Department of Energy
Office of Basic Energy Sciences
Chemical Sciences, Geosciences, & Biosciences (CSGB) Division
Final Technical Report 2006-2009

**DESIGN, SYNTHESIS AND STUDY OF MULTI-COMPONENT AND INTEGRATED
SYSTEMS FOR LIGHT-DRIVEN HYDROGEN GENERATION**

Primary Investigator: Professor Richard Eisenberg
Chemistry Department, University of Rochester, RC Box 270216
Rochester, NY 14514-0216
Phone: (585) 275-5573; Fax: (585) 276-0205
Email: eisenberg@chem.rochester.edu

The final technical report for DE-FG02-90ER14125 (021) covers the period 2006-2009 since the grant represented a one year phase down of the project DE-FG02-90ER14125 (A020). The work during the final year involved completion and publication of studies that are listed at the end of this report. Notable progress was made over the four year period ending February 28, 2010, and the results have contributed to a greater understanding of the complexities and subtleties of this seemingly simple process. In these studies we concentrated on the use of solution luminescent Pt(II) complexes that contain a bi- or terpyridyl ligand for light absorption. These complexes, like the more extensively studied d⁶ Ru(II) complexes with similar hetero-aromatic ligands, possess solution luminescent ³MLCT excited states that can undergo electron transfer reactions.

Two different lines of inquiry were followed in the research conducted during the past four years. The first deals with the photo-generation of H₂ employing a multiple component system consisting of a platinum(II) chromophore, an electron relay, a sacrificial electron source and colloidal Pt as the actual H₂-generating catalyst, while the second concentrates on photoinduced charge separation (PICS) using a similar platinum(II) chromophore covalently connected to spatially specific electron donor and acceptor moieties. The latter has included collaborative transient absorption (TA) measurements on the ns timescale with Professor Russell Schmehl of Tulane University.

Photogeneration of Hydrogen. In 2006, we reported that, like [Ru(bpy)₃]²⁺, complex **1** can promote the photochemical generation of H₂ in a system containing methyl viologen (MV²⁺) as the electron relay, triethanol amine (TEOA) as the sacrificial electron donor and colloidal Pt as the H₂-generating catalyst. The kinetic dependences of both pH and [MV²⁺] on H₂ generation were found to be non-monotonic, suggestive of the involvement of these

species in more than one of the mechanism's steps. Subsequent studies found that other Pt(II) complexes having bi- and terpyridyl ligands with similar $^3\text{MLCT}$ excited states also drive this reaction with light of $\lambda > 410$ nm. Different diquats were used in place of MV^{2+} as the electron relay and compound **2** was found to be most effective with more than 800 turnovers of H_2 and a 67% yield of H_2 based on TEOA for a system containing it. Since **2** was the most difficult to reduce of the different diquats employed (and harder to reduce than MV^{2+}), we concluded that quenching by the electron relay of the excited chromophore was not rate determining and that instead electron transfer from the *reduced* diquat to the colloid is likely turnover limiting.

Two problematic aspects of these initial H_2 -generating systems based on Pt(II) chromophores such as **1** were: (1) the slow decomposition of the electron relay by hydrogenation and (2) the radiation energy needed by these chromophores to effect proton reduction to hydrogen. In order to address the first deficiency, TiO_2 was employed as the electron relay with platinization of the semiconductor nanoparticles providing catalytic sites for H_2 formation. In photolyses ($\lambda > 410$ nm) of **1** with platinized TiO_2 ($\text{TiO}_2\text{-Pt}$) + TEOA, similar turnovers of H_2 were obtained as when MV^{2+} + colloidal Pt + TEOA were present, showing that the chromophores were able to photoinject electrons into the TiO_2 conduction band and that these electrons were collected at the Pt catalytic sites on the surface of the $\text{TiO}_2\text{-Pt}$ particles.

The second problem stimulated a change in the Pt(II) chromophore away from acetylide complexes to corresponding dithiolate systems since these complexes were known from numerous earlier studies to have a lower energy ^3CT state involving a mixed Pt(d)/S(p)/dithiolate HOMO and a π^* diimine LUMO. Importantly, Pt(diimine)(dithiolate) complexes when attached to TiO_2 through carboxylate substituents on the diimine were reported by Arakawa to generate photocurrent. The system shown as **3** was thus found to generate H_2 in the presence of TEOA. While the system efficiency was low, attachment of the chromophore to $\text{TiO}_2\text{-Pt}$ led to greatly improved performance relative to the situation in which the chromophore was not bound to the semiconductor particle. Also, since the charge transfer absorption of the chromophore in **3** was at ~ 530 nm, a lower energy cutoff filter ($\lambda > 455$ nm) was employed, leading to the observation that the system was photostable for more than 180 h while generating H_2 .

Over the last several years, there have been reports of a number of integrated systems for the photogeneration of hydrogen. One such example reported by Sakai contains a $\text{Ru}(\text{bpy})_2(\text{phenanthroline})^{2+}$ moiety envisioned as the light absorber and charge transfer agent, linked via an amide linkage to a $\text{PtCl}_2(\text{dcbpy})$ unit serving as the catalyst for H_2 formation. However, observations by us of the photo-instability for Pt complexes when $\lambda > 410$ nm but not when $\lambda > 455$ nm suggested otherwise and stimulated a multi-pronged examination of whether Pt bi- and terpyridyl chloride complexes are actually capable of functioning as molecular catalysts for H_2 production. The research was undertaken in collaboration with Professor Felix Castellano

of Bowling Green State University, and was published as a communication in *J. Am. Chem. Soc.*

In one set of experiments, TEM images of TiO₂ were obtained before and after photolysis with $\lambda > 410$ nm light to reveal the existence of particles on the TiO₂ surface only after irradiation. The identity of these particles as metallic Pt was supported by EDAX measurements. A second set of experiments involved the use of Hg to sequester or inhibit catalysis by colloids in systems composed of chromophore **1**, either MV²⁺ or TiO₂ as the electron relay, Pt(II) bi- and terpyridyl complexes as catalysts including ones bound directly to TiO₂ and TEOA. The results showed that while Hg did not bind or sequester the Pt(II) complexes, it did inhibit H₂ formation during irradiation. Finally, variants of **3** with the purported Pt(II) "molecular complex catalysts" in place of surface bound Pt islands were examined and found *not* to generate H₂ upon irradiation with $\lambda > 455$ nm light at which energy photodecomposition does not occur. Our study showed that the purported Pt(II) molecular catalysts do not serve to catalyze H₂ formation directly and instead simply act as colloidal metal precursors. During this study, a similar report appeared by Hammarström on the formation of Pd colloids from integrated systems containing Pd(II) diimine chloride moieties thought to be the H₂ generating catalyst. Both reports underscore the necessity of establishing the *absence* of colloidal metal when reporting molecular catalysts for the light-driven production of hydrogen.

One of the directions stated in the DOE Report on Catalysis for Energy Applications is the need to move away from expensive noble metal catalysts to cheaper, more abundant elements. An exciting result that we published was the development of a new solution-based system for H₂ photoproduction in which a cobalt complex functions as the catalyst. This work builds on electrocatalytic studies using Co dimethylglyoximate complexes and derivatives that exhibit low over-potentials for H₂ generation upon reduction. In the system we report, chromophore **1** undergoes both oxidative quenching by Co complex **4** (R = Me) as well as reductive quenching by TEOA. In a subsequent electron transfer, the catalyst is reduced to Co(I) which we think undergoes protonation to give a Co(III)-H species. However, the actual H₂ forming step is yet to be determined. The system containing **1**, **4** and TEOA in MeCN:water (3/2 v/v) generates ~400 and ~1000 turnovers of H₂ after 10 h irradiation with $\lambda > 410$ nm when [TEOA] is 0.016 M and 0.27 M, respectively. This result serves as the basis for some of the proposed studies described below.

Photoinduced Charge Separation in Platinum Chromophore Based Triads and Dyads.

The process of PICS is the key initial step following light absorption in photosynthetic systems that leads to chemical energy storage. Prior to the current grant, the synthesis and photophysical study of several donor-chromophore-acceptor (D-C-A) triads having a Pt(II) bi- or terpyridyl acetylide chromophore were conducted. For one of these systems with a phenothiazine donor and a nitrostilbene acceptor, the D⁺-C⁻ A⁻ charge separated state was observed with a lifetime of 230 ns but its formation was deemed inefficient with only ~25 % of the initial chromophore CT state producing it.

Work during the past four years has yielded several new triad systems such as triad **5** and its nicotinamide analog, together with the corresponding chromophore-acceptor dyads, and analyses of their photophysical properties. The results reveal that **5** exhibits a long-lived transient

characteristic of electron transfer to the viologen in contrast with the nicotinamide and previously published pyridinium acceptors in which electron transfer was not observed. However, the charge separated transient in **5** was formed very inefficiently. In the course of this study, an additional problem was identified with the multi-component systems having pyridinium-type acceptors attached as in **5**. Specifically, the chromophore-acceptor linkage via the N-C(benzylic) bond was

found to be sensitive to cleavage by OH^- which is formed in systems for H_2 generation from H_2O . This sensitivity to base had not been recognized in other studies employing this terpyridyl-acceptor bridge in Ru-based triads studied by TA spectroscopy. For comparison of PICS with other reported triads having phenothiazine (PTZ) donors and nitrobenzene (NB) acceptors, the triad shown as **6** was synthesized using Pd-catalyzed Suzuki coupling chemistry. While the resultant chromophore-acceptor link in this system is robust, electron transfer to NB is *not* found to occur because of poor coupling between the chromophore and the NB moiety, and a lower driving force for the electron transfer compared to that for a neutral Pt phenanthroline bis(acetylide)-based triad.

Vapochromism and the Influence of Pt...Pt Interactions on Emission Energies. The significance of non-covalent interactions on the emission energies of square planar terpyridyl Pt(II) complexes was revealed dramatically for nicotinamide complex **7** in 2004 as its solid state luminescence changed reversibly between orange and red in the presence and absence of MeOH vapors. The change was observed in single crystals that were examined crystallographically in *both* forms, giving strong evidence that the red emission arises as a result of d^8 - d^8 Pt...Pt interactions. During this past year, another vapochromic system shown as **8** was prepared and its structure determined crystallographically in its two different forms, albeit on different crystals. As before, the red emissive form signifies the existence of d^8 - d^8 Pt...Pt interactions that are absent in the green form - *i.e.*, the non-bonding Pt...Pt separations in the

green form are too long to be spectroscopically or electronically significant. The red form further reveals that while its solid state structure possesses both shorter and longer Pt...Pt distances, the excited state energy in that system must migrate to the sites where significant d⁸-d⁸ interactions occur.

DOE Sponsored Publications based on grant DE-FG02-90ER14125, 2006-2009

1. Photocatalytic Generation of Hydrogen from Water Using a Platinum(II) Terpyridyl Acetylide Chromophore, Du, P.; Schneider, J.; Jarosz, P.; Eisenberg, R., *J. Am. Chem. Soc.* **2006**, *128*, 7726-7727.
2. Photoinduced Electron Transfer in Platinum(II) Terpyridyl Acetylide Chromophores: Reductive and Oxidative Quenching and Hydrogen Production, Du, P.; Schneider, J.; Jarosz, P.; Zhang, J.; Brennessel, W. W.; Eisenberg, R., *J. Phys. Chem. B* **2007**, *111*, 6887-6894.
3. Photogeneration of Hydrogen from Water Using an Integrated System Based on TiO₂ and Platinum(II) Diimine Dithiolate Sensitizers, Zhang, J.; Du, P.; Schneider, J.; Jarosz, P.; Eisenberg, R., *J. Am. Chem. Soc.* **2007**, *129*, 7726-7727.
4. The Synthesis and Structural Characterization of a New Vapochromic Pt(II) Complex Based on the 1-Terpyridyl-2,3,4,5,6-Pentaphenylphenyl (TPPPB) Ligand, Du, P.; Schneider, J.; Brennessel, W. W.; Eisenberg, R., *Inorg. Chem.* **2008**, *47*, 69-77.
5. Bi- and Terpyridyl Platinum(II) Chloro Complexes: Molecular Catalysts for the Photogeneration of Hydrogen from Water or Simply Precursors for Colloidal Platinum?, Du, P.; Schneider, J.; Castellano, F.; Eisenberg, R., *J. Am. Chem. Soc.* **2008**, *130*, 5056-5058.
6. Synthesis, Characterization, and Photophysical Properties of Platinum(II) Terpyridyl-based Molecular Assemblies, Jarosz, P.; Thall, J.; Schneider, J.; Kumaresan, D.; Schmehl, R. and Eisenberg, R. *Energy & Environmental Science*, **2008**, 573.
7. A Homogeneous System for the Photogeneration of Hydrogen from Water Based on a Platinum(II) Terpyridyl Acetylide Chromophore and a Molecular Cobalt Catalyst, Du, P.; Knowles, K.; Schneider, J.; and Eisenberg, R., *J. Am. Chem. Soc.* **2008**, *130*, 12576-12577.
8. Platinum(II) Terpyridyl-Acetylide Dyads and Triads with Nitrophenyl Acceptors via a Convenient Synthesis of a Boronated Phenylterpyridine, Jarosz, P.; Lotito, K.; Schneider, J.; Kumaresan, D.; Schmehl, R. and Eisenberg, R., *Inorg. Chem.* **2009**, *48*, 2420-2428.
9. Platinum(II) Terpyridyl Acetylide Complexes on Platinized TiO₂: Towards the Photogeneration of H₂ in Aqueous Media, Jarosz, P.; Du, P.; Schneider, J.; Lee, S.-H.; McCamant, D.; Eisenberg, R., *Inorg. Chem.* **2009**, *48*, 9653-9663.
10. Synthesis, Electrochemistry, Photophysics and Solvatochromism in New Cyclometalated 6-Phenyl-4-(*p*-R-phenyl)-2,2'-bipyridyl (R = CH₃, COOCH₃, P(O)(OEt)₂) (C^NN^N) Platinum(II) Thiophenolate Chromophores, Schneider, J.; Du, P.; Wayn, X.; Brennessel, W. W.; Eisenberg, R., *Inorg. Chem.* **2009**, *48*, 1498-1506.

11. Cyclometalated 6-Phenyl-2,2'-bipyridyl (CNN) Platinum(II) Acetylide Complexes: Structure, Electrochemistry, Photophysics, and Oxidative Reductive Quenching Studies, Schneider, J.; Du, P.; Jarosz, P.; Lazarides, T.; Wang, X.; Brennessel, W. W.; Eisenberg, R., *Inorg. Chem.* **2009**, *48*, 4306-4316.
12. Visible Light-Driven Hydrogen Production from Water Catalyzed by Molecular Cobaloxime Catalysts, Du, P.; Schneider, J.; Luo, G.; Brennessel, W.W.; Eisenberg, R., *Inorg. Chem.* **2009**, *48*, 4952-4962.
13. Energy Upconversion Sensitized by a Platinum(II) Terpyridyl Acetylide Complex, Du, P.; Eisenberg, R., *Chem. Sci.* **2010**, *1*, 502-506.
14. Sensitizing the Sensitizer: The Synthesis and Photophysical Study of Bodipy-Pt(II)(diimine) (dithiolate) Conjugates, Lazarides, T.; McCormick, T.; Wilson, K. C.; Lee, S.; McCamant, D.; Eisenberg, R., *J. Am. Chem. Soc.* **2011**, *133*, 350-364.