize the importance of considering the participation of TEOA and the nature of the solvent when investigating and proposing catalytic pathways.

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Photochemistry and Electrochemistry of a Binuclear Fe(III) Fused Porphyrin

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Controlling multielectron, multiproton reaction networks is central to electrocatalysis and photoelectrosynthesis.[1,2] Although a common approach taken in molecular-based electron transfer assemblies is to "tune" electronic structure to favor charge transfer, the proton-coupled nature of nearly all chemical reactions relevant to solar photochemistry presents a fundamental impasse to applying this design strategy. Leveraging previous work from our group on the two-electron chemistry and electrocatalytic properties of binuclear Cu(II) fused porphyrins,[3] we present the synthesis and characterization of a binuclear Fe(III) fused porphyrin (**Figure 1**).[4] Key features of the fused iron porphyrin include: 1) bimetallic-iron sites, 2) a π-extended ligand capable of delocalizing electrons across the multimetallic scaffold, and 3) the ability to store up to six electrons. These properties are promising in the context of catalyzing multielectron, multisubstrate redox transformations, including oxygen reduction and carbon dioxide reduction half reactions.

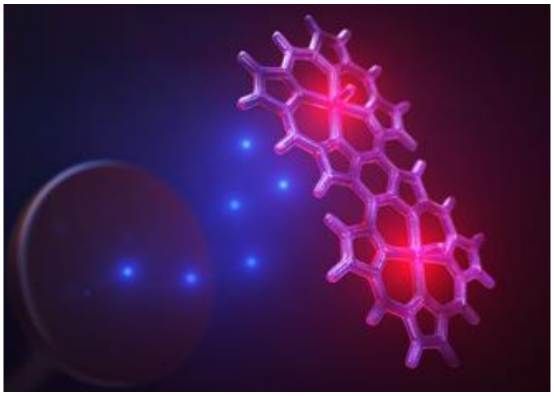

Figure 1. Schematic illustration of charge transfer between an electrode surface and a π-extended, fused metalloporphyrin complex (Image *adapted from the cover of reference 4*).

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Selective and Durable Catalysts for Photochemical CO_2 Reduction to CO and Formate

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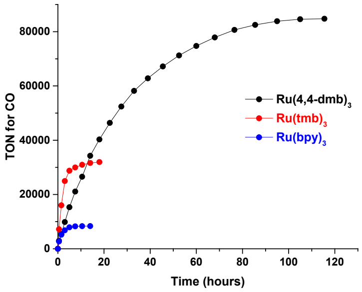
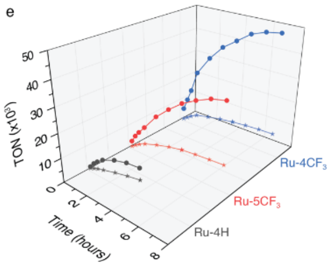
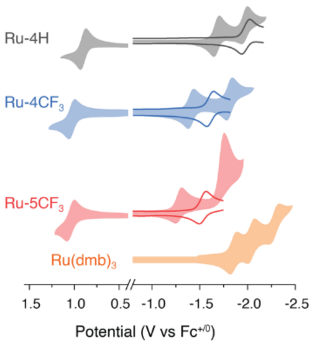
In this poster we will discuss two projects for photochemical CO_2 reduction. The first project focuses on photochemical CO generation using an N-heterocyclic carbene (NHC)-based catalyst. The second project focuses on a new approach to generate highly hydridic metal-hydrides for formate generation. **A)** ***NHC catalysts with controlled selectivity in photochemical CO_2 reduction***. The catalyst $[Ru(tpy)(Mebim\text{-}py)(CH_3CN)]^{2+}$ is one of the most efficient electrocatalysts for CO_2 reduction to CO in terms of selectivity (~90%), TOF (2400 s^{-1}) and robustness. However, photochemical CO_2 reduction has not been reported yet. Interestingly, photocatalysis with the NHC catalyst in a 4-component system using three different $Ru(bpy)_3$-like photosensitizers with different redox potentials ($[Ru(bpy)_3]^{2+}$, $E_{1/2} = -1.75$ V; $[Ru(dmb)_3]^{2+}$, $E_{1/2} = -1.83$ V and $[Ru(tmb)_3]^{2+}$, $E_{1/2} = -1.95$ V) resulted in formate as the dominant CO_2 reduction product under conditions analogous to those used in the electrocatalytic studies. Moreover, the formate/CO ratio is strongly dependent on the reducing power of the photosensitizer and this ratio decreases with the potential of the photosensitizer. In anhydrous acetonitrile using $[Ru(dmb)_3]^{2+}$ as photosensitizer the 4-component system is 100% selective for CO generation with more than *80,000 turnovers*!



B) ***Highly hydridic metal-hydrides with electron-deficient ligands.*** Molecular metal-hydrides have the distinct advantage of allowing tunability of their hydricities by rational ligand modifications, with more electron-rich metal-hydrides being in general more hydridic. We report here a new approach to generate highly hydridic metal hydrides of the type $[Ru(tpy)(NN)(H)]^{n+}$ by introducing electron-withdrawing substituents in the back-bone of the NN ligand. This strategy enables the generation of the $[Ru(tpy)(NN)(H)]^{+}$ metal hydride at mild negative potentials and further one electron reduction to the more hydridic $[Ru(tpy)(NN)(H)]^{0}$ at a potential window that is redox silent by the more electron-rich metal hydride analogue $[Ru(tpy)(bpy)(H)]^{+}$. The parent $[Ru(tpy)(NN)(CH_3CN)]^{2+}$ solvento complexes were then tested as catalysts for the reduction of CO_2 to formate in a 4-component homogenous photochemical approach driven by a Ru(II) sensitizer. The results showed selective (> 91%) formate production with record turnover number of ~50,000 and record turnover frequency of 4.5 s^{-1} when compared to other molecular catalysts.





Progress towards Low Overpotential Reversible Aqueous CO_2/HCO_2^- Electrocatalysis and Activating Formate for > 2 e^- Reduction in a Cascade Catalytic Scheme

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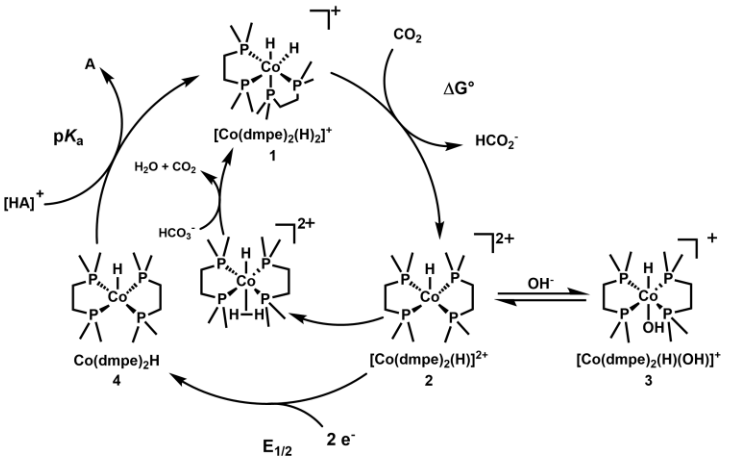
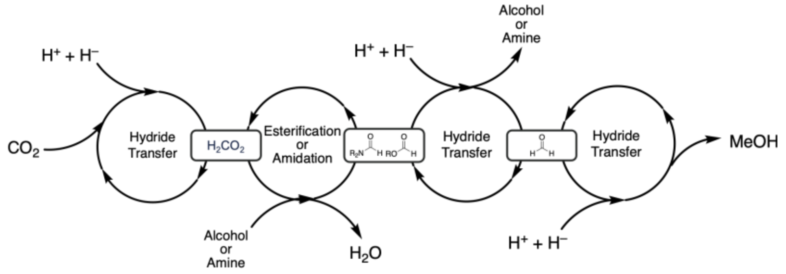
Low Overpotential Reversible Aqueous CO_2/HCO_2^- Electrocatalysis. Reversible catalysis is a hallmark of energy-efficient chemical transformations, but can only be achieved if the changes in free energy of intermediate steps are minimized. In aqueous conditions H^+ can also directly react with MH to form H_2, reducing product selectivity for CO_2 reduction. Therefore, H^+ *and* CO_2 reactivity must be considered for selective, reversible conversion between CO_2 and HCO_2^- (Scheme 1). A metal hydride catalyst with an appropriate aqueous hydricity for ergo-neutral hydride transfer, $[Co(dmpe)_2(H)_2]^+$ (dmpe = 1,2-bis(dimethylphosphino)ethane), was studied for low overpotential, reversible electrocatalysis. A hydroxide bound species, $[Co(dmpe)_2(OH)H]^+$, is formed upon hydride transfer. Increasing amounts of OH^- in solution at higher pH values effectively increases the hydricity of $[Co(dmpe)_2(H)_2]^+$. As a result, the effective $\Delta G°_{H-}$ of $[Co(dmpe)_2(H)_2]^+$ is pH dependent, leading to pH dependent free energies of H^- transfer to CO_2, while the free energy of HER remains the same value at all pH values. Stoichiometric hydride transfer reactions and electrolysis experiments indicate that formate production is more favorable than H_2 evolution only under conditions slightly above 7.4. Above pH 8, H_2 is still the favored product.

Scheme 1.



CO_2 reduction to CH_3OH through Cascade Catalysis. We are exploring the activation of formate to form CH_3OH in a cascade electrocatalytic system (Scheme 2). We have found that activation to form an ester is unfavorable under ambient conditions. However, electron deficient amines can successfully form amide derivatives under mild conditions. Further activation of these amides is being pursued with compatible hydride transfer catalysts to form formaldehyde, which would then be easily reduced to CH_3OH.

Scheme 2



Particle Size Effects on Electron Transfer and Catalysis at Metal/Semiconductor Interfaces

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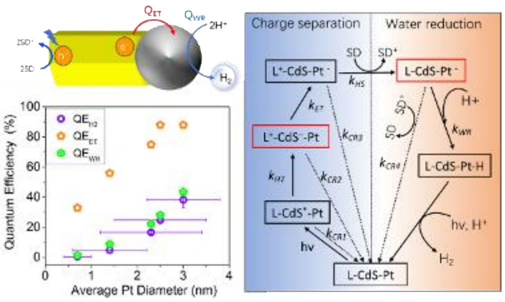
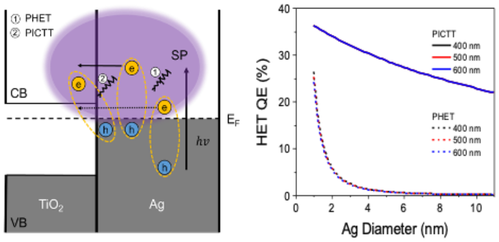
Nanoparticle sizes can have profound effects on the optical and electronic properties of semiconductor and metal. In this presentation, I will discuss our recent works that reveal the importance of metal nanoparticle size in controlling the efficiency of both plasmon induced hot electron transfer and light driven H_2 generation in semiconductor-metal nanoheterostructures.

1). Pt particle size affects both the charge separation and water reduction efficiencies of CdS-Pt nanorod photocatalysts for light-driven H_2 generation. Decreasing the metal catalyst size into nanoclusters or even single atom is an emerging direction of developing more efficient and cost-effective photocatalytic systems. Because the catalyst particle size affects both the catalyst activity and interfacial charge transfer, their effects on the overall photocatalytic efficiency is poorly understood. To answer this question, we study the effect of the Pt catalyst size on light driven H_2 generation quantum efficiency (QE_{H_2}) of Pt-tipped CdS nanorods (NRs). With the increase of the Pt catalyst size from 0.7±0.3 to 3.0±0.8 nm, the QE_{H_2} of CdS-Pt increases from 0.5±0.2% to 38.3±5.1%, by nearly two orders of magnitude. Transient absorption spectroscopy measurement reveals that the electron transfer rate from the CdS NR to the Pt tip increase with the Pt diameter following a scaling law of $d^{5.6}$, giving rise to the increase of electron transfer efficiency at larger Pt sizes. The observed trend can be understood by a simplified kinetic model that assumes the overall efficiency is the product of the quantum efficiencies of charge separation (including hole transfer, electron transfer and hole scavenging) and water reduction steps, and for CdS-Pt NRs, the quantum efficiencies of electron transfer and water reduction steps increase with the Pt sizes. Our findings suggest the importance of improving the quantum efficiencies of both charge separation and catalysis in designing efficient semiconductor-metal hybrid photocatalysts, especially in the regime of small metal particle sizes.



2) Highly Efficient Plasmon Induced Hot-Electron Transfer at Ag/TiO2 Interface. Plasmon induced hot carrier transfer is a promising novel approach for solar energy conversion, but its practical application is often hindered by its low efficiency. This work demonstrates an unprecedented quantum efficiency of plasmonic hot-electron transfer of up to 53 ± 2% from 1.7 nm silver nanoparticles to anatase nanoporous TiO_2 films at 400 nm excitation. This efficient hot electron transfer consists of contributions of both hot electrons generated by plasmon decay through exciting Ag intraband transitions and Ag-to-TiO_2 interfacial charge-transfer transitions. The efficiencies of both pathways increase at smaller Ag particle sizes from 5.9 to 1.7 nm, suggesting that decreasing particle sizes is a promising way towards efficient plasmonic hot-carrier extraction.



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

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Materials that show most promise for many photocatalytic processes (including water splitting) contain a semiconductor light absorber (SC) and an attached metal electrocatalyst (EC). The interface between the SC and EC plays a pivotal role for the performance of these systems. In most cases, this interface evolves spontaneously under reaction conditions. Our project focusses on shedding light on the role of these interfaces by developing appropriate atomistic models that allow us to understand and quantify the underlying physical mechanisms by which they affect the performance of SC/EC systems.

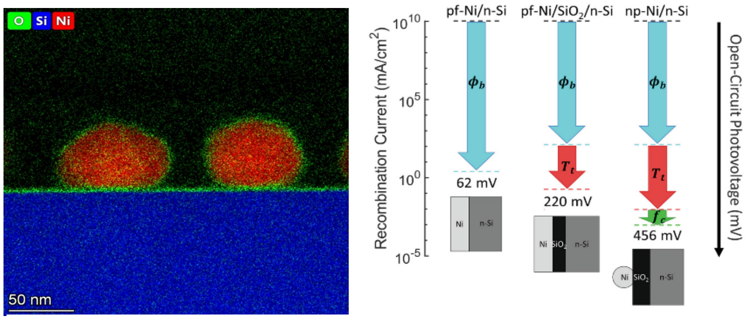

Figure 1: left EDS/STEM cross-sectional micrograph showing Ni nanoparticles on Si after photoelectrocatalytic water oxidation. Evolution of oxide interlayer and oxidized Ni shell is observed. (right) Modeled recombination current densities and photovoltage evaluated at equilibrium and modeled photovoltages for different Ni/Si system. The blue dashed lines represent the recombination current considering only the equilibrium barrier height between Ni and Si, without additional effects. The red dashed lines represent the recombination current after additionally accounting for the impact of the SiO$_2$ layer which limits the probability that the electrons will tunnel through and recombine in the metal. The green dashed represents the recombination current after additionally accounting for the effect of catalyst coverage (i.e., Ni nanoparticle instead of a planar Ni film, the Ni coverage was 22 percent of the Si surface).

We specifically focused on describing the interface of a functioning semiconductor (Si) and nanoparticle electrocatalysts (Ni) in photoelectrochemical water oxidation. We show that to rigorously capture and explain the behavior of EC/SC water splitting photoelectrocatalysts under reaction conditions it is necessary to unearth the atomistic features of the interface. We found that the interface plays a critical role in (1) affecting the fluxes of energetic electrons and holes between SC and EC and therefore modulating the electron/hole recombination rates. In many cases, the physical mechanism that is involved in these processes is quantum tunneling of electrons and holes across thin insulators with high potential barrier, (2) changing the barrier height of the junction by affecting the effective work functions of the SC and EC, and (3) introducing nonidealities which detrimentally impact the performance.[1–1–3] Our analysis shows that all mechanisms have a meaningful impact of the performance, and that any predictive model has to account for all the factor. These findings are important for optimizing nanoparticle catalyst/semiconductor interfaces which are ubiquitous in photoelectrocatalysts.

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Photo-SECM of Single Semiconductor Particles

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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 used photo-SECM to investigate photochemical water splitting at single Al-doped $SrTiO_3$ cubes modified with $Rh_xCr_yO_z$. An SECM tip served as a nanoelectrode and a light guide, and an improved experimental setup was developed in which the nanoprobe is mechanically decoupled from the optical fiber and light is delivered to the back of the tip capillary using a lens system. In this way, we obtained topographic images of Al:$SrTiO_3$ cubes without adding a redox mediator to solution and measured oxygen and hydrogen fluxes generated by a single particle under UV illumination.

A new methodology was developed for photo-electrochemical experiments at a single microcrystal attached to a nanoelectrode that simultaneously served as a light guide. A glass sealed, polished SECM tip was moved vertically toward the upper face of an immobilized cube until the physical contact occurred and the cube stuck to its glass shroud. Fig. 1A shows optical images of an Al:$SrTiO_3$ cube with ~2 µm edge length attached to a 180-nm-radius Pt tip (panel i) and the same arrangement with the through-tip illumination (panel ii). With no electrical connection between the Pt disk and the cube attached to glass, the measured current was either due to the reduction of oxygen or oxidation of hydrogen produced by photochemical water splitting at the Al:$SrTiO_3$ surface. From the current pulses induced by turning on/off the UV light one can evaluate oxygen (Fig. 1B, panel i) and hydrogen (Fig. 1B, panel ii) fluxes generated at the cube surface.

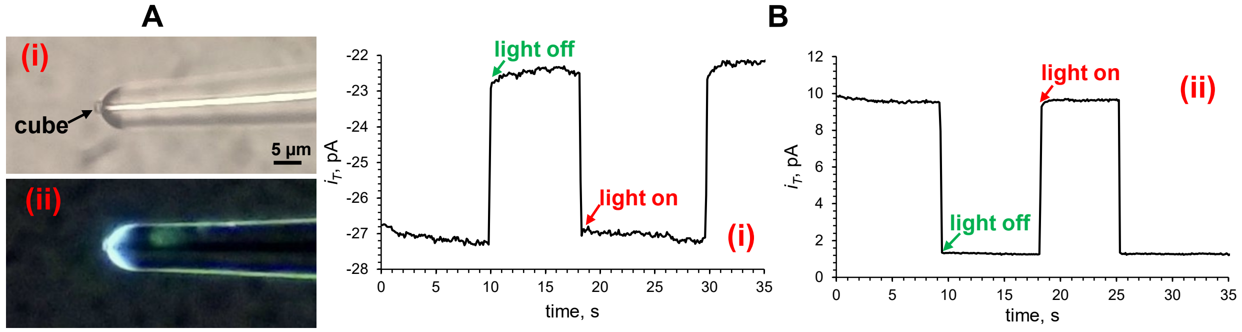

Fig. 1. Probing photochemical water splitting at an Al:$SrTiO_3$ cube attached to a nanoelectrode. (A) Optical micrographs of the SECM tip with an attached cube in the dark (i) and under through-tip illumination (ii). (B) Photo-transients obtained for the reduction of oxygen (i) and oxidation of hydrogen (ii) generated at the same cube. The tip potential was -0.95 V (i) and 0.4 V (ii) vs Hg/$HgSO_4$ reference. Solution contained 10 mM K_2SO_4 and no added redox species except dissolved O_2.

In the future, we will measure photochemical and photoelectrocatalytic rates at single micro/nano-crystals and carry out high-resolution mapping of catalytic cites on surfaces of such particles by using photo-SECM with smaller nanotips.

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A new solar Hub entitled the *Center for Hybrid Approaches in Solar Energy to Liquid Fuels,* or CHASE, was launched in September of 2020. The mission of CHASE is to develop molecule/material hybrid photoelectrodes for cooperative sunlight-driven generation of O_2 and liquid fuels from CO_2, H_2O, and N_2. Emphasis is placed on molecular catalysts integrated with semiconducting materials with precisely controlled microenvironments created around the catalysts. There is a vast, mostly unexplored space at the intersection between molecular catalysts and heterogeneous materials, presenting unique opportunities for advances in photocatalytic durability and product selectivity. CHASE is guided by the overarching hypothesis that the challenge of liquid solar fuel production can only be met through the cooperative interactions of molecules and materials. This hypothesis derives from observations suggesting that *neither* heterogeneous materials alone *nor* homogeneous molecular catalysts alone have proven to be sufficient and that untapped opportunities for cooperativity exist at this interface.

The overarching five-year goal of CHASE is to develop a detailed fundamental molecular level understanding of how hybrid photoelectrodes couple single photon absorptions to multi-electron/proton chemical transformations to generate liquid fuels and O_2 from CO_2, N_2 and H_2O. Through realization of a comprehensive mechanistic picture of the elementary steps that comprise the entire hybrid photoelectrode system, CHASE plans to lead the quest for liquid solar fuels. Guided by theory, photoelectrode architectures that pair light-absorbing materials with molecular fuel-producing catalysts have been constructed. Mechanistic investigations employing a diverse set of *ex situ*, *in situ*, and *operando* surface-specific characterization tools provide new perspectives in our understanding of light-driven chemistry at material–molecule–solution interfaces. This approach targets design principles and foundational insights, rather than a specific solar fuels device design, with the expectation that CHASE findings will be broadly applicable in the development of many different solar fuels technologies. This focus on fundamental science, however, does not preclude the opportunity to demonstrate liquid solar fuel production using hybrid photoelectrodes.

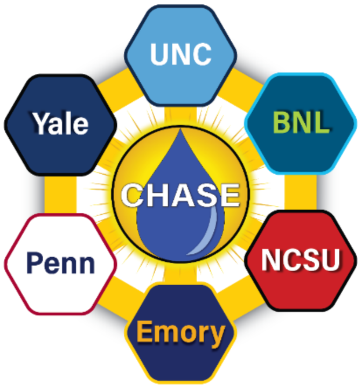

Figure 1. The six partner institutions that comprise CHASE.

To achieve the CHASE mission, an interdisciplinary and multi-institutional team has been assembled with leadership based in the Chemistry Department at the University of North Carolina at Chapel Hill, and partners at Yale University, Brookhaven National Laboratory, the University of Pennsylvania, North Carolina State University and Emory University, Figure 1. As is detailed below, team members contribute to three interrelated thrust research areas that have been initiated to enable the CHASE goal: (1) Understand the fundamental principles that enable the integration of semiconductor light absorbers with molecular catalysts to drive liquid fuel production (Thrust I: Semiconductor-Catalyst

Integration); (2) Tailor the local environment around the catalyst on a molecular scale to direct reactivity along desired pathways (Thrust M: Catalyst ***M***icroenvironments); and (3) Develop design principles that enable the cooperative integrated photosynthesis of liquid fuels through multi-catalyst cascades (Thrust C: Liquid Fuel ***C***ascades), Figure 2.

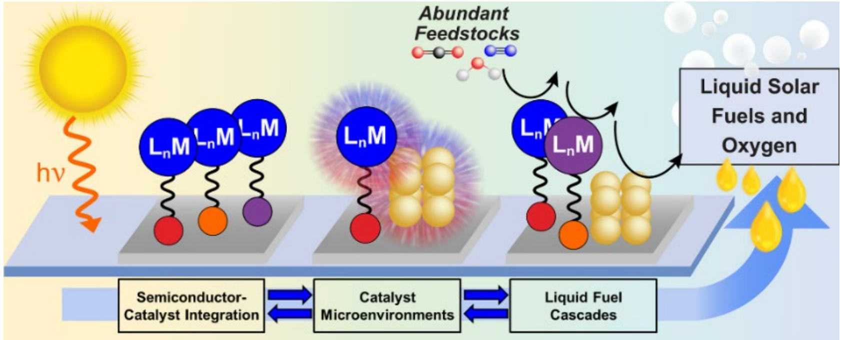

Figure 2. The CHASE five-year goal will be achieved through three synergistic Thrusts.

Thrust I seeks to understand the fundamental principles and design strategies that enable the integration of semiconductor light absorbers with molecular catalysts to drive liquid fuel production. Thrust I bridges the knowledge divide between the semiconductor and molecular catalyst communities to design new hybrid photoelectrodes through systematic construction of new interfaces and fundamental studies of their structure and dynamics from short (femtosecond) to long (day) time scales. Thrust I involves studies on the mechanisms of surface photocorrosion and passivation, design of the interface environment to promote charge transfer, integration of semiconductors that continuously store multiple charges with molecular catalysts that mediate multi-proton and multi-electron events and design of molecular attachment strategies to electronically and physically couple semiconductors and molecular catalysts.

Thrust M seeks to learn how to purposely tailor the local environment around the catalyst on a molecular scale to direct reactivity along desired pathways for the reduction of CO_2 and N_2 to liquid fuels, and for the oxidation of water to O_2. This local catalyst microenvironment forms at the semiconductor–catalyst interface in hybrid photoelectrodes. CHASE investigators will (a) understand the native microenvironment and create catalyst microenvironments containing various chemical functionality in hybrid photoelectrodes, (b) systematically characterize these micro-environments, and (c) understand how the microenvironment influences activity, selectivity, and durability in liquid solar fuel production.

The goal of Thrust C is to develop design principles that enable the cooperative integrated photosynthesis of liquid fuels through multi-catalyst cascades. Despite impressive progress in the generation of H_2, HCO_2H, and CO, the generation of *liquid* fuels with high activity and selectivity remains a central challenge in artificial photosynthesis. Thrust C interrogates innovative strategies to address this problem, based on the guiding hypothesis that multiple catalysts can work synergistically to generate specific liquid fuels, a hypothesis inspired by biological photosynthesis. Few synthetic catalysts can efficiently navigate the generation of liquid fuels by themselves. By simplifying *multi*-proton/*multi*-electron transformations into shorter sequences carried out by multiple catalysts, each catalyst is independently optimized to achieve the overall energy-storing reaction with minimal kinetic barriers**.**

In this presentation, an overview of CHASE activities will be provided with select research advances towards the realization of liquid solar fuels.

Detailed-Balance Efficiency Limits for Protonic Energy Conversion by Aqueous Photoacids

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Charge separation is important for photochemical energy conversion, so much so that "band bending" in typical semiconductor pn-junctions is often thought to be a critical prerequisite. However, it is the preceding step of light absorption that is most important, and when coupled to excited-state recombination, dictate the detailed-balance (Shockley–Queisser) energy conversion efficiency limit.

Given that our overall project goal is to better understand the function of light-driven proton pumps based on photoacid-dye-sensitized bipolar ion-exchange membranes, we developed a methodology to calculate the *protonic* detailed-balance efficiency limit for photoacids in water. Assuming a hypothetical photoacid with a Gaussian molar absorptivity spectrum, detailed-balance absorption and emission of blackbody radiation results in a predicted Stokes-shifted emission spectrum. Using the Strickler and Berg formalism for a two-electronic-state molecular system, calculation of the Einstein A coefficient results in a value for the excited-state radiative lifetime. This key kinetic parameter is then coupled to proton-transfer reactions that follow the Förster cycle square scheme, with thermodynamics that obeys Hess's law and rate constants that either follow the Brønsted model or Marcus–BEBO theory. This results in a zero-dimensional photophysical chemical kinetics model that under detailed-balance conditions enables us to determine the *protonic* solar energy conversion efficiency limit, which is ~10% for ideal photoacids in water under 1 Sun.

In comparison to prior detailed-balance models, ours is unique, because it includes chemically rigorous rate constants and reactivity based solely on mass action, and thus indirectly it assumes that all charges are screened. In this regard, it differs from PEC and PV models that instead rely on charges for current matching and/or interfacial capacitive charging, and where radiative lifetimes are rarely calculated.

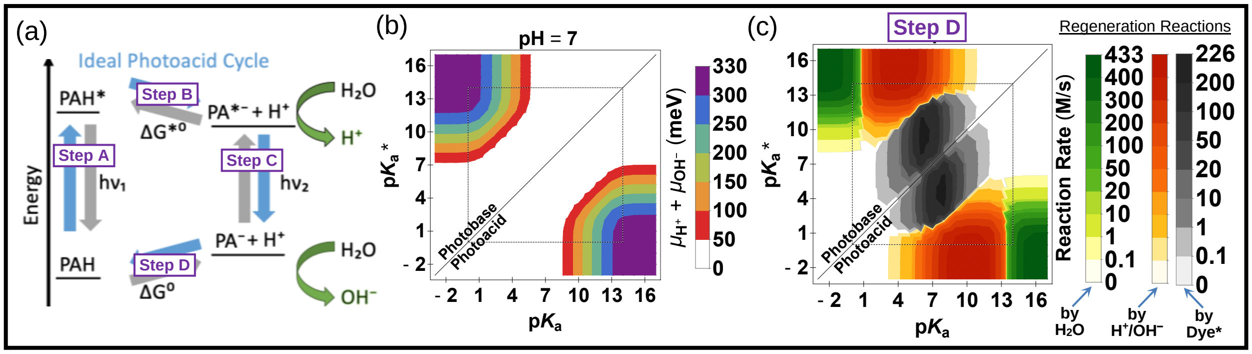

Figure 1. (a) Steps in the Förster cycle for light-to-protonic energy conversion from an optimized photoacid dye, where absorption of light generates both H^+(aq) and OH^-(aq) from water to effect overall heterolytic water dissociation. (b) Simulated detailed-balance-limit protonic quasi-chemical-potential splitting and (c) dominant reactions for *Step D* in panel a, at pH 7 as a function of pK_a and pK_a^*, assuming Brønsted theory for proton-transfer reactions, i.e. $\Delta G^{\neq} = 0$ for $\Delta G^o = 0$.

The Redox Potential of O_2 in the Nonpolar Environment of Molecular Films

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Dioxygen (O_2) is an important molecular species in solar photochemistry. However, being a small molecule, the superoxide ion is expected to be particularly stabilized by ion-pairing and solvation in the conditions used to measure $E^o(O_2)$ with electrochemistry (polar solvent + 0.1 M electrolyte).[1,2] By contrast the redox potentials of larger, highly conjugated molecules used for solar energy conversion are less sensitive to ion pairing and polarity due to charge delocalization.[3] What are these potentials in the nonpolar environment of molecular films ($\varepsilon_r \sim 2 - 4$)? Fig. 1 shows how electrochemical data and computational estimates predict only modest changes until the relative dielectric constant goes below ~10. Below here, the dramatic shifts in E^o are expected to be strongly dependent on the molecular ion size with O_2 predicted to have some of the most dramatic changes.

We seek to use pulse radiolysis to bridge the gap between the environment in which redox potentials can be measured electrochemically and where we wish to know them. Using pulse radiolysis, we have investigated electron transfer equilibria ($D^{-\bullet} + O_2 \leftrightharpoons D + O_2^{-\bullet}$) in a range of conditions that are not commonly accessible with voltammetry (non-polar solvents and electrolyte-free). This region is marked “?” in Fig. 1. We compare our results to predictions from DFT and discuss the implications for stability of devices in ambient conditions.

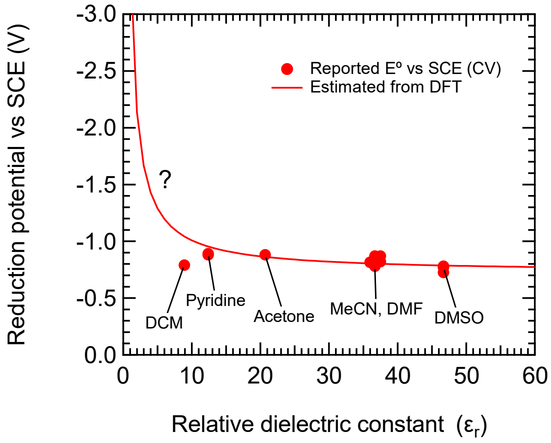

Figure 1. Reported redox potentials from electrochemical measurements (markers) for dioxygen in various solvents (tags) vs ε_r of the solvent. The solid line is a fit to DFT estimates using a simple Born solvation model.

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2. Bird, M. J., Miller, J. R. IntechOpen 2022 DOI:10.5772/intechopen.103003
3. M. J. Bird, M. A. Pearson, S. Asaoka, J. R. Miller, *J.Phys. Chem. A* **2020**, 124, 26, 5487–5495

Controlling Interfacial Charge Separation Energetics and Kinetics: Strong Photoinduced Organic Oxidants for Exploring Marcus Theory at TiO_2 and Driving Water Oxidation

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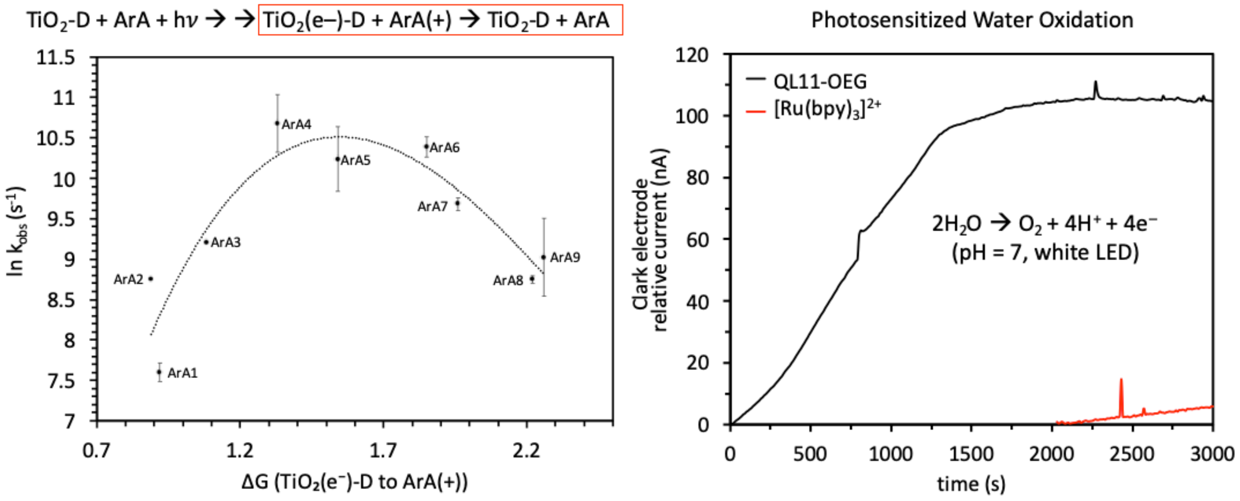
A series of donor-π bridge-acceptor organic dyes have been designed that vary the donor portion of the dye design. The oxidation potentials of the dyes vary over a 1.3 V range with all dyes being suitable for electron injection into TiO_2 while having oxidation potentials as positive as 2.2 V versus NHE. These dyes were all studied with respect to photoinduced electron transfer kinetics at the TiO_2 interface via transient absorption spectroscopy (TAS). Additionally, a series of amines varying oxidation potentials over a 1.4 V range were analyzed via TAS in solution above TiO_2-dye films to probe the rate of electron transfer from reduced TiO_2 to the oxidized amine species formed after photoexcitation of the dye. Additionally, utilizing the dye design elements from this study, a new series of organic photosensitizers were designed using a donor-acceptor-donor construct for solution studies. The sensitizers feature weak aryl donors that become potent photooxidants and a strongly electron withdrawn bridge. A substantial dihedral angle is present between the donor and acceptor groups. These systems have significantly positive excited state reduction potentials (2.49 V versus NHE) and exceptional excited state lifetimes at 16 µs. These photosensitizers were shown to be effective at driving photosensitized water oxidation at a faster rate than benchmark photosensitizer $[Ru(bpy)_3]^{2+}$ under identical conditions (white LED, pH = 7).



Left Image: Electron transfer kinetics plotted versus driving force for electron transfer from reduced TiO_2 to an oxidized aryl amine (ArA^+). The dye bound to TiO_2 is held constant in all of these examples. Right Image: Photocatalyzed O_2 production as observed via a Clark electrode over time with a strong photooxidant (PS: QL11-OEG) compared to $[Ru(bpy)_3]^{2+}$ as a benchmark PS under otherwise identical conditions.

Redox Properties of Strongly Oxidizing Radicals in Organic Solvents Probed by Pulse Radiolysis

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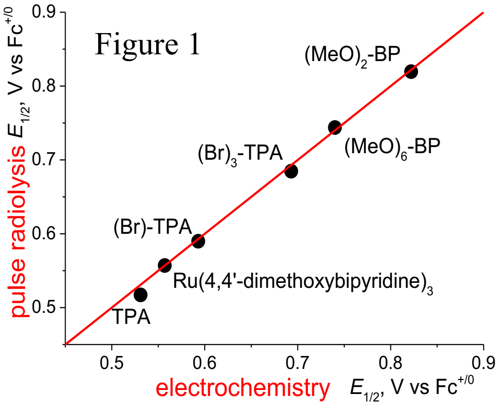
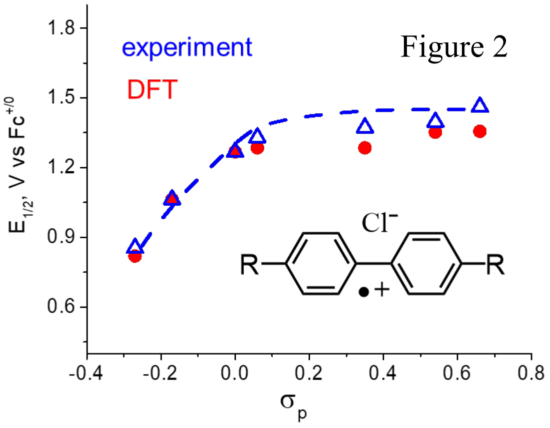


Properties of strongly oxidizing radicals in organic media are important for understanding charge transport in organic solar cells, mechanistic studies of electron transfer in solutions, and probing chemical transformations in nuclear fuel processing. However, investigation of such high energy species is challenging due to their transient nature and limited availability of methods for their generation. Conventional electrochemical techniques, such as cyclic or pulsed voltammetry only yield approximate values of reduction potentials of highly oxidizing radicals due to irreversibility of electron transfer.[1] In this work we employed pulse radiolysis (PR) to generate radical cations of substituted triphenyl amines (TPA) and biphenyls (BP) and measured their reduction potentials using redox equilibrium ladder approach. Potentials of TPA$^{\bullet+}$ and methoxy-substituted biphenyls in 1,2-dichloroethane containing 0.1M TBA PF$_6$ are mild and electrochemically reversible. Potential values measured by PR and electrochemistry show good correlation thus validating PR equilibrium method (Figure 1). Potentials of *p*-substituted biphenyls increase from R = OMe to R = CN, but the trend shows saturation at higher σ_p values (Figure 2). We explain this effect by strong ion pairing between anions present in solution (e.g., Cl$^-$ produced from radiolysis of DCE) and BP$^{\bullet+}$. This interpretation is consistent with reduction potentials of [BP$^{\bullet+}$ Cl$^-$] ion pairs predicted by DFT calculations. Our current work is focused on understanding the effects of added electrolyte or various solvents on measured potentials of biphenyl derivatives.



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Electronic and Nuclear Structural Characterization of Catalytically and Photocatalytically-active Transition Metal Complexes by Static and Transient X-ray Absorption Spectroscopy

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Metal clusters and complexes play important role in electro and photo-catalysis due to their abilities of accommodating multiple redox equivalents for value added products. However, the electronic interactions between the metal centers and their correlations with structures as well as catalytic functions are not always clear. Here we describe our recent work towards understanding the interplay between transition metal center redox/structural properties of catalyst intermediates and catalytic efficiency. In collaboration with Hill Group, we investigated a series of polyoxometallates (POM) of the form $M_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ which are active in water splitting following two electron oxidation for M = Co(II). The oxidized intermediate species for the **Co$_4$** and **Co$_2$Ni$_2$** POMS were generated by ozonolysis and captured via rapid freeze quench. Co K-edge XAS of **Co$_2$Ni$_2$** POM exhibits oxidation of both Co centers from Co(II) to Co(III) (Figure 1). Interestingly, the same measurements on **Co$_2$** POM reveal much lower net oxidation of the Co centers, suggesting that the newly introduced holes are localized across the core in **Co$_2$** POM, but localized on the Co centers in **Co$_2$Ni$_2$**POM. Similarly, EXAFS result shows significant Co-O bond contraction in **Co$_2$Ni$_2$** POM with little change around the Ni centers by the Ni K-edge XAS measurements, while the total structural change in **Co$_4$** POM is diminished. Localization of the hole equivalents on the **Co$_2$Ni$_2$** POM result in great catalytic efficiency towards water splitting than **Co$_4$** POM, demonstrating how electronic communication across the POM core can be tuned to enhance catalytic efficiency.

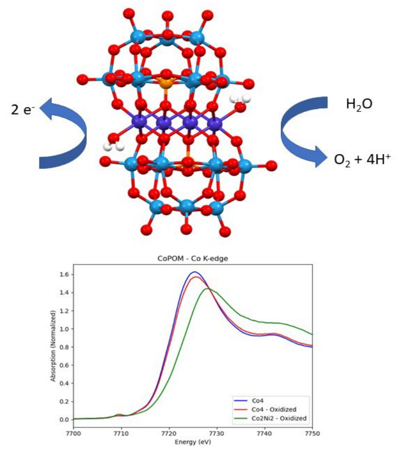

Figure 1: Top: Structure of CoPOM. Bottom: Co K-edge spectra of ground-state CoPOM (blue), oxidized **Co$_4$** POM (red), and oxidized **Co$_2$Ni$_2$** POM (green)

Optical excitation of Ir(III) hydride results in generation of H_2 via collision of two Ir centers. Collaborating with Miller Group, we utilized X-ray transient absorption (XTA) spectroscopy to determine structures of the intermediate species that participate in the H_2 evolution reaction. At early times (~100 ps) following photoexcitation, we observe a difference signal that is consistent with MLCT excitation resulting in a transient Ir(IV) center (Figure 2). One the ns-μs timescales, a different difference signal is observed; here, we a net reduced Ir species is observed, consistent with an Ir(I)/Ir(III) pair, which decays with ~ 3 μs time constant. These results serve as an advancement of our understanding of Ir photocatalysis and serve as an excellent demonstration of the capabilities of pump-probe X-ray spectroscopy to elucidate the many metal-centered intermediates that participate in photocatalysis.

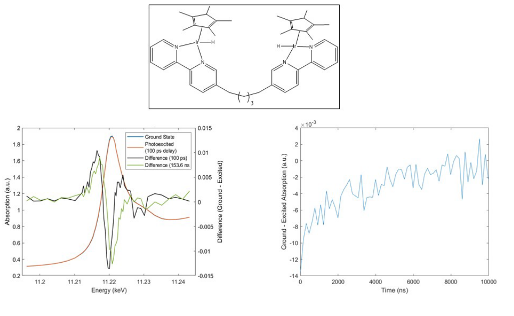

Figure 2: Top: Structure of Ir hydride catalyst. Left: Ir L3-edge XAS spectra of Ir hydride, including difference signals following photoexcitation. Right: Kinetics of recovery of Ir difference signal.

New Photo-Electrode and Water Oxidation Catalyst Dynamics and Mechanistic Studies

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I. Roles of 3d-metals (TM), adjacent to the active site metal, on stability and reactivity of M-$Co_2TM_2P_2$ polyoxometalate (POM) water oxidation catalysts (WOCs). To elucidate the impact of two internal 3d-metal ions (**TM**) on the catalytic activity of the outer Co centers of the previously prepared $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10}$ **Co_4P_2** WOC (Fig. 1), we have synthesized mixed-metal POM WOCs, including $[Co_2Ni_2(PW_9O_{34})_2]^{10-}$, **$Co_2Ni_2P_2$,** and validated location of each 3d-metal in **$Co_2Ni_2P_2$** using multiwavelength synchrotron X-radiation anomalous dispersion scattering (synchrotron XRAS). We demonstrate that XRAS can be widely used for structural characterization of other catalysts with two or more different proximal metals. We revealed that the internal Ni-centers of **$Co_2Ni_2P_2$** impact the WOC activities of the Co-centers by perturbing their electronic properties and coordination environments.

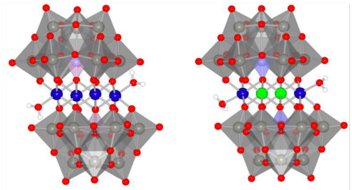

Fig. 1. **Co_4P_2** (left) and **$Co_2Ni_2P_2$** (right) water oxidation catalysts. Co: blue; Ni: green; WO_6, gray octahedra.

II. Counterions (M) effects on redox properties of POM WOCs. We have prepared **M** = Cs^+, Ba^{2+}, La^{3+} and Y^{3+} salts of **M-**$[Co_9(H_2O)_6(OH)_3(HPO_4)_2(PW_9O_{34})_3]^{16-}$ (**M-Co_9P_5**), and studied their X-ray structures (Fig. 2). FT-IR spectroscopy and PXRD studies show no change in the **M-Co_9P_5** complexes after electrocatalytic water oxidation. Significantly, the **M-Co_9P_5** catalysts are stable in acid down to below pH 2. We identified factors impacting structures and stabilities of these complexes, and established that two phosphate units, located outside of the Keggin-cages, interact with the Co centers stabilizing the $Co_9P_2O_xH_y$ core of **M-Co_9P_5**, some of Co centers of which are involved in the water oxidation processes.

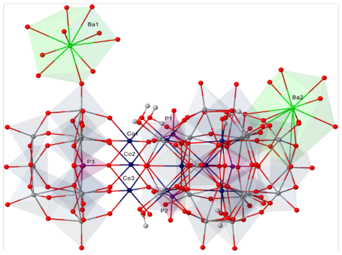

Fig. 2. X-ray structure Ba^{2+} salt of **Co_9P_5**. Co: dark blue balls; PO_4, purple; WO_6, gray; BaO_8, green.

III. Developing novel *in-situ* spectroscopy tools for studying carrier dynamics at planar photoelectrode/liquid interfaces. We have developed two new techniques based on transient reflectance (TR) spectroscopy and time-resolved electric field induced second harmonic generation (EFISH) for *operando* study of planar photoelectrodes. By using these methods, we have shown that: (a) the measured charge separation and water reduction efficiencies, in addition to the overall light-to-current conversion efficiency, will provide detailed insight into the loss mechanisms of these electrodes, and (b) for n-TiO_2 photoanodes under light-driven water oxidation conditions, the charge state of the rate-limiting intermediates depends on the buffer conditions.

IV. Computational approach for interfacial charge transfer (ICT) at the Semiconductor (SC)/Molecule interfaces. We continued development of a hybrid [BA-LCAO]/DFT computational approach to study ICT in the SC/molecule interfaces. To better describe ICT probabilities and rates between nanocrystals (NC) of different size and an acceptor, we extended this approach to include: (a) electron/hole interaction, and (b) exciton-exciton coupling using a many-body expansion theory, i.e. CI singles.

Sequential Surface Synthesis for Operando X-ray Analysis and Few-Atom Cluster Synthesis

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The operando X-ray characterization of photoelectrochemical interfaces competent for solar fuels forming reactions requires photoelectrodes that are compatible with advanced X-ray methods. An overarching goal of this program is to track the sequences of electronic and structural dynamics that underlie solar-to-fuels energy conversion mechanisms. In particular, the amorphous character of many solar fuels catalysts and the complexity of the interfacial architectures that merge semiconductor supports with discrete sites for multi-step catalysis pose challenges for probing those mechanisms. Hard X-ray total scattering pair distribution function (PDF) analysis is especially pertinent to solar fuels forming interfaces as it reveals high-resolution inner and outer coordination sphere structural information of non-extended solids including coordination complexes, amorphous inorganic assemblies, and even solvent interactions. We have developed and implemented high-surface area, micro- to nano porous working electrodes to achieve high-resolution PDF for interfacial catalysts during electrochemical operation. Further, we have developed atomic layer deposition (ALD) synthesis approaches that enable precise deposition of conformal thin film indium oxide-based alloys that are highly conductive yet fully amorphous. This is a significant advance for the design of operando PDF characterization, as these amorphous conductive layers are devoid of Bragg reflections which otherwise swamp PDF signals from interfacial catalyst overlayers. We are characterizing the electrochemical properties of these new electrode architectures designed for operando PDF characterization.

We further explore ALD as a route to the synthesis of few-atom oxide cluster catalysts that might circumvent the scaling relations of bulk oxides for water oxidation. Myriad oxide compositions have been evaluated computationally and experimentally for water oxidation proficiency; however bulk compositions are subject to the thermodynamics of large inorganic assemblies. Few-atom clusters offer the opportunity to access unique "beyond-bulk" compositions, surface sites, and termination. Sequential infiltration synthesis (SIS) utilizes ALD precursors to nucleate inorganic clusters *within* polymer substrates via reversible Lewis acid-base adduction that can be subsequently irreversibly reacted with oxygen sources within ALD tools. The digital synthesis technique affords few-atom oxide clusters with narrow size distribution that are controlled by SIS cycle number, as evaluated by PDF analysis (Figure 1). This work suggests the opportunity to use SIS as an approach to synthesize discrete, size-selected, few-atom TM oxide clusters with elemental composition and terminal capping ligands not achievable by solution synthesis methods, making them exceptional candidates solar fuels catalysis.

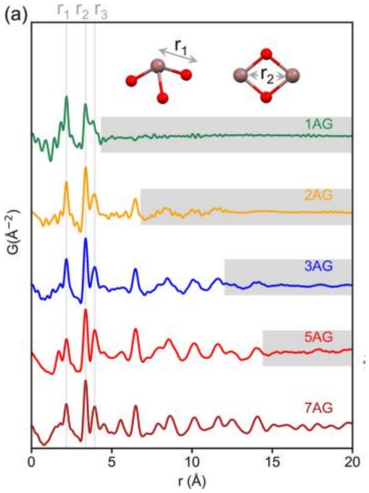

Figure 1. PDFs of as-grown (AG) InO_xH_y clusters in PMMA. More SIS cycles results in larger clusters with longer pair correlated length.

Photoinduced Electron Transfer in $AgInS_2$ and $AgInS_2$-CdS Nanocrystals

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Ternary semiconductors such as $AgInS_2$ with their interesting photocatalytic properties can serve as building blocks to design light harvesting assemblies. The intraband transitions created by the metal ions extend the absorption well beyond the bandgap transition. The interfacial electron transfer of $AgInS_2$ colloidal nanocrystals induced by bandgap and sub bandgap irradiation is probed with steady state photolysis and transient absorption spectroscopy. Capping $AgInS_2$ nanocrystals with CdS shell shifts the emission maximum to the blue and increases the emission yield as the surface defects are remediated. Using ethyl viologen (EV^{2+}) as a probe, we have now elucidated the involvement of conduction band and sub-bandgap states in promoting electron transfer (Figure 1).

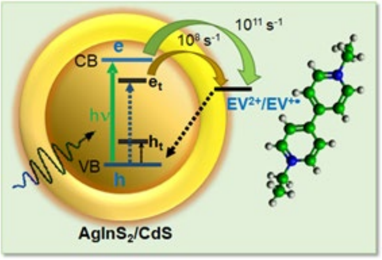

Figure 1. Viologen as a probe to elucidate the interfacial charge transfer processes

Two important conclusions were drawn from these studies. The first one is related to new mechanistic insights into the electron transfer processes of ternary semiconductors. Both bandgap and sub-bandgap excitations induce electron transfer as probed through $EV^{+\bullet}$ formation under wavelength selective irradiation. The quantum yields obtained with sub-bandgap excitation (λ>550 nm) are relatively lower compared to broadband white light (λ>420 nm) irradiation. The transfer of conduction band electrons to EV^{2+} is fast which occurs with a rate constant of $0.6\text{-}2\times10^{11}s^{-1}$ and constitutes a major part of interfacial electron transfer. The electrons trapped at the interstitial defect sites contribute to the reduction of $EV^{2+\cdot}$ with a slower rate ($0.5–2.8 \times 10^8$ s^{-1}). The second interesting conclusion is the stabilization of electron transfer product. Both steady state irradiation and transient absorption measurements indicate suppression of back electron transfer in $AgInS_2$-CdS heterostructures. The beneficial role that CdS layer plays results in enhancement in the electron transfer quantum yield from 14 .5 to 29.3%. As evident from analysis of electron transfer kinetics, the interfacial electron transfer in ternary semiconductors is a kinetically driven process. Careful control of surface interaction of the acceptor molecule and suppression of back electron transfer is needed to maximize the efficiency of photocatalytic reduction. The heterostructures such as $AgInS_2$-CdS heterostructure provide new design strategies to amplify the use of ternary semiconductors in photocatalytic applications.

Kinetically Stable Semiconductor Nanocrystals for Solar Photoconversion

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Synthesis of semiconductor nanocrystals (NCs) with tailored optoelectronic properties can enable their use in several solar photoconversion applications. Plasma-enhanced chemical vapor deposition (PECVD) has emerged as one approach capable of achieving structures that are difficult to prepare using other methods, for example covalently bound semiconductors (Si, III–Vs), highly doped semiconductors exhibiting plasmonic absorption, and metastable phases. Such syntheses are enabled by PECVD synthesis because it operates in a kinetically driven growth regime that facilitates trapping of dopant and other alloying elements within the NC core that would otherwise be expunged using thermodynamically driven processes.

In one example, ternary alloy SiGeSn NCs were synthesized using PECVD synthesis from silane (SiH_4), germane (GeH_4), and tetramethylstannane ($Sn(CH_3)_4$) precursor sources.[1] Incorporation of Sn into a Si/Ge alloy has been predicted to transition the lowest energy, indirect optical bandgap of these semiconductors to a direct gap. We realized these SiGeSn NCs using a secondary injection of SiH_4 and GeH_4 precursor gases in the after-glow region of the plasma, which kinetically traps Sn in the core (Figure 1). Compositional tunability of the SiGeSn NCs can be varied broadly at low Sn concentrations (up to ~2 atomic percent) as revealed by XRD (Figure 1) and ICP-MS analysis. More generally, this study demonstrates how nonthermal PECVD synthesis can be used to produce ternary nanostructured alloys involving thermodynamically insoluble constituents.

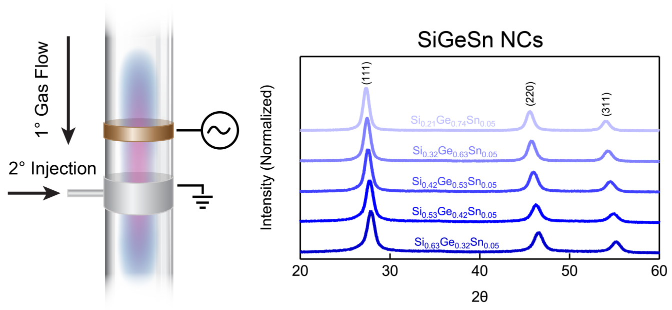

Figure 1. LEFT: Schematic of plasma-enhanced chemical vapor deposition (PECVD) synthesis system enabling synthesis of kinetically stable semiconductor NC phases. RIGHT: XRD patterns of SiGeSn NCs with varying Si:Ge ratios. All samples nominally contain the same composition of Sn (5%) as the $Sn(CH_3)_4$ flow rate was held constant for all experiments.

PECVD synthesis also has enabled III–V and doped Si semiconductor NCs of interest for photochemical conversion of H_2O to H_2 and CO_2 to reduced products. We will present initial studies on GaN NCs produced via PECVD synthesis that have the potential to mimic the intriguing photochemical reduction of CO_2 to CO and oxidation of H_2O to O_2 recently reported by Atwater et al. We will present initial results in collaboration with the LiSA Solar Fuels Hub to unveil the mechanisms of these photochemical redox reactions using these PECVD-synthesized GaN NCs that offer high signal-to-noise owing to their high surface area compared with thin films. Finally, we will describe our initial efforts in exploring doped Si NCs in similar photochemical schemes.

[1] G.F. Pach, F. Urias-Cordero, S. Yazdi, and N. R. Neale, *J. Phys. D: Appl. Phys.* **55**, 074002 (2022).

High Quantum Yield Sensitization of Single Crystal TiO_2 Electrodes with $CsPbBr_3$ Nanocrystals

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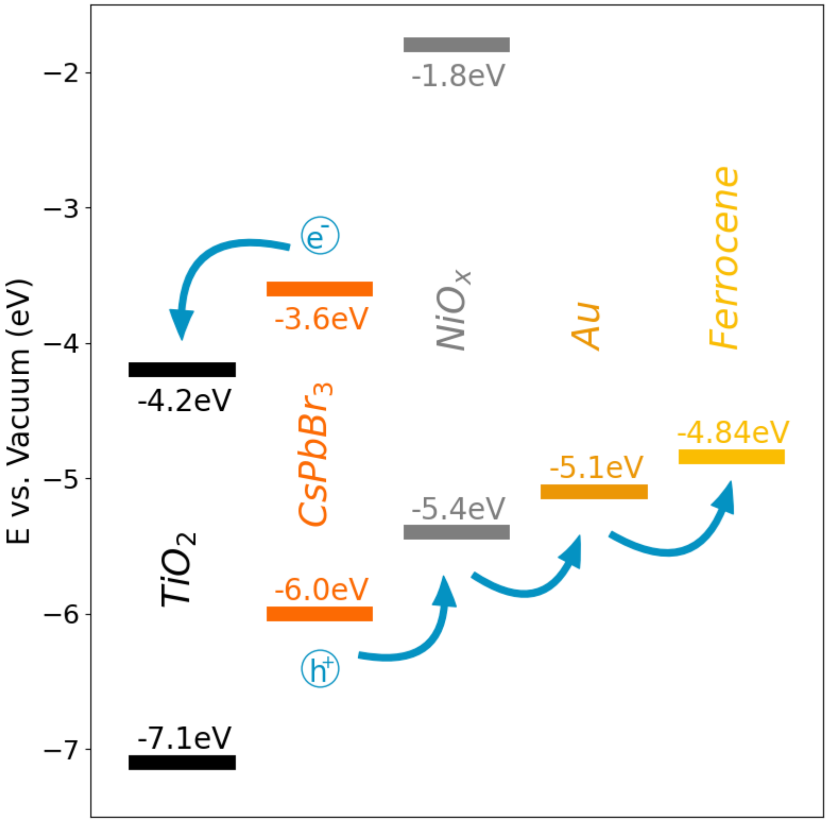
Abstract: Lead halide perovskites are promising materials for solar cells and photodetectors. Nanocrystals of this family of perovskites also have distinct properties. In this study we report the attainment of high quantum yield sensitized photocurrents from stabilized $CsPbBr_3$ perovskite nanocrystals thermally evaporated onto doped single crystal rutile (110) TiO_2 electrodes. The photocurrent stabilization was achieved by capping the nanocrystals with thin NiO_x and Au carrier transport and protection layers respectively as well as the judicious choice of solvent and electrolyte (Scheme 1). We are still working on measuring multiple exciton generation from up-conversion of sub-bandgap radiation now that we have stabilized the conventional sensitization of the nanocrystals.



Scheme 1: Band alignment of materials in the layered device. Blue arrows indicate carrier flow direction.

Regulating Singlet-Triplet Energy Gaps through Substituent-Driven Modulation of the Exchange and Coulomb Interactions

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Controlling the energetic separation between low-lying singlet (S_1) and triplet (T_1) electronically excited states is central to the design of energy efficient light emitting diodes, many solar energy conversion schemes, and photocatalytic transformations. The S_1-T_1 energy gap (ΔE_{ST}) in molecular systems is largely regulated by the exchange interaction, which decays exponentially as the inter-electron distance increases. Time-tested approaches to regulating ΔE_{ST} include: (i) designing extended molecular scaffolds that spatially separate two emitters that serve as distinct singlet and triplet excitation reservoirs, or (ii) modulating the extent of charge delocalization in molecular excited states having charge transfer character, as increased delocalization tracks with reduced exchange interaction magnitudes. While both these tactics have impacted, for example, the development of systems that display thermally-assisted delayed fluorescence (TADF), no systematic methods have been defined that tune ΔE_{ST} in simple chromophoric frameworks that do not rely on the dramatic displacement of excited-state electron density. We describe a strategy that minimizes the energy loss that accompanies S_1-T_1 electronic relaxation in a molecular system where both S_1 and T_1 excitation are confined to a circular absorber. This work demonstrates that for a set of chromophores having a uniform HOMO-LUMO energy gap, the degree of S_1-T_1 electron density overlap may be finely controlled by the porphyrin macrocycle substitution pattern, enabling regulation of absolute S_1 and T_1 state energies and ΔE_{ST} through designed restriction of the electron-electron coulomb (J_{HL}) and exchange (K_{HL}) interaction magnitudes. This systematic modification of J_{HL} and K_{HL} relies upon controlling frontier molecular orbital (MO) density of states (DOSs) and electron density distributions in the singly occupied MOs that characterize the one-electron transitions that describe the S_1 and T_1 state wavefunctions (Fig. 1).

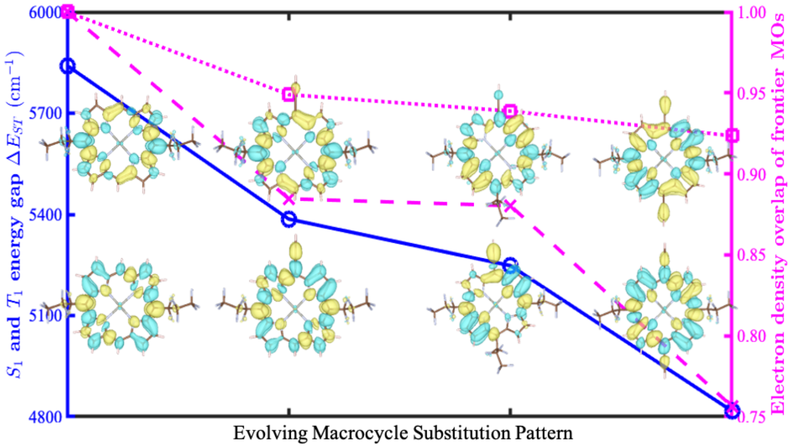

Figure 1. The dependence of the S_1-T_1 energy gap, ΔE_{ST} (solid line; left vertical axis) and the normalized natural transition orbital (NTO) electron density overlap (dashed and dotted lines; right vertical axis) as the macrocycle substitution pattern evolves. This elaboration of the porphyrin macrocycle increasingly distorts the electron distribution between occupied and virtual MOs, diminishing their electron density overlap, and drives a progressive diminution of ΔE_{ST}. The dashed line represents the electron density overlap between the HOMO and LUMO, while the dotted line represents the electron density overlap between the HOMO–1 and LUMO+1.

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

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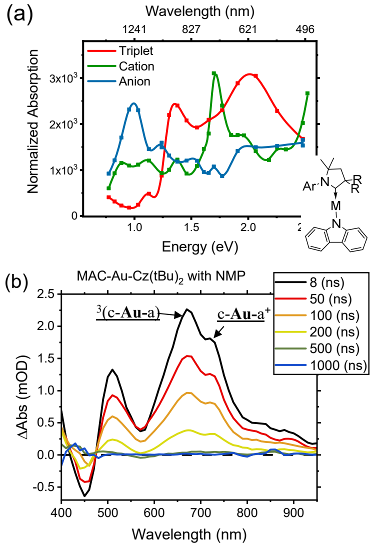
2. Chemistry Department, Brookhaven National Laboratory, Upton, NY 11973

We have developed a large family of monovalent coinage metal sensitizers [i.e. (carbene)M(amide), M = Cu, Ag, Au, c-**M-**a] 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 (light absorption up to 550 nm). These materials have high excited state redox potentials and absorb light in the visible range with ε of 10^3-10^4 $M^{-1}cm^{-1}$. We are investigating these materials as sensitizers for photo-electro-catalysis.

We have expanded our carbene options over those that we started with,* and developed a set of design rules for carbene ligand choices to broaden and red shift absorption. Our initial studies of these c-**M-**a materials showed that they give reversible reduction, but irreversible oxidation waves. Suitable substitution of the amide gives c-**Cu-**a complexes reversible redox waves in CH_2Cl_2, but poor reversibility for oxidation in acetonitrile and DMF. The c-**Au-**a complexes give fully reversible oxidation and reduction in both CH_2Cl_2 and DMF. We believe that the poor oxidative stability for Cu complexes is due to ligand solvolysis in polar solvents.

Irradiation of these c-**M-**a complexes leads to the formation of an interligand charge transfer (ICT) state. The singlet-triplet spacing for these complexes is very small, so the excited state retains high excited state oxidation and reduction potential (verified by quenching studies). We have previously investigated the kinetics of intersystem crossing (ISC) for this ICT state by following fluorescence decay and found time constants of 100-200 ps for the Cu and Ag complexes and ~20 ps for the Au complexes. We have followed up this work with a detailed transient absorbance (TA) study, spanning from 10 fs to 100 μs. To accurately assign the TA spectra we used pulse radiolysis to generate the basis spectra for the T_1 state as well as the oxidized and reduced forms of the c-**M-**a complexes. The ISC rates for Au and Cu complexes agree with those measured by emission decay. The triplet absorption spectrum resembles the sum of the cation and anion spectra for a given c-**M-**a, with a 0.25 eV shift in the spectra of the two charged ions. We have also investigated the oxidative quenching of c-**M-**a complexes by TA spectroscopy. Thus far we have been restricted to toluene solvent and see both the triplet and c-**M-**a cation spectra in the TA formed in < 1 ns. The signatures of the triplet and cation remain in the same ratio and decay over 500 ns. This is likely due the cation and reduced quencher being cage trapped in the toluene solvent. We will be repeating these quenching measurements in THF soon to get a better picture of the rate of electron transfer from c-**M-**a* to the oxidizing quencher.



(a) Triplet, cation and anion spectra of CAAC-**Cu-**Cz from pulse radiolysis. (b) TA spectra of MAC-**Au-**Cz + oxidative quencher.

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

Accelerating Symmetry-breaking Charge Separation in a Perylenediimide Trimer through a Vibronically Coherent Dimer Intermediate

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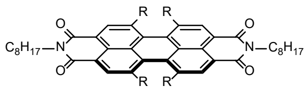
Understanding the photophysics and photochemistry of molecular π-stacked chromophores is important for utilizing them as functional solar energy conversion materials. However, these investigations have been mostly limited to covalent molecular dimers, which can only approximate the electronic and vibronic interactions present in higher oligomers typical of functional organic materials. In this work, we show that a comparison of the excited-state dynamics of a covalent slip-stacked perylenediimide (PDI) dimer (**2**) and trimer (**3**) provides fundamental insights into electronic state mixing and symmetry-breaking charge separation (SB-CS) beyond the dimer limit. We find that coherent vibronic coupling to high-frequency modes facilitates ultrafast state mixing between the Frenkel exciton (FE) and charge transfer (CT) states (Figure 1). Subsequently, solvent fluctuations and interchromophore low-frequency vibrations promote CT character in the coherent FE/CT mixed state. The coherent FE/CT mixed state persists in **2**, while in **3**, low-frequency vibronic coupling collapses the coherence resulting in ultrafast SB-CS between the distal PDI units (Lin, C.; Kim, T.; Schultz, J. D.; Young R. M.; Wasielewski, M. R. *Nat. Chem.* **2022**, https://doi.org/10.1038/s41557-022-00927-y).



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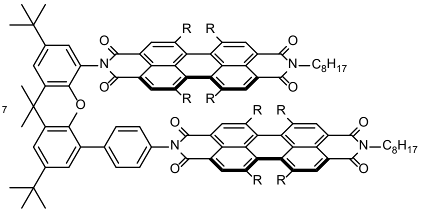

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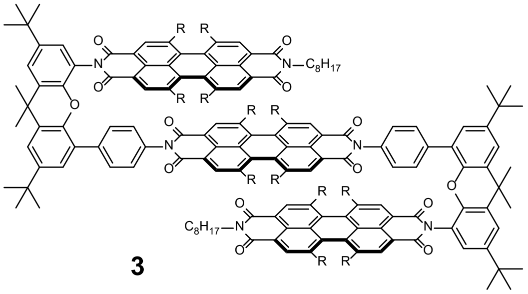

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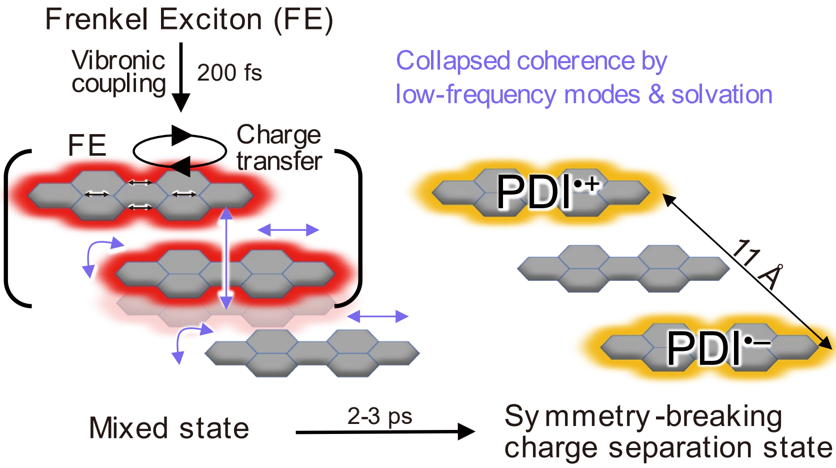

Figure 1. Mechanism of symmetry-breaking charge separation in PDI trimer **3**.

Leveraging Entropy for Solar Photochemistry

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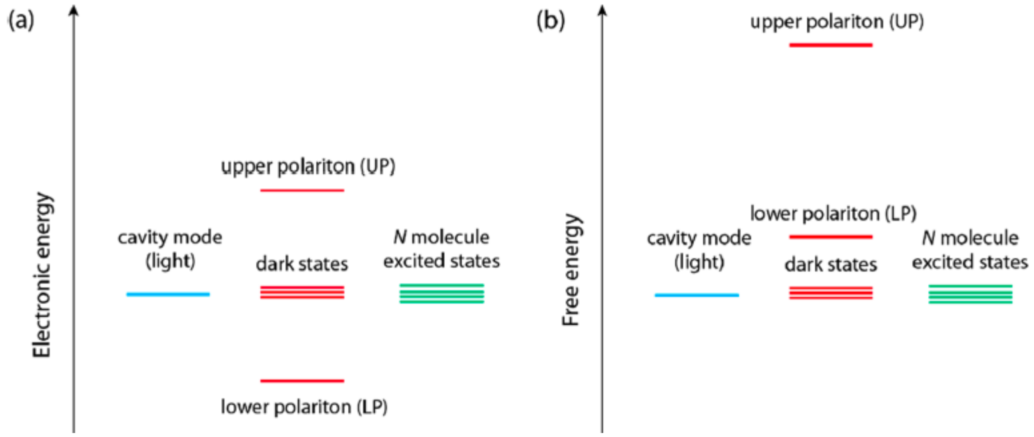
In this forward-looking presentation, I will discuss the delocalization of molecular polaritons and its consequences for solar photochemistry. The main result is that the incredibly long-range phase coherence of the polariton states formed by strong coupling between a photon mode in a cavity and an ensemble of molecules leads to exceptionally low entropy of the upper and lower polariton states, starkly contrasting with the dark states. That result means that spectroscopy does not correctly order the free energy of the excited states because there is a significant entropic contribution to the free energy. The entropic contribution adds to the polariton electronic gap, rendering states surprisingly more reactive that anticipated from the input excitation energy. This apparently 'additional' reactivity, evident from the thermodynamics, suggests how the low entropy of highly coherent states can be exploited as a resource. I will report our recent efforts to find experimental evidence for this prediction.



From Discrete Molecular Catalysts to Multidimensional Architectures: Effects of Charge Delocalization, Electronic Coupling, and Intramolecular Electrostatics on Electrocatalysis

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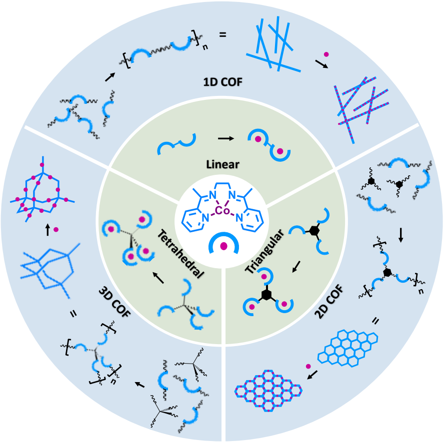
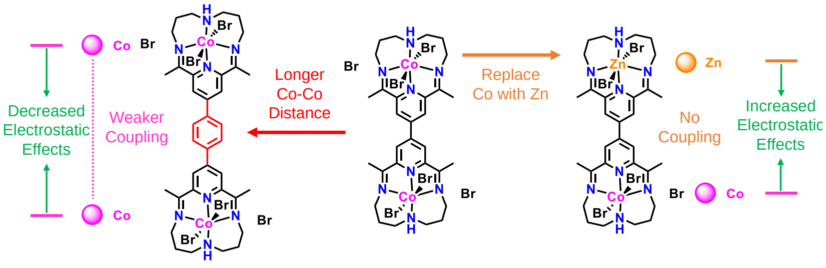
Ann Arbor, MI, 48109

Molecular inorganic complexes show significant promise as electrocatalysts for the selective reduction of CO_2 to solar fuels. An outstanding challenge is incorporating these molecular catalysts into heterogeneous, multidimensional structures that reduce carbon dioxide with high activity and stability, but also maintain the selectivity of discrete, molecular catalysts. This project focuses on determining how the three complicated and interrelated effects of charge delocalization, intramolecular electrostatics, and electronic coupling influence catalytic activity and selectivity in extended multidimensional catalyst architectures. We do this using a bottom-up approach, beginning with simpler model systems to understand these effects and building in complexity towards extended multidimensional structures.



Bottom-up approach for designing new macromolecular catalysts.

Our previous studies focused on exploring two of these effects on CO_2 reduction by discrete molecular catalysts: charge delocalization and intramolecular electrostatics.[1,2] We have expanded our studies to explore the role of all three effects on the catalytic activity of multimetallic molecular assemblies. For example, we have synthesized bimetallic Co-based molecular catalysts that reduce CO_2 with *ca.* 2 orders of magnitude enhanced activity compared to monometallic analogues. Our recent work focuses on altering the distance between the metal sites and the identity of the second metal to tune the electronic coupling and electrostatic effects within the complex and measuring the impact on catalytic activity. We are now focused on incorporating similar molecular building units in larger multimetallic assemblies and coordination polymers to study how these three interrelated effects influence catalytic activity in conjugated macromolecular architectures.



bi-ex-[Co(PDI)] **bi-[Co(PDI)]** **bi-[ZnCo(PDI)]**

Example of a multimetallic molecular assembly in which specific parameters can be tuned systematically to influence catalytic activity.

(1) Nie, W.; Tarnopol, D. E.; McCrory, C. C. L. "Enhancing a Molecular Electrocatalyst's Activity for CO_2 Reduction by Simultaneously Modulating Three Substituent Effects," *J. Am. Chem. Soc.* **2021**, *143*, 3764-3778.
(2) Nie, W.; McCrory, C. C. L. "Strategies for Breaking Molecular Scaling Relationships for the Electrochemical CO_2 Reduction Reaction," *Dalton Trans.* **2022**, *Advance Article*.

Understanding the Multiple Concurring Redox Processes at Semiconductor Photocatalysts

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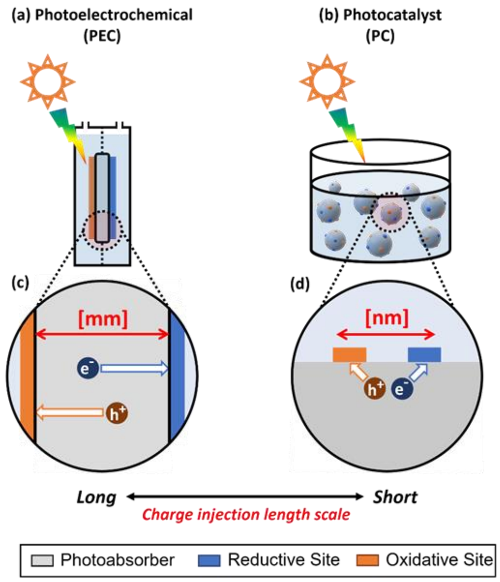
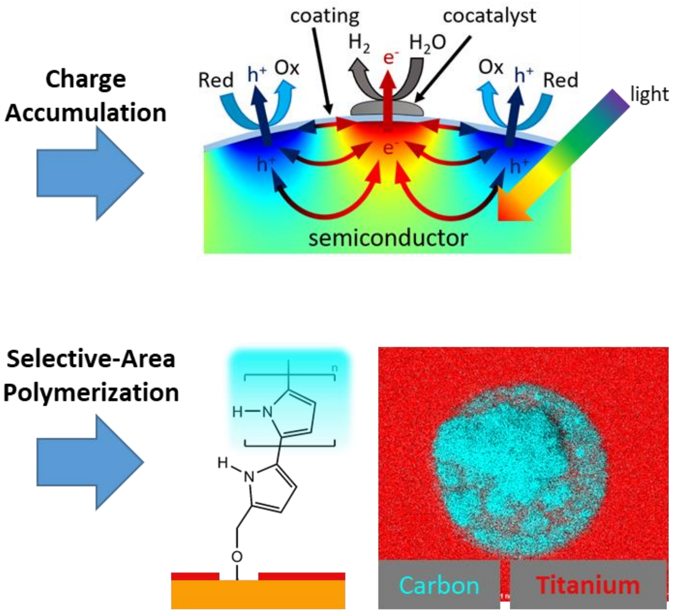
New Haven, CT 06510

Semiconductor photocatalysis refers to coevolving reductive and oxidative reactions at nanoscale proximity. Particulate semiconductors capture sunlight efficiently and support designer molecular co-catalysts to match the photon flux with sufficient rates. The local charge separation and local coevolution have the unique advantages: i) photocatalysts can operate in neutral pH water or water vapor instead of strong acid or base; ii) most semiconductors form a self-passivating layer at corroded surfaces to prevent corrosion propagation; and iii) nanoparticulate photoabsorbers or nanocrystalline films have achieved near-unity quantum efficiency, promising scale-up solar-to-chemical conversion. Photocatalysis involves light absorption, charge separation, charge transfer, surface catalysis, and chemical transport across multiple scales. The timescale mismatch between light absorption and surface catalysis poses a grand challenge in understanding how efficient charge separation can be achieved. Despite the near-unity quantum efficiency achieved for $SrTiO_3$ particles, the Edisonian approach is applied to the vast majority of photocatalysts, thus limiting the progress. We combine local potential and kinetics measurements in a photoelectrochemical cell with semiconductor physics and micro-kinetic modeling, to elucidate the roles of nanoparticle co-catalysts, molecular co-catalysts, and corrosion pinholes in local charge separation. We design the charge separation to achieve multi-electron charge accumulation, selective-area polymerization, and lateral electric field control.





Cathodic Corrosion Mechanisms for p-Type III-V Semiconductor Photoelectrodes

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California Institute of Technology
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Photoelectrochemical (PEC) water-splitting using inorganic semiconductor photoelectrodes provides for one-step generation of hydrogen fuel with water and sunlight as the only inputs. Stability is the most persistent materials challenging limiting the continued development of such systems. Maximizing the achievable efficiency of a water splitting cell requires the use of highly acidic or alkaline electrolytes and thus photoelectrode materials must endure aggressive electrochemical environments. Solar-to-hydrogen energy conversion efficiencies > 15 % have been reported in the literature but are rarely, if ever, maintained for more than a few days in the laboratory. Group III-V semiconductors are attractive candidates for use in solar-driven water-splitting devices due to the potential for high efficiency. We have systematically investigated the stability of GaAs, InP, and GaInP photocathodes, with and without decoration using hydrogen-evolution electrocatalyst materials, for solar-driven hydrogen generation in both acidic and alkaline electrolytes. The principal corrosion pathways observed are summarized graphically in Figure 1.

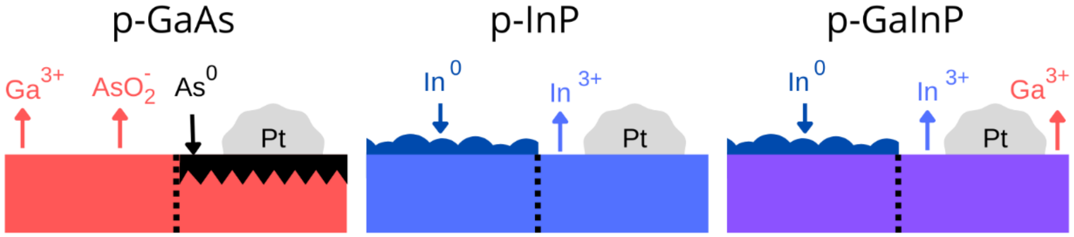

Figure 1. Schematics of corrosion mechanisms for bare and platinized p-GaAs, p-InP, and p-GaInP in acidic conditions. In alkaline media, corrosion of InP and GaInP involves In_2O_3 formation rather than In^{3+} dissolution.

Previously, we have demonstrated that corrosion resistance can be imparted to semiconductor photoelectrodes via protective surficial coating with thin, transparent metal oxide films. Recently, we have fabricated semiconductor anodes composed of arrays of GaAs microislands coated with amorphous TiO_2 films. Such structures enabled analysis of the rate and distribution of pinhole generation that results in failure of the protective coating. Additionally, we have also demonstrated the utility of patterned Ni/NiO_x coatings on Si photoanodes to provide stability in alkaline media under open-circuit conditions. Open-circuit stability is necessary to prevent device failure during nighttime conditions when insolation is unavailable.

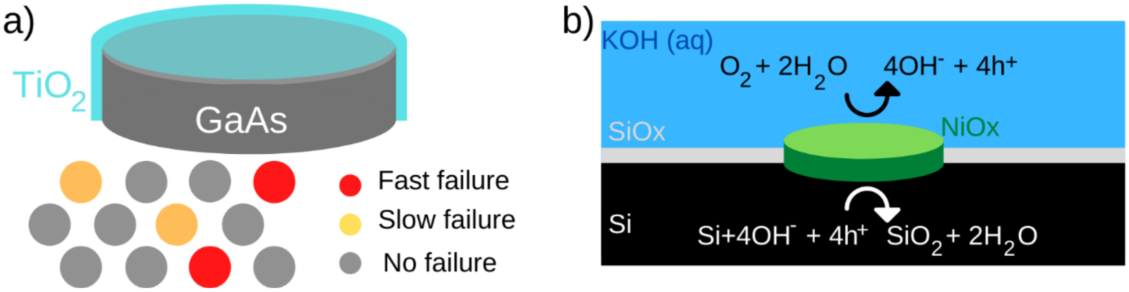

Figure 2. (a) Schematic of a single GaAs microisland protected by TiO_2 and diagram of different failure rates of an array of such islands. (b) Schematic of a NiOx catalyzing the formation of passivating SiOx at the surface of Si photoelectrodes, inhibiting Si etching in the alkaline electrolyte.

Slow Cooling of Hot Excitons in Transition-Metal Dichalcogenides by Ultrastrong Coupling to Plasmon Polaritons

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Golden, Colorado, 80401

In this contribution, we study the effect on excited state dynamics of using ultrastrong coupling between excitons in few-layer molybdenum disulphide (FL-MoS_2) and surface plasmon polaritons on a silver substrate generated in the Kretschmann–Raether configuration (Fig 1). Such strongly coupled polariton states are of interest for controlling hot carrier effects and for driving chemistry at photoelectrochemical fuel-forming interfaces. Hot carrier effects in plasmonically coupled transition metal dichalcogenides (TMDC) have been shown to be active in TMDC systems with solution-grown gold nanoparticles on their surface. Also, it has been shown that the high-energy C exciton has much slower cooling relative to the band gap A exciton in MoS_2 TMDCs. In our current experiments (see Fig 2), we show that when the C exciton in FL-MoS_2 is (ultra) strongly coupled to plasmon polaritons present on a thin silver film substrate it forms two polariton branches: an upper polariton (UP) and a lower polariton (LP). In this case, the lifetime of the coupled UP state is extended by up to a factor of 5.8 with respect to the uncoupled C exciton (Fig 2). This is contrary to the expectation that such a coupled state should decay like the fastest of the decay paths available to either constituent particle—in this case the plasmon polariton—and so one would expect the coupled state to decay much faster than the isolated exciton. We observe the opposite effect. We hypothesize that the delocalization associated with strong coupling strongly suppresses defect scattering, intervalley scattering of band-nested excitations to the K–valley band edges, and exciton–exciton annihilation, leading to the longer lifetimes observed. Polariton coupling therefore can offer control in initiating photochemical reactions by using photoexcited carriers at controlled energies determined by the precise polariton energy tuned by the nanostructure geometry. Such polariton effects are of considerable interest as systems offering control over reaction pathways in fuel-forming reactions.

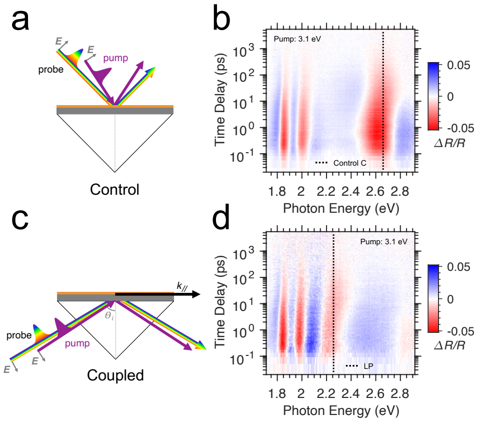

Figure 1. a,c) Transient pump–probe reflection configuration for (a) uncoupled and (c) coupled case. b,d) Differential reflectance as a function of pump–probe time delay and incident probe photon energy for (b) control case and (d) coupled case.

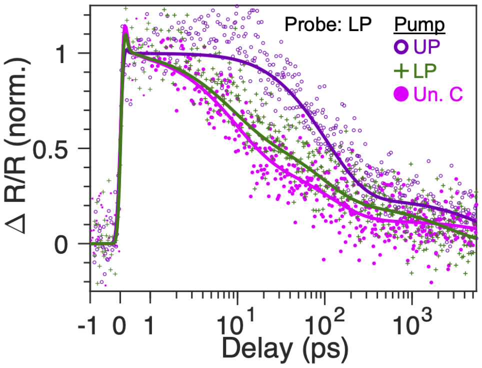

Figure 2. Polariton kinetics when pumping the UP (3.10 eV = 400 nm), LP (2.46 eV = 504 nm), or between the polaritons (2.71 eV = 458 nm). Symbols are data while lines are results from a global analysis fit. Pumping the upper polariton results in a much longer-lived excited state

Transient X-rays and XUV Reveal Element- and Carrier-Specific Semiconductor Photophysics

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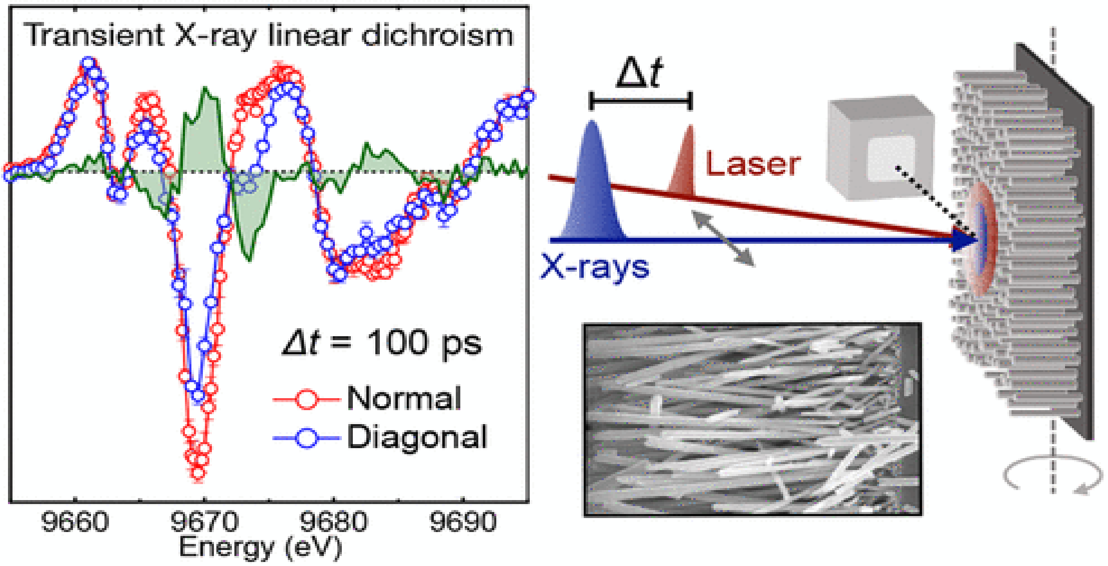
Quantum dot sensitized solar cells (QDSCs) have many potential advantages over traditional dye-sensitized solar cells, such as a larger absorption cross section, high durability, and wavelength tunability via quantum confinement. However, there remain many open questions about the interfacial charge transfer process between the QD and the semiconductor that must be resolved before this architecture can realize its full potential. We seek to develop ultrafast X-ray and XUV spectroscopy as an element- and carrier-specific probe of charge dynamics in multicomponent light harvesting systems.

In work performed at the Advanced Photon Source, we used transient X-ray linear dichroism to reveal carrier dynamics in ZnO nanorods after 355 nm photoexcitation. We observe distinct signals for electron and hole phase-space filling, as well as screening of the core-hole potential by the photoexcited carriers.

To complement this work at user facilities, we developed femtosecond tabletop extreme ultraviolet (XUV) transient absorption spectroscopy as a powerful probe of semiconductor photophysics. We show that in CH3NH3PbBr3, the XUV spectrum provides a band-specific measure of bandgap renormalization, phase-space filling, and carrier cooling. For layered 1D perovskites such as phenethylammonium lead iodide, we show that the Auger recombination rate is largely independent of the cation, contrary to expectations from cation-specific carrier cooling rates observed in lower-flux regimes.



Nano Lett. 2021, 21, 22, 9534

Type-I Hot-Carrier extraction in Monolayer MoS_2 Photoelectrodes

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Quantization effects in photoelectrochemical cells make hot-carrier extraction possible. Established hot-carrier systems such as GaP and InP utilize Type-II hot-carriers (see Figure 1-left). In this scenario, photogenerated electrons transport across the depletion region and react with molecules in solution before they thermalize to the conduction band edge (Step 3 in Figure 1A). Hot-electron injection manifests as a supraband-edge reduction reaction, or the ability to reduce a molecule whose standard reduction potential is higher than the conduction band edge. Unfortunately, the system in Figure 1A loses a large fraction of absorbed solar energy in the bulk because the hot-carriers rapidly lose their excess kinetic energy in ~1 ps (step 2 in Figure 1A). As a result, this Type-II hot-carrier conversion system cannot achieve the theoretical maximum efficiency of 66%.

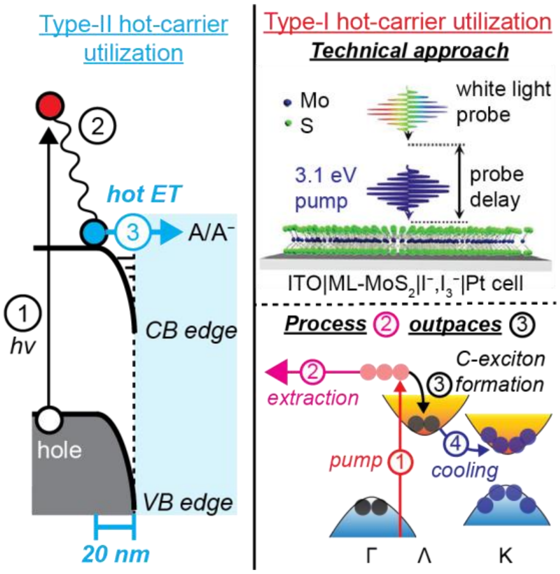

Figure 1. Cartoon illustration of (left) established Type-I hot-carrier utilization in a bulk InP photoelectrochemical cell and (right) technical approach and summary of results for Type-I hot-carrier extraction in ML-MoS_2 photoelectrodes.

Here we test the hypothesis that two-dimensional (2D) semiconductors such as monolayer (ML) MoS_2 have unique physical and photophysical properties that could make Type-I hot-carrier energy conversion possible. The unique electronic structure of ML-MoS_2 extends the hot-carrier lifetime compared to bulk MoS_2 and those hot-carriers need only transport across three atoms to reach electrical contacts and acceptor molecules in a working photoelectrochemical cell. Using a combination of in situ steady state absorption spectroscopy, photocurrent spectroscopy, and ultrafast transient absorption spectroscopy (Figure 1-top right, through an unfunded collaboration with Prof. Amber Krummel at Colorado State University) of a model ITO|ML-MoS_2|I^-, I^{3-}|Pt cell, we demonstrate (1) hot-C exciton dissociation and extraction onsets before A/B-exciton dissociation, likely due to the negligible binding energy of C-excitons compared to A/B-excitons and the orbital character of the states which make up the exciton states are spatially distinct (theoretical calculations performed by unfunded collaborator Prof. Andres Montoya-Castillo at University of Colorado Boulder) and (2) Type-I hot-electron extraction outpaces C-exciton formation (Figure 1-bottom right), which occurs in <50 fs. This research raises interesting questions regarding how to efficiently leverage excitons with weak binding energies for solar fuels production and will likely impact the direction, progress, and thinking in the field because hot-carrier-driven reactions promise to open a new reactivity landscape, one where the thermodynamic considerations for candidate reactions are no longer limited by the relative alignment of semiconductor band edges to reactant molecules.

Ab Initio Quantum Dynamics of Charge Carriers in Advanced Solar Materials

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The methods for modeling excited state dynamics in condensed phase and nanoscale materials, developed in our group, are applied to study photoinduced processes in diverse and modern materials for solar energy harvesting, as exemplified in the figures below.

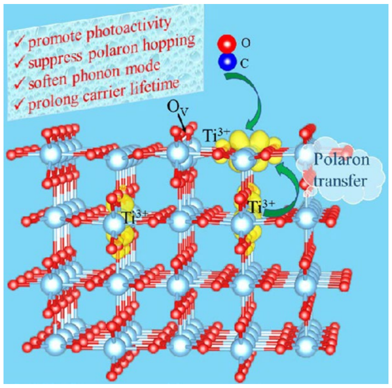

Figure 1. TiO_2 surface electron polarons enhance CO adsorption, while CO attracts electron polarons to the surface, decoupling them from holes and enhancing charge lifetime. CO adsorbes one atom away from electron polaron. [*JACS Au*, **2**, 234 (2022)].

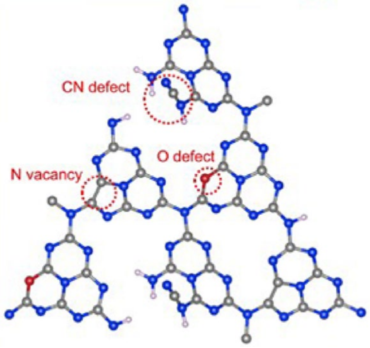

Figure 2. Metal-free graphitic carbon nitride is an excellent and benign photocatalyst for water splitting and many other reactions. We rationalize how defect engineering, realizable experimentally, can improve both oxidation potential and carrier lifetime. [*JPCL*, **13**, 1033 (2022)].

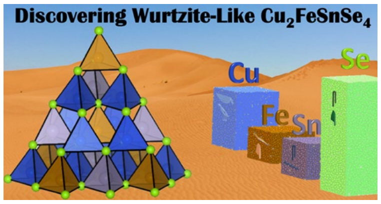

Figure 3. In collaboration with experimentalists, we discover and characterize a new phase of $Cu_2FeSnSe_4$, composed of only earth abundant elements. It exhibits efficient light absorption into the near-infrared, has low toxicity and is a better conductor than the more common phase. The phase is formed through intermediate Cu_3Se_2 nanocrystals that form a structural template for the final product. [*ACS Nano*, **15**, 13463 (2021)].

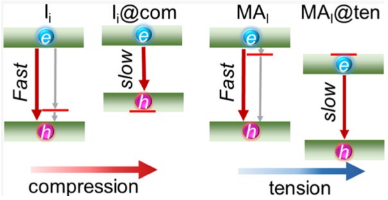

Figure 4. Defect energy levels in $MAPbI_3$ can be controlled by strain. Upon compression, valence band shifts up, and hole traps, such as iodine interstitials, move from midgap into the band and are eliminated. Upon extension, conduction band shifts down, and electron traps, such as MA taking place of iodine, move into the band and are also eliminated. Strain also creates moderate disorder that reduces electron-hole overlap and extends carrier lifetime. [*JACS*, **143**, 9982 (2021)].

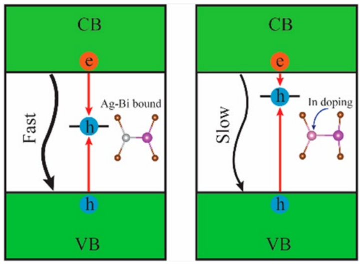

Figure 5. Pb-free double perovskites, such as $Cs_2AgBiBr_6$, are more stable and less toxic than Pb-based perovskites. However, they exhibit new types of defects associated with charge redistribution between the two metals, Ag and Bi. We rationalize how such defects can be efficiently passivated by doping with In that prevents the charge redistribution. [*JPCL*, **12**, 10581 (2021)].

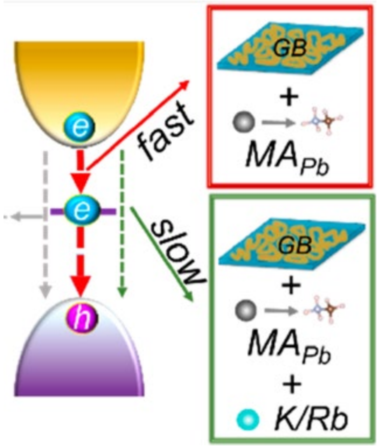

Figure 6. Point defects that are benign in bulk $MAPbI_3$, create charge traps at grain boundary. We rationalize how alkali metals passivate such defects. [*ACS Energ. Lett*, **5**, 3813 (2020)].

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 poster will focus on spectroscopic approaches to monitor fundamental electrochemical processes, including "double-layer" formation of ionic liquids on different printed semiconductor materials and electroabsorbance measurements coupled with impedance spectroscopy to track charge motion in π-conjugated polymers.

In π-conjugated polymers, the three-dimensional electronic structure governing energy/charge transport and transfer is not well-captured by a band-like picture: rather, the electronic structure and charge carriers (i.e., polarons and bipolarons) are highly sensitive to local perturbations and nano-to-microenvironments that derive from intermolecular and interionic interactions. For the prototypical homopolymer poly(3-hexylthiophene), polaron and bipolaron signals exist in the visible to near-IR regions of the electromagnetic spectrum. Tracking these signatures using spectroelectrochemical methods allows one to resolve carrier motion in both energy and frequency domains. First, using electroabsorption coupled with linear-sweep voltammetry and *in situ* conductivity measurements, we can monitor the onset of conductivity via a bleach in the neutral polymer absorbance (460 nm in Figure A) which coincides with formation of polaronic species (800 nm) at approximately 0.4 V vs. Ag/Ag$^+$. These are accompanied by bipolaron signatures at higher anodic potentials, which give rise to a decrease in conductivity despite increasing carrier densities. We hypothesize this is due to a localization of polarons reducing the mobility.

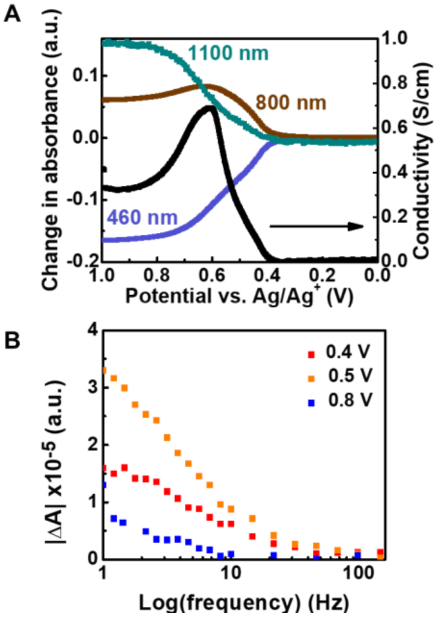

Figure. (A) Electroabsorption and conductivity measurements of poly(3-heyxlthiophene). (B) Color impedance of oscillating carriers as a function of frequency for the polymer/electrolyte provided in A.

Color impedance, which follows the optical modulation of a spectroscopic signature during sinusoidal modulation of the local potential allows for resolution of relative carrier motion. We emphasize the output of color impedance follows the number of polarons (Δpolarons) that oscillate at any given frequency on top of a DC concentration of polarons. In Figure B, we confirm our hypothesis, where increasing anodic potentials from 0.4 to 0.5 V results in an increase in carrier motion (i.e., more carriers oscillate), but at high anodic potentials (0.8 V), carriers become frozen at low frequencies (10 Hz). This approach allows for monitoring of carrier motion within the polymer to better understand mechanisms of charge transfer.

Short and Long-range Electron Transfer Compete to Determine Free-charge Yield in Organic Semiconductors

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We introduce the concept that free-charge generation in organic photovoltaic (OPV) materials may best be described by *competition* between long- and short-range electron transfer events, and that the distribution of rates as a function of distance follows the predictions of Marcus theory. Previous work, both from our group and others, has elucidated these individual concepts; none has put them together into a complete model that quantitatively describes novel experimental data and qualitatively agrees with a broad spectrum of past experimental results in the literature, as we do here. Our results reveal the fundamental connection between solution-phase electron transfer research that has been conducted in the chemistry community over many decades, and the younger materials science effort to develop efficient OPV materials. Our model provides insight into how the microstructure of OPV materials influences the electron transfer process via both entropic and quantum-mechanical mechanisms, and sets the stage for a fundamental understanding of how donor:acceptor energy-offsets interact with the coulomb binding energy to modulate the yield of free charges, and will inform estimates for the ultimate limit of open-circuit voltage in OPV materials.

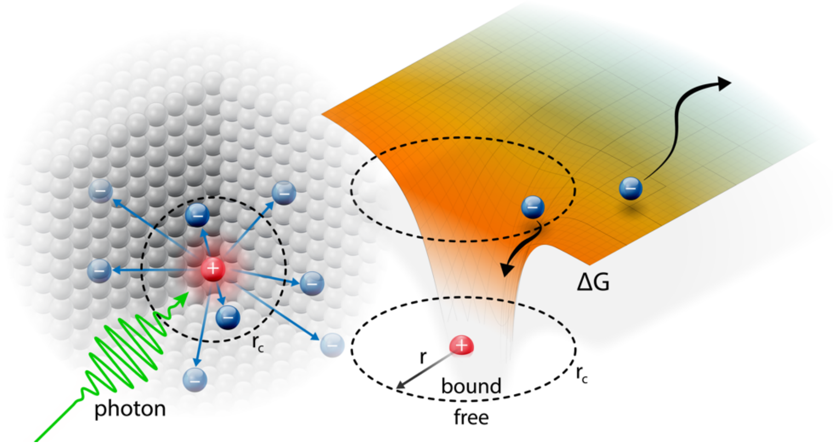

Figure 1 - In a sensitized organic semiconductor, similar to an organic solar cell, light is absorbed by the sensitizer, an electron (-) can remain associated with a hole (+), or transfer beyond a critical radius (r_c) and form a free carrier. Representations: real space (left), Gibbs energy (right).

1. J.M. Carr, T.G. Allen, B.W. Larson, I.G. Davydenko, R.R. Dasari, S. Barlow, S.R. Marder, O.G. Reid, and G. Rumbles. “Short and Long-Range Electron Transfer Compete to Determine Free-Charge Yield in Organic Semiconductors.” *Materials Horizons* 9, no. 1 (January 4, 2022): 312–24. https://doi.org/10.1039/D1MH01331A.

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

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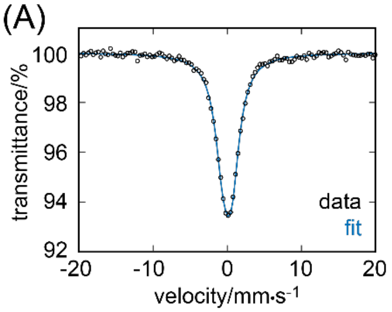
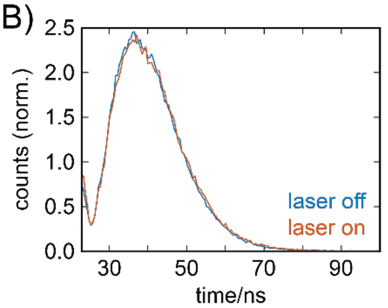
Our research program leverages nuclear resonance techniques (including lab-based radioisotope Mössbauer spectroscopy (MS) and synchrotron-based nuclear forward scattering (NFS) and nuclear resonance inelastic X-ray scattering (NRIXS)) to investigate chemical and physical properties and dynamics of solid-state solar energy conversion materials. We are developing a novel solid-state ultrafast technique, time-resolved synchrotron radiation Mössbauer spectroscopy (TRSRM), which is an element-specific probe of oxidation and spin state dynamics. Optical and X-ray transient absorption characterizations of thin film materials are complicated by laser-induced heating, but TRSRM will provide a complementary approach with exceptional spectral resolution and minimal temperature dependence.

Toward this end, we have recently measured the ^{151}Eu NFS of a 4% Eu^{3+}-doped $Ba_3(PO_4)_2$ glass under intense cw laser illumination on resonance with the $^7F_0 \rightarrow {}^5D_1$ 4*f* ligand field transition of Eu^{3+}. The frequency-domain MS spectrum (Fig. A) shows a single absorption peak comprised of an unresolved quadrupole-split doublet with an isomer shift characteristic of Eu^{3+}. The splitting manifests in the time-domain NFS spectrum of the electronic ground state (Fig. B, blue) as a single quantum beat within the accessible measurement window. Upon illumination, the period of this beat is slightly shifted (Fig. B, red), indicating the presence of another Eu^{3+} species.

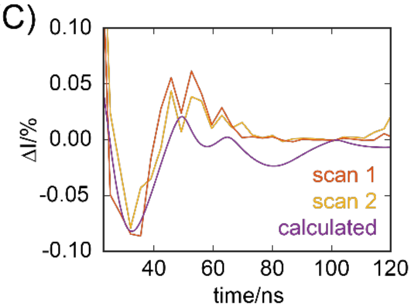
(A)



(B)



(C)



The NFS difference spectra of two independent measurements (Fig. C, red and yellow) demonstrate reproducibility; we also observe no significant difference before vs. after illumination, demonstrating that the difference is indeed transient. The difference spectra also agree with the predicted difference between the $^5D_0$ and $^7F_0$ electronic states (Fig. C, purple), suggesting we are indeed observing the metastable (~2 ms) $^5D_0$ excited state of Eu^{3+}. We are now working to fit the time-domain difference spectra to obtain the $^5D_0$ frequency-domain spectrum, but we believe this is the first-ever nuclear resonance measurement of a transient electronic excited state.

This work represents proof-of-principle for truly time-resolved nuclear resonance measurements. We will perform our first nanosecond-resolved pump-probe NFS experiment in September using SnS_2, a promising earth-abundant and non-toxic material for thin film photovoltaic devices.

Mixed-Metal Oxide Energy Conversion Catalysts for Integration with Photoabsorbers

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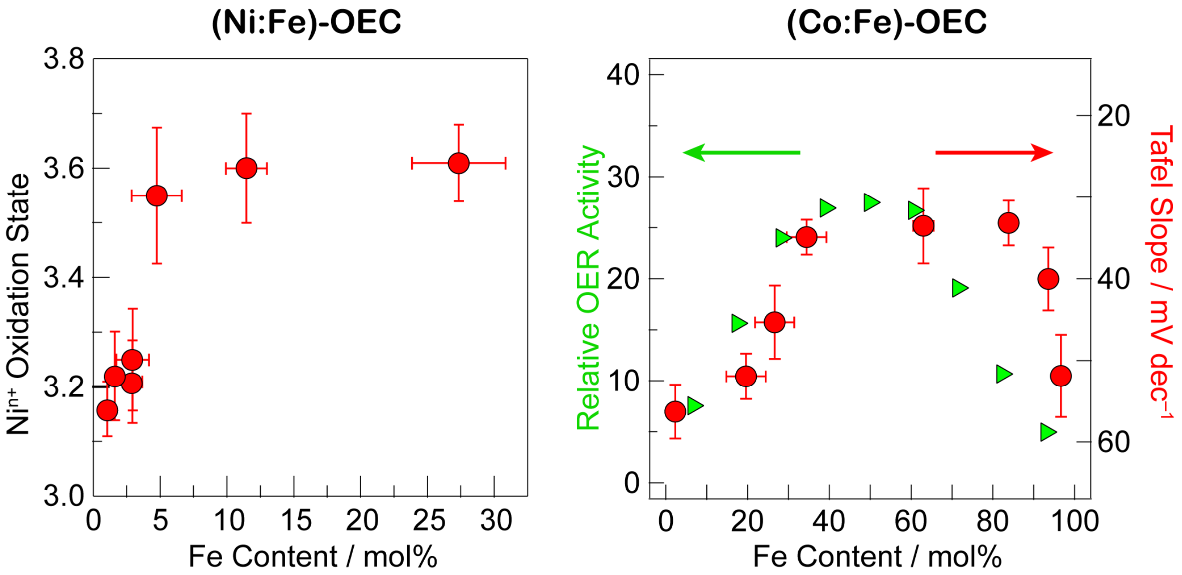
The oxygen evolution reaction (OER) of unary first row oxides may be augmented by alloying to furnish mixed-metal oxides. The introduction of Fe^{3+} into Ni and Co metallate oxygen evolving catalysts (M-OECs) has been shown to be especially effective at increasing OER activity, though the reason for this enhancement continues to be explored. The extent of Fe alloying on activity is notably disparate for M-OECs. Ni-OECs show maximal activity with Fe loadings of ~5 mol% Fe paralleled by an effective Ni valency increase to 3.8. The results are consistent with Fe acting as a Lewis acid to increase the acidity of OH_x (aqua/hydroxo) moieties, giving rise to increased oxyl character ($\text{Ni(IV)}\overset{\cdots}{-}\text{O} \leftrightarrow \text{Ni(III)–O}\bullet$). This Lewis acidity behavior is supported by the observation that Fe doping in $NiPbO_x$ catalysts (which are stable in acid solutions) shows no enhancement in OER at solution pH values commensurate with the pK_a of Fe^{3+}. Conversely, the maximal activity of Co-OECs is observed for Fe loadings >40 mol%. Mossbauer studies show that Fe^{4+} tracks OER activity, suggesting that the Lewis acid properties of Fe^{3+} are augmented by Fe^{4+} being intimately involved as a redox activator of OER. In view of "oxo wall" considerations, and the fact that OER activity decreases with increasing Fe^{4+} content, these results are consistent with Fe^{4+} participating as a cooperative redox center where Fe^{4+} enhances the population of a $\text{Co(IV)}\overset{\cdots}{-}\text{O} \leftrightarrow \text{Co(III)–O}\bullet$ redox level by intermetallic charge transfer.



Correlation of Fe composition with M-OEC activity. For (Ni:Fe)-OEC, plot of coulometric titration data of the Ni valency against the Fe content for NiB_i. Maximal OER activity is observed for 5 mol% Fe. At greater than 50 mol% Fe, OER activity of (Ni:Fe)-OEC degrades. For (Co:Fe)-OEC, overlay of Tafel slope (red circle, ●) with absolute Fe^{4+} (green triangle, ▶) population in $CoFeO_x$ films with increasing Fe content.

Finding Connections Between Light-Activated Excited-States and Electrochemistry for Amorphous Cobalt Oxide Water-Splitting Catalysts

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Niklas B. Thompson, Benjamin J. Reinhart[‡], Sungsik Lee[‡], Lisa M. Utschig, Karen L. Mulfort,
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Chemical Sciences and Engineering, [†]Materials Science, and [‡]X-ray Science Divisions
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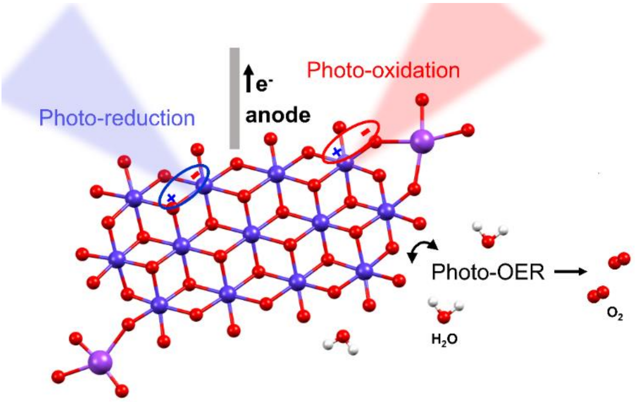
An overarching goal of the Argonne programs is to achieve a fundamental understanding of the mechanisms, structures, and design principles for efficient coupling of photoexcited states to multiple-electron/proton-coupled water-splitting and fuels catalysis. This aspect of the program investigates X-ray approaches for resolving atomic and electronic structures and mechanisms for light-driven oxygen-evolving reactions (OER) using both molecular metal-oxo complexes and "molecular dimensioned" domains in amorphous metal oxide thin film catalysts. Transition metal oxide clusters show optical transitions that include oxo-ligand-to-metal (LMCT), metal-to-metal (MMCT) charge transfer and ligand field *d-d* transitons. We hypothesize that when excited at, or adjacent to, active sites, electron density redistribution in the excited state may trigger catalytic reaction steps. Finding connections between light-activated excited-state chemistry and bond-making/breaking steps in catalysis is of importance as a means to interrogate fundamental mechanisms for solar-to-fuels energy conversion and for exploiting the reactivity of excited states. Here, we report on excitation wavelength-dependent photoelectrochemical responses for the amophorous cobalt oxide formed in the presence of phosphate, CoPi. For example, 415 nm excitation into the LMCT and MMCT bands was found to produce photocathodic currents, while 623 nm excitation elicited photoanodic currents. Both were found to increase with increasing oxidation of the film. Our photocurrent measurements distinguish between photoinduced charge transfer and macroscopic thermal (heat)-driven processes. The results suggest that selective excitation of electronic transitions in metal oxide catalysts can activate electronic and structural dynamics underlying OER catalytic function. The findings suggest new opportunities to probe mechanisms for OER that are triggered by light excitation and to design new modes for enhanced catalysis.



To follow up on these opportunities, this program has been developing approaches to achieve combined resolution of atomic and electronic structures and dynamics for interfacial photocatalysts. In particular, this poster will report on advances in developing computational approaches for extracting high-energy X-ray scattering data and atomic pair distribution profiles for catalysts in complex solution and interfacial environments that are relevant to *operando* analysis of function. In particular, we demonstrate the opportunity to extract information across both inner and outer coordination spheres and to resolve ligand-specific solvent interactions. These methods will be well-suited for extending to ultrafast time-resolved studies.

Probing Water Oxidation Mechanisms on Catalysts with Atomically Defined Active Centers

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Water oxidation is an important reaction for both natural and artificial photosynthesis. The relatively low rate of this reaction on heterogeneous catalysts has been a key challenge in developing solar fuel into a practical technology. Our research goal is to advance solar fuel research by understanding the factors that govern water oxidation on the surface of heterogeneous catalysts. Toward this goal, our project introduces two key innovations. First, we present a new catalyst platform that is derived from molecular precursors ($[Ir(pyalc)(H_2O)_2(\mu\text{-}O)]_2^{2+}$, where pyalc is 2-(2'pyridyl)-2-propanolate). Our preparation procedure preserves the arrangement of the Ir active center of the molecular precursor but removes the organic ligands, resulting in a heterogeneous catalyst whose structure at the active center is resolved. This catalyst offers the structural clarity that is critical to testing various hypotheses of water oxidation mechanisms. Second, we perform the detection of water oxidation intermediates under operando conditions using state-of-the-art spectroscopic tools. When combined with the structural clarity, time-resolved spectroscopic characterization of reaction intermediates provides the clearest understanding on water oxidation. In this presentation, we show our recent results toward the goal of studying water oxidation mechanisms. The catalyst is Ir dinuclear catalyst (Ir DHC) that is synthesized on a variety of substrates that feature different hole (oxidative charge) distribution capabilities, including CeO_2, SiO_2, and indium doped tin oxide (ITO). Importantly, these substrates exhibit low inherent water oxidation activities. As such, the measured reactivity is a direct reporter on the activity of Ir DHC itself. When studied in a classical photochemical system, where $Ru(bpy)_3^{2+}$ serves as a photosensitizer and $Na_2S_2O_8$ works as an electron scavenger, the catalyst exhibits comparable water oxidation activities on the different substrates at room temperature. As the temperature is increased to 50 °C, however, significantly faster reaction rates are measured for Ir DHC on ITO than on CeO_2 or SiO_2. The change in reactivity is understood as a result of improved hole distribution capabilities of ITO at elevated temperatures. The results provide a direct support for the hypothesis that water oxidation activity is sensitive to the propensity for hole accumulation at the active sites. They pave the way toward systematic studies on the implications of this understanding.

Enhancing Photostability of Cu_2O Using Buffer and Protection Layers Prepared by Non-Atomic Layer Deposition Methods

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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. In this presentation, we show our progress on the investigation of buffer and protection layers prepared by inexpensive electrodeposition methods to enhance the efficiency and stability of photoelectrodes.

Cu_2O is a small-bandgap (~2.1 eV) p-type oxide that can be used as a photocathode for solar water reduction, CO_2 reduction, and N_2 reduction. However, Cu_2O suffers from photocorrosion. Fortunately, recent studies have demonstrated that the photostability of Cu_2O can be significantly enhanced by adding a TiO_2 protection layer, which revitalized interest in using Cu_2O as a photocathode. Studies using TiO_2 as a protection layer commonly report that a buffer layer (e.g., ZnO) is necessary between the Cu_2O and TiO_2 layers, suggesting a considerable recombination loss at the Cu_2O/TiO_2 interface. No improvement in photostability is observed without the buffer layer. These studies also report that when ZnO is used as the buffer layer, Al-doping of the ZnO layer is critical. When undoped ZnO is used, the improvement in photostability is not as pronounced as that achieved with Al-doped ZnO.

We note that all buffer and protection layers used in previous multilayer Cu_2O photocathodes were deposited using atomic layer deposition (ALD). This caused us to contemplate if the requirement of adding a buffer layer between Cu_2O and TiO_2 is due to an intrinsic issue of the materials at the Cu_2O/TiO_2 junction, or if it is simply due to the properties of TiO_2 deposited by ALD (e.g. crystallinity, defect type). The same question can be asked about the necessity of Al doping in the ZnO buffer layer. If highly crystalline ZnO can be deposited by non-ALD methods, Al-doping of ZnO may not be needed.

In this presentation, we discuss the preparation and performances of Cu_2O/ZnO, Cu_2O/TiO_2, $Cu_2O/ZnO/TiO_2$ photoelectrodes where ZnO and TiO_2 layers are electrodeposited (Fig. 1). This investigation demonstrates the ability of electrodeposition to produce high quality buffer and protection layers and provides new insights into the construction of multilayer photoelectrodes containing buffer and protection layers.

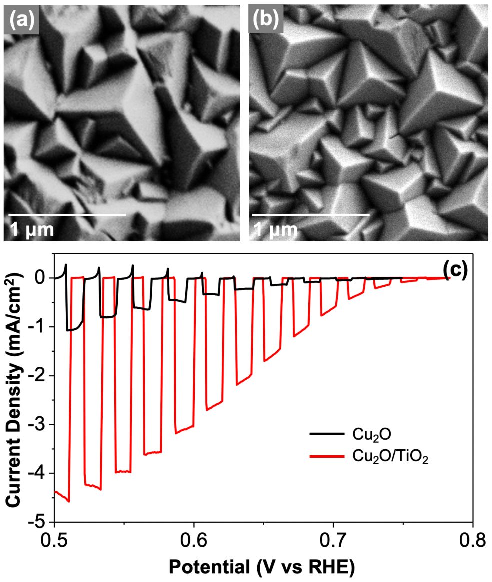

Fig. 1. SEM images of Cu_2O photocathodes (a) before and (b) after the electrodeposition of a TiO_2 layer. (c) J-V plots of Cu_2O and Cu_2O/TiO_2 measured for the reduction of TEMPOL as an electron acceptor at pH 10.6 (AM 1.5G illumination).

Copper Bismuthate Photonic Glass Photoelectrodes for Solar-Driven, Photoelectrochemical Glycerol-to-Hydrogen Evolution

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Fayetteville, AR 72701

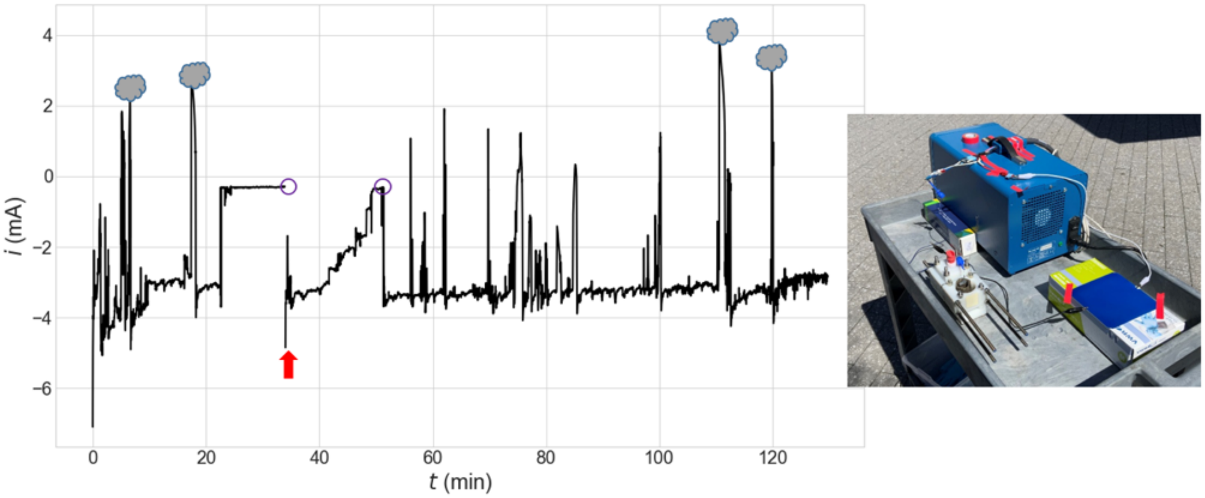

Figure 1 – (left) Sustained current from unbiased solar-to-H_2 generation driven by a single-junction, monocrystalline Si PV cell (right; V_{oc} = 630 mV) using crude glycerol as a sacrificial oxidant on a novel Au-Pt-Bi anode.[1] Dips in the cathodic current due to cloud cover are noted in the scan at several points. These results suggest a glycerol-assisted path to high-yield solar-to-H_2 based on a single junction photoelectrode capable of achieving modest (< 1.0 V) open circuit potentials. We aim to build a photoelectrode for this application by combining a photonic glass photoelectrode structure and copper bismuthate as a light absorber.

Our group is focused on developing photoelectrode structures based on light concentration in a photonic glass. This includes the fabrication of optical cavities in a highly-scattering, random dielectric background which can "self-functionalize" under illumination. In previous work, we have shown that Cu_2O thin films can be grown selectively under photoelectrochemical control. However, Cu_2O is somewhat limited in achievable photovoltage and notoriously unstable under photocathodic operation. Here, we report on our recent work for preparing $CuBi_2O_4$ from photoelectrodeposited Cu_2O as a solid-state precursor. We show that the $CuBi_2O_4$ generates sufficiently high photovoltages to drive the photoelectrochemical solar-to-hydrogen evolution reaction without added bias when glycerol is oxidized on the anode. These initial experiments show that $CuBi_2O_4$ is a candidate for improving overall photocurrents by in the light-concentrating photoelectrode structures we study. Finally, we will report our progress into "designing the disorder" of a photonic glass photoelectrode structure.

(1) Schichtl, Z. G.; Conlin, S. K.; Mehrabi, H.; Nielander, A. C.; Coridan, R. H. Characterizing Sustained Solar-to-Hydrogen Electrocatalysis at Low Cell Potentials Enabled by Crude Glycerol Oxidation. *ACS Appl. Energy Mater.* **2022**, *5* (3), 3863–3875. https://doi.org/10.1021/acsaem.2c00377.

Re-Evaluating Routes of Oxidation of III-V Semiconductor Surfaces

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Physicochemical processes at the photoelectrode and electrolyte interface in photoelectrochemical cells (PECs) lead to spontaneous surface oxidation that can alter chemical and electronic surface properties. Depending on the type of oxides formed, charge carriers can be trapped, thus dampening the effectiveness of water splitting and increasing photocorrosion of the electrode or reducing the dissolution of material and actually improving solar energy conversion. Despite being an inevitable process, such oxidation can be fabricated in a controlled manner if performed under well-adjusted conditions.

Our experimental photoelectroscopic studies combined with *ab initio* simulations on oxidation of III-V semiconductors by oxygen [1] and water [2,3] provided a detailed analysis of oxide structures and their evolution under several pressure and temperature conditions. However, our previous work has failed to track elementary steps in the formation of the surface oxides, their reaction kinetics, and their correlations with the electronic properties at the interface. Therefore, recently we reconsidered a previously studied system, i.e., O_2/GaP(111) interface, to outline a comprehensive picture of the GaP oxidation process and postulate valuable insights for fabricating highly stable III-phosphorous based photoelectrodes with precisely engineered chemical and electronic surface properties.

As previously, we used ambient-pressure X-ray photoelectron spectroscopy assisted by first-principles models, which allowed for analyzing the evolution of surface chemistry without reliance on bulk standards or mechanistic assumptions. We were able to identify and track the distribution of various surface oxides over a wide range of O_2 pressures and temperatures, along with the evolution of atomistic bonding topologies and surface work functions. In addition, we investigated the reaction kinetics of GaP(111) oxidation and determined the activation energies of formation of specific surface oxides. At the initial stage, many oxygen bridges (Ga-O-Ga) were observed, which were formed due to kinetically favorable processes. At the same time, the annealing of the system caused their transformation into more stable and final Ga-O-P configurations.

Such a fundamental understanding of the structural evolution of oxides at the photoelectrodes like GaP upon oxygen exposure is important for monitoring the oxide impact on material properties and ultimately for their practical applications in PEC devices.

[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.

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Energy Materials Chemistry Integrating Theory, Experiment and Data Science

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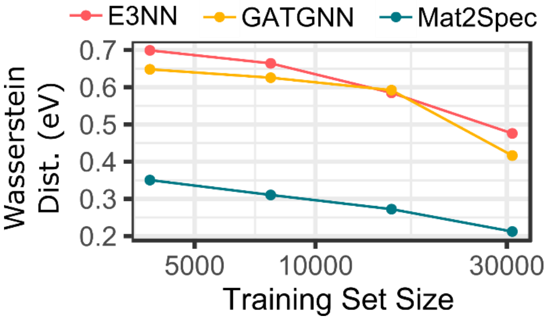
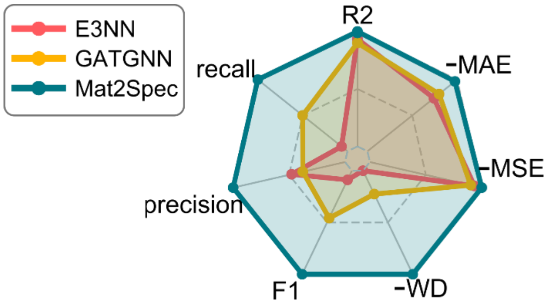
The Energy Materials Chemistry Integrating Theory, Experiment and Data Science (EM-CITED) project is a multidisciplinary research effort focused on accelerating discovery of scientific knowledge via incorporation of data science and artificial intelligence in materials chemistry research. The project aims to advance materials chemistry-aware data science to unify theory and experiment knowledge streams. We will present 2 AI frameworks for materials chemistry - Deep Reasoning Networks (DRNets) and Material-to-Spectrum (Mat2Spec) prediction.

Photoactivity within a given composition system is often 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 that we address through seamless integration of traditionally-distinct AI approaches: *learning* to identify XRD patterns of individual phases and *reasoning* about thermodynamics rules of phase diagrams. The resulting DRNets framework enables new modes of photoanode discovery. [*Nat Mach Intell* **2021**, *3* (9), 1–11. 10.1038/s42256-021-00384-1]



Mat2Spec predicts eDOS with a relatively small amount of data.



Mat2Spec is the best model for both predicting the full eDOS and discovering materials with a specific type of eDOS.

Materials properties for solar photochemistry are most fundamentally rooted in the electronic density of states (eDOS). While AI has shown promise for predicting the properties of materials, the focus to-date has been on individual scalar rather than spectral properties such as eDOS. Mat2Spec is tailored for the prediction of spectral properties by coupling a probabilistic embedding generator with supervised contrastive learning. By exploiting the structure of spectral data, Mat2Spec lowers training data requirements 10-fold and mitigates overfitting, which is critical for predicting the properties of new materials. It outperforms state-of-the-art materials AI methods for predicting eDOS of crystalline materials and for discovering new materials that exhibit specific eDOS features. [*Nat Commun* **2022**, *13* (1), 1–12. 10.1038/s41467-022-28543-x]