

II.K.25 Photoinitiated Electron Collection in Mixed-Metal Supramolecular Complexes: Development of Photocatalysts for Hydrogen Production

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Objectives

The objectives of this research project include goals focused to explore photoinitiated electron collectors as molecular photocatalysts for the reduction of water to hydrogen. Specific research goals are to:

- prepare Ru,Rh,Ru and Os,Rh,Os triads that possess Rh ($d\sigma^*$) based lowest unoccupied molecular orbitals (LUMOs)
- study the redox, spectroscopic and photochemical properties of these complexes focusing on excited state reactions and multi-electron reductions
- explore the photocatalytic properties of these complexes
- utilize the supramolecular nature of these complexes to design larger systems with enhanced functioning.

Technical Barriers

The technical barriers to the development of efficient systems for the production of hydrogen from water are significant including barriers presented by the fundamental understanding of multi-electron chemistry. Specific barriers to efficient solar hydrogen production include the:

- lack of a clear understanding of the factors impacting multielectron photochemical reactions
- lack of understanding of the perturbations imposed on device sub-units upon their incorporation into supramolecular assemblies with reactive metal centers
- lack of molecular systems that can undergo photoinitiated electron collection.

Abstract

Supramolecular complexes used in this forum are large molecular assemblies built of smaller sub-units. Each sub-unit contributes properties to the supramolecular assembly, allowing the assembly to display complex functions. The coupling of multiple charge transfer light absorbing (LA) units in combination with an electron collector (EC) provides light activated collection of reducing equivalents, photoinitiated electron collection (PEC). Supramolecular assemblies coupling two ruthenium light absorbers through bridging ligands (BL) to a central Rh core have been constructed and shown to undergo PEC at the Rh center. These Rh centered supramolecular complexes are capable of producing H_2 from H_2O when excited in the presence of an electron donor. Recently we have shown that all three Ru,Rh,Ru complexes shown in Figure 1 undergo photoinitiated electron collection at the Rh center and photochemically reduce water to hydrogen in the presence of DMA, TEOA or TEA as electron donors. The generality of our approach has been established through the study of these and related systems. The factors impacting hydrogen production efficiency are being uncovered.

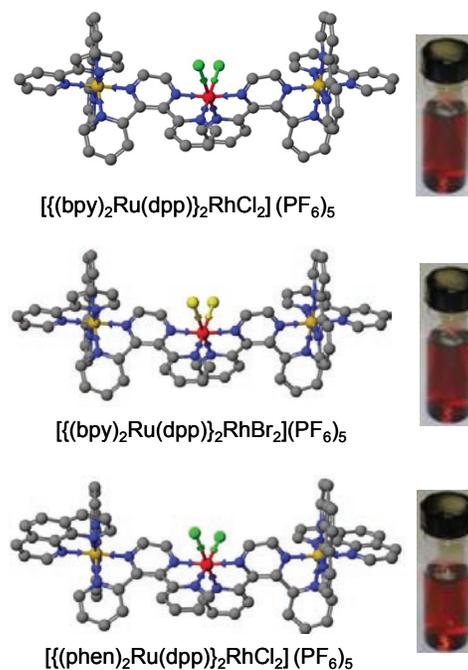


FIGURE 1. Mixed-Metal Supramolecular Photocatalysts for H_2 Production from H_2O .

Recently we have prepared Ru,Rh dyads that still maintain the reactive $\text{Rh}^{\text{III}}\text{Cl}_2$ site. These complexes displayed somewhat unexpected properties. The dyad and triad bridged by dpp are shown in Figure 2. The complexes maintain very similar coordination environments for each metal with both complexes having a reactive $\text{Rh}^{\text{III}}\text{Cl}_2$ site. Electrochemically the triad shows a $\text{Rh}^{\text{III/II}}$ couple prior to the $\text{dpp}^{0/-}$ couples. Orbital inversion is seen in the dyad with the $\text{dpp}^{0/-}$ couple preceding Rh reduction suggesting nearly isoenergetic Rh and dpp orbitals in this structural motif. This is further exemplified by the quenching of the $\text{Ru} \rightarrow \text{dpp}$ CT emission in both systems to a similar degree indicating a low lying $^3\text{MMCT}$ state in both complexes. The photophysical and photochemical properties of these Ru,Rh dyads and triads are being explored in detail.

A new type of molecular architecture that couples multiple LA units through bridging ligands and a central metal has been established to undergo photoinitiated electron collection. These systems collect electrons on bridging ligand acceptor orbitals and include coupled reactive Pt sites. One example of this type of Pt based system is $[\{(\text{bpy})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})\text{PtCl}_2]^{6+}$. We have recently shown that following MLCT excitation, $[\{(\text{bpy})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})\text{PtCl}_2]^{6+}$ undergoes reduction in the presence of an electron donor leading the multielectron reduced form, $[\{(\text{bpy})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})\text{PtCl}_2]^{5+}$. In the presence of H_2O the production of H_2 is seen. Interestingly, Hg addition leads to only minor reduction of H_2 production even though the analogous $[\{(\text{bpy})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})]^{6+}$ and Pt(s) catalytic system is completely shut down by Hg addition. These extended assemblies serve as new forums to study photoinitiated electron collection in systems that can have significant molecular complexity.

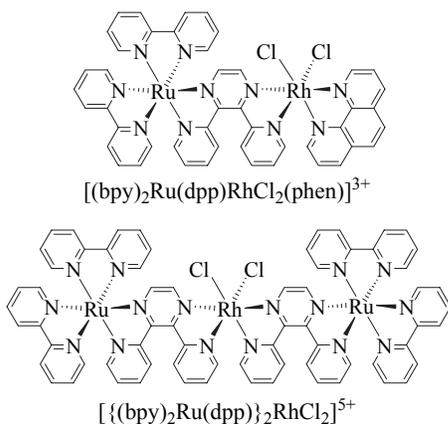


FIGURE 2. Mixed-Metal Supramolecular Ru,Rh dyad and Ru,Rh,Ru triad bridged by dpp.

Publications acknowledging the grant

- “Rhodium Centered Mixed-Metal Supramolecular Complex as a Photocatalyst for the Visible Light Induced Production of Hydrogen,” Mark C. Elvington, Jared Brown, Shamindri Arachchige, Karen J. Brewer *J. Am. Chem. Soc.* **2007**, *129*, 10644-10645.
- “Supramolecular Complexes as Photoinitiated Electron Collectors: Applications in Solar Hydrogen Production,” Mark Elvington, Jared R. Brown, David F. Zigler, Karen J. Brewer, *Proceedings of the SPIE, Optics and Photonics, Solar Hydrogen and Nanotechnology* **2006**, *Proc. of SPIE Vol. 6340*, 63400W1-13. Invited Paper.
- “Photochemical Hydrogen Production from Water Using the New Photocatalyst $[\{(\text{bpy})_2\text{Ru}(\text{dpp})\}_2\text{RhBr}_2](\text{PF}_6)_5$,” Shamindri Arachchige, Jared Brown, Karen J. Brewer *J. Photochem. Photobiol. A. Chem.* **2007**, in press.
- “A Donor-Chromophore Complex Containing the Polyazine Bridging Ligand 2,3-bis(2-pyridyl)pyrazine,” Shamindri M. Arachchige, Karen J. Brewer, *Inorg. Chem. Comm.* **2007**, *10*, 1159-1163.
- “Electrochemistry,” Mark Elvington, Karen J. Brewer, *Encyclopedia of Inorganic Chemistry*, Robert Scott Editor, Wiley and Sons, **2007**, in press.
- “A Structurally Diverse Mixed-Metal Complex with Mixed-Bridging Ligands $[\{(\text{bpy})_2\text{Os}(\text{dpp})\}_2\text{Ru}_2(\text{dpq})](\text{PF}_6)_{12}$,” Ran Miao, Karen J. Brewer, *Inorg. Chem. Commun.* **2007**, *10*, 307-312.
- “Photochemical Molecular Devices Incorporating Reactive Metals as Supramolecular Solar H_2 Photocatalysts,” David F. Zigler, Shamindri Arachchige, Jared Brown, Krishnan Rangan, Eric Chang, Karen J. Brewer, *Prepr. Pap.-Am. Chem. Soc., Div. Pet. Chem.* **2006**, *51 (1&2)*, in press. Invited Paper.
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- “Synthesis and Study of the Spectroscopic and Redox Properties of $\text{Ru}^{\text{II}},\text{Pt}^{\text{II}}$ Mixed-Metal Complexes Bridged by 2,3,5,6-Tetrakis(2-pyridyl)pyrazine,” Shengliang Zhao, Carla Slebodnick, Karen J. Brewer *Inorg. Chem.* **2007**, submitted for publication.

- “A Mixed-Metal Ru(II),Pt(II) Complex as a Photoinitiated Electron Collector Applicable in Solar H₂ Production,” Ran Miao, David F. Zigler, Karen J. Brewer *Inorg. Chem.* **2007**, submitted for publication.
- “Ruthenium(II) Polyazine Light Absorbers Bridged to cis-Dichlororhodium(II) Sites in a Bimetallic Molecular Architecture,” David F. Zigler, Karen J. Brewer *Inorg. Chem.* **2008**, manuscript in preparation.

New mixed-metal complexes with varying terminal ligands, bridging ligands and reactive metals have been constructed and studied. The assembly of a hexametallal complex with Ru and Os light absorbers and dpp and dpq BLs has been studied and provides spectroscopic signatures of each sub-unit. The combination of Ru LAs and Pt reactive metals produces complexes with interesting ground and excited state properties. The complex $[(\text{bpy})_2\text{Ru}(\text{dpp})]_2\text{Ru}(\text{dpq})\text{PtCl}_2]^{6+}$ has been prepared and possesses a lowest energy charge separated state by virtue of the terminal Ru based HOMO and dpq based LUMO. This complex undergoes photoinitiated electron collection, collecting electrons on the dpq and two dpp BLs. In the presence of water this complex photocatalyzes H₂ production. The mechanism appears to have two pathways, one via metallic Pt formation and one without Pt decomplexation which is the major contributor to H₂ formation as assayed via spectroscopy and Hg addition. Our study of the tridentate bridged complexes $[(\text{tpy})\text{Ru}(\text{tppz})\text{PtCl}]^{3+}$ and $[\text{ClPt}(\text{tppz})\text{Ru}(\text{tppz})\text{PtCl}]^{4+}$ reveals that the trimetallic complex is emissive in fluid solution while the bimetallic complex is not (tppz = 2,3,5,6-tetrakis(pyridyl)pyrazine).

Progress Report and Future Directions

The conversion of solar energy into fuels facilitates storage and transportation of this energy source. 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. A major research need identified was the development of systems that convert sunlight into chemical fuels for storage and distribution. The development of solar powered catalysts for energy rich fuel formation was identified as a major research goal. Included were six sub-tasks, three of which are addressed in our work. These tasks include (1) identify new methods for unraveling the mechanisms of complex, coupled reactions for the solar production of fuels; (2) develop

a fundamental understanding of excited-state bond making and breaking processes yielding oxygen and hydrogen; (3) understand the rates and mechanisms of multielectron/atom transfer reactions using new theoretical and experimental approaches. The proposed work addresses these fundamental issues within a molecular architecture that undergoes multi-electron photochemistry and is capable of producing H₂ from water.

The project has facilitated the establishment of supramolecular complexes with reactive metal centers as a unique and exciting structural motif for photoinitiated electron collection and shown the general applicability of this forum to produce new photocatalysts for the multi-electron reduction of water to produce H₂. The first functioning molecular photoinitiated electron collector that catalyzes the reduction of water to H₂ was reported, $[(\text{bpy})_2\text{Ru}(\text{dpp})]_2\text{RhCl}_2(\text{PF}_6)_5$. This system is able to photochemically reduce by multiple electrons. The reduction of $[(\text{bpy})_2\text{Ru}(\text{dpp})]_2\text{RhCl}_2(\text{PF}_6)_5$ leads to structural rearrangement with chloride loss to produce the coordinately unsaturated Rh^I species, $[(\text{bpy})_2\text{Ru}(\text{dpp})]_2\text{Rh}^{\text{I}}]^{5+}$, Figure 3.

The generality of this molecular architecture to produce systems that photochemically collect electrons and produce H₂ was established and the impact of sub-unit on basic chemical properties and photochemistry have been evaluated. The complexes $[(\text{bpy})_2\text{Ru}(\text{dpp})]_2\text{RhCl}_2(\text{PF}_6)_5$, $[(\text{bpy})_2\text{Ru}(\text{dpp})]_2\text{RhBr}_2(\text{PF}_6)_5$, $[(\text{phen})_2\text{Ru}(\text{dpp})]_2\text{RhCl}_2(\text{PF}_6)_5$, $[(\text{bpy})_2\text{Os}(\text{dpp})]_2\text{RhCl}_2(\text{PF}_6)_5$, $[(\text{tpy})\text{RuCl}(\text{dpp})]_2\text{RhCl}_2(\text{PF}_6)_3$, $[(\text{tpy})\text{OsCl}(\text{dpp})]_2\text{RhCl}_2(\text{PF}_6)_3$, and $[(\text{bpy})_2\text{Ru}(\text{dpp})]_2\text{IrCl}_2(\text{PF}_6)_5$ were constructed and evaluated with respect to their functioning as hydrogen photocatalysts (tpy = 2,2':6,2''-terpyridine, phen = 1,10-phenanthroline). With the exceptions of $[(\text{bpy})_2\text{Ru}(\text{dpp})]_2\text{IrCl}_2(\text{PF}_6)_5$ and $[(\text{tpy})\text{OsCl}(\text{dpp})]_2\text{RhCl}_2(\text{PF}_6)_3$, all other complexes demonstrate photocatalytic activity, producing H₂. The functioning systems possess a rhodium localized lowest unoccupied molecular orbital that serves as the site of electron collection and a metal-to-ligand charge-transfer (³MLCT) and/or metal-to-metal charge-transfer (³MMCT) states with sufficient driving forces for excited state reductions by the electron

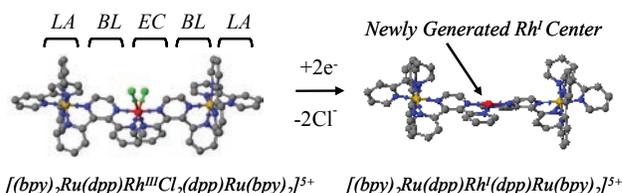


FIGURE 3. Stereochemical rearrangement following electron collection at a Rh^{III} center.

donor. The lack of photocatalytic activity by the first molecular system for photoinitiated electron collection, $[(\text{bpy})_2\text{Ru}(\text{dpp})]_2\text{IrCl}_2(\text{PF}_6)_5$ although multielectron reduction occurs, establishes the significance of the rhodium center in the photocatalytic system. The lack of photocatalytic activity of $[(\text{tpy})\text{OsCl}(\text{dpp})]_2\text{RhCl}_2(\text{PF}_6)_3$ is attributed to the lower energy $^3\text{MLCT}$ state which does not possess sufficient driving force for excited state reduction by the electron donor. The variation of electron donor showed the photocatalysis efficiency to decrease in the order $\text{N,N-dimethylaniline} > \text{triethylamine} > \text{triethanolamine}$. Photocatalysis was controlled by excited state reduction of the catalysts with efficiency not always directly correlating with this factor. These catalysis studies establish the generality of the Rh centered molecular architecture to provide for photoinitiated electron collection and catalysis of water reduction to produce H_2 .

The study of the basic light absorbing, redox and photophysical properties of supramolecular complexes with reactive metals have provided considerable insight into the properties of this important class of supramolecules. The variation of light absorbing metal, terminal ligands and bridging ligand provides a means to specifically tune certain properties of the complexes, Figure 4. The systems with Ru light absorbers and dpp BLs provide for complexes that have emissive $\text{Ru} \rightarrow \text{dpp}$ CT states. These states have been exploited to determine the efficiency with which the $^3\text{MMCT}$ state is populated (ca. 95%) as well as the quenching by added electron donors.

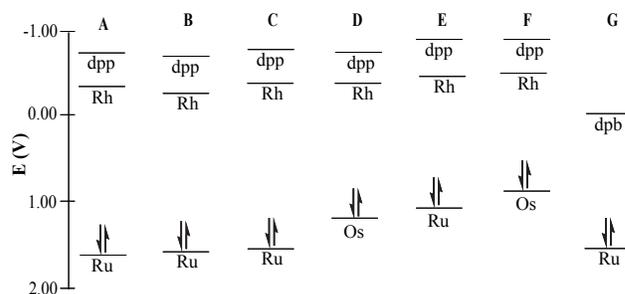


FIGURE 4. Frontier orbital energetics for mixed-metal trimetallic complexes simplified by showing single orbitals from orbital sets with E in V vs Ag/AgCl obtained from cyclic voltammetry
 A = $[(\text{bpy})_2\text{Ru}(\text{dpp})]_2\text{RhCl}_2(\text{PF}_6)_5$, B = $[(\text{bpy})_2\text{Ru}(\text{dpp})]_2\text{RhBr}_2(\text{PF}_6)_5$,
 C = $[(\text{phen})_2\text{Ru}(\text{dpp})]_2\text{RhCl}_2(\text{PF}_6)_5$, D = $[(\text{bpy})_2\text{Os}(\text{dpp})]_2\text{RhCl}_2(\text{PF}_6)_5$,
 E = $[(\text{tpy})\text{Ru}(\text{dpp})]_2\text{RhCl}_2(\text{PF}_6)_5$, F = $[(\text{tpy})\text{OsCl}(\text{dpp})]_2\text{RhCl}_2(\text{PF}_6)_3$, and
 G = $[(\text{bpy})_2\text{Ru}(\text{dpb})]_2\text{IrCl}_2(\text{PF}_6)_5$.

References

1. "Basic Research Needs for the Hydrogen Economy," DOE Report by the Basic Energy Sciences Workshop on H_2 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.