

BES004 Fundamental Design and Mechanisms for Solar Hydrogen Production in Natural and Artificial Photosynthetic Systems

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Objectives

The goal of our program in Solar Photochemistry is to resolve fundamental mechanisms for solar energy capture and conversion in artificial photosynthesis and photosynthetic model compounds. Research goals focus on i) investigation of the interplay between structure, ground and excited-state electronic couplings, and photoinduced energy and electron transfer processes in linked light-harvesting and electron donor-acceptor systems, ii) the phenomena of excited state delocalization and electronic coupling/spin coherence across different parts of molecular and supramolecular systems, and their roles in coupling single photon events to multiple

electron redox processes, and iii) the design, synthesis and structure-function analyses of photosensitizer-catalyst assemblies.

The goal of our program in Photosynthetic Systems is to resolve fundamental mechanisms for light-harvesting and coupling of excited-state photochemistry to proton-coupled electron transfer, water oxidation, and chemical energy conversion in photosynthesis, and to test design concepts in photosynthesis using photosynthetic hybrid systems. Photosynthetic hybrids are developed that include the coupling of abiotic catalytic cofactors to electron transfer within photosynthetic protein complexes, and the insertion of abiotic light-harvesting photochemistry and catalytic functions within redox protein frameworks.

Technical Barriers

A key challenge in solar energy conversion lies in understanding how to efficiently couple light-generated, transient, single-electron excited states to long-lived charge separation and multi-electron, proton-coupled fuels catalysis.

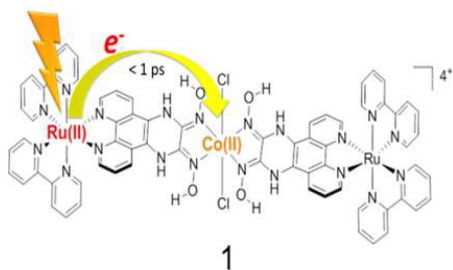
Abstract

This program investigates fundamental mechanisms for coupling photons to fuels in natural and artificial photosynthesis, and tests strategies for the design of sustainable photosynthetic systems for solar energy conversion. The comparison between natural and artificial photosynthesis is used to identify fundamental principles for solar energy conversion and to develop strategies for the design of sustainable photosynthetic systems for solar energy conversion. This presentation will provide examples of chemically-inspired biohybrid designs for multi-electron solar fuels catalysis, and present results on X-ray characterization of amorphous oxide water-oxidation catalyst films as an approach for resolving metal-oxo coordination chemistry underlying solar fuels-dependent water-splitting.

Progress Report

Program highlights accomplished in FY2013-2014 include the following.

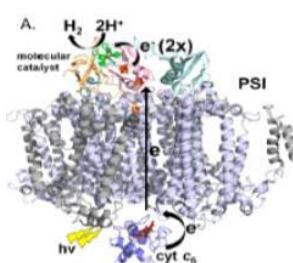
1. Design of linked light-harvesting, hydrogen-evolving catalyst supramolecular assemblies. Key problems for the design of supramolecular assemblies for efficient solar hydrogen production include creating designs that promote efficient photosensitizer-to-catalyst excited-state charge transfer. We succeeded in demonstrating the first example of a dyad assembly, **1**, which accomplishes this transfer in less than 1 ps (Mulfort et. al. 2013 PCCP). The results



are remarkable since they demonstrate a metal-to-metal delocalized excited state analogous to the primary excited state in photosynthesis, and establish a ligand architecture for the design for photo-hydrogen generation.

2. Photosynthetic bio-hybrids for solar hydrogen production.

We demonstrated biohybrids that use Photosystem I (PSI) to drive solar fuel production from a nickel diphosphine molecular catalyst (Utschig et. al. JACS 2013). Upon exposure to visible light, a self-assembled PSI- $[\text{Ni}(\text{P}_2^{\text{Ph}}\text{N}_2^{\text{Ph}})_2](\text{BF}_4)_2$ hybrid generates H_2 at a rate 2 orders of magnitude greater than rates reported for synthetic systems using the same catalyst. In addition, this work developed a strategy for incorporating the Ni molecular catalyst using the native acceptor protein of PSI, flavodoxin. Photocatalysis experiments with this modified flavodoxin demonstrate a new mechanism for biohybrid creation that involves protein-directed delivery of a molecular catalyst to the reducing side of Photosystem I for light-driven catalysis. This work further establishes strategies for constructing functional, inexpensive, earth abundant solar fuel-producing PSI hybrids that use light to rapidly produce hydrogen directly from water.



3. Redox protein biohybrids.

Current research points to the challenges of creating architectures that support the multiple electron and proton transfers needed for solar fuels catalysis, while avoiding a variety of excited-state quenching and charge recombination pathways. This program demonstrated opportunities to exploit the tri-heme cytochromes c7 from

Geobacter sulfurreducens as “molecular wire” components in supramolecular biohybrid synthesis (Tiede et. al. Biochem. 2014). This work has mapped out site-dependent photo-sensitized electron transfer to cofactor hemes using $\text{Ru}(\text{bpy})_3$ derivatives that are covalently linked to cysteine residues placed at a variety of positions on the cytochrome c7 surface through site-directed mutagenesis. Rates of electron transfer were found to vary from 10^{11} s^{-1} to 10^6 s^{-1} depending upon the site and pathway for electron transfer. Photochemical quenching processes are found to track in parallel the site-dependent electron transfer, indicating that both processes follow similar pathway dependences. These results establish criteria for constructing photocatalytic pathways in multi-heme proteins, one that requires multi-step electron transfer to prevent heme-based sensitizer quenching and rapid charge recombination pathways.

4. Amorphous oxides as models for deciphering the chemistry underlying photosynthetic water-splitting and interfacial photochemistry.

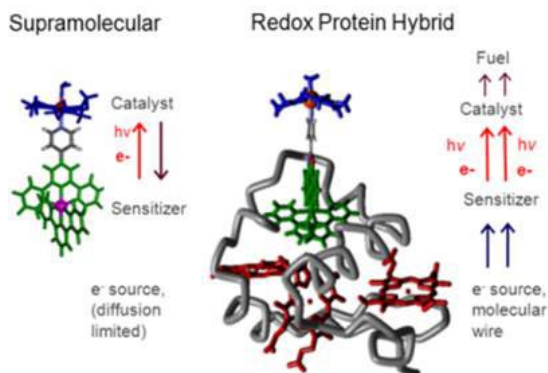
Amorphous thin film oxygen evolving catalysts (OECs) of first-row transition metals are of wide-spread interest for artificial leaf applications, and further serve as models for investigating metal-oxo coordination chemistry underlying photosynthetic water-splitting. We have developed X-ray atomic pair distribution function analysis techniques for the characterization of the “molecular-dimensioned” domain structures within amorphous oxide water-oxidation catalyst films (Tiede et. al. PCCP 2014). Our recent work has extended these measurements to electrode-supported films to resolve structure linked to photochemical energy conversion at electrode interfaces and to develop capabilities that can be extended to molecular-based systems.

Future Directions

Future research will include the following: i) Biomimetic assembly of photocatalyst modules, ii) the development of new redox-active chromophore modules, iii) the development of homogeneous metal-oxide water oxidation catalytic clusters, and iv) Metal-organic frameworks (MOFs) as heterogeneous platforms for solar energy conversion. Within each thrust, we will also describe high-resolution structural and physical characterization techniques which will be critical for in-depth knowledge of the structural factors at the atomic, molecular, and supramolecular levels which impact processes relevant to photocatalysis such as light absorption, photoinduced electron transfer, charge separation and recombination.

Publication list for D.M. Tiede, 2011-2014, acknowledging the DOE grant or contract:

1. Oxyanion Determined Domain Structure for Electrodeposited Amorphous Cobalt Oxide Oxygen Evolving Catalyst Films, Du, P., Ali Han, G. Kwon, O. Kokhan, K.W. Chapman, P.J. Chupas, and D.M. Tiede, (2014) *J.Phys. Chem. Letts.* submitted.



2. Multimerization of Solution-State Proteins by Tetrakis(4-Sulfonatophenyl) Porphyrin. O. Kokhan, N. Ponomarenko, P. Raj Pokkuluri, M. Schiffer, and D.M. Tiede*, (2014) *Biochemistry*, in press.
3. Resolving the Domain Structure for the Amorphous Iridium-oxide Water Oxidation Catalyst by X-ray Pair Distribution Function Analysis, J. Huang, J.D. Blakemore, O. Kokhan, N.D. Schley, R.H. Crabtree,* G.W. Brudvig,* and D.M. Tiede*, (2014) *Phys. Chem. Chem. Phys.*, 16(5): 1814-1819.
4. Detection of a charge-separated catalyst precursor state in a linked photosensitizer-catalyst assembly, A. Mukherjee, O. Kokhan, J. Huang, J. Niklas, L.X. Chen, D.M. Tiede, K.L. Mulfort* (2013) *Phys. Chem. Chem. Phys.*, 15, 21070-21076.
5. “Protein Delivery of a Ni Catalyst to Photosystem I for Light-Driven Hydrogen Production”, Silver, S.C., Niklas, J., Du, P., Poluektov, O.G., Tiede, D.M., and Utschig, L.M, J. Amer. Chem. Soc., (2013) 135(36) 13246-13249.
6. Nanostructured TiO₂/Polypyrrole for Visible Light Photocatalysis, Dimitrijevic, N.M.; Tepavcevic, S.; Liu, Y.; Rajh, T.; Silver, S.C.; Tiede, D.M. (2013) *J. Phys. Chem. C* 117: 15540-15544.
7. Artificial Photosynthesis as a Frontier Technology for Energy Sustainability, T. Faunce, S. Styring, M. R Wasielewski, G.W. Brudvig, A.W. Rutherford, J. Messinger, A.F. Lee, C.L. Hill, H. deGroot, M. Fontecave, D.R. MacFarlane, B. Hankamer, D.G. Nocera, D.M. Tiede, H. Dau, W. Hillier, L. Wang (2013) *Energy Environ. Sci.*, 6, 1074–1076
8. Characterization of an amorphous iridium water oxidation catalyst electrodeposited from organometallic precursors, J.D. Blakemore, M.W. Mara, M.N. Kushner-Lenhoff,† N.D. Schley, S.J. Konezny, I. Rivalta, C.F.A. Negre, R.C. Snoeberger, O. Huang, A. Stickrath, L.A. Tran, M.L. Parr, L.X. Chen,* D.M. Tiede,* V.S. Batista,* R. Crabtree,* and G.W. Brudvig*, (2013) *Inorgan. Chem.* 52: 1860-1871.
9. Structure-based analysis of solar fuels catalysts using *in-situ* X-ray scattering analyses, Karen L. Mulfort*, Anusree Mukherjee, Oleksandr Kokhan, Pingwu Du, David M. Tiede* (2013) *Chem. Soc. Rev.* 42, 2215-2227.
10. A novel ruthenium(II)–cobaloxime supramolecular complex for photocatalytic H₂ evolution: synthesis, characterisation and mechanistic studies, D.M. Crokek, A. Metz, A.M. Müller, H.B. Gray, T. Horne, D.C. Horton, O. Poluektov, D.M. Tiede, R.T. Weber, W.L. Jarrett, J.D. Phillips and A.A. Holder (2012) *Dalton Trans.*, 41, 13060-13073.
11. Elucidating the Domain Structure of the Cobalt-oxide Water Splitting Catalyst by X-ray Pair Distribution Function Analysis, P. Du, O. Kokhan, K.W. Chapman, P.J. Chupas, and D.M. Tiede* (2012) *J. Am. Chem. Soc.* 134(27):11096-11099.
12. Resolution of Cofactor-Specific Excited States and Charge Separation Pathways in Photosynthetic Reaction Centers by Single Crystal Spectroscopy, L. Huang, N. Ponomarenko, G.P. Wiederrecht, and D.M. Tiede (2012) *Proc. Nat. Acad. Sci. USA* 109(13), 4851-4856.
13. X-ray Capabilities on the Picosecond Timescale at the Advanced Photon Source, B. Adams, M. Borland, L.X. Chen, P. Chupas, N. Dashdor, G. Doumy, E. Dufresne, S. Durbin, H. Dürr, P. Evans, T. Graber, R. Henning, E.P. Kanter, D. Keavney, C. Kurtz, Y. Li, A.M. March, K. Moffat, A. Nassiri, S.H. Southworth, V. Srajer, D.M. Tiede, D. Walko, J. Wang, H. Wen, L. Young, X. Zhang, and A. Zholents, (2012) *Synchrotron Rad. News* 25(2): 6-10.
14. Highly Efficient Ultrafast Electron Injection from the Singlet MLCT Excited State of CuI-Diimine Complexes to TiO₂ Nanoparticles, J. Huang, O. Buyukcakir, M.W. Mara, A. Coskun, N.M. Dimitrijevic, G. Barin, O. Kokhan, A.B. Stickrath, R. Ruppert, D.M. Tiede, J.F. Stoddart, J.-P. Sauvage, and L.X. Chen, *Angew. Chem. Intl. Ed.* 51, 12711–12715. (2012).
15. The Hydrogen Catalyst Cobaloxime – a Multifrequency EPR and DFT Study of Cobaloxime’s Electronic Structure, Niklas, J., Mulfort, K.L., Rakhimov, R.R, Mardis, K.L., Tiede, D.M., and Poluektov, O.G. (2012) *J. Phys. Chem. B*, 116, 2943-2957.
16. Nature-Driven Photochemistry for Catalytic Solar Hydrogen Production: A Photosystem I–Transition Metal Catalyst Hybrid, L.M. Utschig, S.C. Silver, K.L. Mulfort, and D.M. Tiede (2011) *J. Am. Chem. Soc.* 133:16334-16337.
17. Metal Nanoparticle Plasmon-Enhanced Light-Harvesting in a Photosystem I Thin Film, I. Kim, S.L. Bender, J. Hranisavljevic, L.M. Utschig, L. Huang, G.P. Wiederrecht, and D.M. Tiede (2011) *Nano Letts.* 11 (8): 3091–3098.
18. Comparing Photosynthetic and Photovoltaic Efficiencies and Recognizing the Potential for Improvement, R. E. Blankenship*, D.M. Tiede*, J. Barber, G.W. Brudvig, G. Fleming, M. Ghirardi, M.R. Gunner, W. Junge, D.M. Kramer, A. Melis, T.A. Moore, C.C. Moser, D.G. Nocera, A.J. Nozik, D.R. Ort, W.W. Parson, R.C. Prince, R.T. Sayre (2011) *Science* 332: 805-809.
19. Photocatalytic Hydrogen Production from Noncovalent Biohybrid Photosystem I/Pt Nanoparticle Complexes, L.M. Utschig, N.M. Dimitrijevic, O.G. Poluektov, S.D. Chemerisov, K.L. Mulfort, and D.M. Tiede (2011) *J. Phys. Chem. Letts.* 2: 236-241. *Highlighted in Chemical & Engineering News*, 2011, 89(5), 44-45.