

# Discovering the Balance of Steric and Electronic Factors Needed To Provide a New Structural Motif for Photocatalytic Hydrogen Production from Water

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**S** Supporting Information

**ABSTRACT:** Ru,Rh,Ru supramolecules are known to undergo multielectron photoreduction and reduce H<sub>2</sub>O to H<sub>2</sub>. Ru, Rh bimetallics were recently shown to photoreduce but not catalyze H<sub>2</sub>O reduction. Careful tuning of sterics and electronics for [(TL)<sub>2</sub>Ru(dpp)RhCl<sub>2</sub>(TL')]<sup>3+</sup> produce active bimetallic photocatalysts (TL = terminal ligand). The system with TL,TL' = Ph<sub>2</sub>phen photocatalytically reduces H<sub>2</sub>O to H<sub>2</sub> while TL,TL' = phen,bpy or bpy,<sup>t</sup>Bu<sub>2</sub>bpy do not.

Solar energy conversion schemes to produce fuels are of great interest in the quest for renewable energy resources. Solar energy conversion via water splitting to produce H<sub>2</sub> fuel is an attractive alternative energy source that is carbon neutral. Sunlight provides sufficient energy to drive this thermodynamically uphill, multi-electron reaction.<sup>1–4</sup> Complex systems that efficiently absorb solar light and undergo multielectron catalysis must be designed to facilitate this complicated multielectron reaction.

Multiple component systems with light absorbers, electron relays, and catalysts photocatalytically reduce H<sub>2</sub>O to H<sub>2</sub>.<sup>5–7</sup> An early example incorporating a [Ru(bpy)<sub>3</sub>]<sup>2+</sup> light absorber, a [Rh(bpy)<sub>3</sub>]<sup>3+</sup> electron relay, Pt colloid catalyst, and triethanolamine electron donor produces H<sub>2</sub> using λ = 450 ± 20 nm (bpy = 2,2'-bipyridine).<sup>5–7</sup>

Covalent coupling of multiple molecular components whose individual acts contribute to the overall functioning generates supramolecules.<sup>8,9</sup> Supramolecules that use light to collect reducing equivalents are photoinitiated electron collectors<sup>10–15</sup> with [(bpy)<sub>2</sub>Ru(dpb)}<sub>2</sub>IrCl<sub>2</sub>]<sup>5+</sup> being the first, collecting electrons on the dpb bridging ligand (BL) π\* orbitals (dpb = 2,3-bis-(2-pyridyl)benzoquinoline).<sup>12,13</sup> The complex [(phen)<sub>2</sub>Ru(BL)-Ru(phen)<sub>2</sub>]<sup>4+</sup> (BL = 9,11,20,22-tetraazatetrapyrido[3,2-a:2'3'-c:3'',2''-1:2''',3'''-n]pentacene (tatpp) or 9,11,20,22-tetraazatetra-pyrido-[3,2-a:2'3'-c:3'',2''-1:2''',3'''-n]pentacene10,21]quinone (tatpq); phen = 1,10-phenanthroline) collect multiple electrons on bridging ligand π\* orbitals.<sup>10,11</sup> The complex [(bpy)<sub>2</sub>Ru(pbn)]<sup>2+</sup> undergoes proton-coupled, two electron reduction (pbn = 2-(2-pyridyl)benzo[b]-1,5-naphthyridine).<sup>14,15</sup> These important early systems store electrons but do not photocatalytically reduce H<sub>2</sub>O.

Recently, single-component supramolecular photocatalysts for H<sub>2</sub> production have appeared including systems that couple Ru or Os light absorbers to Pt, Pd, Co, Rh, or diiron dithiolate catalysts functioning with added electron donors as well as dirhodium complexes, Table 1.<sup>16–27</sup>

**Table 1. Illustrative Single-Component H<sub>2</sub> Photocatalysts**

complex	TON <sup>a</sup>	time (h) <sup>b</sup>	ref
[(bpy) <sub>2</sub> Ru(phenNHCO-(COOHbpy))PtCl <sub>2</sub> ] <sup>2+</sup>	5	10	26
[ <sup>t</sup> Bu <sub>2</sub> bpy) <sub>2</sub> Ru(tpphz)PdCl <sub>2</sub> ] <sup>2+</sup>	56	30	27
[(bpy) <sub>2</sub> Ru(L-pyr)Co(dmgbF <sub>2</sub> ) <sub>2</sub> (OH <sub>2</sub> )] <sup>2+</sup>	103	15	19
[(ppy) <sub>2</sub> Ir(L-pyr)Co(dmgbF <sub>2</sub> ) <sub>2</sub> (OH <sub>2</sub> )] <sup>+</sup>	210	15	18
[Rh <sub>2</sub> <sup>0,0</sup> (dfpma) <sub>3</sub> (PPh <sub>3</sub> )(CO)]	27/h	3	20
[PtCl(tpy)]Cl	3	7	25

<sup>a</sup>TON = turnover number; mol H<sub>2</sub>/mol catalyst. <sup>b</sup>Photolysis time.

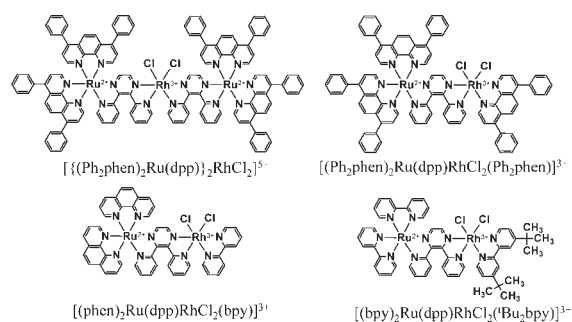
Ru,Rh,Ru trimetallics, [(TL)<sub>2</sub>Ru(dpp)}<sub>2</sub>RhX<sub>2</sub>]<sup>5+</sup> (TL = bpy, phen, Ph<sub>2</sub>phen; X = Cl, Br), undergo photoinitiated electron collection to generate Rh(I) centered trimetallics and photocatalytically reduce H<sub>2</sub>O to H<sub>2</sub>.<sup>28–33</sup> Recently, we reported the related Ru,Rh bimetallic [(phen)<sub>2</sub>Ru(dpp)RhCl<sub>2</sub>(bpy)]<sup>3+</sup> undergoes photoinitiated electron collection to generate a Rh(I) complex, but this motif does not reduce H<sub>2</sub>O to H<sub>2</sub>. Dimerization of the sterically accessible Rh(I) site deactivates this bimetallic motif for photocatalysis highlighting the role of the supramolecule in active photocatalysts.<sup>34</sup> These supramolecules possess energetically close bridging ligand(π\*) and Rh(dσ\*) orbitals. We postulate that discovery of requirements for careful simultaneous tuning of electronics and sterics necessary to maintain a Rh(dσ\*) LUMO and steric protection for the photoproduced Rh(I) center will provide active bimetallic photocatalysts.

Herein, we report the new Ru,Rh bimetallic complexes [(Ph<sub>2</sub>phen)<sub>2</sub>Ru(dpp)RhCl<sub>2</sub>(Ph<sub>2</sub>phen)](PF<sub>6</sub>)<sub>3</sub> and [(bpy)<sub>2</sub>-Ru(dpp)RhCl<sub>2</sub>(<sup>t</sup>Bu<sub>2</sub>bpy)](PF<sub>6</sub>)<sub>3</sub> (Figure 1) with comparison to the photocatalytically inactive TL' = bpy system. This series of Ru, Rh bimetallic complexes illustrates careful modulation of sterics and electronics at Rh is possible to generate requirements that highlight how to develop a new structural motif for photoinitiated electron collection that is photocatalytically active. This provides a new supramolecular architecture for single-component photocatalytic reduction of H<sub>2</sub>O to H<sub>2</sub> and establishes that a single Ru light absorber can photoreduce Rh(III) to Rh(I) and bimetallics can be designed as active photocatalysts for H<sub>2</sub>O reduction.

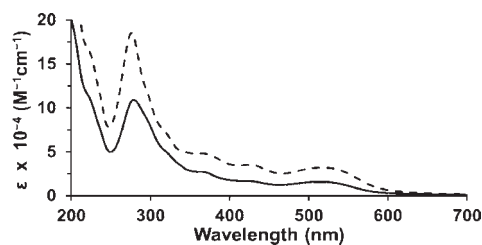
The new Ru,Rh bimetallic complexes were synthesized using a building block approach which covalently couples a Ru(II) polypyridine light absorber to [RhCl<sub>3</sub>(CH<sub>3</sub>OH)(TL')] (TL' = Ph<sub>2</sub>phen

**Received:** July 27, 2011

**Published:** August 29, 2011



**Figure 1.** Structures of Ru,Rh bimetallic and Ru,Rh,Ru trimetallic supra-molecular complexes.

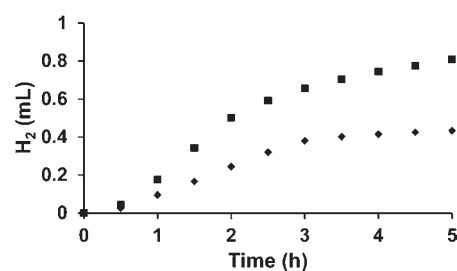


**Figure 2.** Electronic absorption spectra of  $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{RhCl}_2(\text{Ph}_2\text{phen})]^{3+}$  (solid line) and  $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})]_2\text{RhCl}_2]^{5+}$  (dashed line) in  $\text{CH}_3\text{CN}$  at room temperature.

or  ${}^t\text{Bu}_2\text{bpy}$ ) (Scheme S1, Supporting Information).<sup>35,36</sup> The cyclic voltammogram (Figure S1) displays reversible, one-electron  $\text{Ru}^{\text{II/III}}$  oxidations, +1.58 V ( $\text{Ph}_2\text{phen}$ ) and +1.62 V ( ${}^t\text{Bu}_2\text{bpy}$ ) versus  $\text{Ag}/\text{AgCl}$ . A reversible  $\text{dpp}^{\text{0/-}}$  ( $E_{1/2} = -0.39$  V) reduction is observed for  $\text{TL}' = {}^t\text{Bu}_2\text{bpy}$ , while irreversible  $\text{Rh}^{\text{III/II}}$  and  $\text{Rh}^{\text{II/I}}$  ( $E_p^a = -0.42$  and  $-0.79$  V) couples occur for  $\text{TL}' = \text{Ph}_2\text{phen}$ . This demonstrates the close energetic proximity of the  $\text{Rh}(d\sigma^*)$  and  $\text{dpp}(\pi^*)$  orbitals in this motif. The LUMO is Rh-based with  $\text{TL}' = \text{Ph}_2\text{phen}$  or  $\text{bpy}$  while  $\text{dpp}$ -based for the electron donating  ${}^t\text{Bu}_2\text{bpy}$ . While both  $\text{Ph}_2\text{phen}$  and  ${}^t\text{Bu}_2\text{bpy}$  provide steric protection at the Rh site, the previously reported  $\text{bpy}$  and new  $\text{Ph}_2\text{phen}$  provide the Rh LUMO needed for photo-initiated electron collection at Rh, suggesting that only the new  $\text{Ph}_2\text{phen}$  system should provide the necessary sterics and electronics with appropriate orbital energetics to provide active photocatalysis.

The Ru,Rh bimetallic complexes absorb light efficiently throughout the UV and visible (Figure 2, Figure S2). The UV is dominated by intense  $\text{TL}$ ,  $\text{TL}'$ , and  $\text{dpp}$  based intraligand  $\pi \rightarrow \pi^*$  transitions with  $\text{Ru}(d\pi) \rightarrow \text{TL}(\pi^*)$  and  $\text{dpp}(\pi^*)$  CT ( ${}^1\text{MLCT}$ ) transitions in the visible. The lowest energy transition (514 nm) is  $\text{Ru}(d\pi) \rightarrow \text{dpp}(\pi^*)$  CT ( $\epsilon = 15\,800\ \text{M}^{-1}\text{cm}^{-1}$ ), with half the absorptivity of the Ru,Rh,Ru trimetallic complex.

Photoinitiated electron collection of  $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{RhCl}_2(\text{Ph}_2\text{phen})]^{3+}$  was probed via spectrophotochemical and spectroelectrochemical analyses (Figure S3). When photolyzed,  $\lambda > 460$  nm, with DMA, the  $\text{Ru}(d\pi) \rightarrow \text{dpp}(\pi^*)$   ${}^1\text{MLCT}$  transition blue-shifts, mirroring the spectroscopic changes for electrochemical reduction of  $\text{Rh}^{\text{III}}$  to  $\text{Rh}^{\text{I}}$ .  $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{RhCl}_2(\text{Ph}_2\text{phen})]^{3+}$  undergoes photoinitiated electron collection at the Rh metal center providing the activation needed for multielectron reduction of  $\text{H}_2\text{O}$  to  $\text{H}_2$ , as observed for  $[(\text{phen})_2\text{Ru}(\text{dpp})\text{RhCl}_2(\text{bpy})]^{3+}$ .<sup>34</sup> Unlike the previously reported photoreduced  $[(\text{phen})_2\text{Ru}(\text{dpp})\text{Rh}^{\text{I}}(\text{bpy})]^{3+}$ ,



**Figure 3.**  $\text{H}_2$  production profile upon 470 nm excitation in  $\text{CH}_3\text{CN}$ , 65  $\mu\text{M}$  photocatalyst, 1.5 M DMA, and 0.62 M  $\text{H}_2\text{O}$ .  $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{RhCl}_2(\text{Ph}_2\text{phen})]^{3+}$  ( $\blacklozenge$ ),  $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})]_2\text{RhCl}_2]^{5+}$  ( $\blacksquare$ ).

$[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Rh}^{\text{I}}(\text{Ph}_2\text{phen})]^{3+}$  is sterically impeded from dimerization at the  $\text{Rh}^{\text{I}}$  site (Figure S4).

Photocatalytic studies with  $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{RhCl}_2(\text{Ph}_2\text{phen})]^{3+}$  demonstrate our success in careful control of sterics and electronics showing photocatalytic reduction of  $\text{H}_2\text{O}$  to  $\text{H}_2$  establishing a new motif for photocatalytic  $\text{H}_2$  generation. Initial photocatalysis assays in  $\text{CH}_3\text{CN}$  containing 65  $\mu\text{M}$  catalyst, 1.5 M DMA, 0.62 M  $\text{H}_2\text{O}$ , and 0.11 mM  $[\text{CF}_3\text{SO}_3^-][\text{DMAH}^+]$  (light flux =  $2.36 \pm 0.05 \times 10^{19}$  photons/min; effective pH ca. 9.1) showed, after 20 h,  $0.48 \pm 0.08$  mL of  $\text{H}_2$  ( $70 \pm 10$  TON; max overall  $\Phi_{\text{H}_2} = 0.005$ ) establishing this as the first Ru,Rh bimetallic photocatalyst providing roughly 50% activity of the analogous trimetallic  $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})]_2\text{RhCl}_2]^{5+}$  ( $1.1 \pm 0.1$  mL of  $\text{H}_2$ ,  $150 \pm 10$  TON; max overall  $\Phi_{\text{H}_2} = 0.009$ ), Figure 3, consistent with the ca. 50% absorptivity of the bimetallic system.<sup>28</sup> To provide equal absorptivity, a system with a 2-fold increase in  $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{RhCl}_2(\text{Ph}_2\text{phen})]^{3+}$  concentration (130  $\mu\text{M}$ ) showed  $0.69 \pm 0.05$  mL of  $\text{H}_2$ ,  $49 \pm 4$  TON, and max overall  $\Phi_{\text{H}_2} = 0.007$  after 20 h. The  $[(\text{bpy})_2\text{Ru}(\text{dpp})\text{RhCl}_2({}^t\text{Bu}_2\text{bpy})]^{3+}$  system and previously reported  $[(\text{phen})_2\text{Ru}(\text{dpp})\text{RhCl}_2(\text{bpy})]^{3+}$  do not produce  $\text{H}_2$ , establishing the importance of careful steric and electronic tuning in this motif. These studies demonstrate that  $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{RhCl}_2(\text{Ph}_2\text{phen})]^{3+}$  represents a new homogeneous, single-component structural motif for photoinitiated electron collection and photoreduction of  $\text{H}_2\text{O}$  to  $\text{H}_2$ , one of only a few motifs known to display this function.

As the catalytic center is expected to cycle between  $\text{Rh}^{\text{III/II/I}}$ , replacing  $\text{CH}_3\text{CN}$  with the weaker ligating DMF should enhance photocatalytic functioning as observed for Ru,Rh,Ru trimetallic complexes.<sup>28,37</sup> Photolysis of 130  $\mu\text{M}$   $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{RhCl}_2(\text{Ph}_2\text{phen})]^{3+}$ , 1.5 M DMA, 0.62 M  $\text{H}_2\text{O}$ , and 0.11 mM  $[\text{CF}_3\text{SO}_3^-][\text{DMAH}^+]$  in DMF produced  $1.1 \pm 0.1$  mL of  $\text{H}_2$  ( $81 \pm 5$  TON; max overall  $\Phi_{\text{H}_2} = 0.007$ ) after 20 h. Further modification increasing  $[\text{DMA}]$  to 3.1 M provides increased  $\text{H}_2$  production with  $1.3 \pm 0.1$  mL of  $\text{H}_2$  ( $93 \pm 5$  TON; max overall  $\Phi_{\text{H}_2} = 0.01$ ) after 20 h.

Careful choice of molecular components within the Ru,Rh supra-molecular architecture is critical to functioning as molecular devices for photoinitiated electron collection and photocatalysis. Steric protection of the photogenerated  $\text{Rh}(\text{I})$  center is needed while maintaining a  $\text{Rh}(d\sigma^*)$  LUMO. The previously reported  $[(\text{phen})_2\text{Ru}(\text{dpp})\text{RhCl}_2(\text{bpy})]^{3+}$  possesses a  $\text{Rh}(d\sigma^*)$  LUMO and undergoes photoinitiated electron collection at the Rh metal center but does not function as a photocatalyst, dimerizing upon  $\text{Rh}(\text{I})$  formation. Increasing steric bulk with the  ${}^t\text{Bu}_2\text{bpy}$  TL provides steric protection of the Rh center but increased electron density at Rh, destabilizing the  $\text{Rh}(d\sigma^*)$  orbital, preventing

photoinitiated electron collection or photocatalytic functioning with a dpp( $\pi^*$ ) LUMO. The new bimetallic complex achieves the delicate steric and electronic balance and  $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{RhCl}_2(\text{Ph}_2\text{phen})]^{3+}$  undergoes photoinitiated electron collection and photocatalytically generates  $\text{H}_2$  from  $\text{H}_2\text{O}$ . The  $\text{Ph}_2\text{phen}$  TL provides enhanced steric bulk at the Rh center without destabilizing the  $\text{Rh}(d\sigma^*)$  orbital. This study provides insight into the structural and electronic requirements for the design of supramolecules for photoinitiated electron collection and multielectron photoreduction of  $\text{H}_2\text{O}$  to  $\text{H}_2$ , highlighting the role of supramolecular architecture and orbital energetics for active photocatalysts. The herein reported active bimetallic motif is one of the few functional single component photocatalysts functioning by photoinitiated electron collection activation and provides systems more amendable to mechanistic studies with fewer needed structural components. Continued research to probe this in detail is ongoing in our laboratory.

## ■ ASSOCIATED CONTENT

**S Supporting Information.** Syntheses, experimental methods, cyclic voltammograms and tabulated data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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## ■ ACKNOWLEDGMENT

Acknowledgment is made to the Chemical Sciences, Geosciences and Biosciences Division, Office of Basic Energy Sciences, Office of Sciences, U.S. Department of Energy DE FG02-05-ER15751 for their generous financial support of our research. The authors wish to also thank Jing Wang and Rongwei Zhou for their assistance with this work.

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