

## II.G.19 Argonne-Northwestern Solar Energy Research (ANSER) Center

Michael R. Wasielewski, Director  
Northwestern University  
2145 Sheridan Rd.  
Evanston, IL 60208  
Phone: (847) 467-1423  
Email: m-wasielewski@northwestern.edu

DOE Program Manager: Dr. Chris Fecko  
Phone: (301) 903-1303  
Email: Christopher.fecko@science.doe.gov

### Objectives

The long-term vision of the ANSER Center is to develop the fundamental understanding, materials and methods necessary to create dramatically more efficient technologies for solar fuels and electricity production. ANSER will realize this vision by understanding and characterizing the basic phenomena of solar energy conversion dynamics, by designing and synthesizing new nanoscale and mesoscale architectures with extraordinary functionality, and by linking basic solar energy conversion phenomena across time and space to create emergent energy conversion systems operating with exceptional performance.

### Technical Barriers

The ANSER Center's goals are to answer the following four fundamental questions essential to both solar fuels and solar electricity production:

**Question 1:** How can multi-scale predictive theory and computational modeling lead to the design and discovery of novel organic, inorganic, and hybrid systems?

**Question 2:** How do molecular and materials structure and order determine the efficiency of light capture, charge separation, and long-range charge transport?

**Question 3:** What are the fundamental multi-scale temporal and spatial requirements for efficient charge transport across interfaces to deliver multiple redox equivalents to catalysts and electrodes?

**Question 4:** How can molecular and materials properties be tailored to exploit hierarchical assembly for solar fuels and electricity systems scalable from the nanoscale to the mesoscale?

### Abstract

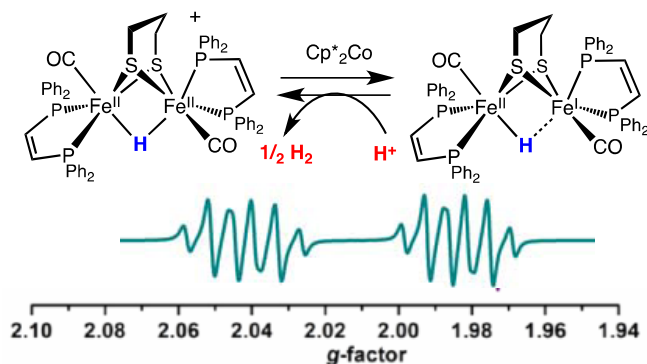
ANSER is investigating coupling light-driven charge generation to multi-electron catalysts for H<sub>2</sub>O splitting and

H<sub>2</sub> production, focusing on how the structure of photodriven donor-acceptor-catalyst systems determines their charge transfer dynamics at all relevant time scales. Selected highlights of research accomplishments are presented here.

### Progress Report

**1. Photodriven Proton Reduction Catalysts.** ANSER focused on understanding hydrogen evolution catalysts made from earth-abundant metals, e.g. the diiron dithiolato complexes found in natural hydrogenases, and providing them with photogenerated redox equivalents. One deficiency with traditional “bioinspired” systems is the photolability of the iron carbonyl group. ANSER discovered that diiron catalysts stabilized by diphosphine ligands are photostable. They also isolated and crystallized the long sought doubly-protonated catalytic intermediate in Fe<sub>2</sub>S<sub>2</sub> hydrogenase mimics and showed it to be highly active for H<sub>2</sub> formation. The mixed valence intermediate was characterized by EPR and crystallographic studies, and remarkably the bridging hydride (**Fig. 1**) persisted throughout catalytic turnover.

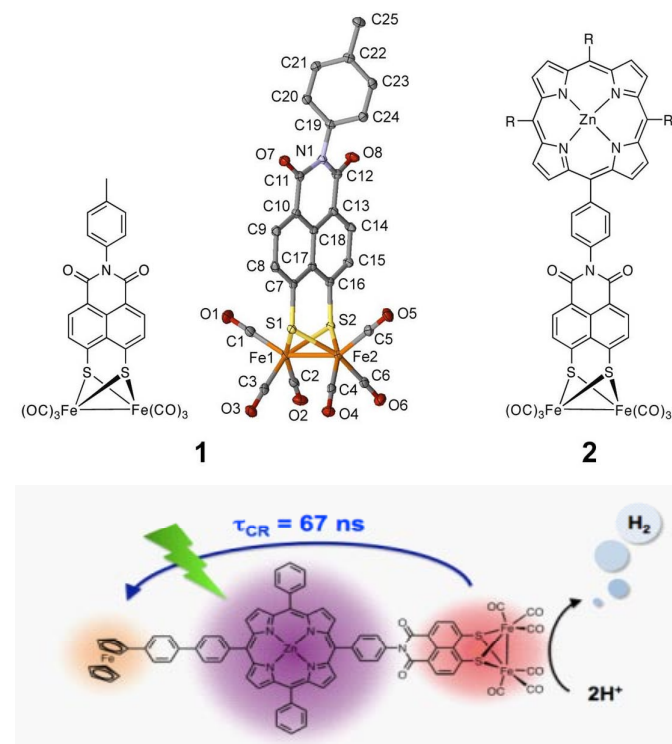
ANSER developed photodriven H<sup>+</sup> reduction catalysts that mimic the active cofactor within hydrogenase enzymes, yet do so in simplified structures. For example, in the dithiolate diiron complex **1** in **Fig. 2**, the electron-withdrawing naphthalene monoimide (NMI) ligand makes the diiron complex among the most easily reduced hydrogenase mimics reported to date. In the presence of triflic acid, **1** shows electrocatalytic H<sub>2</sub> production. Selective femtosecond laser excitation of the Zn porphyrin in **2** yields charge separation and charge recombination dynamics of 20 ps and 62 ps, respectively. Time-resolved X-ray absorption spectroscopy (at the APS, Argonne) on the electrochemically-generated reduced Fe<sub>2</sub> complex shows that both the Fe-Fe and Fe-CO bonds lengthen as the complex is reduced.



**FIGURE 1.** Fe-Fe hydrogenase mimic and the EPR spectrum of the Fe(II)-Fe(I) state.

To extend the lifetime of the reduced diiron state of **1**, an electron donor-acceptor triad (**Fig. 2, 3**) was prepared. Here, charge recombination occurs with  $\tau_{CR} = 67$  ns in  $\text{CH}_2\text{Cl}_2$ , an increase of >1000-fold relative to the dyad. These results show that rapid energy transfer from the photoexcited Zn porphyrin to the low-lying d-d states of the iron complexes does not compete with the desired photoreduction of  $\text{NMI-Fe}_2\text{S}_2(\text{CO})_6$ . Photoexcitation of the triad in the presence of trifluoroacetic acid generates one mole of  $\text{H}_2$  for every two photons absorbed.

**2. Self-assembly of Hierarchical Systems for Photocatalytic Proton Reduction.** ANSER developed a novel class of biomimetic chalcogenides, “chalcogels”, which are air-stable porous, high surface area ( $150 \text{ m}^2/\text{g}$ ) materials resistant to hydrolysis. These gels have a high degree of synthetic flexibility, allowing a wide range of light-driven processes relevant to solar fuels production. For example, using a simple ion-exchange process, a  $\text{Ru}(\text{bpy})_3^{2+}$  photosensitizer was incorporated into a chalcogel containing a  $\text{Fe}_4\text{S}_4$  cluster which serves as a  $\text{H}^+$  reduction catalyst. Visible light irradiation results in  $\text{H}_2$  evolution for days. Importantly, the chalcogel framework provides a flexible design scaffold for assembling integrated systems for solar fuels formation (**Fig. 3**), and this work was extended to high-performance  $\text{FeMoS}$  clusters, where the relevant transient redox states responsible for  $\text{H}_2$  formation were identified. ANSER also

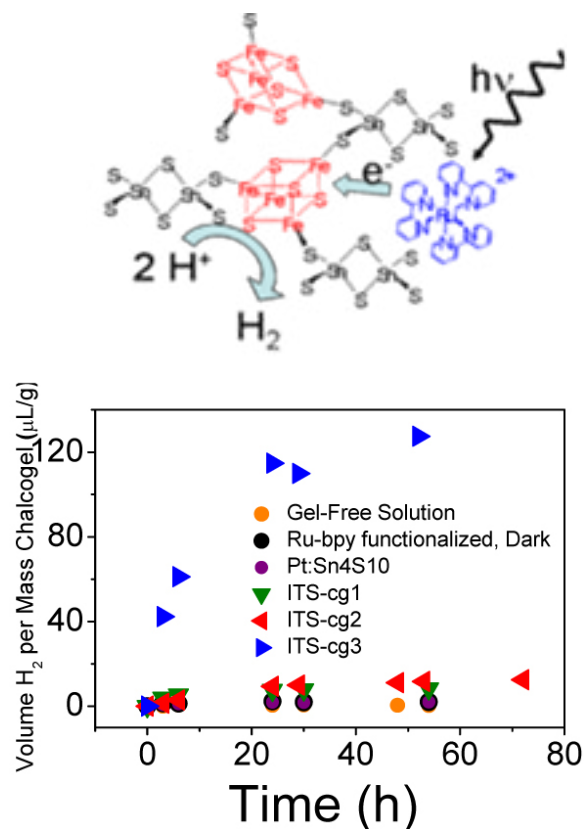


**FIGURE 2.** Top left: chemical structure of **1**. Top Center: X-ray structure of **1**. Top Right: chemical structure of **2** ( $\text{R} = n\text{-C}_5\text{H}_{11}$ ). Bottom: chemical structure of **3**.

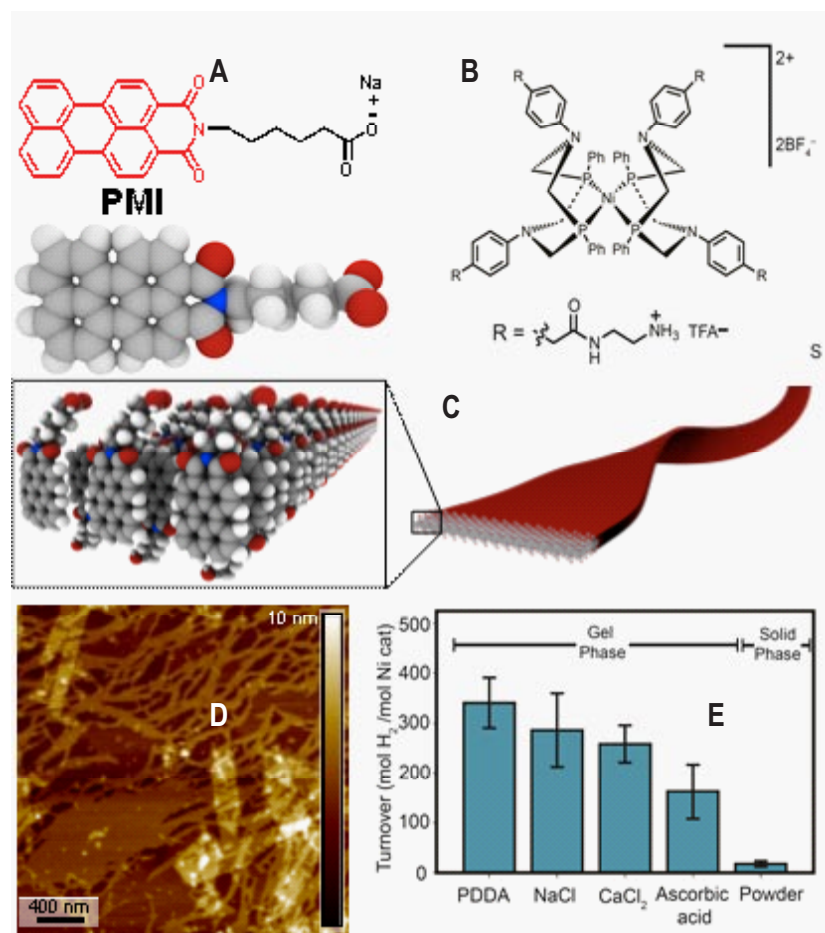
examined the effect of third metal cations (in addition to the  $\text{Fe}_4\text{S}_4$  clusters) on the electrochemical and electrocatalytic properties of the chalcogels. They found that ternary biomimetic chalcogels containing Ni or Co show increased efficiency in  $\text{CO}_2$  to formate conversion and can be thought of as solid-state analogues of enzymatic NiFe or NiFeS reaction centers.

ANSER also demonstrated control of the electrochemical redox potential of biomimetic  $\text{Fe}_4\text{S}_4$  clusters by varying the size of the bridge between them. As a result, the light to  $\text{H}_2$  conversion efficiency of the dye-functionalized chalcogels,  $([\text{Fe}_4\text{S}_4]_x[\text{Sn}_n\text{Sn}_{2n+2}]_y[\text{Ru}(\text{bpy})_3]_z)$  was enhanced by using three different Fe/S chalcogels with increasingly larger bridges of  $[\text{SnS}_4]^{4-}$ ,  $[\text{Sn}_2\text{S}_6]^{4-}$ , and  $[\text{Sn}_4\text{S}_{10}]^{4-}$  (ITS-cg1, ITS-cg2, and ITS-cg3, respectively, **Fig. 3**). The anion sizes define the inter- $\text{Fe}_4\text{S}_4$  cluster spacing and modulate the redox potentials. Transient spectroscopy shows that increased  $\text{H}_2$  production for ITS-cg3 tracks the longer charge separation lifetime for this system.

A negatively-charged perylene-monoimide (PMI) carboxylate derivative and a positively charged polyelectrolyte was used to self-assemble hierarchically-ordered supramolecular membrane materials that strongly



**FIGURE 3.** Top: Schematic of photo-sensitized of  $\text{H}_2$  production using a  $\text{Fe}_4\text{S}_4\text{-Sn}_2\text{S}_6$  chalcogel. Bottom:  $\text{H}_2$  production as a function of photolysis time and cluster porosity.



**FIGURE 4.** (A) Amphiphilic PMI photosensitizer; (B) Ni(II)-phosphine<sub>4</sub> catalyst; (C) schematic of self-assembled PMI ribbon; (D) AFM image of ribbons; (E) H<sub>2</sub> evolution in gels.

absorb visible light and are mechanically robust and acid stable (**Fig. 4A-E**). ANSER showed that the PMI carboxylate acts as a photosensitizer to drive photocatalytic H<sub>2</sub> production from H<sup>+</sup> and light with a positively-charged DuBois-type<sup>7</sup> Ni(II)-phosphine catalyst with a sacrificial donor (**Fig. 4E**). In fact, the cationic catalyst itself induces PMI ribbon formation as an emergent property. This result shows that it is possible to associate and compartmentalize catalysts in a self-assembled light-harvesting system to achieve photodriven catalytic H<sub>2</sub> evolution.

## Future Directions

Our greatest challenge is efficient fuel production at acceptable rates and driving forces. The ANSER team will use a hierarchical approach to designing, synthesizing, modeling, characterizing, assessing, and understanding catalyst and photocatalyst function. The focus will be on theory-guided and hypothesis-driven design and discovery of superior catalysts, and integration of catalysts with light-harvesting/charge generation molecules and materials. Catalysts will span the range from molecules to clusters, nanoparticles, and bulk materials. Molecules and clusters offer the possibility of full atomic-scale characterization and investigation, while studies of bulk materials will point toward issues that may be relevant for eventual technologies. Nanoparticles provide a useful functional and conceptual bridge between these two limits. The work will be organized around four cross-cutting questions outlined under Technical Barriers.

## Publication list (including patents)

See official list from [www.energyfrontier.us](http://www.energyfrontier.us) website. As of April 30, 2014, there are 209 cumulative peer-reviewed publications acknowledging ANSER EFRC funding, resulting in 2750+ citations and an h-index of 32.