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Tetra- and Heptametallic Ru(II),Rh(III) Supramolecular Hydrogen Production Photocatalysts

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Supporting Information Placeholder

ABSTRACT: Supramolecular mixed metal complexes combining the trimetallic chromophore $[(\text{bpy})_2\text{Ru}(\text{dpp})]_2\text{Ru}(\text{dpp})^{6+}$ (**Ru₃**) with $[\text{Rh}(\text{bpy})\text{Cl}_2]^+$ or $[\text{RhCl}_2]^+$ catalytic fragments to form $[(\text{bpy})_2\text{Ru}(\text{dpp})]_2\text{Ru}(\text{dpp})\text{RhCl}_2(\text{bpy})(\text{PF}_6)_7$ (**Ru₃Rh**) or $[(\text{bpy})_2\text{Ru}(\text{dpp})]_2\text{Ru}(\text{dpp})\text{RhCl}_2(\text{PF}_6)_{13}$ (**Ru₃RhRu₃**) (bpy = 2,2'-bipyridine and dpp = 2,3-bis(2-pyridyl)pyrazine) catalyze the photochemical reduction of protons to H₂. This first example of a heptametallic Ru,Rh photocatalyst produces over 300 turnovers of H₂ upon photolysis of a solution of acetonitrile, water, triflic acid, and *N,N*-dimethylaniline as an electron donor. In contrast, the tetrametallic **Ru₃Rh** produces only 40 turnovers of H₂ due to differences in the excited state properties and nature of the catalysts upon reduction as ascertained from electrochemical data, transient absorption spectroscopy, and flash-quench experiments. While the lowest unoccupied molecular orbital of **Ru₃Rh** is localized on a bridging ligand, it is Rh-centered in **Ru₃RhRu₃** facilitating electron collection at Rh in the excited state and reductively quenched state. The Ru→Rh charge separated state of **Ru₃RhRu₃** is endergonic with respect to the emissive Ru→dpp ³MLCT excited and cannot be formed by static electron transfer quenching of the ³MLCT state. Instead, a mechanism of subnanosecond charge separation from high lying states is proposed. Multiple reductions of **Ru₃** and **Ru₃Rh** using sodium amalgam were carried out to compare UV-vis absorption spectra of reduced species and to evaluate the stability of highly reduced complexes. The **Ru₃**⁶⁺ can be reduced by ten electrons to a stable tetra-anion, while the **Ru₃Rh**⁷⁺ can be reduced to the trianion. In the final states, all bridging ligands are reduced twice and all bpy ligands are reduced once.

INTRODUCTION

Hydrogen is a desirable alternative to fossil fuels for its high energy density and its availability from the reduction of water. Cost effective water splitting on the large scale is limited by efficient catalysis of the multiproton/multielectron oxidation and reduction of water. In principle, H₂ can be produced with solar photovoltaics supplying the current for water electrolysis or by direct solar-to-chemical energy conversion by artificial photosynthesis (AP).¹⁻¹³ The homogeneous approach to solar H₂ by AP is complex and requires synergy among multiple components specializing in light absorption, charge separation, and catalysis. Given the importance of this problem, intense efforts have been dedicated to the discovery and optimization of new catalysts and chromophores and to unraveling the mechanisms of photocatalysis.¹⁴⁻²⁷

The supramolecular approach to AP pursues covalent linkage of the chromophore and catalyst through a bridging ligand.²⁸⁻⁴⁹ This strategy is motivated by the opportunity to eliminate diffusion controlled bimolecular electron transfers between the individual components and is a step toward functional photochemical devices for multielectron reactions.⁵⁰⁻⁵¹ Developing efficient supramolecular photocatalysts requires overcoming numerous challenges including unpredicted alterations of the properties of each component upon assembly and ensuring that the bridging ligand is electrochemically stable and capable of promoting electron transfer without acting as an electron sink.⁵² While covalent linkage can improve the efficiency of electron transfer to the catalyst, it also facilitates charge recombination, which is highly exergonic, on timescales many orders of magnitude faster than catalysis of

the water reduction. Consequently, the supramolecules must be stable to many photo-excitation/relaxation cycles relative to catalytic turnovers. Strategies to suppress charge recombination include synthesis of donor-chromophore-catalyst triads for which charge separation occurs over a large distance and the recombination rates are slowed in the Marcus inverted region.⁵³

Understanding the electronic structures, charge transfer kinetics and thermodynamics, and catalysis mechanisms is essential for improving photocatalysis, and numerous spectroscopic techniques have proven valuable in these investigations. The photocatalysts comprising $(\text{bpy})_2\text{Ru}(\text{tpphz})^{2+}$ (bpy = 2,2'-bipyridine, tpphz = tetrapyrido[2,3-*a*:2',3':3'',2'',*h*:2''',3'''-]phenazine) chromophores bridged to PdCl₂ or PtCl₂ catalytic centers are well known and provide instruction regarding the factors that control catalysis. Coordination of PdCl₂ to the chromophore accelerates excited state relaxation from a Ru→phen MLCT (metal to ligand charge transfer) state to a Ru→pyrazine MLCT state. A final 310 ps charge transfer to Pd occurs with dissociation of chloride.³¹ If the Ru→phen charge transfer state is stabilized, the energy gradient and rate of charge transfer to Pd are lowered, relaxation to the ground state is accelerated, and photocatalytic turnovers decrease from 210 to 67.⁵⁴ X-ray absorption experiments showed that showed the Ru-tpphz-PdCl₂ catalyst decomposed to active Pd colloids within 35 minutes while the PtCl₂ catalyst remained stable and catalytically active.⁵⁵ A significantly increased TON of 276 was achieved by substitution of PtI₂ for PtCl₂ (TON = 7), and was attributed to an increase in electron density at the Pt catalyst.

Supramolecules of $[(\text{bpy})_2\text{Ru}(2,2':5',2''\text{-terpyridine})]^{2+}$ chromophores bound to $[\text{PdCl}(\text{CH}_3\text{CN})]^+$ produced 130 turnovers of H₂.³⁶

Interestingly, optical excitation populates charge transfer states of the peripheral and bridging ligand with subsequent relaxation by $\text{bpy} \rightarrow \text{tpy}$ intraligand electron transfer to the $\text{Ru} \rightarrow \text{tpy}$ CT state with a 32.5 ps time constant.⁴⁰ Related complexes with Pt as the active catalyst are sensitive to the peripheral ligand on Ru, with electron-withdrawing groups on bpy promoting enhanced activity.⁴⁷ The difference in activity was attributed to ultrafast localization of the excited state on the bpy ligands, which functioned as electron reservoirs and decreased the rate of relaxation to the ground state.⁴⁸ Improved catalysis in this system is counterintuitive to the general goal of excited state charge transfer in the direction of the bridge/catalyst being necessary for photocatalysis; however, the concept could be relevant to other systems as illustrated by differences between $[(\text{bpy})_2\text{Ru}(2,5\text{-dpp})\text{PdCl}_2]^{2+}$ (dpp = bis(2-pyridyl)pyrazine), which is not catalytic, vs $[(4,4'\text{-CO}_2\text{Et-bpy})_2\text{Ru}(2,5\text{-dpp})\text{PdCl}_2]^{2+}$, which yields H_2 with a TON of 400.³⁴

Most of the examples discussed above are bimetallic complexes with 1:1 sensitizer to catalyst ratios. In contrast, Photosystems I and II of green plants operate at the opposite extreme and contain hundreds of light harvesting pigments that capture and transfer solar energy to the reaction centers within 100 picoseconds.^{56–60} Comparatively few multi-chromophore supramolecular photocatalysts have been tested for hydrogen production despite the improved light absorption per catalytic center. These include Ru,Rh,Ru complexes that function efficiently in fully aqueous media,^{61–62,26} multinuclear Ru,Pt complexes,⁶³ and a metal organic cage with eight Ru chromophores and six Pd catalysts.⁶⁴

The Brewer group has investigated supramolecular photocatalysts coupling multiple Ru(II) chromophores to Rh(III) or Pt(II) catalytic centers in numerous arrangements including $[(\text{TL})_2\text{Ru}(\text{dpp})\text{RhX}_2(\text{dpp})\text{Ru}(\text{TL})_2]^{5+}$ (**Ru,Rh,Ru**), $[(\text{TL})_2\text{Ru}(\text{dpp})]\text{Ru}\{(\text{TL})(\text{BL})\text{PtCl}_2\}^{4+}$ (**Ru}_2\text{Pt}**), and $[(\text{TL})_2\text{Ru}(\text{dpp})]_2\text{Ru}(\text{BL})\text{PtCl}_2]^{6+}$ (**Ru}_3\text{Pt}**). In these abbreviations, TL = “terminal ligand” which is typically a bipyridine-type diimine and BL = a “bridging ligand” capable of bis-bidentate coordination of two metals.^{65–71} Photocatalysis by the Rh complexes typically requires a Rh-based lowest unoccupied molecular orbital (LUMO) in combination with quenching of ³MLCT emission due to intramolecular excited state electron transfer to Rh; however, these properties alone cannot predict turnover numbers or efficiencies. Under electrochemical conditions, H_2 is released upon reduction of a bridging ligand after formation of a Rh hydride showing that reductions of both Rh and ligand sites are involved in catalysis.⁷² The **Ru}_3\text{Pt}** complexes also produce H_2 photocatalytically. Activation of the Pt center for catalysis requires charge transfer from the peripheral $\text{Ru} \rightarrow (\mu\text{-Ru,Ru-dpp})$ ³MLCT state to low energy $\text{Ru} \rightarrow \text{BL}$ charge separated (³CS) state.⁶⁸

We envisioned improving photocatalysis with a hybrid approach that combines the light-harvesting **Ru}_3** chromophore of **Ru}_3\text{Pt}** with the more reactive Rh metal as tetrametallic $[(\text{bpy})_2\text{Ru}(\text{dpp})]_2\text{Ru}(\text{dpp})\text{RhCl}_2(\text{bpy})]^{7+}$ (**Ru}_3\text{Rh}**) and heptametallic $[(\text{bpy})_2\text{Ru}(\text{dpp})]_2\text{Ru}(\text{dpp})]_2\text{RhCl}_2]^{13+}$ (**Ru}_3\text{RhRu}_3**) (Chart 1). The **Ru}_3\text{RhRu}_3** functions as photocatalyst with higher turnovers at lower concentration than all other smaller **Ru,Rh** photocatalysts in the dpp-bridged family of complexes. In contrast, **Ru}_3\text{Rh}** is nearly inactive for hydrogen production. Experiments reveal that **Ru}_3\text{Rh}** can be reduced to Rh(I), but only after a second reduction due to its ligand-localized LUMO. Conversely, **Ru}_3\text{RhRu}_3** possesses a Rh-based LUMO and begins to accumulate charge on Rh in the excited state and in the singly reduced complex. Transient absorption data show that ¹MLCT excitation of **Ru}_3\text{RhRu}_3** populates a mixture of ³MLCT and ³MMCT (metal-to-metal charge transfer) excited states on the sub-nanosecond timescale presumably via charge separation from high energy ³MLCT states of the $[\text{Ru}(\text{dpp})_3]^{2+}$ portion of the chromophore. This ³MMCT state is not observed for **Ru}_3\text{Rh}**. The photophysical

differences are presumably retained in pertinent intermediates and can explain the relative catalytic efficiencies of the two structures.

Chart 1. New **Ru}_3\text{Rh} tetrametallic and **Ru}_3\text{RhRu}_3** heptametallic complexes.^a**

^a The **Ru}_3\text{Rh}** and **Ru}_3\text{RhRu}_3** complexes were prepared by the reaction of **Ru}_3** with $[\text{RhCl}_2(\text{bpy})(\text{DMF})]$ or $\frac{1}{2}$ equiv. $\text{RhX}_3 \cdot n\text{H}_2\text{O}$, respectively, and are isolated as PF_6 salts. bpy = 2,2'-bipyridine and dpp = 2,3-bis(2-pyridyl)pyrazine.

RESULTS AND DISCUSSION

Electrochemistry. As mentioned in the Introduction, a Rh-based LUMO is typically required for efficient photochemical proton reduction using Ru,Rh supramolecules. The redox potentials of **Ru}_3\text{Rh}** and **Ru}_3\text{RhRu}_3** were measured by cyclic and square wave voltammetry in CH_3CN to assess the relative energetics of redox active components. Figure 1 shows the CV of **Ru}_3** as a reference and as an illustration of the relative order of increasingly negative ligand reductions expected for dpp-bridged polymetallic complexes.⁷³ The redox assignments of **Ru}_3** are: two sequential $(\mu\text{-Ru,Ru-dpp})^{0/-}$ couples (A at -0.48 and -0.62 V), the non-bridging $\text{dpp}^{0/-}$ couple (B at -1.05 V), and two $(\mu\text{-Ru,Ru-dpp})^{-2/-}$ couples (C at -1.17 and -1.32 V).⁷⁴ Bipyridine reductions will occur cathodic of -1.3 V, but these couples are unresolved because the neutral complex precipitates on the electrode. Two terminal $\text{Ru}^{\text{III/II}}$ couples of **Ru}_3** overlap at $E^\circ = 1.56$ V vs Ag/AgCl as expected for electronically independent couples.⁷⁵

Figure 1 also shows the CV of **Ru}_3\text{Rh}**. The addition of $[\text{RhCl}_2(\text{bpy})]^+$ has no effect on the $\text{Ru}^{\text{III/II}}$ or $(\mu\text{-Ru,Ru-dpp})^{0/-}$ potentials (wave A); however, there are additional reductive processes. The first reduction is a quasi-reversible $1e^-$ process with the cathodic peak potential $E_p^c = -0.26$ V (peak D). The two $(\mu\text{-Ru,Ru-dpp})^{0/-}$ couples (A) are distorted due to overlap with an irreversible $1e^-$ process (E) as verified by the consumption of $4e^-$ during bulk electrolysis at -0.8 V. For related molecules, the irreversible $\text{Rh}^{\text{III/II}}$ reduction of $[(\text{bpy})_2\text{Ru}(\text{dpp})]_2\text{RhCl}_2]^{5+}$ occurs at -0.39 V⁷⁶ while the ligand-centered $(\mu\text{-Ru,Pt-dpp})^{0/-}$ reduction of the **Ru}_3\text{Pt}** tetrametallic $[(\text{bpy})_2\text{Ru}(\text{dpp})]_2\text{Ru}(\text{dpp})\text{PtCl}_2]^{6+}$ occurs -0.40 V⁷⁴ showing that Rh- or dpp-localized reductions are possible at similar potentials in this coordination environment. Wave D is reversible, suggesting a ligand-centered process. This was verified by the absence of the $2\text{Cl}^-/\text{Cl}_2$ couple in an oxidative scan after exhaustive $1e^-$ electrolysis and shows that Rh(I) is not formed at this potential (Figure S2).⁷⁷ Assignment of wave D to a largely dpp-localized orbital with partial mixing with the Rh center is appropriate.

After $4e^-$ reduction, chloride oxidation was detected consistent with reduction to the Rh(I)^{78} complex $[(\text{bpy})_2\text{Ru}(\text{dpp}^-)]_2\text{Ru}(\text{dpp})\text{Rh}^{\text{I}}(\text{bpy})]^{5+}$ with two reduced $(\mu\text{-Ru,Ru-dpp}^-)$ ligands. This behavior, in which the first reduction is ligand-localized but a second reduction yields Rh(I) and the neutral bridging ligand is known for bimetallic Rh(III) and Ir(III) complexes in which $[\text{M}^{\text{III}}(\text{BL}^-)\text{M}^{\text{III}}] + e^- \rightarrow [\text{M}^{\text{III}}(\text{BL}^0)\text{M}^{\text{I}}]$.⁷⁹ A two-step reduction was observed for Ru,Rh bimetallic complexes with the ratios of current for each step dependent on the rate of

halide dissociation.⁸⁰ In contrast, our chloride detection experiments verify the stability of the Rh(III) coordination environment in the singly reduced species. Wave F (−1.04 V) is assigned to the (μ-Ru,Rh^I-dpp)^{0/−} couple of the Rh(I) complex by comparison to the non-bridging ligand potential of **Ru3** while two C waves (−1.16, −1.32 V) are assigned as the second reductions of the (μ-Ru,Ru-dpp) ligands similarly to **Ru3**.

Figure 1. Cyclic voltammograms of **Ru3** [(bpy)₂Ru(dpp)]₂Ru(dpp)]⁶⁺ (top), and **Ru3Rh** [(bpy)₂Ru(dpp)]₂Ru(dpp)RhCl₂(bpy)]⁷⁺ (bottom) in CH₃CN with a 100 mV s^{−1} scan rate and 0.1 M Bu₄NPF₆ electrolyte. Arrows indicate the applied potentials of bulk electrolyses and equivalents of charge consumed. For simplicity, peak E is labelled as a Rh^{III/II} couple and is justified due to mixing of the (μ-Ru,Rh-dpp)^{0/−} with Rh(III) in peak D, but the actual process is: [(bpy)Rh^{III}Cl₂(dpp[−])] + e[−] → [(bpy)Rh^I(dpp⁰)]⁺ + 2Cl[−].

The electrochemistry of **Ru3RhRu3** is complicated due to the number of electroactive units in similar environments, and square-wave voltammograms (Figure 2) show the redox couples with greater clarity than CV. Interpretation of the data is assisted by comparison to the known ruthenium congener **Ru3RuRu3**.⁸¹

The first reduction of **Ru3RhRu3** at −0.22 V is comparable in potential to the first reduction of **Ru3Rh**; however, it is irreversible in the heptametallic complex and has no counterpart in the **Ru3RuRu3**, suggesting a Rh^{III/II/I} process. The waves at −0.50 and −0.62 are each assigned as two overlapping 1e[−] (μ-Ru,Ru-dpp)^{0/−} couples by comparison to the analogous processes in **Ru3RuRu3**. At more negative potentials, reductions are observed at −0.75 V and −1.05 V. These are comparable to the inner (μ-Ru,Ru-dpp)^{0/−} reductions of **Ru3RuRu3** at −0.74 V and −0.87 V, which are coupled through the central metal, and therefore appear separately. The **Ru3RhRu3** waves at −0.74 V and −1.05 V are also identical in potential to the first and second ligand reductions of [(bpy)₂Ru(dpp)]₂RhCl₂]⁵⁺, supporting assignment as consecutive (μ-Ru,Rh^I-dpp)^{0/−} reductions. The second reduction of the (μ-Ru,Ru-dpp) ligands occurs cathodic of −1.2 V.

There are several notable differences between the electrochemistry of **Ru3Rh** and **Ru3RhRu3** that could influence the excited state properties and catalysis. The first reduction of **Ru3Rh** is quasi-reversible and ligand-localized, but **Ru3RhRu3** is first reduced from Rh(III) to Rh(I). Therefore, photochemical electron collection at Rh is expected in **Ru3RhRu3**. Despite the ligand based first reduction, the Rh(I) oxidation state of **Ru3Rh** is still attainable photochemically by two excitation / quenching reactions since the potential of the [Rh^{III}Cl₂(dpp[−])] + e[−] → [Rh^I(dpp⁰)]⁺ + 2Cl[−] reaction (Figure 1, wave E) lies near *E*⁰ of the (μ-Ru,Ru-dpp)^{0/−}, which is the source of reducing power of the photochemically quenched state. Next, there is a significant dif-

ference between *E*⁰ of Rh-bridged dpp ligands, (μ-Ru,Rh^I-dpp)^{0/−}, in the Rh(I) complexes. In **Ru3Rh^I**, the potential is −1.04 V while the analogous potential in **Ru3Rh^IRu3** is less negative at −0.74 V and is electronically coupled to the second (μ-Ru,Rh^I-dpp)^{0/−} reduction −1.05 V. The difference may arise from distribution of Rh(I)→dpp(π*) backbonding among two π-accepting dpp ligands in **Ru3Rh^IRu3** while the (μ-Ru,Rh^I-dpp) ligand of **Ru3Rh^I** is more electron rich due to stronger backbonding induced by the σ-donating, but poor π-accepting nature of the bpy ligand on Rh(I).

Figure 2. Reductive square wave voltammetry of [(bpy)₂Ru(dpp)]₂Ru(dpp)]⁶⁺ (top), [(bpy)₂Ru(dpp)]₂Ru(dpp)]₂RhCl₂]¹³⁺ (middle), and [(bpy)₂Ru(dpp)]₂Ru(dpp)]₂RuCl₂]¹²⁺ (bottom) in CH₃CN with 0.1 M Bu₄NPF₆ electrolyte. Step = 4 mV, amplitude = 25 mV, and frequency = 25 Hz.

Absorption and Emission Spectroscopy. The electronic absorption spectra of **Ru3**, **Ru3Rh**, and **Ru3RhRu3** (Figure 3, Table S2) show features of each component of the supramolecules with intraligand (IL) π→π* transitions of bpy (280 nm) and dpp (350 nm) in the UV and Ru(dπ)→bpy(π*) (400 nm) and Ru(dπ)→dpp(π*) (540 nm) charge transfer bands in the visible.⁸² Coordination of the Rh fragment in **Ru3Rh** induces minor changes in the low energy band shape and in the region from 300 to 380 nm by perturbation of the Ru(dπ)→dpp(π*) charge transfer band and dpp π→π* transitions.⁸³ Extinction coefficients (ε) for **Ru3RhRu3** are roughly double those of **Ru3Rh** as expected for non-interacting **Ru3** subunits. In the visible maxima, extinction coefficients in **Ru3RhRu3** approach 80,000 M^{−1} cm^{−1}, and are greatly enhanced over [(bpy)₂Ru(dpp)]₂RhCl₂]⁵⁺ (25,000 M^{−1} cm^{−1})⁷⁶ showing a substantial increase in the absorption cross section and suggesting possible catalysis at lower concentration or low light intensity.

Steady state emission can be used to evaluate the coupling between the Ru→dpp ³MLCT state and the Rh catalyst. Each supramolecule is emissive in fluid CH₃CN with λ_{max} = 765 nm (Figure 3). These data show that the terminal Ru→dpp ³MLCT emissive state is populated as expected for dendritic Ru(II) complexes with the peripheral [(bpy)₂Ru(dpp)]₂²⁺ unit.^{84–85} The energy of this state is not altered by the Rh; however, the quantum yields of emission (Φ_{em}) and emission lifetimes (τ) (Table 1) are attenuated for **Ru3Rh** and **Ru3RhRu3** relative to **Ru3** due to additional excited state decay mechanisms such as electron transfer, energy transfer, or vibrational deactivation.

Figure 3. Absorption (left) and emission (right) spectra of $[(\text{bpy})_2\text{Ru}(\text{dpp})]_2\text{Ru}(\text{dpp})^{6+}$ (**Ru3**), $[(\text{bpy})_2\text{Ru}(\text{dpp})]_2\text{Ru}(\text{dpp})\text{RhCl}_2(\text{bpy})^{7+}$ (**Ru3Rh**), and $[(\text{bpy})_2\text{Ru}(\text{dpp})]_2\text{Ru}(\text{dpp})]_2\text{RhCl}_2^{13+}$ (**Ru3RhRu3**) in CH_3CN .

In prior work, the comparably reduced Φ and τ in bimetallic and trimetallic Ru,Rh supramolecules relative to model complexes with similar excited states, such as $[(\text{bpy})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})_2]^{4+}$, was viewed as evidence for static intramolecular electron transfer quenching by the appended Rh(III).⁸⁶ The putative ³MMCT state had no detectable signature in the spectroscopic methods employed. Equal rates of radiative (k_r) and nonradiative (k_{nr}) decays for the Ru,Rh complexes and model compounds were assumed and the electron transfer rates (typically $\sim 10^7 \text{ s}^{-1}$) were estimated by $k_{ET} = (\tau^{-1} - \tau_o^{-1})$, where τ_o is the lifetime of the model complex. In contrast, recent transient absorption data⁸⁷ revealed picosecond spectral evolution suggesting that excited state ET might occur faster than 10^{11} s^{-1} and the original assumption using equivalent k_r and k_{nr} could be an oversimplification.

While the lifetimes of **Ru3Rh** and **Ru3RhRu3** are $\sim 20\%$ shorter than **Ru3**, the quantum yields are reduced by 40% and 74%, respectively, precluding analysis of ³MLCT quenching by electron transfer using the equation $k_{ET} = (\tau^{-1} - \tau_o^{-1})$. A comparable decrease in lifetime at 77 K suggests that the lifetime attenuation at room temperature is merely caused by a decrease in k_r or an increase in k_{nr} upon Rh coordination. Indeed, the ligand-localized LUMO and transient absorption data (see below) support the absence of ET to Rh in **Ru3Rh** and the drop in Φ_{em} and τ are attributed to approximate 25% reduction in k_r and 25% increase in k_{nr} relative to **Ru3**.

Table 1. Excited State Properties of Ru,Rh Supramolecules.^a

Complex	293 K			77 K	
	λ_{em} (nm)	$\Phi_{em} \times 10^4$	τ (ns)	λ_{em} (nm)	τ (μs)
Ru3	766	5.3	55	705	2.1
Ru3Rh	769	3.2	43	715	1.9
Ru3RhRu3	769	1.4	45	718	1.7

^a Room temperature data were collected in argon-saturated CH_3CN . 77 K data were collected in frozen butyronitrile glasses. Spectra were corrected for the PMT response.

The reason for quenched emission of **Ru3RhRu3** is more complicated than simple variation in k_r and k_{nr} , and transient absorption experiments (see below for details) provide evidence for the existence of a second state reasonably assigned as the terminal Ru→Rh ³MMCT charge separated state. The pathway to the ³MMCT warrants thermodynamic consideration. The free energy

change, ΔG_{ET} , for static electron transfer quenching of the ³MLCT can be estimated as 12.5 kJ mol^{-1} (0.13 eV) by equation 1

$$\Delta G_{ET} = -nF\Delta E = -nF(E_{Rh^{3+/2+}}^o - E_{Ru^{3+/2++}}^o) \quad (1)$$

where F is the Faraday constant 96485 C mol^{-1} , the $\text{Rh}^{3+/2+}$ potential is -0.26 V , and $E_{Ru^{3+/2++}}^o$ is the excited state oxidation potential of the terminal Ru→dpp ³MLCT state (-0.13 eV) state calculated using equation 2.

$$E_{Ru^{3+/2++}}^o = E_{Ru^{3+/2+}}^o - E^{oo} \quad (2)$$

In equation 2 E^{oo} is estimated as 1.73 eV from the emission maximum at 77 K. The analysis shows that intramolecular ET quenching of the ³MLCT state is endergonic. Similar conclusions are drawn from comparison of the 1.73 ³MLCT energy to the 1.85 eV ³MMCT state, for which the energy is estimated as the difference between $\text{Ru}^{III/II}$ and $\text{Rh}^{III/II}$ potentials.

An alternate pathway for quenched emission is charge separation from higher energy MLCT states of the central Ru chromophore prior to relaxation by energy transfer. This mechanism of charge transfer ³MLCT states has been invoked to explain the photophysics of tetrametallic **Ru3Pt** complexes in which the quantum yields of emission are also attenuated much more than the lifetimes due to inefficient population of the emissive triplet.⁶⁸ In this proposed mechanism, charge separation competes with intramolecular energy transfer and must occur on the sub ns time-scale.

To summarize, the emission data for **Ru3Rh** do not support quenching by excited state electron transfer. In contrast **Ru3RhRu3** is weakly emissive compared to the **Ru3** chromophore, but the lifetime is barely attenuated, suggesting inefficient population of the emissive triplet due to excited state electron transfer from higher energy non-relaxed triplet or singlet MLCT states. A high energy state is needed to initiate charge separation because ET from the terminal Ru→dpp ³MLCT is endergonic by $\sim 0.13 \text{ eV}$.

Chemical Reduction. Reduction of **Ru3** and **Ru3Rh** with sodium amalgam was performed and monitored by UV-vis spectroscopy in attempt to correlate the spectral changes with the electrochemical assignments and to examine the stability of highly reduced species. In subsequent discussion, the chemical reduction results will be compared to the transient spectra of singly reduced species obtained by flash-quench experiments.

The bimetallic complex $[(\text{bpy})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})_2]^{4+}$ was reduced as a model for spectral changes accompanying single or double reduction of the dpp and bpy ligands (Figure S3). The results corroborate an earlier spectroelectrochemical study in DMF⁸⁸ with minor exceptions that our data include $\lambda < 320 \text{ nm}$ and six-electron reduction to the dianion. Upon the first dpp reduction, the low energy absorption maximum shifts from 532 to 470 nm. During the second dpp reduction, bands appear at 345 and 625 nm while absorptivity at 470 nm decreases. Reduction of four bpy ligands occurs in two steps from the +2 to 0 and 0 to -2 overall charge. Both steps are characterized by disappearance of the 293 nm $\text{bpy } \pi \rightarrow \pi^*$ absorption and growth of bands at 335 nm and 490-535 nm associated with reduced bpy.⁸⁸

Figure 4 shows spectral changes during reduction of **Ru3**⁶⁺ to **Ru3**⁴⁻ and reduction of **Ru3Rh(III)**⁷⁺ to **Ru3Rh(I)**³⁻. The two ($\mu\text{-Ru,Ru-dpp}$)^{0/-} couples differ in potential by less than 0.15 V, and it was not possible to separate single and double reduction as shown by the imperfect isosbestic points during progression from **Ru3**⁶⁺ to **Ru3**⁴⁻ (see SI). Similarly, the individual second reduction

of (μ -Ru,Ru-dpp) ligands and the first reduction of non-bridging dpp were not resolved. Therefore, the blue spectrum in Figure 4A, which is the last spectrum before bpy-based reductions occur, is assigned as the 5-electron reduced species. The red spectrum shows characteristics of bpy reduction with simultaneous reduction of the first bpy ligand of each $[\text{Ru}(\text{dpp})(\text{bpy})_2]^{2+}$. In the final spectrum four bpy ligands are reduced, and double reduction of the non-bridging dpp ligand is assumed since the potential of this couple should be less negative than the second bpy $^{0/-}$ couple.

Figure 4. Sodium amalgam reduction of $[(\text{bpy})_2\text{Ru}(\text{dpp})]_2\text{Ru}(\text{dpp})^{6+}$ (A) and $[(\text{bpy})_2\text{Ru}(\text{dpp})]_2\text{Ru}(\text{dpp})\text{RhCl}_2(\text{bpy})^{7+}$ (B) in CH_3CN . Intermediate spectra and data for $[(\text{bpy})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})_2]^{4+}$ are provided as Supporting Information.

Spectra of reduced $\text{Ru}_3\text{Rh}(\text{III})^{7+}$ species correlate well with those of Ru_3 . Electrochemical data showed Rh reduction coincident with the (μ -Ru,Ru-dpp) reduction, and the second spectrum is assigned to the $\text{Rh}(\text{I})$ species with two singly reduced (μ -Ru,Ru-dpp) ligands. The light blue spectrum is the final stage prior to bpy reductions, and is assigned as the species with all bridging ligands doubly reduced. The bpy reductions occur in two steps as discussed above. The $\text{Rh}(\text{I})$ complexes show higher absorptivity from 450 to 530 nm relative to the reduced Ru_3 chromophore consistent with the low energy absorption band of $\text{Rh}(\text{dpp})^{2+}$ having an extinction coefficient of $ca. 4000 \text{ M}^{-1} \text{ cm}^{-1}$ as shown in Figure S7.

The following conclusions regarding the chemical reduction results are summarized: (1) The complexes are stable in highly reduced states in dry CH_3CN , some of which might store charges during photocatalysis, (2) The spectral changes associated with reduction of the Rh center are thoroughly masked by those of the ligand reductions due to greater extinction coefficients of transitions associated with the latter, and (3) The first and second reductions could not be resolved, but the $1e^-$ reduced complex can be obtained by transient absorption experiments in the presence of a quencher (see below).

Hydrogen Production. For initial screening, hydrogen production was tested using Ru_3Rh under conditions previously optimized for Ru,Rh,Ru complexes (Table 2). 67 H_2 was obtained with < 3 turnovers, and marginal improvements were realized upon increasing the acidity to $0.67 \text{ M CF}_3\text{SO}_3\text{H}$ ($\text{TON} = 7$).

Noting the ligand-based (μ -Ru,Rh-dpp) $^{0/-}$ first reduction possibly mixed with $\text{Rh}^{\text{III/II}}$ character and the necessity of a second reduction to reduce Rh^{III} to Rh^{I} we hypothesized that the second intramolecular ET from (μ -Ru,Ru-dpp $^-$) could be accelerated by sequestering Cl^- . Photolysis with 2 equiv. $\text{CF}_3\text{SO}_3\text{Ag}$ improved the H_2 TON to 20 ± 2 in CH_3CN and 41 ± 2 in DMF suggesting that Cl^- removal indeed promotes the charge shift from ligand localized orbitals to the reactive Rh while opening vacant coordination sites for catalysis. Proton reduction by Ag^+ or Ag^0 was ruled out by control experiments in the absence of Ru_3Rh or with the Ru_3 chromophore and Ag^+ which produced a negligible amount of H_2 . The production of H_2 shows that photoinitiated electron collection at Rh^{I} can occur, but the process is inefficient compared to catalyst deactivation.

Figure 5. Photocatalytic H_2 production using $20 \mu\text{M Ru}_3\text{RhRu}_3$ in CH_3CN or $40 \mu\text{M Ru}_3\text{Rh}$ in DMF each containing $0.6 \text{ M H}_2\text{O}$, $0.67 \text{ M CF}_3\text{SO}_3\text{H}$, and $1.5 \text{ M } N,N\text{-dimethylaniline}$ (optimized conditions). Data for Ru_3RhRu_3 are shown with or without 2 equivalents of $\text{CF}_3\text{SO}_3\text{Ag}$ and a control experiment is shown using $40 \mu\text{M}$ of the Ru_3 chromophore and $80 \mu\text{M CF}_3\text{SO}_3\text{Ag}$.

Ru_3RhRu_3 was tested for H_2 production using conditions optimized for Ru_3Rh and achieved a significantly higher TON of 302 ± 15 (Figure 5, Table 1) with an initial rate and quantum yield of 33 h^{-1} and 0.002, respectively, using only $20 \mu\text{M}$ of the complex. The Ag^+ additive was necessary for high activity. Although the quantum efficiencies are lower than simpler Ru,Rh , or Ru,Rh,Ru photocatalysts, the overall TONs achieved by Ru_3RhRu_3 are significantly higher with the same light source. We did not attempt to improve the TON by manipulating photon flux or catalyst concentration. Although specific deactivation pathways are not well known, one major design difference is the location of a stored reducing equivalent immediately after reductive quenching. This electron is located in the (μ -Ru,Rh-dpp) ligand in Ru,Rh and Ru,Rh,Ru photocatalysts, but is stored remotely in the (μ -Ru,Ru-dpp) ligand of Ru_3RhRu_3 . The chemical reduction experiments above show that species with electrons stored in the (μ -Ru,Ru-dpp) ligands are very stable. Furthermore, Ru_3RhRu_3 is capable of storing several reducing equivalents since each Ru_3 chromophore should function independently with negligible coupling across Rh.

Table 2. Photocatalytic Hydrogen Production a

Complex	μM	$[\text{Ag}^+]$ μM	$[\text{H}^+]$ mM	H_2 (μL)	TON^c
Ru_3Rh	40	0	0.11	< 12	< 3
Ru_3Rh^b	40	80	0.67	165 ± 8	41 ± 2

Ru₃RhRu₃	20	0	0.67	54 ± 4	25 ± 2
Ru₃RhRu₃	20	40	0.67	650 ± 30	302 ± 15
Ru₃	40	80	0.67	6.3 ± 0.1	< 2
Ru₃RhRu₃^b	20	40	0.67	530 ± 50	240 ± 20
Ru₃Rh^d	65	0	0.11	480 ± 8	70 ± 10
Ru₃Rh₂Ru₃^e	65	0	0.11	1100 ± 100	150 ± 10

^aPhotolysis experiments were performed in CH₃CN using a 470 nm LED light source (flux = $2.36 \pm 0.05 \times 10^{19}$ photons min⁻¹) in a 4.5 mL solution and 15.8 mL headspace with 0.6 M H₂O, 1.5 M *N,N*-dimethylaniline (DMA), and CF₃SO₃H as the source of H⁺.
^bIn DMF. ^cTurnover number after 20 h.
^d[(Ph₂phen)₂Ru(dpp)RhCl₂(Ph₂phen)]³⁺, reference 35.
^e[(Ph₂phen)₂Ru(dpp)]₂RhCl₂³⁺, reference 67.

The different photophysical properties among **Ru₃Rh** and **Ru₃RhRu₃** as shown by emission data is a possible reason for a drastic difference in catalytic activity. In attempt to understand the properties of reduced intermediates and the photochemical reactions that trigger catalysis, steady state photo-reduction and nanosecond transient absorption measurements of the excited state and singly reduced species were performed.

Photo-reduction. Solutions of **Ru₃Rh** or **Ru₃RhRu₃** and 10 equiv. DMA were irradiated with a 405 nm diode laser in attempt to obtain evidence for production of Rh^I. The spectral changes and their respective quantum yields were compared to **Ru₃**. Upon photolysis of **Ru₃** two sequential spectral changes were observed (see Figures S8-S10 for spectra). The first reductive quenching reaction yields a (μ-Ru,Ru-dpp⁻) ligand as shown by decreased absorptivity of the low energy MLCT bands due to population of dpp(π*) orbitals, and was complete within 5 minutes with a quantum yield, Φ, of 9×10^{-4} . The second reduction was much less efficient and was not pursued to completion. A second photochemical reaction shows that the second (μ-Ru,Ru-dpp) ligand is also reduced via reductive quenching; however, this process is inefficient since bimolecular quenching by DMA competes with intramolecular quenching of the ³MLCT state by the (μ-Ru,Ru-dpp⁻) radical.

Photoreduction of **Ru₃Rh** and **Ru₃RhRu₃** occurred with Φ = 3×10^{-4} for the first UV-vis sensitive reaction. The three-fold decrease in Φ relative to **Ru₃**, despite the similar photophysical properties of all three molecules, is suggestive of reactivity beyond single reduction of a (μ-Ru,Ru-dpp) ligand. Given the three-fold reduction in quantum yields to achieve qualitatively similar spectroscopic changes for **Ru₃Rh** and **Ru₃RhRu₃**, we propose that the first observable spectral change corresponds to the photo-initiated collection of three electrons: two for reduction of Rh^{III} to Rh^I and one stored as (μ-Ru,Ru-dpp⁻). Similar to **Ru₃**, a shift in the isosbestic points indicated the end point of the first reduction.

Transient Absorption. Steady state photolysis of **Ru₃Rh** and **Ru₃RhRu₃** in the presence of an electron donor suggested that the same triply reduced state, i.e. Rh(I) / (μ-Ru,Ru-dpp⁻) is formed in both complexes with identical quantum yields. Thus, the disparity in photocatalytic efficiency is not explained by the efficiency of forming Rh(I). Nanosecond transient absorption experiments were pursued to compare the excited states and singly reduced states of **Ru₃Rh** and **Ru₃RhRu₃** and to correlate the data to differences in photocatalysis. The **Ru₃** chromophore was studied as a model for which the ³MLCT state decays exponentially to the ground state.

Figure 6A shows the transient difference spectra of **Ru₃**, **Ru₃Rh**, and **Ru₃RhRu₃** 80 ns after excitation with intensities normalized to the ground state bleach of **Ru₃** at 560 nm. The **Ru₃RhRu₃** contains twice as many Ru(II) centers; therefore, upon a single photon excitation, the pre-normalized ΔA is approximate-

ly half those of **Ru₃** and **Ru₃Rh**. The transients of each molecule are nearly identical and are qualitatively identical to those of [(bpy)₂Ru(dpp)Ru(bpy)₂]⁴⁺, supporting a terminal Ru(II)→dpp ³MLCT excited state assignment for each supramolecule.⁸⁹ The broad excited state absorptions for λ > 650 nm are consistent with LMCT states. The bleaches at 420 and 520 nm indicates depletion of Ru(II)→bpy and Ru(II)→dpp ¹MLCT absorptions. Excited state absorptions at 380 and 450 nm are appropriately assigned as transitions of the dpp radical anion, and the bleach at 330 nm is consistent with depletion of the dpp(π→π*) absorption due to population of the dpp(π*) orbital in the ³MLCT state.

Figure 6. **A.** Transient absorption difference spectra of **Ru₃**, **Ru₃Rh**, and **Ru₃RhRu₃** in CH₃CN. The intensities have been normalized to the 560 nm excited state bleach. **B.** Kinetics of excited state relaxation monitored at 560 nm with fits to the appropriate exponential or biexponential functions.

The excited states of **Ru₃**, **Ru₃Rh**, and **Ru₃RhRu₃** decay to the ground state without spectral shifts and with complete recovery of the ground state (Figure S11). Despite the qualitatively similar spectra, there is a significant difference in the relaxation kinetics as shown in Figure 6B. At all wavelengths, decay traces for **Ru₃** and **Ru₃Rh** are fit single exponential kinetics with lifetimes of 55 and 43 ns, respectively. In contrast, the decay kinetics of the 560 nm excited state bleach in **Ru₃RhRu₃** required a bi-exponential fit with time constants of 51 and 13 ns. Interestingly, for **Ru₃RhRu₃** a single exponential decay with a time constants around 50 ns was suitable for the 380 nm absorption. This disparity between double exponential fits in the spectral regions dominated by the Ru(III) bleach vs dpp radical absorptions is evidence for the decay of two non-equilibrated excited states.

The excited state decays provide insight into excited state electron transfer. For **Ru₃Rh**, the spectral similarity to **Ru₃**, the absence of spectral evolution, and the single exponential decay suggest that only the ³MLCT state is observed. The minor decreases in the steady emission quantum yield and the lifetime could arise from slow static intramolecular ET in which case the charge separated state would not be observed if charge recombination occurred more rapidly. Conversely, slight differences in radiative and non-radiative decay kinetics are equally valid explanations for the shorter lived excited state of **Ru₃Rh**, especially in consideration of the ligand-centered LUMO observed electrochemically.

The difference spectra of **Ru₃RhRu₃** are qualitatively identical to the **Ru₃** chromophore, but the relaxation kinetics of **Ru₃RhRu₃** required biexponential fits for wavelengths where spectral features are associated with oxidation of Ru(II). Decay kinetics of excited state absorptions of the dpp radical anion were fit to single exponential functions matching the longer lived component of the biexponential decay in the Ru(II) ground state bleach. These observations suggest that two states are formed within the 6 ns laser pulse. The 51 ns time constant matches the emission lifetime and is assigned to the ³MLCT excited state. The short-lived component is only found in the 560 nm bleach, suggesting a state with Ru(III) character in which the electron does not reside on the dpp ligand. We tentatively assign the short-lived state to a charge separated ³MMCT with the hole on a peripheral Ru(III) and the electron on Rh.

As discussed above, electron transfer from the emissive ³MLCT state is uphill by 0.13 eV and the previously used method of estimating $k_{ET} = (\tau^{-1} - \tau_0^{-1}) = 4 \times 10^6 \text{ s}^{-1}$ is not appropriate. The time constant for ET computed by this method would be 250 ns and is 5 times greater than decay by emission, but both states are observed immediately following the 6 ns laser pulse. As an alternative to static electron transfer, we propose that charge separation from hot triplet MLCT states of the central Ru(II) competes with energy transfer to the emissive ³MLCT state. The diminished emission quantum yield of **Ru₃RhRu₃** despite the marginal decrease in lifetime relative to **Ru₃** is also evidence for ET in competition with energy transfer. If the 77 K emission energy⁹⁰ of $[\text{Ru}\{(\text{dpp})\text{PtCl}_2\}_3]^{2+}$ is used to estimate E^{oo} of the $[\text{Ru}^{\text{II}}(\text{dpp})_3]^{2+} \rightarrow [\text{Ru}^{\text{III}}(\text{dpp})_2(\text{dpp}^-)]^{2+}$ charge transfer state, then ΔG_{ET} is favorable with a maximum value of -0.02 eV. The actual ΔG_{ET} will be more negative if the higher standard potential of the central Ru^{III/II} relative to the outer Ru^{III/II} is considered.

In order to compete with relaxation to the emissive triplet, ET from a hot state must be rapid. Charge separation prior to excited state relaxation is sometimes observed in multimetallic complexes and in charge injection into semiconductors.⁹¹ Excitation of $[(\text{bpy})_2\text{Ru}^{\text{II}}(\text{tpphz})\text{Co}^{\text{III}}(\text{bpy})_2]^{5+}$ yields a 13 Å Ru(III)-Co(II) charge separated state with the remarkable rate of $1.4 \times 10^{12} \text{ s}^{-1}$ and quantum yield of 0.77.⁹² X-ray emission spectroscopy and X-ray scattering revealed the non-equilibrium dynamics of optically dark states and found that initial charge transfer from Ru to an electronically excited state of Co is 20 times faster than local thermalization of the solvent.⁹³ Among bimetallic complexes, ultrafast experiments reveal the participation of hot and relaxed excited states on the charge transfer mechanisms within the same chromophore.⁹⁴

The kinetics of internal conversion, vibrational relaxation, intersystem crossing and energy transfer must be considered to estimate the rate of ET in photo-excited **Ru₃RhRu₃**. In $[\text{Ru}(\text{bpy})_3]^{2+}$, intersystem crossing to the triplet manifold occurs within 300 fs,⁹⁵⁻⁹⁸ but vibrational cooling may require several picoseconds.⁹⁹ Vibrational relaxation occurs within 800 fs in $[\text{Ru}\{(\text{dpp})\text{Ru}(\text{bpy})_2\}_3]^{8+}$ and dpp-bridged Os and Ru multimetallic complexes.^{100,81} Ultrafast singlet-singlet energy transfer (< 60 fs) may occur from nonthermalized states in competition with intersystem crossing and vibrational cooling.¹⁰⁰⁻¹⁰¹ The limiting value needed to estimate the minimum ET rate in **Ru₃RhRu₃** describes energy transfer from a vibrationally relaxed central $[\text{Ru}^{\text{II}}(\text{dpp})_3]^{2+} \rightarrow [\text{Ru}^{\text{III}}(\text{dpp})_2(\text{dpp}^-)]^{2+}$ ³MLCT to the outer $[(\text{bpy})_2\text{Ru}^{\text{II}}(\mu\text{-dpp})]^{2+} \rightarrow [(\text{bpy})_2\text{Ru}^{\text{III}}(\mu\text{-dpp}-)]^{2+}$ ³MLCT state. A similarly natured process was measured with a 600 fs time constant for $[\text{Os}\{(\text{dpp})\text{Ru}(\text{bpy})_2\}_3]^{8+}$,¹⁰¹ while slow energy transfer from a Ru→tpy ³MLCT state to a linked Fe→tpy ³MLCT state required 15 ps.¹⁰² Comparison of the 0.6 to 15 ps range for energy transfer with the 3 to 18 ps ET rates reported for bi- and trimetallic complexes^{103,87} suggests that 0.6 to 18 ps is a reasonable range

of time constants for ET in **Ru₃RhRu₃**. Slower ET on the 300 ps timescale such as from Ru(II)→phenazine ³MLCT states to Pd or Pt centers in $[(\text{bpy})_2\text{Ru}^{\text{II}}(\text{tpphz})\text{MCl}_2]^{2+}$ (M = Pt, Pd) photocatalysts^{31,55} is also reasonable. An investigation of the femtosecond dynamics of **Ru₃RhRu₃** is necessary to clarify the suggested kinetics.

The initial charge transfer will yield a species with ³MMCT character with a formally oxidized $[\text{Ru}^{\text{III}}(\mu\text{-dpp})_3]^{3+}$ core. This state could relax immediately to the ground state by charge recombination or could undergo further charge separation to the lower energy $[(\text{bpy})_2\text{Ru}^{\text{III}}(\mu\text{-dpp})]^{3+} \rightarrow \text{Rh}$ ³MMCT state by hole transfer. This step should be rapid considering that hole transfer over a longer distance in the similarly structured **Ru₃RuRu₃** from the $[(\text{dpp})_2\text{RuCl}_2]$ core to the outer Ru→dpp MLCT state was complete within a 300 fs laser pulse.⁸¹ Therefore, 13 ns decay of the transient signal is interpreted as relaxation of the long-distance 1.85 eV ³MMCT charge separated state (Scheme 1).

The ³MMCT state may be viewed as a donor-chromophore-acceptor triad that can relax by charge recombination through the intermediacy of the emissive ³MLCT state¹⁰⁴ or directly to the ground state. The k_{CR} of $7.7 \times 10^7 \text{ s}^{-1}$ is much slower than observed in Ru-Rh(bpy)₃ dyads where charge separation is much slower than recombination, even in weakly coupled donor/acceptor pairs.¹⁰⁵⁻¹⁰⁶ According to the classical expression of Marcus theory for electron transfer, the rate of charge recombination will be controlled by nuclear terms (the solvent reorganization energy, λ , and the change in free energy, ΔG^0) and an electronic term (H_{ET}).¹⁰⁷ The H_{ET} is a function of the coupling between the initial and final states and the virtual states involving bridge orbitals that promote ET through hole and/or electron transfer superexchange pathways.¹⁰⁸ At present, we cannot distinguish between charge recombination to the emissive ³MLCT state or directly to the ground state; however, with ΔG values of -0.13 and -1.85 eV, respectively, decay to the ground state is favored unless the ET is slowed by lying in the Marcus inverted regime.

Under photocatalytic conditions, the complexes are irradiated in the presence of a large concentration of a sacrificial reductant, prompting investigation of the transient absorption data in the presence of DMA. Figure 7 shows the 60 ns difference spectra of **Ru₃**, **Ru₃Rh**, and **Ru₃RhRu₃** after quenching. The spectrum of **Ru₃**⁵⁺ contains a strong absorption band from 350 to 500 nm, a slight bleach of the **Ru₃** low energy ¹MLCT absorption (550 nm), and a low-intensity absorption for $\lambda > 600 \text{ nm}$. These changes are consistent with the spectra of the 1e⁻ reduced species obtained by steady state photolysis or Na/Hg reduction. The intense feature at 460 nm absorption is a characteristic feature of a $(\mu\text{-Ru,Ru-dpp}^-)$ radical anion in good agreement with the spectrum of singly reduced $[(\text{bpy})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})_2]^{4+}$.¹⁰⁹

The transient spectrum of **Ru₃Rh** after reductive quenching shows weak absorptions at 450 nm and at 620 nm. The one-electron reduced spectrum of **Ru₃Rh** lacks the strong 460 nm absorption of the $(\mu\text{-Ru,Ru-dpp}^-)$ radical anion as explained by electrochemical data that showed the first reduction is largely localized on the $(\mu\text{-Ru,Rh-dpp})$ ligand. The result suggests that reductive quenching of the terminal ³MLCT excited state is followed by fast electron transfer to the $(\mu\text{-Ru,Rh-dpp})$ ligand. In this experiment, bimolecular quenching by DMA is rate-limiting and the $(\mu\text{-Ru,Ru-dpp}^-)$ radical anion was not observed as an intermediate.

Figure 7. Transient absorption difference spectra of **Ru₃**, **Ru₃Rh**, and **Ru₃RhRu₃** after 60 ns in CH₃CN following reductive quenching with DMA.

The transient difference spectrum of quenched **Ru₃RhRu₃** shows a small absorption 450 nm and minor changes for the rest of the spectrum. The 620 nm band of reduced **Ru₃Rh** is absent, showing that the 4- and 7-metal supramolecules have different electronic structures after 1e[−] reduction. In relation to the electrochemical data these changes are consistent with a Rh-based LUMO for **Ru₃RhRu₃** for which reduction would induce minimal changes in the singlet charge transfer absorptions of the Ru(II) centers. Disproportionation of a formally Rh^{II} center is expected, but the subsequent kinetics were not observed due to the weak signals and second order kinetics with a low initial concentration of Rh^{II}. The excited state processes are summarized in Scheme 1.

Scheme 1. Summary of excited state charge separation and quenching in the Ru₃RhRu₃ heptametallic complex.^a

^a (a) Excited state charge separation in **Ru₃RhRu₃** from high energy ³MLCT states of the central [Ru(dpp)₃]²⁺. The emissive ³MLCT and ³MMCT₁ are populated within the 6 ns laser pulse and the 0.6 to 18 ps rate of formation of the ³MMCT is estimated based on available literature data (see text). The rapid decay from the hot upper-lying MLCT levels to the MMCT state(s) can also involve singlet states, not necessary triplet states as is shown here

for simplicity. (b) Reductive quenching followed by ground state electron transfer. Abbreviations: k_{ISC} = rate of intersystem crossing from singlet to triplet MLCT states, k_{ET} = rate of intramolecular electron transfer, k_{EN} = rate of intramolecular energy transfer, k_{HT} = rate of intramolecular hole transfer, k_{CR} = rate of charge recombination, k_Q = bimolecular rate constant for reductive quenching.

CONCLUSIONS

In summary, mixed metal supramolecular complexes **Ru₃Rh** and **Ru₃RhRu₃** have been designed to function as antenna photocatalysts for production of H₂. While the tetrametallic complex is an ineffective photocatalyst with turnover numbers near 40, the heptametallic complex yields over 300 turnovers of H₂. The difference in activity has been traced to differences in the electrochemical and photophysical properties. While the LUMO is largely ligand-localized in **Ru₃Rh**, it is localized on Rh in **Ru₃RhRu₃**, presumably due to a slight decrease in Rh d-orbital energies induced by coordination of the weaker σ -donating, but better π -accepting dpp ligand. The effects of this energy difference are clear in the electron transfers that initiate catalysis.

The transient absorption experiments suggest **Ru₃RhRu₃** forms a ³MMCT state with an outermost oxidized Ru and a reduced Rh and a 13 ns lifetime while **Ru₃Rh** does not undergo excited state electron transfer. The energetics and kinetics of this charge separation are notable: the ³MMCT state is endergonic with respect to the relaxed ³MLCT state and it is formed rapidly on the sub-nanosecond timescale. Additionally, the steady state emission intensity of **Ru₃RhRu₃** is largely quenched relative to **Ru₃** while the lifetimes are similar suggesting incomplete population of the emissive state after excitation. Taken together, these observations are evidence for charge separation from upper ³MLCT states associated with the central Ru(II) meaning electron transfer necessarily competes with energy transfer to the lowest emitting MLCT state of the outermost Ru(II). During photocatalysis, the reducing equivalents are provided by a sacrificial reagent in large excess. Transient absorption spectra were recorded for the singly reduced species obtained by reductive quenching and show that reduced **Ru₃Rh** and **Ru₃RhRu₃** do not share the (μ -Ru,Ru-dpp[−]) radical anion of reduced **Ru₃**. In addition, the spectra of singly reduced **Ru₃Rh** and **Ru₃RhRu₃** differ significantly with singly reduced **Ru₃RhRu₃** showing a nearly featureless spectrum. This result supports fast intramolecular ET to yield a (μ -Ru,Rh-dpp[−]) radical anion in reduced **Ru₃Rh**, and a Rh-reduced complex after quenching of **Ru₃RhRu₃**.

The experiments presented here pertain only to the initial catalyst activation steps, but further electron transfer reactions are needed during catalysis and the differences in excited state and reduced species might be extrapolated to catalytic intermediates. The facile reduction of the Rh center in the excited state or quenched state of **Ru₃RhRu₃** is clearly advantageous in the photocatalytic potential of this heptametallic complex. The supramolecule features an exceptional absorption cross section due to the cumulative absorbance of six Ru(II) chromophores and begins to expand the ratio of chromophores to catalytic centers while efficiently transferring charge to the Rh catalyst. The unusual mechanism of long distance charge separation from non-relaxed ³MLCT states provides a pathway unavailable to supramolecules with low chromophore: catalyst ratios (i.e. 1:1 Ru,Rh). Another feature that deserves further experimentation is the ability to store multiple reducing equivalents in the four (μ -Ru,Ru-dpp) bridging ligands upon reductive quenching. This is a clear advantage if H₂-evolving reactions are slower than excited state relaxation, charge recombination, or quenching. We hope the results presented in this article will inspire research to better mimic Photosystem I and

II by using antenna-type chromophores in supramolecular homogeneous photocatalysis.

Experimental Details

Instrumentation. Cyclic and Osteryoung square wave voltammograms were recorded using Bio-Analytical System (BAS) Epsilon potentiostat using a Pt disc working electrode, Pt wire counter electrode, and Ag/AgCl (3M NaCl) reference electrode in freshly distilled, Ar-saturated CH₃CN. Tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) was used as the supporting electrolyte for all electrochemical experiments. Electronic absorption spectra were measured in CH₃CN using a Hewlett-Packard 8453 diode array spectrophotometer. Sodium amalgam reductions were performed in two-compartment homemade vessels consisting of quartz cuvettes separated from a second chamber by a fine glass frit. Small portions of analyte solutions were briefly exposed to the amalgam and transferred back to the optical cuvette for data collection. The sequence was repeated until no further spectral changes occurred or until thermal decomposition was noticed. Steady state emission spectra were recorded using a Photon Technologies, Inc. (PTI) QuantaMaster Model QM-200-45E, and data are corrected for PMT response. Quantum yields of emission were measured relative to [Os(bpy)₃](PF₆)₂ in deoxygenated CH₃CN (Φ = 0.0046). 77 K measurements were performed in a butyronitrile frozen glass rigid matrix in 5 mm NMR tubes submerged in liquid nitrogen in a double walled quartz finger dewar. Lifetimes measurements at 77 K were performed using a pulsed PTI PL2300 nitrogen laser equipped with a PTI PL 201 tunable dye laser. The signal was digitized and visualized using a LeCroy 9361 300 MHz oscilloscope with final data collected as the average of 300 decay curves.

Transient Absorption. Samples for transient absorption were prepared such that the ground state absorbance at wavelengths above 350 nm were less than 1 and the absorbance at 532 nm was approximately 0.5–0.7. All samples were prepared in anhydrous CH₃CN in septum-sealed cuvettes and deoxygenated with a stream of argon. The spectra of one-electron reduced species were recorded in the presence of *N,N*-dimethylaniline (20 μ M) at a concentration sufficient to induce rapid quenching. Since the reaction is irreversible, the sample was changed frequently for full data collection. Samples were pumped with a continuously tunable OPO (Spectral Physics QuantaRay Lab170) pumped by a Q-switched Nd:YAG at 355 nm. The instrument was operated at 5 Hz with 3 mJ per pulse and ~8 ns pulse width. The sample was probed at 90° with a pulsed 75 W Xe arc lamp. The probe light was filtered where appropriate and focused on an ISA monochromator. The signal was detected using a Hamamatsu R955 PMT and digitized with an oscilloscope. Kinetic data were fit to single or double exponentials decays as appropriate. Emission lifetimes in solution were recorded using the same system.

Materials. [(bpy)₂RuCl₂] $\cdot$ 2H₂O, RuCl₃ $\cdot$ *n*H₂O, and NH₄PF₆ were purchased from Strem Chemicals. Silver trifluoromethanesulfonate, RhCl₃ $\cdot$ 3H₂O, and spectrophotometric grade acetonitrile were purchased from Alfa Aesar. *N,N*-dimethylaniline, trifluoromethanesulfonic acid, trifluoroacetic acid, 2,2'-bipyridine (bpy), and 2,3-bis(2-pyridyl)pyrazine (dpp) were purchased from Aldrich. Spectroscopic grade DMF was purchased from Honeywell. Bu₄NPF₆ for electrochemical measurements was prepared by metathesis of Bu₄NCl with HPF₆ and recrystallized several times from hot ethanol. [Rh(dpp)₂Cl₂]PF₆ was prepared by literature methods.¹¹⁰ The trimetallic complex [(bpy)₂Ru(dpp)]₂Ru(dpp)](PF₆)₆ was prepared using a modified literature procedure.⁸¹ A mixture of [(bpy)₂Ru(dpp)]₂Ru(Cl₂)](PF₆)₄ and AgOTf (4 equiv.) was

refluxed in ethanol for 4 h. The hot mixture was transferred dropwise to a warm solution of dpp (5 equiv.) in an equal volume of ethylene glycol and refluxed for 4 days. The solution was cooled and decanted into a stirred aqueous solution of NH₄PF₆ to induce precipitation. The precipitate was collected by vacuum filtration, washed thoroughly with water and ether, and dried in an oven at 80 °C. Purification was achieved by size-exclusion chromatography on Sephadex LH-20 eluting with 2:1 ethanol/acetonitrile. Typical yields were 75–80%.

Synthesis of [RhCl₃(bpy)(DMF)]. A solution of RhCl₃ $\cdot$ 3H₂O (0.101 g) was dissolved in 2 mL DMF with gentle heating. A solution of bpy (0.060 g, 1 equiv.) in 1 mL DMF was added. The mixture was heated at 60 °C for 3 h, cooled to ambient temperature, and triturated with 20 mL diethyl ether. The yellow solid was filtered, washed thoroughly with water and ether, and dried in a 70 °C oven to provide 0.107 g of the desired complex in 63 % yield. ¹H NMR (400 MHz (CD₃)₂SO, 27 °C, *fac*-isomer): δ 9.62 (d, *J* = 5.6 Hz, 1H), 8.97 (d, *J* = 5.2 Hz, 1H), 8.72 (d, *J* = 8.0 Hz, 1H), 8.67 (d, *J* = 8.4 Hz, 1H), 8.36–8.33 (m, 2H), 8.29 (t, *J* = 7.6 Hz, 1H), 7.92 (t, *J* = 6.4 Hz, 1H), 7.82 (t, *J* = 6.4 Hz, 1H), 3.19 (s, 3H), 3.18 (s, 3H).

Synthesis of [(bpy)₂Ru(dpp)]₂Ru(dpp)RhCl₂(bpy)](PF₆)₇. To a warm solution of [(bpy)₂Ru(dpp)]₂Ru(dpp)](PF₆)₆ (0.132 g) in 2:1 ethanol:water (15 mL) was added solid [RhCl₃(bpy)(DMF)] (0.023 g, 1 equiv.). The mixture was refluxed for 3 h. After cooling to ambient temperature, an excess of solid NH₄PF₆ (*ca.* 0.25 g) was added. Water (35 mL) was added to induce precipitation. The crude solid was collected by vacuum filtration, washed with water and dried. Purification was achieved by size-exclusion chromatography on LH-20 eluting with 2:1 ethanol:acetonitrile. Fractions which were isoabsorptive throughout the UV and visible and exhibited identical quantum yields of emission when excited at 540 nm were combined and concentrated to *ca.* 1–2 mL. Precipitation in diethyl ether afforded 0.110 g of the product as a purple solid in 70% yield. ESI–HRMS: *m/z* 1342.9967 [M–2(PF₆)]²⁺ *calcd.* 1342.9963; 1270.5181 [M–3(PF₆)]²⁺ (*calc'd.* 1270.5412); 847.0126 [M–3(PF₆)]³⁺ *calcd.* 847.0275; 798.6936 [M–4(PF₆)]³⁺ (*calcd.* 798.6881); 599.0185 [M–4(PF₆)]⁴⁺ (*calcd.* 599.0161).

Synthesis of [(bpy)₂Ru(dpp)]₂Ru(dpp)]₂RhCl₂](PF₆)₁₃. The complex was prepared by the reaction of RhCl₃ $\cdot$ *n*H₂O with two equivalents of [(bpy)₂Ru(dpp)]₂Ru(dpp)](PF₆)₆ in refluxing 2:1 ethanol/water for 4 h. The crude mixture was precipitated in aqueous NH₄PF₆, filtered, and purified by size-exclusion chromatography on Sephadex LH-20. Precipitation from ether afforded the product as a purple solid in 55–65% yield. The complex ionized as [M–3PF₆]³⁺ by high resolution ESI with *m/z* = 1629.0095 for [Ru₃RhCl₂Ru₃](PF₆)₁₀ (*calcd.* 1629.0015).

ASSOCIATED CONTENT

Supporting Information

Tabulated photophysical and electrochemical data, photochemical or chemical reduction spectra, and transient absorption data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interests.

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