Increased Photocatalytic Activity in Ru(II),Rh(III) Supramolecular Bimetallic Complexes with Terminal Ligand Substitution

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Abstract

Three new Ru(II),Rh(III) supramolecular bimetallic complexes of the design $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{RhCl}_2(\text{R}_2\text{-bpy})](\text{PF}_6)_3$ ($\text{R} = \text{CH}_3$ (**Ru-Rh(Me₂bpy)**), H (**Ru-Rh(bpy)**), or COOCH_3 (**Ru-Rh(dmeb)**); $\text{Ph}_2\text{phen} = 4,7$ -diphenyl-1,10-phenanthroline; $\text{dpp} = 2,3$ -bis(2-pyridyl)pyrazine; $\text{dmeb} = 4,4'$ -dimethyl ester-2,2'-bipyridine; $\text{bpy} = 2,2'$ -bipyridine; $\text{Me}_2\text{bpy} = 4,4'$ -dimethyl-2,2'-bipyridine) have been synthesized and analyzed to determine the impact that the polypyridyl terminal ligand (TL) coordinated to the cis-dihalide rhodium(III) metal center has on the photocatalytic activity for water reduction. The bimetallic complexes demonstrate that a correlation exists between the σ -donating ability of the substituted bipyridine ligand, the rate of chloride dissociation upon electrochemical reduction and the activity towards photocatalytic hydrogen production. The weaker σ -donating $-\text{COOCH}_3$ substituent in **Ru-Rh(dmeb)** increases the rate constant for Cl^- dissociation ($k_{-\text{Cl}} = 0.7 \text{ s}^{-1}$) and the amount of H_2 produced photocatalytically ($37 \pm 4 \text{ } \mu\text{mol H}_2$, 63 ± 7 turnovers after 20 hr; turnovers = mol H_2 /mol photocatalyst) when compared to $-\text{H}$ and $-\text{CH}_3$ substituted complexes **Ru-Rh(bpy)** ($k_{-\text{Cl}} = 0.2 \text{ s}^{-1}$, $21 \pm 2 \text{ } \mu\text{mol H}_2$, 35 ± 3 turnovers) and **Ru-Rh(Me₂bpy)** ($k_{-\text{Cl}} = 0.2 \text{ s}^{-1}$, $18 \pm 2 \text{ } \mu\text{mol H}_2$, 30 ± 4 turnovers), respectively. Varied catalytic activity with respect to the σ -donor capacity of the Rh-TL is attributed to the relative ease of ligand dissociation and the ability to afford rapid electron collection at the Rh metal center.

Keywords: supramolecular photocatalysis, water reduction, electron-withdrawing, ligand variation

1. Introduction

The utilization of sunlight to drive thermodynamically demanding reactions that generate alternative fuels (e.g. H_2O splitting to H_2 and O_2) is an attractive solution to the rise in global energy demands [1-4]. To store solar energy in the form of chemical bonds, light absorbing components harness incident photons that provide the necessary energy and subsequent electrons to reduce H_2O to H_2 fuel. Significant research efforts have focused on the design of multi-component, homogeneous photocatalytic systems for H_2O reduction that rely on bimolecular, diffusion-based collisions between each component within the photocatalytic system [5-8]. In an effort minimize the number of required bimolecular collisions and to better understand the photocatalytic processes at the molecular level, supramolecular complexes that function as

photochemical molecular devices (PMDs) have been developed by covalently coupling the molecular components [9-12].

Photochemical molecular devices that serve to collect multiple reducing equivalents upon photoexcitation are labeled as photoinitiated electron collectors (PECs) and function by collecting electrons in low-lying, unoccupied ligand- or metal-based MOs. Early examples of complexes that collect electrons within the bridging ligand (BL) π^* molecular orbitals include $[(\text{bpy})_2\text{Ru}(\text{dpb})]_2\text{IrCl}_2^{5+}$ (dpb = 2,3-bis(2-pyridyl)benzoquinoxaline) and $[(\text{phen})_2\text{Ru}(\text{BL})\text{Ru}(\text{phen})_2]^{4+}$ (phen = 1,10-phenanthroline; BL = tatpp = 9,11,20,22-tetraazatetrapyrido[3,2-*a*:2',3'-*c*:3'',2''-*I*:2''',3'''-*n*]pentacene; tatpq = 9,11,20,22-tetraazatetrapyrido[3,2-*a*:2',3'-*c*:3'',2''-*I*:2''',3'''-*n*]pentacene-10,21-quinone), yet these systems do not serve as photocatalysts for H_2O reduction [12-14]. Modification of the BL and reactive metal (RM) of $[(\text{bpy})_2\text{Ru}(\text{dpb})]_2\text{IrCl}_2^{5+}$ to form $[(\text{bpy})_2\text{Ru}(\text{dpp})]_2\text{RhCl}_2^{5+}$ (dpp = 2,3-bis(2-pyridyl)pyrazine) generated the first PMD for PEC at a metal site to function as a photocatalyst for H_2O reduction [15, 16]. In the presence of the sacrificial electron donor *N,N*-dimethylaniline (DMA) and light, the $[(\text{bpy})_2\text{Ru}(\text{dpp})]_2\text{RhCl}_2^{5+}$ trimetallic complex functions *via* successive photoexcitations of the Ru-based LA to transfer electrons to the *cis*- $\text{Rh}^{\text{III}}\text{Cl}_2$ site which dissociates two halide ligands and generates a coordinatively unsaturated, four coordinated Rh^{I} species, $[(\text{bpy})_2\text{Ru}(\text{dpp})]_2\text{Rh}^{\text{I}}^{5+}$, that is capable of H_2O reduction to H_2 .

Structural and component modifications of systems that couple LA subunits to a RM center through a polypyridyl BL have resulted in an array of photocatalytically-active architectures for H_2O reduction to H_2 [17-23]. Within the Ru(II),Rh(III),Ru(II) trimetallic architecture $[(\text{TL})_2\text{Ru}(\text{dpp})]_2\text{RhX}_2^{5+}$ (TL = bpy, phen, Ph_2phen ; X = Cl^- , Br^- , OH^-), bidentate and monodentate ligand variation has produced a library of complexes with varied electrochemical and photophysical properties and photocatalytic H_2O reduction activity [24-28]. The light absorbing and excited state properties of the Ru-based LA subunit are strongly impacted by the choice of polypyridyl TL, while the catalytic activity at the Rh-based RM center is tuned by monodentate X identity. The trimetallic complex $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})]_2\text{RhBr}_2^{5+}$ is a highly active H_2O reduction photocatalyst when compared with the $[(\text{phen})_2\text{Ru}(\text{dpp})]_2\text{RhBr}_2^{5+}$ trimetallic analogue, producing 1640 vs. 180 $\mu\text{mol H}_2$, respectively, after 20 h photolysis in a *N,N*-dimethylformamide (DMF) solution containing DMA electron donor [27]. This minor

change to the polypyridyl TL structure significantly enhances photocatalytic activity and thereby emphasizes the importance of design considerations when developing new H₂O reduction photocatalysts.

Substitution of one LA subunit with a polypyridyl TL in the Ru(II),Rh(III),Ru(II) trimetallic architecture has produced Ru(II),Rh(III) bimetallic complexes of the general formula $[(TL)_2Ru(BL)RhX_2(TL')]^{3+}$ in an effort to better understand the role and necessity of the second LA subunit [29]. The judicious choice of molecular components throughout the Ru(II),Rh(III) bimetallic architecture dictates photocatalytic activity towards H₂O reduction through a careful balance of sterics, electronics, light absorption, and ion pairing throughout the photocatalytic cycle [30-34]. The bimetallic complexes $[(Ph_2phen)_2Ru(dpp)RhX_2(Ph_2phen)]^{3+}$ ($X = Cl^-$ or Br^-) represent a systematic study undertaken to determine the influence that the σ -donating ability and degree of ion pairing imparted by the monodentate halide ligands have on the photocatalytic H₂O reduction activity [30]. Previous reports that vary the electronic character (σ -donor/ π -acceptor) of the bidentate polypyridyl ligand coordinated to Rh within a monometallic complex, $[Rh(R_2-bpy)_2Cl_2]^+$ ($R = H$ or $C(CH_3)_3$) [35] and $[Rh(BL)_2Br_2]^+$ ($BL = dpp, dpq, \text{ or } dpb$) [36], display how differences in electron density at the Rh metal center can impact the observed catalysis. Conversely, a systematic study to decipher the electronic contributions at the Rh site *via* variation of the polypyridyl TL's σ -donating ability has yet to be reported for the $[(TL)_2Ru(BL)RhX_2(TL')]^{3+}$ bimetallic architecture and necessitates such analysis.

Herein we report the synthesis, characterization, and photocatalytic activity of a series of Ru(II),Rh(III) bimetallic complexes of the design $[(Ph_2phen)_2Ru(dpp)RhCl_2(R_2-bpy)]^{3+}$ ($R = CH_3$ (**Ru-Rh(Me₂bpy)**), H (**Ru-Rh(bpy)**), or $COOCH_3$ (**Ru-Rh(dmeb)**); **Fig. 1**) to investigate what impact electronic variation of the Rh-TL σ -donating ability will have on the observed photocatalytic reduction of H₂O to H₂. The Ru-based LA subunit, $(Ph_2phen)_2Ru^{II}(dpp)$, is not altered in an effort to minimize any contributions that the light absorber component would have on the Rh-TL electronic comparisons. The pK_a values for similarly substituted pyridinium compounds (4-methoxycarbonylpyridinium = 3.26; pyridinium = 5.23; 4-methylpyridinium = 5.97) [37] can provide an approximation for the σ -bonding character of the polypyridyl TL (σ -donor ability: $Me_2bpy \sim bpy > dmeb$). Inclusion of stronger ($-CH_3$) vs. weaker ($-COOCH_3$) σ -type electron-donating substituents on 2,2'-bipyridine modulates electron density on the Rh

center and not only impacts the rate constant for halide dissociation upon electrochemical reduction (k_{-Cl} : **Ru-Rh(dmeb)** > **Ru-Rh(Me₂bpy)** ~ **Ru-Rh(bpy)**), but also the ability to catalyze H₂O reduction ($\mu\text{mol of H}_2$: **Ru-Rh(dmeb)** > **Ru-Rh(Me₂bpy)** ~ **Ru-Rh(bpy)**).

Fig. 1. Structural representation of $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{RhCl}_2(\text{R}_2\text{-bpy})](\text{PF}_6)_3$ complexes (R = CH₃, H, or COOCH₃).

2. Experimental

2.1. Materials and methods

All materials for syntheses and characterizations were used as received unless otherwise stated. RuCl₃·xH₂O, RhCl₃·xH₂O, 4,7-diphenyl-1,10-phenanthroline (Ph₂phen), 2,3-bis(2-pyridyl)pyrazine (dpp), 2,2'-bipyridine (bpy), and Sephadex® LH-20 resin were purchased from Aldrich. 4,4'-Dimethyl-2,2'-bipyridine (Me₂bpy) was purchased from Atomax Chemicals. Neutral, activated alumina was purchased from Alfa Aesar and deactivated using methanol. Spectrophotometric grade acetonitrile was purchased from Spectrum Chemicals. 4,4'-Dimethyl ester-2,2'-bipyridine (dmeb) [38], $[(\text{Ph}_2\text{phen})_2\text{RuCl}_2]$ [39], $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})](\text{PF}_6)_2$ [40] and $[\text{Rh}(\text{bpy})\text{Cl}_3(\text{MeOH})](\text{MeOH})$ [41] were synthesized as previously reported.

2.2. Syntheses

2.2.1. $[\text{Rh}(\text{Me}_2\text{bpy})\text{Cl}_3(\text{DMF})]$

The new Rh monometallic complex was synthesized using a similar procedure reported for [Rh(bpy)Cl₃(DMF)] (DMF = *N,N*-dimethylformamide) [34]. RhCl₃·xH₂O (0.20 g, 0.75 mmol) and 4,4'-dimethyl-2,2'-bipyridine (0.017 g, 0.92 mmol) were heated at 60 °C in 2 mL DMF for 2 h with rapid stirring. The resultant orange-yellow solution was allowed to cool to room temperature and was added dropwise to stirring diethyl ether to induce precipitation. The orange precipitate was collected by vacuum filtration, dissolved in chloroform, and filtered into a clean flask. The solvent was removed from the yellow filtrate by rotary evaporation to produce a yellow solid (yield = 67%, 0.24 g, 0.51 mmol). ESI-MS: [M – Cl]⁺ m/z = 430.85.

2.2.2. [Rh(*dmeb*)Cl₃(DMF)]

The new Rh monometallic complex was synthesized as described above using RhCl₃·xH₂O (0.20 g, 0.76 mmol) and 4,4'-dimethyl ester-2,2'-bipyridine (0.26 g, 0.92 mmol) Yield = 79 %, 0.34 g, 0.61 mmol. ESI-MS: [M + NH₄⁺]⁺ m/z = 570.98.

2.2.3. [(Ph₂phen)₂Ru(dpp)RhCl₂(Me₂bpy)](PF₆)₃ (**Ru-Rh(Me₂bpy)**)

The new Ru(II),Rh(III) bimetallic complex was synthesized using a similar procedure reported for [(bpy)₂Ru(dpp)RhCl₂(phen)](PF₆)₃ [29]. [(Ph₂phen)₂Ru(dpp)](PF₆)₂ (0.48 g, 0.37 mmol) and [Rh(Me₂bpy)Cl₃(DMF)] (0.24 g, 0.51 mmol) were heated at reflux in 30 mL 2:1 ethanol/water (v/v) for 3 h with rapid stirring. The dark red solution was cooled to room temperature and precipitated in aqueous NH₄PF₆. The dark red precipitate was collected by vacuum filtration and rinsed with water and diethyl ether. The crude product was purified using size exclusion chromatography with Sephadex® LH-20 resin as the stationary phase and a 2:1 ethanol/acetonitrile (v/v) solvent mixture as the mobile phase. Multiple fractions were collected and analyzed by electronic absorption and emission spectroscopies to ensure the absence of the emissive [(Ph₂phen)Ru(dpp)](PF₆)₂ monometallic (λ_{em} = 680 nm) when excited at λ_{abs} = 520 nm. Fractions which did not emit at 680 nm were combined and the solvent removed by rotary evaporation. The product was dissolved in minimal acetonitrile and added to stirring ether to induce precipitation. The precipitate was collected by vacuum filtration and dried in air to produce a dark red solid (yield = 15 %, 0.10 g, 0.074 mmol). ESI-MS: [M – PF₆]⁺ m/z = 1647.12.

2.2.4. [(Ph₂phen)₂Ru(dpp)RhCl₂(*dmeb*)](PF₆)₃ (**Ru-Rh(*dmeb*)**)

The new Ru(II),Rh(III) bimetallic complex was synthesized as described above using $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})](\text{PF}_6)_2$ (0.48 g, 0.37 mmol) and $[\text{Rh}(\text{dmeb})\text{Cl}_3(\text{DMF})]$ (0.29 g, 0.51 mmol). Yield = 18 %, 0.12 g, 0.083 mmol. ESI-MS: $[\text{M} - \text{PF}_6^-]^+$ $m/z = 1735.10$.

2.2.5. $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{RhCl}_2(\text{bpy})](\text{PF}_6)_3$ (**Ru-Rh(bpy)**)

The new Ru(II),Rh(III) bimetallic complex was synthesized as described above using $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})](\text{PF}_6)_2$ (0.47 g, 0.37 mmol) and $[\text{Rh}(\text{bpy})\text{Cl}_3(\text{MeOH})](\text{MeOH})$ (0.21, 0.50 mmol). Yield = 35 %, 0.23 g, 0.17 mmol. ESI-MS: $[\text{M} - \text{PF}_6^-]^+$ $m/z = 1619.10$.

2.3. Physical measurements

Cyclic voltammograms (CV) were performed at room temperature using a BAS Epsilon potentiostat with a glassy carbon disk working electrode, platinum wire auxiliary electrode and Ag/AgCl reference electrode (3 M NaCl) in 0.1 M $^n\text{Bu}_4\text{NPF}_6/\text{CH}_3\text{CN}$ electrolyte. Solutions were purged with argon prior to measurement and blanketed with argon during CV scans. The rate constants for halide dissociation ($k_{-\text{Cl}}$) were determined by comparing experimental voltammograms with those of simulated voltammograms using BASi DigiSim® version 3.0 simulation software for cyclic voltammetry [42, 43]. Simulated voltammograms were fit using the formulae for quasi-reversible couples that possess an electron transfer step (E) followed by a chemical reaction step (C) as shown in **Eqs. 1** and **2**, respectively.

Other pertinent parameters included $v = 100$ and 1000 mV/s, resistance = $100 - 300$ ohms, $T = 298$ K, $E^0 = -0.38$ V for **Ru-Rh(dmeb)** and $E^0 = -0.41$ for **Ru-Rh(Me₂bpy)** and **Ru-Rh(bpy)**, $\alpha/\lambda = 0.5$ eV and $K_{\text{eq}} = 1 \times 10^{10}$.

A Hewlett-Packard 8452A diode array spectrophotometer was employed for electronic absorption spectroscopy and spectra were collected in spectrophotometric grade CH_3CN using a 1 cm quartz cuvette (Starna Cells; Atascadero, CA). Extinction coefficient values were measured in triplicate. Steady-state luminescence spectroscopy was performed with a water-cooled 150 W xenon arc lamp with a 540 nm excitation using a Quanta Master Model QA-200-45E fluorimeter from Photon Technologies International and a thermo-electric cooled Hamamatsu R2658

photomultiplier tube. Time-resolved luminescence spectroscopy was carried out with an Edinburgh Instruments FLS920 time-correlated single photon counter with a 508.6 nm excitation wavelength and monitoring 790 nm emission.

Photocatalytic hydrogen production experiments were performed similar to a previously reported method [30]. The photolysis setup consisted of a locally designed LED array [44] and H₂scan HY-OPTIMA 700 hydrogen sensors (Valencia, CA) to permit real time monitoring of hydrogen evolution. Empty, air-tight photolysis reaction cells were connected to hydrogen sensors and deoxygenated using argon gas. Stock catalyst solutions prepared in DMF were combined with acidified deionized water (pH = 2 with CF₃SO₃H) in the air-tight photolysis cells and were further deoxygenated. The *N,N*-dimethylaniline (DMA) electron donor was purged separately with argon gas and injected into the catalyst solutions immediately prior to photolysis. The total solution volume was 4.5 mL, consisting of 130 μ M catalyst, 1.5 M DMA, 0.62 M H₂O and 0.11 mM [DMAH⁺][CF₃SO₃⁻] with a 15.5 mL headspace. The solutions were photolyzed with 470 nm light (light flux = $2.36 \pm 0.05 \times 10^{19}$ photons/min). The reported value for H₂ production is the average of three experiments.

3. Results and discussion

3.1. Synthesis

The title Ru(II),Rh(III) bimetallic complexes were synthesized using a building block approach outlined in **Fig. 2**. The [(Ph₂phen)₂RuCl₂] starting material was prepared by reacting two equivalents of the Ph₂phen terminal ligand with RuCl₃·xH₂O, followed by alumina column chromatography to remove the highly emissive [Ru(Ph₂phen)₃]²⁺ impurity. The [(Ph₂phen)₂Ru(dpp)]⁺ light absorber subunit was prepared by substituting the labile Cl⁻ ligands with the bis-bidentate dpp BL. Separately, the [Rh(R₂-bpy)Cl₃(DMF)]⁺ monometallic complexes were synthesized by gently heating a solution of RhCl₃·xH₂O and one equivalent of the bidentate TL in DMF, followed by precipitation with diethyl ether and rinsing with H₂O to remove unreacted RhCl₃·xH₂O starting material. The Ru(II) and Rh(III) monometallic precursors were heated at reflux in 2:1 (v/v) EtOH/H₂O solution and purified using size-exclusion chromatography to produce the new bimetallic complexes **Ru-Rh(Me₂bpy)**, **Ru-Rh(bpy)**, and **Ru-Rh(dmeb)**. The Ru(II),Rh(III) bimetallic complexes were characterized using ESI-MS, electrochemical analysis, and steady-state and time-resolved spectroscopic techniques.

Fig. 2. General building block synthetic approach for the preparation of **Ru-Rh(Me₂bpy)**, **Ru-Rh(bpy)**, **Ru-Rh(dmeb)** bimetallic complexes (see Experimental for details). ^aReference [39]. ^bReference [40].

3.2. Electrochemistry

Electrochemistry provides information pertaining to the frontier molecular orbital energies and the subsequent chemical reactivity following heterogeneous electron transfer [45]. Cyclic voltammograms (CVs) of the title Ru(II),Rh(III) complexes (**Fig. 3**) display similar redox-activity and features as those for previously reported polyazine-bridged Ru(II),Rh(III) bimetallic complexes that possess a *cis*-Rh^{III}X₂ center [29-33, 46]. Anodic scans display a reversible, one-electron Ru^{II/III} oxidation at $E_{1/2} = +1.60 \text{ V}$ vs. Ag/AgCl for all three bimetallic complexes, indicative of minimal-to-negligible electronic communication between the Ru(II) metal center and the terminal ligand coordinated to Rh(III). Similarly, Ru^{II/III} oxidation of the previously

reported $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{RhX}_2(\text{Ph}_2\text{phen})]^{3+}$ ($\text{X} = \text{Cl}^-$ or Br^-) bimetallic complexes occurs at $E_{1/2} = +1.59$ V vs. Ag/AgCl, providing further evidence of electronic isolation between Ru(II) and Rh-TL [30].

Fig. 3. Cyclic voltammograms of **Ru-Rh(Me₂bpy)** (a), **Ru-Rh(bpy)** (b) and **Ru-Rh(dmeb)** (c) measured at RT under Ar atm in 0.1 M ⁿBu₄NPF₆ supporting electrolyte in CH₃CN solvent at a scan rate of 100 mV/s.

Cathodic scans present somewhat complicated electrochemistry given the nearly isoenergetic nature of the $\text{dpp}(\pi^*)$ and $\text{Rh}(\text{d}\sigma^*)$ unoccupied MOs and the competitive electrochemical mechanisms upon reduction [32]. The bimetallic complexes display a reversible reduction at -0.41 V vs. Ag/AgCl for **Ru-Rh(Me₂bpy)** and **Ru-Rh(bpy)** and a quasi-reversible reduction at -0.38 V vs. Ag/AgCl for **Ru-Rh(dmeb)** (**Fig. 3**). This first cathodic couple is labeled as an ECEC process consisting of a $\text{Rh}^{\text{III/II}}\text{Cl}_2$ reduction followed by chloride dissociation and subsequent $\text{Rh}^{\text{II/I}}\text{Cl}$ reduction prior to cleavage of the second Rh-Cl bond [32]. Varied reversibility of the first cathodic couple is attributed to differing rates of chloride dissociation following the first reduction. The rate constant for chloride dissociation ($k_{-\text{Cl}}$) was further investigated using DigiSim® to model the first reductive couple with an EC mechanism from **Eqs. 1 and 2** (**Fig. 4**). Simulations provide an estimated $k_{-\text{Cl}}$ value of 0.2 s^{-1} for **Ru-Rh(Me₂bpy)**

and **Ru-Rh(bpy)** and 0.7 s^{-1} for **Ru-Rh(dmeb)**. The second cathodic couple is labeled an EECC process whereby a portion of the one-electron reduced species, $\text{Rh}^{\text{II}}\text{Cl}_2$, does not dissociate chloride rapidly and undergoes further reduction prior to dissociation of both chloride ligands [32]. The second cathodic couple shifts from $E_p^c = -0.82\text{ V}$ vs. Ag/AgCl for **Ru-Rh(Me₂bpy)** and $E_p^c = -0.80\text{ V}$ vs. Ag/AgCl for **Ru-Rh(bpy)** to $E_p^c = -0.68\text{ V}$ vs. Ag/AgCl for **Ru-Rh(dmeb)** which supports more rapid chloride dissociation with the methyl ester-substituted TL. The faster rate of chloride dissociation following reduction for **Ru-Rh(dmeb)** suggests increased formation of a coordinatively-unsaturated Rh metal center for potential catalysis, an important factor in the generation of a highly active catalyst. Importantly, the frontier molecular orbitals within this Ru(II),Rh(III) architecture are described as primarily Ru(II) HOMO and Rh(III) LUMO in character.

Fig. 4. Experimental CVs of the first cathodic couple (solid line) and simulated CVs using DigiSim® (dashed line) of **Ru-Rh(Me₂bpy)** (a), **Ru-Rh(bpy)** (b) and **Ru-Rh(dmeb)** (c) with a scan rate of 100 mV/s in 0.1 M ⁿBu₄NPF₆/CH₃CN.

3.3. Electronic absorption spectroscopy

The light absorbing ability of the Ru(II),Rh(III) bimetallic complexes was measured using electronic absorption spectroscopy and are tabulated in **Table 1**. As observed with similar complexes [29-31, 33, 46], **Ru-Rh(Me₂bpy)**, **Ru-Rh(bpy)** and **Ru-Rh(dmeb)** are strong light absorbers throughout the UV and visible with polypyridyl $\pi \rightarrow \pi^*$ intraligand (^1IL) transitions in the UV and Ru($d\pi$) $\rightarrow$ ligand(π^*) metal-to-ligand charge transfer ($^1\text{MLCT}$) transitions in the visible (**Fig. 5**). For all three bimetallic complexes, the lowest energy transition is ascribed to the

$\text{Ru}(\text{d}\pi) \rightarrow \mu\text{-dpp}(\pi^*)$ $^1\text{MLCT}$ transition at $\lambda_{\text{max}} = 512$ nm for **Ru-Rh(Me₂bpy)** and **Ru-Rh(bpy)** and at $\lambda_{\text{max}} = 520$ nm for **Ru-Rh(dmeb)**. The small $^1\text{MLCT}$ energy difference throughout the series of $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{RhCl}_2(\text{TL})]^{3+}$ complexes ($\lambda_{\text{max}} = 514$ nm for $\text{TL} = \text{Ph}_2\text{phen}$ [30]) is not surprising given the same $(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})$ LA subunit dominates the UV-Vis spectrum, as well as possessing a $\text{RhCl}_2(\text{TL})$ RM subunit. Modification of the Rh-TL does not strongly alter the $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{RhCl}_2(\text{TL})]^{3+}$ complexes' light absorbing ability and maintains the $\text{Ru}(\text{d}\pi) \rightarrow \mu\text{-dpp}(\pi^*)$ $^1\text{MLCT}$ as the lowest energy transition to direct electron density towards the $\text{RhCl}_2(\text{TL})$ RM subunit upon photoexcitation.

Table 1. Light absorbing properties of Ru(II),Rh(III) bimetallic complexes

Complex ^a	λ^{abs} (nm)	$\epsilon \times 10^{-4}$ ($\text{M}^{-1} \text{cm}^{-1}$)	Assignment
Ru-Rh(Me₂bpy)	278	10.2	$\text{Ph}_2\text{phen } \pi \rightarrow \pi^*$
	426	1.9	$\text{Ru}(\text{d}\pi) \rightarrow \text{Ph}_2\text{phen}(\pi^*)$ ^1CT
	512	2.0	$\text{Ru}(\text{d}\pi) \rightarrow \mu\text{-dpp}(\pi^*)$ ^1CT
Ru-Rh(bpy)	278	10.2	$\text{Ph}_2\text{phen } \pi \rightarrow \pi^*$
	426	1.9	$\text{Ru}(\text{d}\pi) \rightarrow \text{Ph}_2\text{phen}(\pi^*)$ ^1CT
	512	1.9	$\text{Ru}(\text{d}\pi) \rightarrow \mu\text{-dpp}(\pi^*)$ ^1CT
Ru-Rh(dmeb)	278	10.2	$\text{Ph}_2\text{phen } \pi \rightarrow \pi^*$
	426	1.9	$\text{Ru}(\text{d}\pi) \rightarrow \text{Ph}_2\text{phen}(\pi^*)$ ^1CT
	520	1.8	$\text{Ru}(\text{d}\pi) \rightarrow \mu\text{-dpp}(\pi^*)$ ^1CT
Ru-Rh(Ph₂phen) ^b	278	10.7	$\text{Ph}_2\text{phen } \pi \rightarrow \pi^*$
	414	1.7	$\text{Ru}(\text{d}\pi) \rightarrow \text{Ph}_2\text{phen}(\pi^*)$ ^1CT
	514	1.6	$\text{Ru}(\text{d}\pi) \rightarrow \mu\text{-dpp}(\pi^*)$ ^1CT

^aMeasured at RT in spectrophotometric grade CH₃CN using a 1 cm quartz cuvette. ^bValues reported from reference [30]; **Ru-Rh(Ph₂phen)** corresponds to $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{RhCl}_2(\text{Ph}_2\text{phen})]^{3+}$.

Fig. 5. Electronic absorption of **Ru-Rh(Me₂bpy)** (blue), **Ru-Rh(bpy)** (black) and **Ru-Rh(dmeb)** (red) measured in CH₃CN at RT.

3.4. Emission spectroscopy

Steady-state and time-resolved emission spectroscopies provide insight into the excited state dynamics of the title Ru(II),Rh(III) bimetallic complexes and these properties are summarized in **Table 2**. A simplified Jablonski diagram is shown in **Fig. 6** to provide an overview of possible excited state deactivation processes. Upon visible light photoexcitation, population of the Ru(d π) $\rightarrow$ μ -dpp(π^*) ¹MLCT excited state (ES) is followed by intersystem crossing to populate the weakly emissive Ru(d π) $\rightarrow$ μ -dpp(π^*) ³MLCT ES. The ³MLCT emission energy (λ^{em}), emission quantum yield (Φ^{em}), and ES lifetime (τ^{em}) are similar for all three Ru(II),Rh(III) bimetallic complexes, indicating that minimal electronic perturbations are imparted on the ES dynamics upon Rh-TL variation. Weak emission from the ³MLCT ES is due to low-lying, unoccupied Rh(d σ^*) MOs which permit facile intramolecular electron transfer to populate a non-emissive Ru(d π) $\rightarrow$ Rh(d σ^*) ³MMCT (metal-to-metal charge transfer) ES. The rate constant for intramolecular electron transfer (k_{et}) was calculated (**Eqs. 3-5**) using the homobimetallic model complex, [(Ph₂phen)₂Ru]₂(dpp)]⁴⁺ (labeled **(Ph₂phen)₂Ru-Ru**), which also emits from a Ru(d π) $\rightarrow$ μ -dpp(π^*) ³MLCT but does not possess a ³MMCT ES. The rate constants for ³MLCT ES radiative (k_r) and non-radiative (k_{nr}) decay of the **(Ph₂phen)₂Ru-Ru** model complex are used as an estimate for the Ru(II),Rh(III) bimetallic complexes given the similar ES manifold [47].

$$\tau_{Ru,Rh} = \frac{1}{k_r + k_{nr} + k_{et}} \quad (3)$$

$$\tau_{Ru,Ru} = \frac{1}{k_r + k_{nr}} \quad (4)$$

$$k_{et} = \frac{1}{\tau_{Ru,Rh}} - \frac{1}{\tau_{Ru,Ru}} \quad (5)$$

As shown in Table 2, the k_{et} values for the title Ru(II),Rh(III) bimetallic complexes are similar and further imply that efficient population of the $^3\text{MMCT}$ ES occurs regardless of Rh-TL identity. Equally important is the large order of magnitude (10^7 s^{-1}) calculated for intramolecular electron transfer that produces a formally oxidized Ru(III) and formally reduced Rh(II) species in the absence of a sacrificial quencher species such as *N,N*-dimethylaniline (DMA). Rapid, directional charge separation is vital to the formation of photochemically-active excited states towards the photocatalytic reduction of H_2O to H_2 .

Table 2. Excited state properties of Ru(II),Rh(III) bimetallic complexes

Complex ^a	λ^{em} (nm)	Φ^{em} (10^{-4})	τ^{em} (ns)	k_r (10^4 s^{-1})	k_{nr} (10^6 s^{-1})	k_{et} (10^7 s^{-1})
Ru-Rh(Me₂bpy)	808	5.2	20	1.0	5.9	4.4
Ru-Rh(bpy)	808	4.7	19	1.0	5.9	4.7
Ru-Rh(dmeb)	787	6.4	19	1.0	5.9	4.8
(Ph₂phen)₂Ru-Ru ^b	754	17.3	170	1.0	5.9	-

^aMeasured at RT in Ar-deoxygenated, spectrophotometric grade CH_3CN using a 1 cm quartz cuvette.

^bValues reported from reference [48]; **(Ph₂phen)₂Ru-Ru** corresponds to $[\{(\text{Ph}_2\text{phen})_2\text{Ru}\}_2(\text{dpp})]^{4+}$.

Fig. 6. Simplified Jablonski diagram depicting potential excited states and deactivation processes within the Ru(II),Rh(III) bimetallic architecture. GS = ground state, MLCT = metal-to-ligand charge transfer, MMCT = metal-to-metal charge transfer, k_{isc} = rate constant for intersystem

crossing, k_v = rate constant for vibrational relaxation, k_r = rate constant for radiative decay, k_{nr} = rate constant for non-radiative decay, k_{et} = rate constant for intramolecular electron transfer, k_{-Cl} = rate constant for Cl^- dissociation.

3.5. Photocatalysis studies

Photocatalytic H_2O reduction experiments were performed in an effort to elucidate the impact of Rh-TL identity within the Ru(II),Rh(III) bimetallic architecture. The new bimetallic complexes **Ru-Rh(Me₂bpy)**, **Ru-Rh(bpy)**, and **Ru-Rh(dmeb)** are active photocatalysts for H_2 production when excited with 470 nm light in DMF solvent in the presence of H_2O substrate and DMA electron donor, **Fig. 7**. Although the light absorbing and excited state properties of the modified Rh-TL complexes are similar, the photocatalytic activity displays a large disparity between the **Ru-Rh(dmeb)** complex ($37 \pm 4 \mu\text{mol } H_2$, 63 ± 7 TON after 20 hr) and the **Ru-Rh(Me₂bpy)** and **Ru-Rh(bpy)** complexes ($18 \pm 2 \mu\text{mol } H_2$, 30 ± 4 TON; $21 \pm 2 \mu\text{mol } H_2$, 35 ± 3 TON, respectively) (**Table 3**). Maximum quantum yields for H_2 evolution after 4 h photolysis (Max. Φ) with **Ru-Rh(Me₂bpy)**, **Ru-Rh(bpy)** and **Ru-Rh(dmeb)** are 0.002, 0.003 and 0.004, respectively. Recent reports by our group [30] and Rau and co-workers [18] have demonstrated that the halide ligand coordinated to the reactive metal center, $RhCl_2$ vs. $RhBr_2$ in the former and $PtCl_2$ vs. PtI_2 in the latter, dictates photocatalytic activity toward H_2 production regardless of the similar photophysical properties within each series. The weaker σ -donating Br^- vs. Cl^- ligand in $[(Ph_2phen)_2Ru(dpp)RhX_2(Ph_2phen)]^{3+}$ is proposed to more rapidly form the active Ru(II),Rh(I) species, as well as minimize the degree of ion pairing that impedes catalyst activity throughout the photocatalytic cycle. With regards to the weaker σ -donating dmeb ligand in **Ru-Rh(dmeb)**, more rapid Cl^- dissociation upon photoexcitation generates the proposed $[(Ph_2phen)_2Ru(dpp)Rh^I(dmeb)]^{3+}$ more efficiently to interact with H_2O and evolve H_2 . The photocatalytic robustness of **Ru-Rh(dmeb)** is enhanced when compared with **Ru-Rh(Me₂bpy)** and **Ru-Rh(bpy)**, which suggests the methyl-ester substituents inhibit catalyst deactivation until later times.

Table 3: Hydrogen evolution turnover numbers (TON) and maximum quantum yields for **Ru-Rh(Me₂bpy)**, **Ru-Rh(bpy)** and **Ru-Rh(dmeb)**.

Complex	k_{-Cl} (s^{-1})	TON ^a	Max. Φ
Ru-Rh(Me₂bpy)	0.2	30 ± 4	0.002

Ru-Rh(bpy)	0.2	35 ± 3	0.003
Ru-Rh(dmeb)	0.7	63 ± 7	0.004

^aMole H₂ per mole catalyst after 20 h photolysis.

The rate constants for excited state intramolecular electron transfer (10^7 s^{-1}) and deactivation ($10^3 - 10^6 \text{ s}^{-1}$), as well as bimolecular quenching by a sacrificial electron donor ($4.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for [(bpy)₂Ru(dpp)RhCl₂(bpy)]³⁺ and DMA) [46], are several orders of magnitude greater than the electrochemically determined rate constants for chloride loss (10^{-1} s^{-1}). Intramolecular electron transfer to populate the ³MMCT excited state and bimolecular quenching from DMA occur rapidly to create a state similar to the electrochemically reduced product, [(Ph₂phen)₂Ru^{II}(dpp)Rh^{II}Cl₂(R₂-bpy)]²⁺. In this scenario, chloride dissociation represents a potential rate limiting step in water reduction catalysis and the weaker σ -donating methyl ester substituents on bpy facilitate more rapid chloride dissociation.

Fig. 7. Photocatalytic H₂ production and catalyst turnover numbers (TON) for **Ru-Rh(Me₂bpy)** (triangles), **Ru-Rh(bpy)** (circles), and **Ru-Rh(dmeb)** (squares). Conditions: $\lambda^{\text{exc}} = 470 \text{ nm}$, solvent = DMF, [photocatalyst] = 130 μM , [H₂O] = 0.62 M, [DMA] = 1.5 M, [DMAH⁺][CF₃SO₃⁻] = 110 μM .

4. Conclusions

The new Ru(II),Rh(III) bimetallic complexes **Ru-Rh(Me₂bpy)**, **Ru-Rh(bpy)**, and **Ru-Rh(dmeb)** were synthesized and characterized to investigate the influence that Rh-TL variation

has on the electrochemical, photophysical, and photocatalytic properties. Electrochemical data indicate a Ru-based HOMO and Rh-based LUMO for all three bimetallics. The bimetallic complexes are efficient light absorbers throughout the UV and visible with the lowest energy transition displaying $\text{Ru}(\text{d}\pi) \rightarrow \mu\text{-dpp}(\pi^*)$ $^1\text{MLCT}$ character. Photoexcitation results in population of a weakly-emissive, short-lived $\text{Ru}(\text{d}\pi) \rightarrow \mu\text{-dpp}(\pi^*)$ $^3\text{MLCT}$ excited state that undergoes intramolecular electron transfer to populate a non-emissive, photochemically-active $\text{Ru}(\text{d}\pi) \rightarrow \text{Rh}(\text{d}\sigma^*)$ $^3\text{MMCT}$ excited state. The above properties are important requirements for the design of photocatalysts for H_2O reduction *via* photoinitiated electron collection at a Rh metal center. The new bimetallic complexes are able to catalyze the reduction of H_2O to H_2 in the presence of light and a sacrificial electron donor and the **Ru-Rh(dmeb)** complex displayed enhanced activity compared to the **Ru-Rh(Me₂bpy)** and **Ru-Rh(bpy)** complexes. Although the photophysical properties of the three complexes did not vary greatly, the rate constant for chloride dissociation ($k_{-\text{Cl}}$) was impacted and the weaker σ -donating $-\text{COOCH}_3$ substituted bipyridine TL possessed a larger $k_{-\text{Cl}}$ value (0.7 s^{-1}) compared to the stronger σ -donating $-\text{CH}_3$ and $-\text{H}$ substituted bipyridine TL ($k_{-\text{Cl}} = 0.2 \text{ s}^{-1}$). Substitution with ester groups decreases the σ -donating ability of the bipyridine ligand, thereby stabilizing the $\text{Rh}(\text{d}\sigma^*)$ orbitals and expediting cleavage of the Rh-Cl bond to form the active catalytic species.

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Graphical Abstract

Ru-Rh(NN)

Enhanced photocatalytic hydrogen production with weaker σ -donor terminal ligand on Rh in Ru(II),Rh(III) supramolecular bimetallic complexes.