

# Photoinitiated Electron Collection in Mixed-Metal Supramolecular Complexes: Development of Photocatalysts for Hydrogen Production

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## Objectives

- Design and study of new supramolecular complexes for the production of H<sub>2</sub> from H<sub>2</sub>O using molecular devices for photoinitiated electron collection.
- Understand the mechanisms of complex, coupled reactions for the solar production of fuels as facilitated by supramolecular complexes.
- Probe the role of sub-unit variation on the functioning of supramolecular H<sub>2</sub> production photocatalysts to explore the impact of modulation of orbital energetics and excited state dynamics on this complicated photochemistry.
- Develop a fundamental understanding of the rates and mechanisms of multielectron photochemistry and photocatalysis in supramolecular complexes.

## Technical Barriers

- Controlling the high purity assembly of multicomponent supramolecular complexes with reactive metal centers needed to photocatalyze H<sub>2</sub>O reduction to H<sub>2</sub> in single component systems is a developing field that requires considerable synthetic expertise to prepare target systems.
- Few molecular systems are known that photochemically collect reducing equivalents and less are known that collect electrons at a reactive site.
- Understanding the factors that control multielectron photochemistry is still in its infancy and developing this understanding in supramolecular assemblies presents additional challenges.
- The process of collecting reducing equivalents on a molecular system followed by delivery to a H<sub>2</sub>O substrate requires a series of carefully controlled and coordinated reactions, high overall efficiency reliant on the product of efficiency of individual steps.

## Abstract

The growing energy needs of our Nation require that we explore and harness a variety of new energy sources within the coming decades. Fossil fuels are currently used to supply much of our Nation's energy needs, often derived from the sun's energy, as harnessed and converted by plants into biomaterials. The rate of our use of fossil fuels makes it necessary to explore alternative means to harvest this energy or alternative energy sources. One appealing alternative energy source is solar energy harnessed without the use of plants. In the Report of the Basic Energy Sciences Workshop on H<sub>2</sub> Production, Storage and Use in 2003, catalyst design for H<sub>2</sub> production was identified as an important goal with emphasis on nanoscale systems.<sup>1</sup> In the report of the Basic Energy Sciences Workshop on Solar Utilization, sunlight is identified as by far the largest of all carbon-neutral energy sources with  $4.3 \times 10^{20}$  J per hour reaching the earth's surface.<sup>2</sup> This represented more energy than that consumed on the planet in a year. The report from the Basic Energy Sciences committee in 2008 states "The ultimate transport solution would be solar fuels, made from using sunlight to split water and produce hydrogen..."<sup>3</sup> A major research need identified in the Workshop on H<sub>2</sub> Production was the development of systems that convert sunlight into chemical fuels for storage and distribution. This project addresses these fundamental issues within a molecular architecture that undergoes multielectron photochemistry and is capable of producing H<sub>2</sub> from water. Importantly the work aims to develop a deeper understanding of the fundamental nature of the multiple steps involved in the complex processes needed to use light energy to promote multielectron reactions as well as the catalysis of the multielectron reduction of substrates to produce transportable fuel. The basic structural motifs of interest focus on the use of Ru and Os MLCT light absorbers (LA) coupled through polyazine bridging ligands (BL) to reactive metal centers, typically Rh. These complexes contain the basic building blocks needed to prepare complexes that undergo photoinitiated electron collection (PEC) and catalyze the reduction of H<sub>2</sub>O to produce H<sub>2</sub>. Functioning single component systems have been developed with our understanding of their functioning allowing for substantial increases in photocatalytic turnover and quantum efficiency. Studies have focused on a development of a knowledge base concerning the role of device sub-units and excited state dynamics on functioning as well as elucidating the mechanism of functioning.

## Progress Report

This project is aimed at developing and studying a class of mixed-metal supramolecular complexes with promising

redox and excited state properties. These systems couple charge transfer light absorbing metals to reactive metals such as rhodium(III) that will allow these systems to undergo PEC while possessing reactive metal sites capable of delivering collected electrons to a substrate such as  $\text{H}_2\text{O}$  to facilitate the production of  $\text{H}_2$ . The factors impacting multi-electron photochemistry and the reduction of water to produce  $\text{H}_2$  have been explored aimed at providing a detailed understanding of the mechanism of action of these unique photocatalysts and the factors that impact functioning. The synthetic pathway to prepare these systems is illustrated in Figure 1 and represents a building block method that allows stepwise assembly and careful purification at each step.

The Rh centered supramolecular complexes must undergo a complex series of steps in order to undergo PEC and deliver collected electrons to a substrate to produce a fuel. This includes the absorption of a series of photons, excited state electron transfer reactions, and the delivery of multiple electrons to the water substrate including the bond breaking and making processes needed to produce hydrogen. The coupling of Ru polyazine light absorbers to Rh centers with low lying  $d\sigma^*$  orbitals results in many low energy excited states providing for complicated excited state dynamics. Figure 2 shows the two lowest lying triplet states that are thought to be engaged in the excited state electron transfer leading to reduction of the photocatalysts. To explore the role of each state in the PEC process a series of complexes have been studied that vary the energy of the  $^3\text{MLCT}$  and  $^3\text{MMCT}$  states as a function of device components as well as a system able to undergo PEC but without a reactive Rh metal center. These studies illustrated that while the  $^3\text{MMCT}$  seems to play a role in PEC, the  $^3\text{MLCT}$  state when alone is able to undergo excited state reduction still leading to PEC and production of  $\text{H}_2$  from water. The absence of a Rh metal center, using an Ir centered photoinitiated electron collector does not lead to  $\text{H}_2$  production, pointing out the role of Rh in the photocatalysis. The addition of  $\text{Hg}(\text{I})$  to our photocatalytic system does not impact  $\text{H}_2$  production, indicative of the lack of colloidal metal functioning as a catalytic surface in our system.

We have investigated the photophysics and photocatalytic properties of a series of Ru,Rh,Ru trimetallic complexes (the  $\{[(\text{TL})_2\text{Ru}(\text{dpp})]_2\text{RhX}_2\}(\text{PF}_6)_5$  structural motif) as well as related bimetallic systems which couple one Ru light absorber to a cis-Rh<sup>III</sup>Cl<sub>2</sub> moiety (the  $[(\text{TL})_2\text{Ru}(\text{dpp})$

$\text{RhCl}_2(\text{TL})](\text{PF}_6)_3$  structural motif). The systems with  $\text{X} = \text{Cl}$  or  $\text{Br}$  and  $\text{TL} = \text{bpy}$ ,  $\text{phen}$  and most recently  $\text{Ph}_2\text{phen}$  have been studied. We have found that these complexes emit from their  $\text{Ru} \rightarrow \text{dpp}$   $^3\text{MLCT}$  excited state and this emission is quenched at RT due to electron transfer to generate a lower lying  $^3\text{MMCT}$  excited state. The use of  $\text{Br}$  bound to the Rh center in place of  $\text{Cl}$  leads to systems with lower emission quantum yields and excited state lifetimes but larger quantum yields for  $\text{H}_2$  production. The use of  $\text{phen}$  as the TL in place of  $\text{bpy}$  provides systems with shorter lifetimes and lower emission quantum yields in stark contrast to the typical extension of lifetimes in related  $\{[(\text{phen})_2\text{Ru}]_2(\text{dpp})\}^{4+}$  and  $[(\text{phen})_2\text{Ru}(\text{dpp})]^{2+}$  systems relative to the  $\text{bpy}$  analogs. The newly prepared and soon to be reported  $\text{Ph}_2\text{phen}$  systems provide for photocatalysts with higher  $\text{H}_2$  production rates and yields. The newly prepared Ru,Rh bimetallic motif,  $[(\text{TL})_2\text{Ru}(\text{dpp})\text{RhCl}_2(\text{TL})](\text{PF}_6)_3$ , has recently been established to have similar excited state dynamics with a low lying  $^3\text{MMCT}$  excited state quenching the emission of the  $^3\text{MLCT}$  excited state. We have recently shown this bimetallic motif undergoes photoinitiated electron collection generating Rh(I) systems. We have also demonstrated that despite this the Ru,Rh bimetallics are not photocatalysts for water reduction to produce  $\text{H}_2$ , as the Rh(I) form dimerizes. This is a very significant result that provides insight into the mechanism of the photocatalysis with our trimetallic systems and provides strong evidence that the supramolecular architecture remains intact and is critical to active photocatalysis.

We have explored the modification of our photocatalytic system showing our system can tolerate changes in solvent,

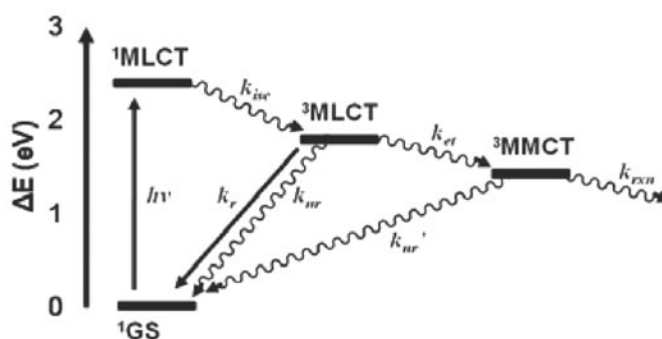


FIGURE 2. State diagram for  $\{[(\text{TL})_2\text{Ru}(\text{dpp})]_2\text{RhX}_2\}^{5+}$  systems

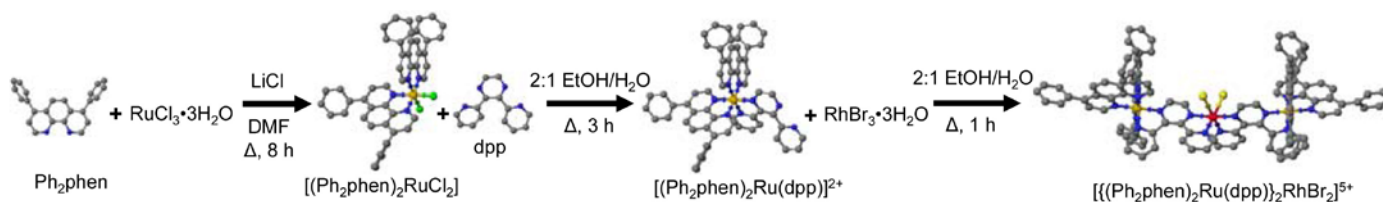
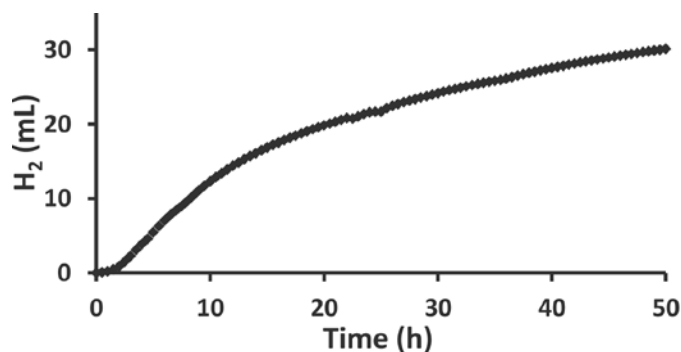


FIGURE 1. Building block method to prepare the TL-LA-BL-EC-BL-LA-TL assembly,  $\{[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})]_2\text{RhBr}_2\}(\text{PF}_6)_5$ , a photocatalyst for  $\text{H}_2\text{O}$  reduction to  $\text{H}_2$ .



**FIGURE 3.** Real time H<sub>2</sub> production by supramolecular photocatalyst-{(bpy)<sub>2</sub>Ru(dpp)}<sub>2</sub>RhBr<sup>5+</sup> in DMF.

electron donor, light flux, etc.. Our system represents the first report of a PEC system that functions in water and our system also produces H<sub>2</sub>. We have shown that DMF as a solvent impacts photocatalytic yield producing higher amounts of H<sub>2</sub>, Figure 3.

### Future Directions

The understanding of the mechanistic details of our photocatalytic system remains an overriding goal. We have made considerable progress on this goal. The use of varied sub-units in our Ru,Rh,Ru trimetallic motif has provided insight into the role of the various excited states and the driving force for excited state electron transfer on photocatalysis. We have investigated the role of the supramolecular architecture and shown through our studies with the new Ru,Rh bimetallics that simply producing a system in which Rh(I) is generated is not sufficient to produce active photocatalysts. The studies of the bimetallic systems have uncovered the possible role of Rh-Rh bond formation as a deactivating pathway in non-functioning Rh systems. We have moved to the direct synthesis of Rh(I) complexes. This work has progressed and preliminary results show with the proper design we can produce Ru(II),Rh(I) systems that can be active photocatalysts through the protection of the Rh site with a bulky ligand. Studies are ongoing to explore the mechanistic aspects of our important photocatalysis and photoreduction reactions.

### References

1. "Basic Research Needs for the Hydrogen Economy," DOE Report by the Basic Energy Sciences Workshop on H<sub>2</sub> Production, Storage and Use, May 2003.
2. "Basic Research Needs for Solar Energy Utilization," DOE Report of the Basic Energy Sciences Workshop on Solar Utilization, Department of Energy, April 2005.
3. "New Science for a Secure and Sustainable Energy Future A Report from the Basic Energy Sciences Advisory Committee," Chair: John Hemminger University of California, Irvine U.S. Department of Energy, December 2008.

### Publication list (selected) acknowledging the DOE grant or contract

1. "A New Structural Motif for Photoinitiated Electron Collection: Ru, Rh Bimetallic Providing Insight into H<sub>2</sub> Production via Photocatalysis of Water Reduction by Ru,Rh,Ru Supramolecular," J. Wang, T.A. White, S.M. Arachchige, K.J. Brewer, *Chem. Comm.* **2011**, in press.
2. "High Turnover in a Photocatalytic System for Water Reduction to Produce Hydrogen Using a Ru,Rh,Ru Photoinitiated Electron Collector," S.M. Arachchige, R. Shaw, T.A. White, V. Shenoy, H.-M. Tsui, and K.J. Brewer\*, *ChemSusChem* **2011**, in press.
3. "Photocatalytic Hydrogen Production from Water," S.M. Arachchige, K.J. Brewer, *Energy Production and Storage-Inorganic Chemical Strategies for a Warming World, Encyclopedia of Inorganic Chemistry*, Robert Crabtree Editor, John Wiley and Sons, **2010**, in press.
4. "Solar Energy Conversion Using Photochemical Molecular Devices: Photocatalytic Hydrogen Production From Water Using Mixed-Metal Supramolecular Complexes," K. Rangan, S.M. Arachchige, J.R. Brown and K.J. Brewer, *J. Energy and Environ. Sci.* **2009**, 2(4), 410-19.
5. "Synthesis, Characterization, and Study of the Photophysics and Photocatalytic Properties of the Photoinitiated Electron Collector [{"(phen)<sub>2</sub>Ru(dpp)}<sub>2</sub>RhBr<sub>2</sub>](PF<sub>6</sub>)<sub>5</sub>," T.A. White, K. Rangan, K.J. Brewer, *J. Photochem. Photobiol. A: Chem.* **2010**, 209, 203-209.
6. "Supramolecular Complexes as Photoinitiated Electron Collectors: Applications in Solar Hydrogen Production," S.M. Arachchige, K.J. Brewer, *On Solar Hydrogen and Nanotechnology*, Lionel Vayssieres Editor, John Wiley and Sons, **2010**, 589-617.
7. "Mixed-Metal Supramolecular Complexes Coupling Polyazine Light Absorbers and Reactive Metal Centers," S.M. Arachchige, K.J. Brewer, in *Macromolecules Containing Metal and Metal Like Elements: Supramolecular and Self-Assembled Metal-containing Materials*, Volume 9, John Wiley and Sons, Martel Zeldin, Editor, **2009**, 295-366.
8. "Design Considerations for a System for Photocatalytic Hydrogen Production from Water Employing Mixed-Metal Photochemical Molecular Devices for Photoinitiated Electron Collection," S.M. Arachchige, J.R. Brown, E. Chang, A. Jain, D.F. Zigler, K. Rangan, K.J. Brewer *Inorg. Chem.* **2009**, 48, 1989-2000.
9. "Ruthenium(II) Polyazine Light Absorbers Bridged to cis-Dichlororhodium(II) Sites in a Bimetallic Molecular Architecture," D.F. Zigler, J. Wang, K.J. Brewer *Inorg. Chem.* **2008**, 47, 11342-11350.
10. "Photochemical Hydrogen Production from Water Using the New Photocatalyst [{"(bpy)<sub>2</sub>Ru(dpp)}<sub>2</sub>RhBr<sub>2</sub>](PF<sub>6</sub>)<sub>5</sub>," S.M. Arachchige, J. Brown, K.J. Brewer *J. Photochem. Photobiol. A. Chem.* **2008**, 197, 13-17.
11. "Rhodium Centered Mixed-Metal Supramolecular Complex as a Photocatalyst for the Visible Light Induced Production of Hydrogen," M.C. Elvington, J. Brown, S.M. Arachchige, K.J. Brewer *J. Am. Chem. Soc.* **2007**, 129, 10644-10645.