Angewandte Chemie International Edition

Photocatalysis

DOI: 10.1002/anie.201105170

Efficient Photocatalytic Hydrogen Production in a Single-Component System Using Ru,Rh,Ru Supramolecules Containing 4,7-Diphenyl-1,10-Phenanthroline**

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Light-to-chemical energy conversion schemes are of considerable interest in the quest for renewable, alternative energy resources.[1] One approach to this issue is the photochemical reduction of H_2O to H_2.[2] Converting solar energy to H_2 fuel through H_2O splitting is challenging as it involves separating charges to generate a potential at the molecular scale, collecting multiple reducing equivalents to provide for energetically feasible reactions, and breaking and forming chemical bonds. Molecular photocatalysts are attractive as the basic redox, spectroscopic, and photophysical properties can be tuned at the molecular level to understand system function using traditional techniques. Herein we report an efficient, high-turnover single-component system for H_2O reduction to H_2 with superior photocatalytic functioning. This system uses a single molecule to absorb light, generate charge separation, multiply reduce a metal center and deliver reducing equivalents to H_2O to produce H_2.

Multi-component H_2 photocatalysts provide the backdrop for the development of single-component photocatalysts. Multi-component photosystems incorporating separate molecular light absorbers (LA), electron relays, and catalysts have been developed.[3] A photosystem comprising a $[Ru(bpy)_3]^{2+}$ LA, $[Rh^{III}(bpy)_3]^{3+}$ electron relay, Pt catalyst, and triethanolamine electron donor (ED) produces H_2 from H_2O with a turnover number (TON) of 80 (per Rh site) when irradiated at $\lambda = 450 \pm 20$ nm (bpy = 2,2′-bipyridine).[3] Recently, multi-component systems have been reported that utilize a cyclometalated Ir LA with a Rh or Pt catalyst, as well as a Pt LA with a Co catalyst.[4]

Covalent coupling of multiple subunits whose individual acts lead to a complex function provides for supramolecular complexes acting as molecular devices.[5] Photoinitiated electron collectors (PECs) are supramolecules that use photons to multiply reduce an electron collector (EC). The first device for PEC, $[\{(bpy)_2Ru(dpb)\}_2IrCl_2](PF_6)_5$ (dpb = 2,3-bis(2-pyridyl)benzo-quinoxaline) collects reducing equivalents on the dpb π^* orbitals functioning through electronic decoupling of the two Ru LA by the intervening Ir site.[6] $[(phen)_2Ru(BL)Ru(phen)_2](PF_6)_4$ collects electrons on the BL π^* orbitals using a remote acceptor decoupled from optical excitation (phen = 1,10-phenanthroline; BL = bridging ligand = tatpp, tatpq).[7] $[(bpy)_2Ru(pbn)]^{2+}$ couples a Ru LA to a NAD^+/NADH (NAD = nicotinamide adenine dinucleotide) model ligand that undergoes proton-coupled, two-electron reduction to generate $[(bpy)_2Ru(pbnHH)]^{2+}$.[8] These pioneering PEC systems store electrons on ligands but do not perform multi-electron photocatalysis or produce H_2 fuel.

The use of supramolecular architecture allows for the coupling of the light absorbers to the catalytically reactive metals, providing unique structural motifs functioning as single-component H_2 photocatalysts.[2d,e] Rh-centered PECs $[\{(TL)_2Ru(dpp)\}_2RhX_2]^{5+}$ (TL = terminal ligand = bpy, phen; X = Cl or Br; dpp = 2,3-bis(2-pyridyl)pyrazine) photocatalyze H_2 from H_2O with $\Phi \approx 0.01$.[9] Bimetallic $[(TL)_2Ru(dpp)RhCl_2(TL')]^{3+}$ photoreduce but dimerize in the Rh^I form preventing photocatalysis.[9f] Photochemical H_2 production from hydrohalic acids with a $\Phi \approx 0.01$ and 27 turnovers per hour in the first 3 h use $[Rh_2^{0,0}(dfpma)_3(PPh_3)(CO)]$ (dfpma = $MeN(PF_2)_2$), with a halogen atom trap.[2b,10] Ru,Pt bimetallic systems photocatalyze H_2 production from H_2O.[11] Ru,Pd bimetallic systems photochemically produce H_2 providing 56 turnovers in ca. 30 h.[12] Recent studies on Pt[13] and Pd[14] systems suggest that colloidal metal formation, due to Pt or Pd decomplexation, may be catalytically active. Zn-porphyrin LA coupled to a bio-inspired diiron catalyst photocatalyzes H_2 production with a low turnover.[15] The $[(bpy)_2Ru(L\text{-}pyr)Co(dmgBF_2)_2(OH_2)]^{2+}$ affords 56 turnovers in 4 h.[16] The Ir-based system, $[(ppy)_2Ir(pyr)Co(dmgBF_2)_2(OH_2)]^+$ (ppy = 2-phenylpyridine), demonstrates 200 turnovers in 15 h. Generation of an Os,Rh bimetallic complex in situ provides 87 turnovers and $\Phi = 0.007$.[17] It is clear from initial studies that single-component systems that function as LA and catalysts for H_2O reduction to H_2 can be prepared and modification of molecular design can enhance functioning. Few systematic studies are undertaken and surprising results are often encountered. A stable, efficient single-component system for H_2 production remains elusive requiring sustained work in this field.

Reported herein are $[\{(Ph_2phen)_2Ru(dpp)\}_2RhCl_2](PF_6)_5$ and $[\{(Ph_2phen)_2Ru(dpp)\}_2RhBr_2](PF_6)_5$ (Ph_2phen = 4,7-diphenyl-1,10-phenanthroline; Figure 1), two new supramolecules that undergo PEC and photocatalyze the reduction of H_2O to H_2 with substantially enhanced photocatalytic efficiency and high photocatalytic system turnover. This substantial enhancement in catalytic functioning through use of

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[**] Acknowledgements is made to the Chemical Sciences, Geosciences and Biosciences Division, Office of Basic Energy Sciences, Office of Sciences, U.S. Department of Energy DE FG02-05ER15751 for their generous financial support of our research.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201105170.

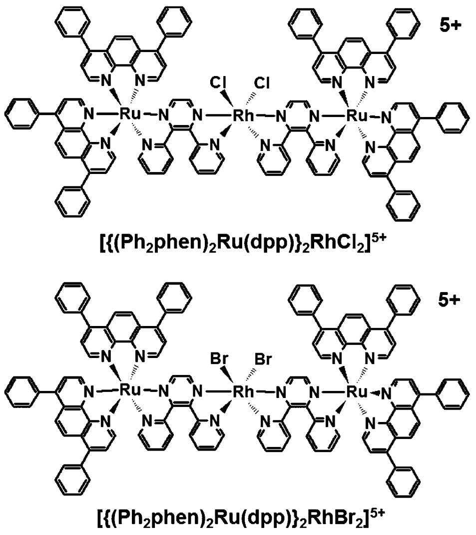

Figure 1. Ru,Rh,Ru supramolecular complexes as photoinitiated electron collectors for the photocatalytic production of H_2 from H_2O.

the Ph$_2$phen TL in place of bpy or phen is remarkable and unexpected given the Ru→dpp and Ru→Rh charge-transfer (CT) nature of the two lowest-lying and photoactive excited states in this Ru,Rh,Ru trimetallic motif. The synthesis, redox, photophysical, and photocatalytic properties of the new PECs are reported with an analysis of the factors modulated by the use of the Ph$_2$phen TL. The new bimetallic system [{(Ph$_2$phen)$_2$Ru}$_2$(dpp)](PF$_6$)$_4$, which lacks a Rh center, but possesses the same Ru→dpp CT state has also been synthesized and the redox and photophysical properties reported serving as a model for photophysics of the Ru→dpp ^{3}MLCT state with a Ph$_2$phen TL. The title trimetallics photochemically collect electrons at the Rh metal center and represent two of only a handful of PECs capable of multi-electron photocatalysis. The title trimetallics have unusually high quantum efficiency and turnover (maximum $\Phi = 0.073$; overall $\Phi = 0.050$ (5 h); TON = 1300 mol H_2/mol Rh with long-term photolysis) for a single-component system that is substantially enhanced relative to analogous bpy- and phen-containing systems which themselves are already superior single-component systems.

The new bimetallic complex [{(Ph$_2$phen)$_2$Ru}$_2$(dpp)](PF$_6$)$_4$ and trimetallic complexes [{(Ph$_2$phen)$_2$Ru(dpp)}$_2$RhCl$_2$](PF$_6$)$_5$ and [{(Ph$_2$phen)$_2$Ru(dpp)}$_2$RhBr$_2$](PF$_6$)$_5$ were synthesized in good yield using a building-block approach (Scheme S1, Supporting Information).[9b,18] The electrochemistry of the Ru,Rh,Ru trimetallic complexes (Figure S1, Table S1) show two overlapping, one-electron oxidations (+1.58 V vs. Ag/AgCl, $\Delta E_p \approx 150$ mV) indicative of the largely electronically uncoupled Ru centers and Ru(dπ)-based HOMOs. Both complexes display irreversible Rh$^{III/II/I}$ reductions ($E_p^c = -0.35$ (Cl) and -0.32 (Br) vs. Ag/AgCl), with two reversible one-electron dpp$^{0/-}$ couples that follow demonstrating Rh(dσ*)-based LUMOs. The weaker σ-donating ability of Br versus Cl shifts the Rh$^{III/II/I}$ reduction potential positive for the Br analogue.[19] The LUMO is dpp(π*)-based in the Ru,Ru bimetallic.

The title Ph$_2$phen bimetallic and trimetallic complexes are efficient light absorbers (Figure 2) with intraligand (IL) π→π* transitions in the UV and Ru(dπ)→ligand(π*) ^{1}MLCT transitions in the visible (Table S2). The lowest-energy transitions are Ru(dπ)→dpp(π*) metal-to-ligand charge transfer (^{1}MLCT) transitions. The variation of halide bound to Rh does not change the optical properties but use of Ph$_2$phen TL provides for enhanced absorptivity in the UV and visible providing significant enhancement in the 360–460 nm region due to increased molar absorptivity for the Ru→Ph$_2$phen CT transition.

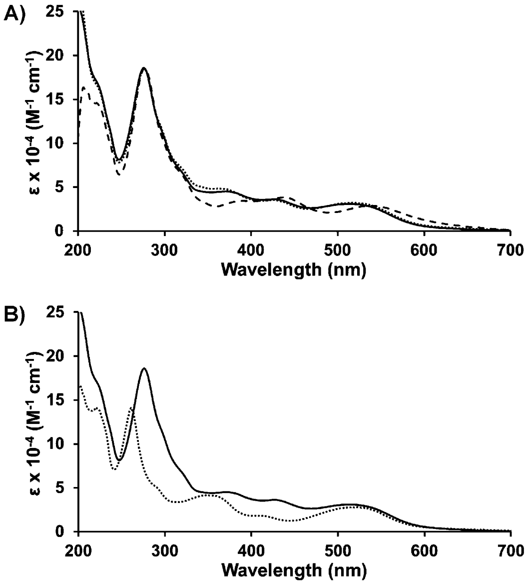

Figure 2. Electronic absorption spectra of A) [{(Ph$_2$phen)$_2$Ru}$_2$(dpp)]$^{4+}$ (– – –), [{(Ph$_2$phen)$_2$Ru(dpp)}$_2$RhCl$_2$]$^{5+}$ (-----) and [{(Ph$_2$phen)$_2$Ru(dpp)}$_2$RhBr$_2$]$^{5+}$ (——); B) [{(phen)$_2$Ru(dpp)}$_2$RhBr$_2$]$^{5+}$ (-----) and [{(Ph$_2$phen)$_2$Ru(dpp)}$_2$RhBr$_2$]$^{5+}$ (——) in CH$_3$CN at room temperature.

Steady-state and time-resolved emission spectroscopy was utilized to provide insight into the complex excited-state dynamics (Table S3). At room temperature, both trimetallic complexes display a low-energy, weak emission ([{(Ph$_2$phen)$_2$Ru(dpp)}$_2$RhCl$_2$]$^{5+}$: $\lambda^{em} = 770$ nm, $\Phi^{em} = 2.4 \times 10^{-4}$, $\tau = 52$ ns; [{(Ph$_2$phen)$_2$Ru(dpp)}$_2$RhBr$_2$]$^{5+}$: $\lambda^{em} = 770$ nm, $\Phi^{em} = 2.0 \times 10^{-4}$, $\tau = 40$ ns) from the Ru(dπ)→dpp(π*) ^{3}MLCT excited state. This emission is substantially quenched compared to the model Ru,Ru bimetallic system [{(Ph$_2$phen)$_2$Ru}$_2$(dpp)]$^{4+}$ ($\lambda^{em} = 754$ nm, $\Phi^{em} = 1.7 \times 10^{-3}$, $\tau = 192$ ns). Efficient quenching of the ^{3}MLCT emission is due to intramolecular electron transfer (k_{et}) to populate the non-emissive Ru(dπ)→Rh(dσ*) metal-to-metal charge transfer (^{3}MMCT) excited state (Figure 3). Using k_r (9.0×10^3 s^{-1}) and k_{nr} (5.2×10^6 s^{-1}) from the model Ru,Ru bimetallic complex, k_{et} for intramolecular electron transfer for [{(Ph$_2$phen)$_2$Ru(dpp)}$_2$RhX$_2$]$^{5+}$ are 1.4×10^7 s^{-1} (Cl) and 2.0×10^7 s^{-1} (Br). At 77 K in a rigid matrix, quenching of the ^{3}MLCT emission is impeded with $\tau = 1.9$ μs for the Ph$_2$phen trimetallic and bimetallic model systems, consistent with an intramolecular

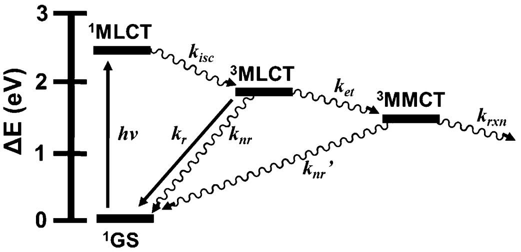

Figure 3. State diagram of $[\{(Ph_2phen)_2Ru(dpp)\}_2RhX_2](PF_6)_5$ (X = Cl or Br).

electron transfer mechanism quenching the ^{3}MLCT emission at room temperature.

Electrochemical and photochemical reduction of the Ph_2phen trimetallic complexes were performed to observe the ability of these two new trimetallics to undergo PEC at the Rh^{III} center (Figure S2). Similar to previously studied Ru,Rh,Ru systems,[9c] the Ph_2phen trimetallic complexes photoreduce with the sacrificial electron donor DMA illuminated at $\lambda > 460$ nm (photochemical reduction), which generates spectroscopy consistent with electrochemical reduction to Rh^I establishing these new systems as photochemical molecular devices for photoinitiated electron collection.

With the knowledge that $[\{(Ph_2phen)_2Ru(dpp)\}_2RhCl_2]^{5+}$ and $[\{(Ph_2phen)_2Ru(dpp)\}_2RhBr_2]^{5+}$ photochemically collect electrons generating Rh^I-centered supramolecules, photocatalytic studies were undertaken. In the presence of DMA, both title trimetallics photocatalytically reduce H_2O to produce H_2 (Table 1). In CH_3CN with 65 μM trimetallic photocatalyst, 1.5 M DMA, 0.62 M H_2O and 0.11 mM $[DMAH^+][CF_3SO_3^-]$ (light flux $= 2.36 \pm 0.05 \times 10^{19}$ photons/min, effective pH ≈ 9.1), for comparison to other trimetallic photocatalysts, $[\{(Ph_2phen)_2Ru(dpp)\}_2RhX_2]^{5+}$ produced 1.1 ± 0.1 mL H_2 (Cl) and 1.4 ± 0.1 mL H_2 (Br) after 20 h. This demonstrated superior photocatalysis relative to known Ru,Rh,Ru photocatalysts and other single-component systems. The weaker σ-donating ability of the Br analogue as compared to the Cl complex affords efficient generation of the reduced Rh species and provides for enhanced driving force to generate the MMCT state. This Br-containing complex was further studied under recently optimized conditions.[20] Changing just the solvent system from CH_3CN to the weaker ligating DMF enhanced photocatalytic activity with 2.1 ± 0.1 mL of H_2 and 280 ± 10 TON after 20 h, indicating solvent ligation impacts conversion between $Rh^{III/II/I}$ through the catalytic cycle as the light-absorbing properties were not greatly influenced (Figure S3). Based on prior studies with related photocatalysts, increased solution volume, light flux, [photocatalyst] and [DMA][9] provides with this new photocatalyst an efficient and stable photocatalytic system (44 ± 6 mL; 610 ± 90 TON; maximum $\Phi = 0.073$; overall $\Phi = 0.050$ after 5 h; overall $\Phi = 0.029$ after 20 h) that far outperforms related Ru,Rh,Ru photocatalysts and known single-component systems. The long-term photostability was investigated with 63 mL of H_2 produced representing 870 TON after 46 h (Figure 4) and continued photolysis providing 1300 TON. The previously reported lead photosystem, $[\{(bpy)_2Ru(dpp)\}_2RhBr_2]^{5+}$, produced 20 mL of H_2, maximum $\Phi = 0.023$ and overall $\Phi = 0.013$, after 20 h.[20] The phen analogue, $[\{(phen)_2Ru(dpp)\}_2RhBr_2]^{5+}$, produced even less H_2 with 4.5 mL of H_2, maximum $\Phi = 0.008$ and overall $\Phi = 0.003$ after 20 h. Inclusion of phenyl substituents in this motif provides for substantially enhanced photocatalytic activity, long-term stability and greater than three-fold enhancement in quantum efficiency. Such disparity in H_2 production between photosystems is surprising given the similar nature of the Ru→dpp ^{3}MLCT and Ru→Rh ^{3}MMCT excited states in this $[\{(TL)_2Ru(dpp)\}_2RhX_2]^{5+}$ molecular architecture.

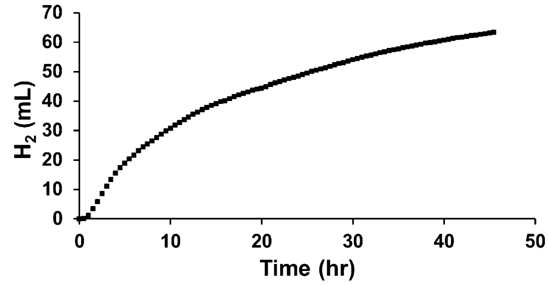

Figure 4. H_2 production profile using $[\{(Ph_2phen)_2Ru(dpp)\}_2RhBr_2]^{5+}$ (120 μM) in DMF photolyzed at 460 nm in the presence of H_2O (0.62 M) and the electron donor DMA (3.1 M).

Table 1: Photocatalytic hydrogen production from water using Ru,Rh,Ru photocatalysts under various experimental parameters.

Complex[a]	[Complex] [μM]	[DMA] [M]	Solvent	H_2 [mL]	H_2 [μmol]	TON[b]	Max. Φ
$[\{(phen)_2Ru(dpp)\}_2RhBr_2]^{5+}$	65	1.5	CH_3CN	0.25 ± 0.03	10 ± 1	36 ± 4	0.006
$[\{(Ph_2phen)_2Ru(dpp)\}_2RhCl_2]^{5+}$	65	1.5	CH_3CN	1.1 ± 0.1	44 ± 3	150 ± 10	0.013
$[\{(Ph_2phen)_2Ru(dpp)\}_2RhBr_2]^{5+}$	65	1.5	CH_3CN	1.4 ± 0.1	58 ± 4	200 ± 10	0.022
$[\{(bpy)_2Ru(dpp)\}_2RhBr_2]^{5+}$[c,d]	120	3.1	DMF	20	810	270	0.023
$[\{(phen)_2Ru(dpp)\}_2RhBr_2]^{5+}$[c]	120	3.1	DMF	4.5	180	62	0.008
$[\{(Ph_2phen)_2Ru(dpp)\}_2RhBr_2]^{5+}$[c]	120	3.1	DMF	44 ± 6 (63)	1640 ± 340 (2400)	610 ± 90 (870)	0.073

[a] Results correspond to 20 h photolysis time using 470 nm LED light source (light flux $= 2.36 \pm 0.05 \times 10^{19}$ photons/min; reaction solution volume = 4.5 mL; head space volume = 15.2 mL). [b] Values correspond to turnovers per Rh catalytic center. [c] Experiment was performed using an increased reaction solution volume (24.8 mL), head space volume (25.0 mL), and light flux ($6.27 \pm 0.01 \times 10^{19}$ photons/min). Values correspond to 20 h photolysis time unless otherwise stated. Values in parenthesis correspond to 46 h photolysis time. [d] Reference [20].

Many factors contribute to the significantly enhanced photocatalytic efficiency by the $[\{(Ph_2phen)_2Ru(dpp)\}_2RhBr_2]^{5+}$ system. The thermodynamic driving force (E_{redox}) for the reductive quenching of the ^{3}MLCT and ^{3}MMCT excited states using the sacrificial electron donor DMA is thermodynamically favorable for $[\{(Ph_2phen)_2Ru(dpp)\}_2RhBr_2]^{5+}$ ($E_{redox} = 0.60$ V and 0.23 V vs. Ag/AgCl, respectively) and similar in value to $[\{(bpy)_2Ru(dpp)\}_2RhBr_2]^{5+}$ (0.52 V and 0.13 V) and $[\{(phen)_2Ru(dpp)\}_2RhBr_2]^{5+}$ (0.58 V and 0.19 V). This slight increase in E_{redox} does not alone account for the enhanced photocatalysis by the Ph$_2$phen systems. Insight into the interaction between DMA and the ^{3}MLCT excited state is provided using a Stern–Volmer analysis to obtain a bimolecular quenching rate constant (k_q = reductive quenching of ^{3}MLCT state and bimolecular deactivation of ^{3}MLCT state).[9c] Values for k_q of $[\{(Ph_2phen)_2Ru(dpp)\}_2RhBr_2]^{5+}$ ($2.9 \times 10^9\,\text{M}^{-1}\text{s}^{-1}$), $[\{(bpy)_2Ru(dpp)\}_2RhBr_2]^{5+}$ ($3.2 \times 10^9\,\text{M}^{-1}\text{s}^{-1}$), and $[\{(phen)_2Ru(dpp)\}_2RhBr_2]^{5+}$ ($5.9 \times 10^9\,\text{M}^{-1}\text{s}^{-1}$) are near the diffusion control limit and indicate efficient quenching by DMA. The ^{3}MLCT excited state lifetime (τ) is largest for the new Ph$_2$phen systems, 40 ns vs. 30 ns for phen and 34 ns for bpy. The product of τ and k_q the Stern–Volmer quenching constant and is $120\,\text{M}^{-1}$, $110\,\text{M}^{-1}$ and $180\,\text{M}^{-1}$ for $[\{(Ph_2phen)_2Ru(dpp)\}_2RhBr_2]^{5+}$, $[\{(bpy)_2Ru(dpp)\}_2RhBr_2]^{5+}$ and $[\{(phen)_2Ru(dpp)\}_2RhBr_2]^{5+}$, respectively. The similarity of these values indicates that extension of the ^{3}MLCT lifetime alone is not responsible for the enhanced photocatalysis by the Ph$_2$phen system. Extention of the formally Ru(dπ) HOMO onto the Ph$_2$phen TL may result in an enhanced photoreduction yield for these complexes due to slower back electron transfer providing for enhanced photocatalysis. The sterically demanding Ph$_2$phen ligand may provide enhanced protection of the reactive Rh center during redox cycling, relative to the bpy and phen systems, to provide superior photocatalytic functioning. The steric constraints imposed by the two Ru LA units was recently discovered to play a critical role in photocatalysis in a study that showed Ru,Rh bimetallics undergo PEC but do not photocatalyze H$_2$ production due to dimerization of the Rh^I form of the bimetallic.[9f] The combination of the steric constraints imposed by the Ph$_2$phen ligand, the extended ^{3}MLCT lifetime, extension of the formally Ru(dπ) HOMO onto the TL and enhanced driving force for photoreduction likely all combine to provide for the superior photocatalytic functioning reported herein.

The two new polyazine-bridged, supramolecular photocatalysts $[\{(Ph_2phen)_2Ru(dpp)\}_2RhCl_2](PF_6)_5$ and $[\{(Ph_2phen)_2Ru(dpp)\}_2RhBr_2](PF_6)_5$ have been synthesized and studied, as well as the $[\{(Ph_2phen)_2Ru\}_2(dpp)](PF_6)_4$ model system. The photophysical properties show that photoexcitation populates the emissive ^{3}MLCT excited states, which are efficiently quenched by intramolecular electron transfer to populate the non-emissive ^{3}MMCT excited states at room temperature. Photochemical reduction of $[\{(Ph_2phen)_2Ru(dpp)\}_2RhCl_2]^{5+}$ and $[\{(Ph_2phen)_2Ru(dpp)\}_2RhBr_2]^{5+}$ converts the synthesized Rh^{III} form to a multi-reduced Rh^I form establishing these as molecular devices for photoinitiated electron collection. Reductive quenching of both the ^{3}MLCT and ^{3}MMCT excited states by the DMA electron donor is thermodynamically favorable with quenching of the ^{3}MLCT emission by DMA occuring rapidly, near the diffusion control limit. The two new trimetallic complexes show substantially enhanced photocatalytic activity compared to the previously reported $[\{(phen)_2Ru(dpp)\}_2RhX_2](PF_6)_5$ and $[\{(bpy)_2Ru(dpp)\}_2RhX_2](PF_6)_5$ systems with $[\{(Ph_2phen)_2Ru(dpp)\}_2RhBr_2](PF_6)_5$ being a far superior photocatalyst providing a maximum $\Phi = 0.073$ and an overall $\Phi = 0.050$ in 5 h. Continued photolysis provides large TON of 1300 mol H$_2$/mol catalyst with some functioning persistent even at this stage. This system functions at relatively low photocatalyst concentrations (120 μM) at basic pH ($\approx$9.5) with relatively high quantum efficiency and TON for a single-component photocatalyst coupling the light absorber and catalytic metal in one supramolecule. The steric demands of the Ph$_2$phen ligand may provide protection of the photogenerated Rh^I center, prohibiting undesirable side reactions subject to deactivation in our photocatalytic system and assist in halide loss needed upon Rh reduction.[9] Studies are underway to explore additional factors that impact photocatalysis by these Ru,Rh,Ru supramolecules as well as probing the properties of these systems in more detail.

Received: July 22, 2011
Revised: September 5, 2011

Keywords: photocatalysis · rhodium · ruthenium · supramolecular complexes · water splitting

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[1] N. D. McDaniel, S. Bernhard, *Dalton Trans.* **2010**, *39*, 10021–10030.

[2] a) A. J. Bard, M. A. Fox, *Acc. Chem. Res.* **1995**, *28*, 141–145; b) M. J. Esswein, D. G. Nocera, *Chem. Rev.* **2007**, *107*, 4022–4047; c) D. G. Nocera, *Inorg. Chem.* **2009**, *48*, 10001–10017; d) M. Wang, Y. Na, M. Gorlov, L. C. Sun, *Dalton Trans.* **2009**, 6458–6467; e) L. L. Tinker, N. D. McDaniel, S. Bernhard, *J. Mater. Chem.* **2009**, *19*, 3328–3337.

[3] a) G. M. Brown, S. F. Chan, C. Creutz, H. A. Schwarz, N. Sutin, *J. Am. Chem. Soc.* **1979**, *101*, 7638–7640; b) S. F. Chan, M. Chou, C. Creutz, T. Matsubara, N. Sutin, *J. Am. Chem. Soc.* **1981**, *103*, 369–379; c) M. Kirch, J. M. Lehn, J. P. Sauvage, *Helv. Chim. Acta* **1979**, *62*, 1345–1384.

[4] a) E. D. Cline, S. E. Adamson, S. Bernhard, *Inorg. Chem.* **2008**, *47*, 10378–10388; b) P. N. Curtin, L. L. Tinker, C. M. Burgess, E. D. Cline, S. Bernhard, *Inorg. Chem.* **2009**, *48*, 10498–10506; c) P. W. Du, K. Knowles, R. Eisenberg, *J. Am. Chem. Soc.* **2008**, *130*, 12576.

[5] a) V. Balzani, A. Juris, M. Venturi, S. Campagna, S. Serroni, *Chem. Rev.* **1996**, *96*, 759–833; b) V. Balzani, L. Moggi, F. Scandola in *Supramolecular Photochemistry* (Ed.: V. Balzani), Reidel, Dordrecht, **1987**, pp. 1–28.

[6] a) S. M. Molnar, G. E. Jensen, L. M. Vogler, S. W. Jones, L. Laverman, J. S. Bridgewater, M. M. Richter, K. J. Brewer, *J. Photochem. Photobiol. A* **1994**, *80*, 315–322; b) S. M. Molnar, G. Nallas, J. S. Bridgewater, K. J. Brewer, *J. Am. Chem. Soc.* **1994**, *116*, 5206–5210.

[7] a) M. J. Kim, R. Konduri, H. W. Ye, F. M. MacDonnell, F. Puntoriero, S. Serroni, S. Campagna, T. Holder, G. Kinsel, K. Rajeshwar, *Inorg. Chem.* **2002**, *41*, 2471–2476; b) R. Konduri, H. W. Ye, F. M. MacDonnell, S. Serroni, S. Campagna, K.

Rajeshwar, *Angew. Chem.* **2002**, *114*, 3317–3319; *Angew. Chem. Int. Ed.* **2002**, *41*, 3185–3187. tatpp = 9,11,20,22-tetraazatetrapyrido[3,2-*a*:2′3′-*c*:3″,2″-1:2‴,3‴-*n*]pentacene, tatpq = 9,11,20,22-tetraazatetrapyrido[3,2-*a*:2′3′-*c*:3″,2″-1:2‴,3‴-*n*]pentacene-10,21-quinone.

[8] a) D. Polyansky, D. Cabelli, J. T. Muckerman, E. Fujita, T. Koizumi, T. Fukushima, T. Wada, K. Tanaka, *Angew. Chem.* **2007**, *119*, 4247–4250; *Angew. Chem. Int. Ed.* **2007**, *46*, 4169–4172; b) D. E. Polyansky, D. Cabelli, J. T. Muckerman, T. Fukushima, K. Tanaka, E. Fujita, *Inorg. Chem.* **2008**, *47*, 3958–3968. pbn = 2-(2-pyridyl)benzo[*b*]-1,5-naphthyridine.

[9] a) S. A. Arachchige, J. Brown, K. J. Brewer, *J. Photochem. Photobiol. A* **2008**, *197*, 13–17; b) S. M. Arachchige, J. R. Brown, E. Chang, A. Jain, D. F. Zigler, K. Rangan, K. J. Brewer, *Inorg. Chem.* **2009**, *48*, 1989–2000; c) M. Elvington, K. J. Brewer, *Inorg. Chem.* **2006**, *45*, 5242–5244; d) M. Elvington, J. Brown, S. M. Arachchige, K. J. Brewer, *J. Am. Chem. Soc.* **2007**, *129*, 10644–10645; e) T. A. White, K. Rangan, K. J. Brewer, *J. Photochem. Photobiol. A* **2010**, *209*, 203–209; f) J. Wang, T. A. White, S. A. Arachchige, K. J. Brewer, *Chem. Commun.* **2011**, *47*, 4451–4453.

[10] a) A. J. Esswein, A. S. Veige, D. G. Nocera, *J. Am. Chem. Soc.* **2005**, *127*, 16641–16651; b) A. F. Heyduk, D. G. Nocera, *Science* **2001**, *293*, 1639–1641.

[11] H. Ozawa, M. A. Haga, K. Sakai, *J. Am. Chem. Soc.* **2006**, *128*, 4926–4927.

[12] S. Rau, B. Schafer, D. Gleich, E. Anders, M. Rudolph, M. Friedrich, H. Gorls, W. Henry, J. G. Vos, *Angew. Chem.* **2006**, *118*, 6361–6364; *Angew. Chem. Int. Ed.* **2006**, *45*, 6215–6218.

[13] P. Du, J. Schneider, L. Fan, W. Zhao, U. Patel, F. N. Castellano, R. Eisenberg, *J. Am. Chem. Soc.* **2008**, *130*, 5056.

[14] P. Lei, M. Hedlund, R. Lomoth, H. Rensmo, O. Johansson, L. Hammarstrom, *J. Am. Chem. Soc.* **2008**, *130*, 26.

[15] X. Q. Li, M. Wang, S. P. Zhang, J. X. Pan, Y. Na, J. H. Liu, B. Akermark, L. C. Sun, *J. Phys. Chem. B* **2008**, *112*, 8198–8202.

[16] a) A. Fihri, V. Artero, A. Pereira, M. Fontecave, *Dalton Trans.* **2008**, 5567–5569; b) A. Fihri, V. Artero, M. Razavet, C. Baffert, W. Leibl, M. Fontecave, *Angew. Chem.* **2008**, *120*, 574–577; *Angew. Chem. Int. Ed.* **2008**, *47*, 564–567; c) C. Li, M. Wang, J. X. Pan, P. Zhang, R. Zhang, L. C. Sun, *J. Organomet. Chem.* **2009**, *694*, 2814–2819. L-pyr = [(4-pyridine) oxazolo(4,5-*f*)phenanthroline], dmgBF$_2$ = (difluoroboryl)dimethyl glyoximate.

[17] Y. Miyake, K. Nakajima, K. Sasaki, R. Saito, H. Nakanishi, Y. Nishibayashi, *Organometallics* **2009**, *28*, 5240–5243.

[18] C. H. Braunstein, A. D. Baker, T. C. Strekas, H. D. Gafney, *Inorg. Chem.* **1984**, *23*, 857–864.

[19] D. Amarante, C. Cherian, C. Ernmel, H. Y. Chen, S. Dayal, M. Koshy, E. G. Megehee, *Inorg. Chim. Acta* **2005**, *358*, 2231–2238.

[20] S. A. Arachchige, R. Shaw, T. A. White, V. Shenoy, H.-M. Tsui, K. J. Brewer, *ChemSusChem* **2011**, *4*, 514–518.