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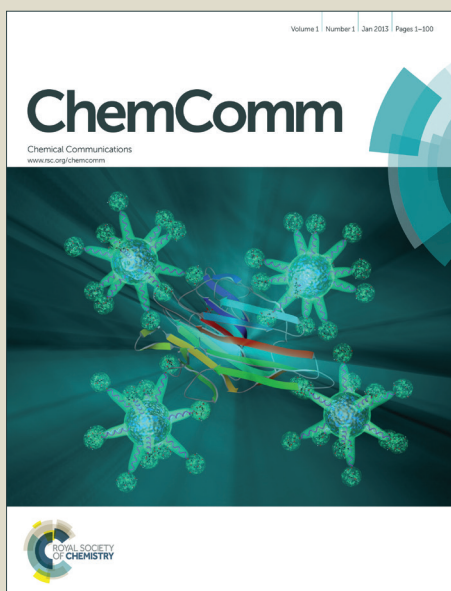
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A New Ru^{II}Rh^{III} Bimetallics with a Single Rh-Cl Bond as a Supramolecular Photocatalyst for Proton Reduction

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

Solar water splitting to generate H$_2$ has gained considerable interest as a method to produce an alternative fuel to meet future energy demands.[1] Robust systems which absorb visible light, facilitate electron transfer and catalyze H$_2$ 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.[2] In contrast to the bimolecular electron transfer (ET) reactions in the multi-component photocatalytic water reduction systems developed in the 1970's,[3] the supramolecular approach exploits intramolecular ET. Supramolecular complexes coupling metal-based chromophores to a catalytic center photocatalytically reduce water to H$_2$ under varied conditions.[4] Impediments to engineering supramolecular complexes for solar H$_2$ production include the small number of molecular systems capable of photochemically collecting reducing equivalents and the lack of fundamental understanding of the multielectron photochemistry.

In seeking an efficient and robust supramolecular photocatalyst, a series of Ru^{II}Rh^{III}-containing supramolecular complexes coupling polypyridyl Ru^{II} chromophores to a Rh^{III} catalytic center via a bridging ligand dpp (2,3-bis(2-pyridyl)pyrazine) were explored. The first photocatalyst of this type, [{(bpy)$_2$Ru(dpp)}$_2$RhCl$_2$](PF$_6$)$_5$, inspired the development of Ru^{II}Rh^{III}Ru^{II} trimetallics with the architecture of [{(TL)$_2$Ru(dpp)}$_2$RhX$_2$](PF$_6$)$_5$ (TL = bpy, 1,10-phenanthroline (phen), or 4,7-diphenyl-1,10-phenanthroline (Ph$_2$phen); X = Cl or Br) to explore factors which control photoinitiated electron collection (PEC) and catalytic activity.[4f, 5] The presence of a Rh(dσ*)-based LUMO (lowest unoccupied molecular orbital) in the Ru^{II}Rh^{III}Ru^{II} complexes is a key energetic requirement for PEC at the Rh^{III} catalytic center.[6] PEC on the Rh^{III} center forms the proposed active species, Ru^{II}Rh^{I}Ru^{II} upon sequential reductive quenching of the ^{3}MLCT (metal-to-ligand

charge transfer) excited state by a sacrificial electron donor.[6c] Recent studies also show that two Ru^{II} chromophores are not required for photocatalysis. Active Ru^{II}Rh^{III} bimetallics require a Rh-based LUMO and steric protection around the photogenerated Rh^{I} center to prevent dimerization that leads to catalytic deactivation.[4g] These Ru^{II}Rh^{III}Ru^{II} and Ru^{II}Rh^{III} motifs represent homogenous single-component photocatalysts for H$_2$ generation.

To the best of our knowledge, all reported dpp-bridged Ru^{II}Rh^{III} and Ru^{II}Rh^{III}Ru^{II} photocatalysts have two labile halide ligands (Cl or Br) on the Rh^{III}. 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^{II}Rh^{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 Rh^{I} center.

The ligand tpy (2,2':6',2"-terpyridine) has been widely used in coordination chemistry with meridional tridentate (η^3) chelation being the most common coordination mode. Taking advantage of the tridentate binding mode, the new Ru^{II}Rh^{III} complex, [(bpy)$_2$Ru(dpp)RhCl(tpy)](PF$_6$)$_4$ (Ru^{II}Rh^{III}Cl(tpy)), has been prepared to test the hypotheses described above. For comparative purposes, we have studied the *cis*-Rh^{III}Cl$_2$ analogue [(bpy)$_2$Ru(dpp)RhCl$_2$(bpy)](PF$_6$)$_3$ (Ru^{II}Rh^{III}Cl$_2$(bpy)). Herein we reported the electrochemical, photochemical, and catalytic properties of these two RuRh supramolecular complexes. It was found that Ru^{II}Rh^{III}(tpy) was an active photocatalyst for H$_2$ production. The result suggested that two Rh–Cl bonds were not required for photocatalysis. All synthetic details, including ^{1}H NMR spectra, are provided in the supporting information (Fig. S1-3, ESI†).

Cyclic voltammetry (CV) was utilized to investigate the influence of TL variation on the redox properties of the Rh^{III} center. Fig. 1 shows that both complexes possess a reversible Ru$^{III/II}$ couple at similar potential (*ca.* 1.60 V vs Ag/AgCl) indicating that the Ru(dπ) orbital energy is insensitive to the variation of the remote TL on Rh^{III}. Reductively, Ru^{II}Rh^{III}Cl$_2$(bpy) shows a quasi-reversible Rh$^{III/II}$ couple at −0.43 V (ΔE = 60 mV), an irreversible Rh$^{II/I}$ couple at E$_p^c$ = −0.79 V, and a reversible dpp$^{0/–}$ at −1.01 V. The assignments are confirmed by coulometric experiments and consistent with [(bpy)$_2$Ru(dpp)RhCl$_2$(phen)]$^{3+}$.[7] In Ru^{II}Rh^{III}Cl(tpy), the first

reduction appears as an irreversible wave at E_p^c = −0.35 V vs Ag/AgCl and comprises 2e$^-$/molecule. The appearance of the 2Cl$^-$/Cl$_2$ oxidation couple in the CV of the reduced solution (Fig. S4, ESI†) suggests dissociation of the Cl$^-$ ligand from Rh^{III} upon reduction, providing an assignment of Rh$^{III/II/I}$ for the first reduction. Unlike Ru^{II}Rh^{III}Cl$_2$(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 Ru^{II}Rh^{III}Cl(tpy), geometry requires the Cl$^-$ ligand to be *trans* to dpp whereas the Ru^{II}Rh^{III}Cl$_2$(bpy), has one Cl$^-$ *trans* to dpp and one Cl$^-$ *trans* to bpy. This uncovers an important consideration in controlling the rate of halide loss critical to providing an active site in the reduced Rh^I species. The single Rh$^{III/II/I}$ couple in Ru^{II}Rh^{III}Cl(tpy), is in marked contrast with two separate Rh reductions in Ru^{II}(*cis*-Rh^{III}Cl$_2$) bimetallics. The effect is traced to rapid halide loss and instability of the 1e$^-$ reduced species of Ru^{II}Rh^{III}Cl(tpy) toward disproportionation whereas the 1e reduced Ru^{II}Rh^{III}Cl$_2$(bpy) likely possesses dpp•$^-$ character and is comparatively more stable. The Ru-based first oxidation and Rh-based first reduction establish the Ru(dπ) HOMO and the Rh(dσ*) LUMO in both complexes with a lowest-lying MMCT (metal-to-metal charge transfer) excited state predicted to undergo PEC at the Rh^{III} center producing active photocatalysts.
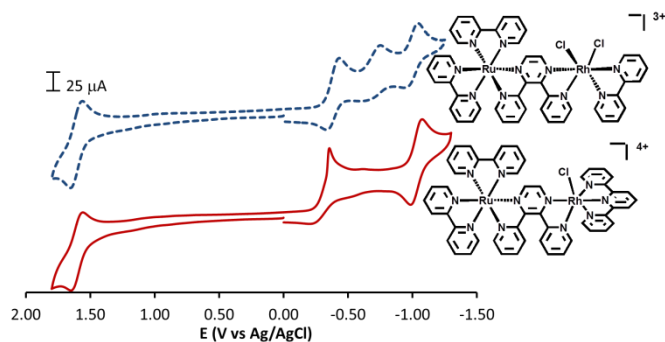

Fig. 1. CVs and structures of Ru^{II}Rh^{III}Cl$_2$(bpy) (blue dashed) and Ru^{II}Rh^{III}Cl(tpy) (red solid) in 0.1 M Bu$_4$NPF$_6$ acetonitrile.

The electronic absorption spectra of Ru^{II}Rh^{III}Cl(tpy) and Ru^{II}Rh^{III}Cl$_2$(bpy) are provided in Fig. S6, ESI†. The UV is dominated by intense ligand centered π→π* transitions. The Ru^{II}Rh^{III}Cl(tpy) displays a higher absorption intensity (ε = 74,200 M^{-1} cm^{-1}) at 280 nm than Ru^{II}Rh^{III}Cl$_2$(bpy) (ε = 59,300 M^{-1} cm^{-1}). A broad band between 400 – 500 nm is ^{1}MLCT in character with lower energies attributed to Ru(dπ)→dpp(π*) ^{1}MLCT transitions and higher energies attributed to Ru(dπ)→bpy(π*) ^{1}MLCT transitions. The spectra of the two bimetallics are nearly identical in the visible region, indicating that the structural difference at Rh does not impact the Ru^{II} ^{1}MLCT transitions.

Emission spectroscopy was used to investigate the photophysical properties of these Ru^{II}Rh^{III} complexes. The emission spectra of Ru^{II}Rh^{III}Cl$_2$(bpy), Ru^{II}Rh^{III}Cl(tpy), and a model complex [{(bpy)$_2$Ru}$_2$(dpp)](PF$_6$)$_4$ were measured at room temperature (Fig. S7, ESI†) and 77 K (Table S1, ESI†). Both Ru^{II}Rh^{III} complexes are weak emitters at room temperature from the ^{3}MLCT state (λ_{em}^{max} = 750 nm, Φ_{em} =1.3 × 10^{-4}, τ = 40 ns for Ru^{II}Rh^{III}Cl$_2$(bpy); Φ_{em} = 6.5 × 10^{-5}, τ =30 ns for Ru^{II}Rh^{III}Cl(tpy)) and are dramatically quenched compared to the model complex [{(bpy)$_2$Ru}$_2$(dpp)](PF$_6$)$_4$ (Φ_{em} = 8.9 × 10^{-4}, τ = 130 ns). The quenching is due to intramolecular electron transfer from dpp to Rh to populate the ^{3}MMCT excited state. Using k_r and k_{nr} from this model complex, k_{et} was obtained as 2.6 × 10^7 s^{-1} for Ru^{II}Rh^{III}Cl(tpy) and 1.7 × 10^7 s^{-1} for

Ru^{II}Rh^{III}Cl$_2$(bpy). Intramolecular ET is impeded at 77 K and results in a long-lived ^{3}MLCT emission. At 77 K in an ethanol/methanol (4:1, v/v) glass matrix, the emissions of Ru^{II}Rh^{III}Cl(tpy) and Ru^{II}Rh^{III}Cl$_2$(bpy) are blue-shifted to 715 nm (λ_{max}) with a dramatic increase in the intensity and lifetime (τ = 2.3 μs for Ru^{II}Rh^{III}Cl$_2$(bpy) and 2.1 μs for Ru^{II}Rh^{III}Cl(tpy)) comparable to 2.4 μs for the model.

Spectrophotochemical and spectroelectrochemical analyses on the title Ru^{II}Rh^{III} complexes demonstrated PEC at the Rh^{III} center. PEC is essential for Ru^{II}Rh^{III} systems to provide active photocatalysts. Fig 2 and Fig S8, ESI† illustrate spectroscopic changes which accompany reduction at −0.65 V for Ru^{II}Rh^{III}Cl(tpy) and −0.95 V vs Ag/AgCl for Ru^{II}Rh^{III}Cl$_2$(bpy) to generate the Rh^I species. The changes upon reduction are analogous to the changes upon the photolysis of Ru^{II}Rh^{III}Cl(tpy) and Ru^{II}Rh^{III}Cl$_2$(bpy) in the presence of *N,N*-dimethylaniline (DMA), establishing both complexes as molecular devices for PEC. Upon reduction, the Ru(dπ)→dpp(π*) ^{1}MLCT transitions blue shift, consistent with dpp bound to electron rich Rh^I. Reduction of Rh^{III} 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 undegoes 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]
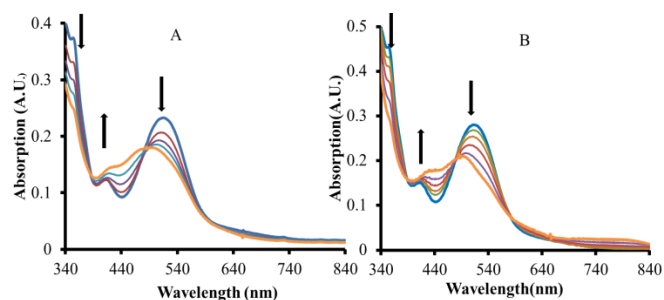

Fig. 2: Electronic absorption spectra generated from the electrochemical reduction (A, reduced at −0.65 V vs Ag/AgCl) and photochemical reduction (B) of Ru^{II}Rh^{III}Cl(tpy) in deoxygenated acetonitrile at room temperature.

Reductive quenching of the ^{3}MLCT excited state by DMA (E(DMA$^{+/0}$) = 0.86 V vs Ag/AgCl) is reported as the primary pathway to generate Ru^{II}Rh^I during photolysis of Ru^{II}Rh^{III}.[8] Using the ground state reduction potential, E(CAT^{n+}/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 λ_{em}^{max} (77 K) as 1.73 eV, the thermodynamic driving force for reductive quenching, E_{redox}, 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).[5c] This driving force demonstrates that reduction of Ru^{II}Rh^{III} to Ru^{II}Rh^{II} using DMA is thermodynamically favorable. Quenching of the new Ru^{II}Rh^{III}Cl(tpy) is more favorable than Ru^{II}Rh^{III}Cl$_2$(bpy) and [{(bpy)$_2$Ru(dpp)}$_2$RhCl$_2$](PF$_6$)$_5$ (0.49 V).[5c] Greater driving force for reductive quenching facilitates the formation of the Rh^I active species and is hypothesized to enhance the photochemical 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 H2 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 μmol H$_2$ with 33 TONs 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 μmol

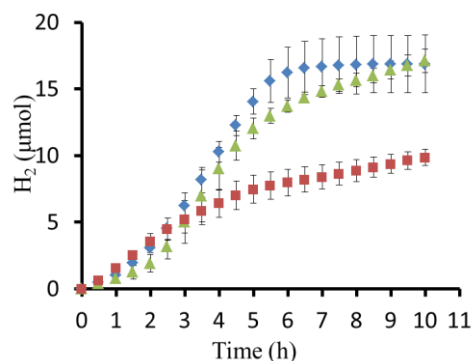H_2 and 58 TONs showing improvements relative to strongly ligating CH_3CN. [4h]

Fig. 3. Photolycatalytic H_2 production of $Ru^{II}Rh^{III}Cl(tpy)$ (65 µM) in acetone (blue diamond), DMF (green triangle), and CH_3CN (red square) solution with 1.5 M DMA and 0.6 M H_2O irradiated under 470 nm LED (light flux = $(2.36 \pm 0.05) \times 10^{19}$ photons/min).

Photocatalytic H_2 production by $Ru^{II}Rh^{III}Cl_2(bpy)$ and trimetallic $[\{(bpy)_2Ru(dpp)\}_2RhCl_2](PF_6)_5$ was also conducted in DMF and CH_3CN for comparison (Fig S10 and Fig. S11, ESI†). The catalytic activity of $Ru^{II}Rh^{III}Cl(tpy)$ is better than $Ru^{II}Rh^{III}Cl_2(bpy)$ and comparable with $[\{(bpy)_2Ru(dpp)\}_2RhCl_2](PF_6)_5$ under similar conditions (Table S2, ESI†). The $Ru^{II}Rh^{I}$ state is proposed as the active species for proton reduction.[6] For $Ru^{II}Rh^{III}Cl_2(bpy)$, the electrochemical reduction leads to the formation of $[(bpy)_2Ru(dpp)Rh^{I}(bpy)]^{3+}$ following halides loss, confirmed by ESI mass spectrometry (m/z, = 302.3; $Calc'd$ = 302.3, M = $[(bpy)_2Ru(dpp)Rh^{I}(bpy)]^{3+}$) (Fig. S12–S13, ESI†). In $Ru^{II}Rh^{III}Cl(tpy)$, Cl^- dissociation was also observed (Fig. S4, ESI). Electrochemical reduction of the simple model $[Rh^{III}Cl(tpy)dpp](PF_6)_2$ showed halide loss (Fig. S14, ESI†) to form $[Rh^{I}(tpy)(dpp)]^{+}$ (m/z = 570.0; $clac'd.$ = 570.0, M= $[(dpp)Rh^{I}(tpy)]^{+}$ Fig. S15, ESI†). The variable η^3–tpy or η^2–tpy coordination, of which the latter has been seen in some Re and Rh complexes,[9] facilitates the necessary geometry change as Rh^{III} is reduced to Rh^{I} to form $[[(bpy)_2Ru(dpp)Rh^{I}(\eta^2\text{-tpy})]^{3+}$. Additional support for the formation of $[[(bpy)_2Ru(dpp)Rh^{I}(\eta^2\text{-tpy})]^{3+}$ is provided in the detailed photolysis studies of $Ru^{II}Rh^{III}Cl(tpy)$. The addition of Cl^- to the photocatalytic system reduced H_2 production, whereas added tpy did not impact H_2 production, consistent with chloride, not tpy, loss occurring in the photocatalytic pathway . This η^2–tpy gives steric protection on the Rh^{I} site and prevents deactivation of the catalyst by Rh^{I} dimerization.[6b] Switching between η^2 and η^3 coordination at tpy provides a new mechanism to stabilize the supramolecule as it cycles the redox states at Rh in the catalytic cycle. Furthermore, one free pyridine of η^2–tpy may assist catalysis through secondary coordination sphere effects.[10] The improved functionality of $Ru^{II}Rh^{III}Cl(tpy)$ over $Ru^{II}Rh^{III}Cl_2(bpy)$ results from the enhanced driving force for reductive quenching by DMA, the rapid rate of halide loss and the steric protection of the photogenerated Rh^{I} imparted by the tpy ligand.[4g,6b]

In conclusion, a new photocatalyst, $Ru^{II}Rh^{III}Cl(tpy)$, with one Cl ligand and a tridentate ligand on Rh^{III} 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_{redox} 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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