A new Ru\textsuperscript{II}Rh\textsuperscript{III} bimetallic with a single Rh–Cl bond as a supramolecular photocatalyst for proton reduction†

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A new Ru\textsuperscript{II}Rh\textsuperscript{III} structural motif \((\text{bpy})_2\text{Ru}(dpp)\text{RhCl}(tpy))^4+ with one halide on the Rh\textsuperscript{III} center demonstrates light-driven proton reduction ability, establishing that two halide ligands are not mandatory despite all prior systems containing a cis-RhCl\textsubscript{2} catalytic site. This new design provides a novel approach to modulate Rh\textsuperscript{III} redox behavior and catalytic activity with insight into catalytic intermediates.

Solar water splitting to generate H\textsubscript{2} has gained considerable interest as a method to produce an alternative fuel to meet future energy demands.\textsuperscript{1} Robust systems that absorb visible light, facilitate electron transfer and catalyze H\textsubscript{2} formation are required for achieving solar energy conversion. To this end, supramolecular complexes incorporating separate units with individual properties offering unique functions to the entire molecule have been designed.\textsuperscript{2} In contrast to the bimolecular electron transfer (ET) reactions in the multi-component photocatalytic water reduction systems developed in the 1970s,\textsuperscript{3} the supramolecular approach exploits intramolecular ET. Supramolecular complexes coupling metal-based chromophores to a catalytic center photocatalytically reduce water to H\textsubscript{2} under various conditions.\textsuperscript{4} Impediments to engineering supramolecular complexes for solar H\textsubscript{2} production include the small number of molecular systems capable of photochemically collecting reducing equivalents and the lack of fundamental understanding of multielectron photochemistry.

In seeking an efficient and robust supramolecular photocatalyst, a series of Ru\textsuperscript{II}Rh\textsuperscript{III}-containing supramolecular complexes coupling polypyridyl Ru\textsuperscript{II} chromophores to a Rh\textsuperscript{III} catalytic center via a bridging ligand dpp (2,3-bis(2-pyridyl)pyrazine) were explored. The first photocatalyst of this type, \([(\text{bpy})_2\text{Ru}(dpp)\text{RhCl}(tpy)]^+\text{PF}_6\), inspired the development of Ru\textsuperscript{II}Rh\textsuperscript{III} trimettalics with the architecture of \([(\text{TL})_2\text{Ru}(dpp)\text{RhCl}_2]^+\text{PF}_6\), (TL = bpy, 1,10-phenanthroline (phen), or 4,7-diphenyl-1,10-phenanthroline (Ph\textsubscript{2}phen); X = Cl or Br) to explore factors that control photoinitiated electron collection (PEC) and catalytic activity.\textsuperscript{5} The presence of a Rh(d*)-based LUMO (lowest unoccupied molecular orbital) in the Ru\textsuperscript{II}Rh\textsuperscript{III} complex is a key energetic requirement for PEC at the Rh\textsuperscript{III} catalytic center.\textsuperscript{6} PEC on the Rh\textsuperscript{III} center forms the proposed active species, Ru\textsuperscript{II}Rh\textsuperscript{III}, upon sequential reductive quenching of the \(^3\)MLCT (metal-to-ligand charge transfer) excited state by a sacrificial electron donor.\textsuperscript{6b} Recent studies also show that two Ru\textsuperscript{II} chromophores are not required for photocatalysis. Active Ru\textsuperscript{II}Rh\textsuperscript{III} bimetallics require a Ru-based LUMO and steric protection around the photogenerated Rh\textsuperscript{III} center to prevent dimerization that leads to catalytic deactivation.\textsuperscript{6g} These Ru\textsuperscript{II}Rh\textsuperscript{III}Ru\textsuperscript{II} and Ru\textsuperscript{II}Rh\textsuperscript{III} motifs represent homogenous single-component photocatalysts for H\textsubscript{2} generation.

To the best of our knowledge, all reported dpp-bridged Ru\textsuperscript{II}Rh\textsuperscript{III} and Ru\textsuperscript{II}Rh\textsuperscript{III}Ru\textsuperscript{II} photocatalysts have two labile halide ligands (Cl or Br) on the Rh\textsuperscript{III} center. Here we propose the replacement of one halide ligand with an N donor of a polypyridyl ligand as a means to (1) modulate the electrochemical properties of the catalytic Rh center, (2) test the hypothesis that only one labile halide ligand is needed in the dpp-bridged Ru\textsuperscript{II}Rh\textsuperscript{III} pre-catalyst for photocatalytic water reduction, (3) expand the scope of structural designs for competent Rh-containing supramolecular photocatalysts, and (4) provide a new mechanism of steric protection of the Rh\textsuperscript{III} center.

The ligand tpy (2,2′:6′,2″-terpyridine) has been widely used in coordination chemistry with meridional tridentate (η\textsuperscript{3}) chelation being the most common coordination mode. Taking advantage of the tridentate binding mode, the new Ru\textsuperscript{II}Rh\textsuperscript{III} complex, \([(\text{bpy})_2\text{Ru}(dpp)\text{RhCl}(tpy)]^+\text{PF}_6\), has been prepared to test the hypotheses described above. For comparative purposes, we have studied the cis-RhCl\textsubscript{2} analogue \([(\text{bpy})_2\text{Ru}(dpp)\text{RhCl}_2(bpy)]^+\text{PF}_6\) (Ru\textsuperscript{II}Rh\textsuperscript{III}Cl\textsubscript{2}(bpy)). Herein we report the electrochemical, photochemical, and catalytic properties...
of these two RuRh supramolecular complexes. It was found that RuII RhIII(tpy) is an active photocatalyst for H₂ production. The results suggested that two Rh–Cl bonds were not required for photocatalysis. All synthetic details, including 1H NMR spectra, are provided in the ESI† (Fig. S1–S3).

Cyclic voltammetry (CV) was utilized to investigate the influence of TL variation on the redox properties of the RhIII center. Fig. 1 shows that both complexes possess a reversible RuII couple at a similar potential (ca. 1.60 V vs. Ag/AgCl) indicating that the Ru(dr) orbital energy is insensitive to the variation of the remote TL on RhIII. Reductively, RuIII RhIICl₂(bpy) shows a quasi-reversible RhIII couple at –0.43 V (ΔE = 60 mV), an irreversible RhI/I couple at EP = –0.79 V, and a reversible dpp0+ at –1.01 V. The assignments are confirmed by coulometric experiments and consistent with [(bpy)₂Ru(dpp)RhCl₂(phen)]³⁺. In RuIII RhIII Cl(tpy), the first reduction appears as an irreversible wave at EP = –0.35 V vs. Ag/AgCl and comprises 2e⁻/molecule. The appearance of the 2Cl⁻/Cl₂ oxidation couple in the CV of the reduced solution (Fig. S4, ESI†) supports the dissociation of the Cl⁻ ligand from RhIII upon reduction, providing an assignment of RhIII/I for the first reduction. Unlike RuIII RhIICl₂(bpy), very little current is seen in the anodic wave associated with the first reduction even upon increasing the scan rate to 1.0 V s⁻¹ (Fig. S5, ESI†), establishing that Cl⁻ loss is faster in the tpy complex than the bpy complex. The RuIII RhIII Cl(tpy) geometry requires the Cl⁻ ligand to be trans to dpp whereas RuIII RhIICl₂(bpy) has one Cl⁻ trans to dpp and one Cl⁻ trans to tpy. This uncovers an important consideration in controlling the rate of halide loss critical to providing an active site in the reduced RhI species. The single RhIII/I couple in RuII RhIII Cl(tpy) is in marked contrast to two separate Rh reductions in RuII cis-RhIII Cl₂ bimetals. The effect is traced to rapid halide loss and instability of the 1e⁻ reduced species of RuII RhIII Cl(tpy) toward disproportionation whereas the 1e reduced RuIII RhIICl₂(bpy) likely possesses dpp⁻ character and is comparatively more stable. The Ru-based first oxidation and Rh-based first reduction establish the Ru(dr) HOMO and the Rh(dr*) LUMO in both complexes with a lowest-lying MMCT (metal-to-metal charge transfer) excited state predicted to undergo PEC at the RhIII center producing active photocatalysts.

The electronic absorption spectra of RuII RhIII Cl(tpy) and RuII RhIICl₂(bpy) are provided in Fig. S6 (ESI†). The UV spectrum is dominated by intense ligand centered π → π* transitions. RuII RhIII Cl(tpy) displays a higher absorption intensity (ε = 74 200 M⁻¹ cm⁻¹) at 280 nm than RuII RhIICl₂(bpy) (ε = 59 300 M⁻¹ cm⁻¹). A broad band between 400 and 500 nm is 1MLCT in character with lower energies attributed to Ru(dr) → dpp(π⁻) 1MLCT transitions and higher energies attributed to Ru(dr) → bpy(π⁻) 1MLCT transitions. The spectra of the two bimetals are nearly identical in the visible region, indicating that the structural difference at Rh does not impact the 1MLCT transitions.

Emission spectroscopy was used to investigate the photophysical properties of these RuII RhIII complexes. The emission spectra of RuII RhIII Cl₂(bpy), RuII RhIICl₂(tpy), and a model complex [[(bpy)₂Ru₂(dpp)][PF₆]₄ were recorded at room temperature (Fig. S7, ESI†) and 77 K (Table S1, ESI†). Both RuII RhIII complexes are weak emitters at room temperature from the 1MLCT state (λem = 750 nm, φem = 1.3 × 10⁻⁴, τ = 40 ns for RuII RhIICl₂(bpy); λem = 6.5 × 10⁻⁵, τ = 30 ns for RuII RhIICl₂(tpy)) and are dramatically quenched compared to the model complex [[(bpy)₂Ru₂(dpp)][PF₆]₄ (φem = 8.9 × 10⁻⁴, τ = 130 ns). The quenching is due to intramolecular electron transfer from dpp to Rh to populate the 3MMCT excited state. Using kₗ and kᵣ from this model complex, kᵣ was obtained as 2.6 × 10⁶ s⁻¹ for RuIIRhIIICl(tpy) and 1.7 × 10⁵ s⁻¹ for RuIIRhIICl₂(bpy). Intramolecular ET is impeded at 77 K and results in a long-lived 3MLCT emission. At 77 K in an ethanol/methanol (4 : 1, v/v) glass matrix, the emissions of RuIIRhIIICl₂(tpy) and RuIIRhIICl₂(bpy) are blue-shifted to 715 nm (λem) with a dramatic increase in the intensity and lifetime (τ = 2.3 µs for RuIIRhIIICl₂(bpy) and 2.1 µs for RuIIRhIII Cl(tpy)) comparable to 2.4 µs for the model.

Spectrophotochemical and spectroelectrochemical analyses of the title RuII RhIII complexes demonstrated PEC at the RhIII center. PEC is essential for RuII RhIII systems to provide active photocatalysts. Fig. 2 and Fig. S8 (ESI†) illustrate spectroscopic changes which accompany reduction at –0.65 V for RuII RhIICl₂(tpy) and –0.95 V vs. Ag/AgCl for RuII RhIICl₂(bpy) to generate the RhI species. The changes upon reduction are analogous to the changes upon the photolysis of RuII RhIICl₂(tpy) and RuII RhIICl₂(bpy) in the presence of N,N-dimethylaniline (DMA), establishing both complexes as molecular devices for PEC. Upon reduction, the Ru(dr) → dpp(π⁻) 1MLCT transitions blue shift, consistent with dpp bound to electron rich RhI. Reduction of RhIII is...
accompanied by halide loss as the Rh\(^{I}(d^8)\) reduces its coordination number to adopt a square planar geometry. This demonstration of PEC establishes Ru\(^{II}Rh^{III}Cl(tpy)\) as the first Ru\(^{II}Rh^{III}\) system that undergoes PEC where the Rh\(^{III}\) is coordinated to a single halide, removing the previously employed design constraint that two coordinated halides are needed to promote PEC in Ru\(^{II}Rh^{III}\) supramolecules as well as greatly expanding the potential supramolecular motifs available as single-component photocatalysts for proton reduction to produce H\(_2\) fuel.\(^5\)

Reductive quenching of the 3MLCT excited state by DMA (\(E(DMA/AgCl) = 0.86\) V vs. Ag/AgCl) is reported as the primary pathway to generate Ru\(^{II}Rh^{I}\) during the photolysis of Ru\(^{II}Rh^{III}\)

Using the ground state reduction potential, \(E(CAT^{III}/CAT^{n-1})\), of 0.35 V for Ru\(^{II}Rh^{III}Cl(tpy)\) and 0.43 V for Ru\(^{II}Rh^{III}Cl_2(bpy)\), and \(E^{0,0}\) estimated from \(\lambda_{\text{em}}\) (77 K) as 1.73 eV, the thermodynamic driving force for reductive quenching, \(E_{\text{reduction}}\) is determined to be 0.52 V for Ru\(^{II}Rh^{III}Cl(tpy)\) and 0.44 V for Ru\(^{II}Rh^{III}Cl_2(bpy)\). This driving force demonstrates that reduction of Ru\(^{II}Rh^{III}\) to Ru\(^{II}Rh^{I}\) using DMA is thermodynamically favorable.

Quenching of the new Ru\(^{III}Rh^{III}Cl(tpy)\) is more favorable than Ru\(^{II}Rh^{III}Cl_2(bpy)\) and [(bpy)Ru(dpp)]\(^{2+}\)RhCl\(_2\)(PF\(_6\))\(^{-}\)(0.49 V).\(^5\) Greater driving force for reductive quenching facilitates the formation of the Rh\(^{I}\) active species and is hypothesized to enhance the photocatalytic reactivity for proton reduction.

Photocatalytic H\(_2\) production from water–organic mixtures using Ru\(^{II}Rh^{III}Cl(tpy)\) was studied to test the hypothesis that two photolabile halides are not necessary for H\(_2\) generation in the dpp-bridged Ru\(^{II}Rh^{III}\) photocatalysts. As shown in Fig. 3, in CH\(_3\)CN Ru\(^{II}Rh^{III}Cl(tpy)\) produced 9.8 \(\mu\)mol H\(_2\) with a TON of 33 and an overall quantum efficiency of 0.08% in 10 hours. Photocatalytic H\(_2\) production was also observed in DMF and acetone with ca. 17 \(\mu\)mol H\(_2\) and a TON of 58 showing improvements relative to strongly ligating CH\(_3\)CN.\(^4\)

Photocatalytic H\(_2\) production by Ru\(^{II}Rh^{III}Cl_2(bpy)\) and trinmetallic [(bpy)\(_2\)Ru(dpp)]\(^{2+}\)RhCl\(_3\)(PF\(_6\))\(^{-}\) was also conducted in DMF and CH\(_3\)CN for comparison (Fig. S10 and S11, ESI†). The catalytic activity of Ru\(^{II}Rh^{III}Cl(tpy)\) is better than Ru\(^{II}Rh^{III}Cl_2(bpy)\) and comparable to [(bpy)\(_2\)Ru(dpp)]\(^{2+}\)RhCl\(_3\)(PF\(_6\))\(^{-}\) under similar conditions (Table S2, ESI†). The Ru\(^{II}Rh^{I}\) state is proposed as the active species for proton reduction.\(^6\) For Ru\(^{II}Rh^{III}Cl_2(bpy)\), electrochemical reduction leads to the formation of [(bpy)Ru\(^{II}Rh^{III}Cl_2(bpy)\)]\(^{2+}\) following halides loss, confirmed by ESI mass spectrometry (\(m/z = 302.3\); calcld = 302.3, M = [(bpy)Ru(dpp)-Rh\(^{III}Cl\)(bpy)]\(^{3+}\)) (Fig. S12 and S13, ESI†). In Ru\(^{II}Rh^{III}Cl(tpy)\), Cl\(^{-}\) dissociation was also observed (Fig. S4, ESI†). Electrochemical reduction of the simple model [Rh\(^{III}Cl(tpy)dpp\)](PF\(_6\)) showed halide loss (Fig. S14, ESI†) to form [Rh\(^{II}Cl(tpy)dpp\)]\(^{-}\) (\(m/z = 570.0\); calcld = 570.0, M = [(dpp)]\(^{-}\)) (Fig. S15, ESI†). The variable \(\eta^3\)-tpy or \(\eta^3\)-tpy coordination, of which the latter has been seen in some Re and Rh complexes,\(^8\) facilitates the necessary geometry change as Rh\(^{III}\) is reduced to Rh\(^{I}\) to form [(bpy)Ru\(^{II}Rh^{III}Cl(tpy)dpp\)]\(^{-}\) (Fig. S16, ESI†). Additional support for the formation of [(bpy)Ru(dpp)Rh\(^{III}\)]\(^{3+}\) is provided in the detailed photoysis studies of Ru\(^{II}Rh^{III}Cl(tpy)\).

In conclusion, a new photocatalyst, Ru\(^{II}Rh^{III}Cl(tpy)\), with one Cl ligand and a tridentate ligand on the Rh\(^{III}\) center has shown light-driven H\(_2\) production from water. This established that two labile halide ligands on the Rh\(^{III}\) center are not mandatory for photocatalysis. The replacement of one halide with a pyridyl ligand successfully increases the rate of halide loss and the \(E_{\text{reduction}}\) for reductive quenching of the 3MLCT excited state by DMA. Increased driving force for intramolecular electron transfer from reduced dpp to Rh also increases photocatalytic efficiency. This study shows that photocatalytic activity can be controlled by tuning the Rh redox properties and demonstrates a new approach to design photocatalysts for H\(_2\) generation.

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Notes and references


