

II.K.11 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 H₂ from H₂O 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 H₂ 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 H₂O reduction to H₂ 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 H₂O 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 H₂ Production, Storage and Use in 2003, catalyst design for H₂ production was identified as an important goal with emphasis on nanoscale systems.¹ 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 4.3×10^{20} J per hour reaching the earth's surface.² 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..."³ A major research need identified in the Workshop on H₂ 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 H₂ 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 H₂O to produce H₂. 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 H₂O to facilitate the production of H₂. The factors impacting multi-electron photochemistry and the reduction of water to produce H₂ 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 dσ* 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 ³MLCT and ³MMCT 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 ³MMCT seems to play a role in PEC, the ³MLCT state when alone is able to undergo excited state reduction still leading to PEC and production of H₂ from water. The absence of a Rh metal center, using an Ir centered photoinitiated electron collector does not lead to H₂ production, pointing out the role of Rh in the photocatalysis. The addition of Hg(I) to our photocatalytic system does not impact H₂ 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 $[(TL)_2Ru(dpp)]_2RhX_2(PF_6)_5$ structural motif) as well as related bimetallic systems which couple one Ru light absorber to a cis-Rh^{III}Cl₂ moiety (the $[(TL)_2Ru(dpp)]$

$RhCl_2(TL)](PF_6)_3$ structural motif). The systems with X = Cl or Br and TL = bpy, phen and most recently Ph₂phen have been studied. We have found that these complexes emit from their Ru→dpp ³MLCT excited state and this emission is quenched at RT due to electron transfer to generate a lower lying ³MMCT excited state. The use of Br bound to the Rh center in place of Cl leads to systems with lower emission quantum yields and excited state lifetimes but larger quantum yields for H₂ production. The use of phen as the TL in place of bpy provides systems with shorter lifetimes and lower emission quantum yields in stark contrast to the typical extension of lifetimes in related $[(phen)_2Ru]_2(dpp)^{4+}$ and $[(phen)_2Ru(dpp)]^{2+}$ systems relative to the bpy analogs. The newly prepared and soon to be reported Ph₂phen systems provide for photocatalysts with higher H₂ production rates and yields. The newly prepared Ru,Rh bimetallic motif, $[(TL)_2Ru(dpp)RhCl_2(TL)](PF_6)_3$, has recently been established to have similar excited state dynamics with a low lying ³MMCT excited state quenching the emission of the ³MLCT 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 H₂, 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,

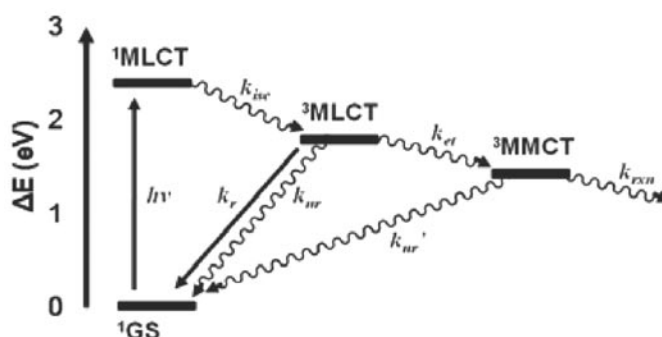


FIGURE 2. State diagram for $[(TL)_2Ru(dpp)]_2RhX_2^{5+}$ systems

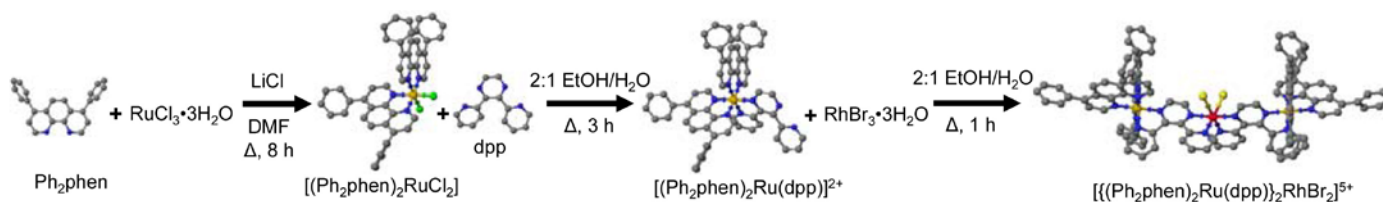


FIGURE 1. Building block method to prepare the TL-LA-BL-EC-BL-LA-TL assembly, $[(Ph_2phen)_2Ru(dpp)]_2RhBr_2(PF_6)_5$, a photocatalyst for H₂O reduction to H₂.

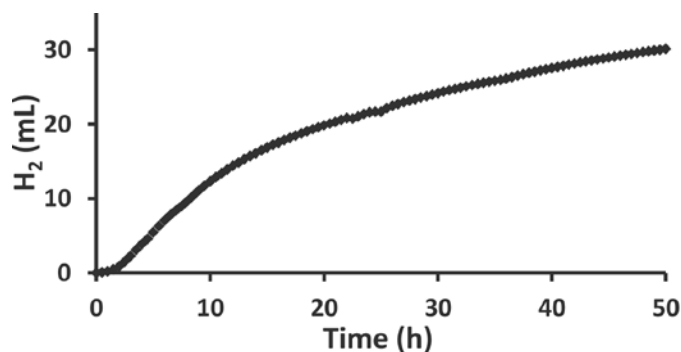


FIGURE 3. Real time H₂ production by supramolecular photocatalyst-{(bpy)₂Ru(dpp)}₂RhBr⁵⁺ in DMF.

electron donor, light flux, etc.. Our system represents the first report of a PEC system that functions in water and our system also produces H₂. We have shown that DMF as a solvent impacts photocatalytic yield producing higher amounts of H₂, 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.

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