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Photochemical hydrogen production from water using the new photocatalyst $[\{(bpy)_2Ru(dpp)\}_2RhBr_2](PF_6)_5$

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Abstract

The synthesis, electrochemical, and photochemical properties of the new photocatalyst $[\{(bpy)_2Ru(dpp)\}_2RhBr_2](PF_6)_5$ (bpy = 2,2′-bipyridine, dpp = 2,3-bis(2-pyridyl)pyrazine) which couples two ruthenium light absorbing metal centers to a reactive rhodium center is reported. The substitution of the bromide in lieu of the chloride in the $RhX_3 \cdot nH_2O$ starting material provides the bromo analog in high yield and purity. The basic chemical properties of the bromide complex are very similar to the chloride system $[\{(bpy)_2Ru(dpp)\}_2RhCl_2](PF_6)_5$, being an efficient metal-to-ligand charge-transfer (MLCT) light absorber in the visible while possessing a lowest lying metal-to-metal charge-transfer (^{3}MMCT) state. In the presence of an electron donor and visible light, $[\{(bpy)_2Ru(dpp)\}_2RhBr_2](PF_6)_5$ undergoes excited state intramolecular electron transfer affording photoinitiated electron collection on the reactive rhodium center to generate the Rh^I complex, $[\{(bpy)_2Ru(dpp)\}_2Rh^I](PF_6)_5$. The new complex affords photocatalytic hydrogen production from water with $\Phi \approx 0.01$, generating higher hydrogen yields than the chloride analog, 10.9 versus 8.2 μmol H_2 over a 4 h photolysis period.

Keywords: Metal-to-ligand charge-transfer; Metal-to-metal charge-transfer; Multi-electron photochemistry; Hydrogen photocatalysis; Ruthenium polyazine light absorber; Bridging ligand

1. Introduction

Considerable effort has been aimed towards light to energy conversion research chiefly stimulated by the urgent need for alternative energy sources [1,2]. The long lived metal-to-ligand charge-transfer (MLCT) excited state of $[Ru(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridine) light absorber (LA) has inspired photochemical and photophysical studies leading to light to energy conversion schemes [1–5]. The MLCT excited state of $[Ru(bpy)_3]^{2+}$ and its analogs have the required energy to split water into hydrogen and oxygen, yet complicated multi-component systems are required for functioning. Work in this solar energy water splitting arena has demonstrated that systems capable of multi-electron photochemistry are potential photocatalysts for water splitting. Despite this significance, designing systems that can successfully afford multi-electron photochemistry, has remained a challenge [6–8]. We recently reported the photochemical hydrogen production from water with a $\Phi \approx 0.01$ using the photocatalyst $[\{(bpy)_2Ru(dpp)\}_2RhCl_2](PF_6)_5$ (dpp = 2,3-bis(2-pyridyl)pyrazine) using a sacrificial electron donor [9]. The ability of this system to undergo photoinitiated electron collection on the rhodium center with its molecular architecture remaining intact, allows use in multi-electron photochemistry promoting hydrogen photocatalysis from water [9,10]. MacDonnell [6], Bocarsly [7], and Nocera [8] have reported other systems capable of multi-electron photochemistry, with only Nocera's system affording photoinduced hydrogen production using hydrohalic acids and a halogen trap [8]. Creutz and Sutin have reported a multi-component system that can photochemically produce hydrogen from water employing a $[Ru(bpy)_3]^{2+}$ LA, $[Rh(bpy)_3]^{3+}$ electron acceptor, and metallic platinum which acts as the catalyst [11]. Systems using a platinum terpyridine chromophore reported by Eisenberg function similarly with

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colloidal platinum catalysts [12]. Ruthenium polypyridyl linked platinum-based catalyst reported by Sakai provides hydrogen with a low turnover [13].

In this study we report the photochemical hydrogen production from water using the new photocatalyst $[\{(bpy)_2Ru(dpp)\}_2RhBr_2](PF_6)_5$. Similar to $[\{(bpy)_2Ru(dpp)\}_2RhCl_2](PF_6)_5$ [9,10], incorporation of the ruthenium polypyridyl LAs and the reactive electron collector within the same molecular assembly eliminates the need for molecular collision prior to relaxation of the ^{3}MLCT excited state affording efficient electron and energy transfer during energy conversion schemes [5]. The preparation and characterization of the new complex including its function as a photocatalyst in photochemical hydrogen production from water is presented.

2. Experimental details

2.1. Materials

Ruthenium(III) chloride hydrate (Alfa Aesar), rhodium(III) bromide hydrate (Alfa Aesar), 2,2′-bipyridine (bpy) (Aldrich), 2,3-bis(2-pyridyl)pyrazine (dpp) (Aldrich), (80–200 mesh) adsorption alumina (Fisher), potassium hexafluorophosphate (KPF_6) (Fluka), tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) (Fluka), spectral grade acetonitrile (Burdick and Jackson), ACS grade toluene, ethanol (AAPER), and re-distilled *N*,*N*-dimethylaniline (Aldrich) were all used as received. ESI mass spectral analysis was performed by M-Scan Incorporated, West Chester, Pennsylvania.

2.2. Synthesis of $[\{(bpy)_2Ru(dpp)\}_2RhBr_2](PF_6)_5$

The complex $[(bpy)_2Ru(dpp)](PF_6)_2$ was prepared using a slightly modified procedure of that reported by Gafney [14] in which the PF_6^- salt was obtained by metathesis of the $C1^-$ salt with KPF_6 in aqueous solution. Purification of the PF_6^- salt was achieved by column chromatography on a methanol deactivated adsorption alumina column with 2:3 acetonitrile:toluene eluent. The complex $[\{(bpy)_2Ru(dpp)\}_2RhBr_2](PF_6)_5$ was prepared using a modified procedure for that used to prepare the chloride analog [9] by heating at reflux for 1 h $[(bpy)_2Ru(dpp)](PF_6)_2$ (0.32 g, 0.34 mmol) and $RhBr_3{\cdot}3H_2O$ (0.074 g, 0.22 mmol), in a EtOH:H_2O (15 mL, 2:1) mixture. The cooled solution was added drop wise to a saturated aqueous solution of KPF_6 (100 mL) to induce precipitation of the PF_6^- salt. The dark red precipitate was washed with water and diethyl ether, dried in a vacuum desiccator, dissolved in minimum volume of acetonitrile and flash precipitated in diethyl ether. The complex $[\{(bpy)_2Ru(dpp)\}_2RhBr_2](PF_6)_5$ was isolated as a deep red solid by vacuum filtration (0.30 g, 77%). Purity of the complex to >99.5% necessary for emission spectroscopy was provided by careful purification of $[(bpy)_2Ru(dpp)](PF_6)_2$ starting material by adsorption chromatography on alumina coupled with re-precipitation of the crude product $[\{(bpy)_2Ru(dpp)\}_2RhBr_2](PF_6)_5$ from hot ethanol (0.18 g, 46%). ESI-MS: $[M-PF_6]^+$, $m/z = 2138$.

2.3. Electrochemistry

The cyclic voltammetry experiment was conducted with a Bioanalytical Systems (BAS) electrochemical analyzer using a platinum wire auxillary electrode, platinum disk working electrode, and measured against a Ag/AgCl reference electrode calibrated versus ferrocene, ($FeCp_2/FeCp_2^+ = 0.67$ V vs. NHE).

2.4. Electronic absorption spectroscopy

The electronic absorption spectrum was recorded at room temperature using a Hewlett-Packard 8452 diode array spectrophotometer with 2 nm resolution. Data was collected at room temperature in Burdick and Jackson UV-grade acetonitrile in 1 cm quartz cuvettes.

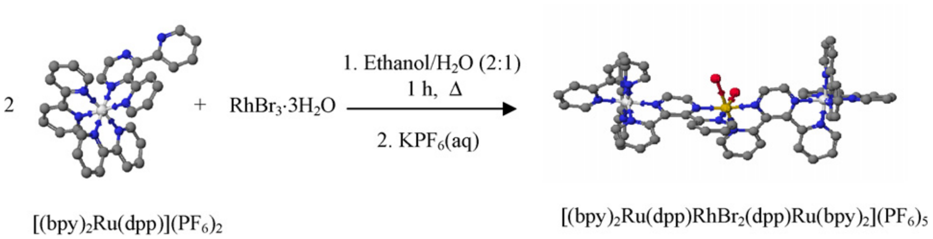
2.5. Emission spectroscopy

The emission spectra were recorded in a deoxygenated acetonitrile solution using a modified QuantaMaster Model QM-200-45E fluorimeter from Photon Technology Inc. The system was modified to use a 150 W cooled xenon lamp excitation source collected at a right angle by a thermoelectrically cooled Hamamatsu 1527 photomultiplier tube operating in photon counting mode with 0.25 nm resolution. A solution of $[\{(bpy)_2Ru(dpp)\}_2RhBr_2](PF_6)_5$ was dissolved in acetonitrile to have an absorbance matched at the wavelength of excitation (520 nm) to the $[(bpy)_2Ru(dpp)Ru(bpy)_2](PF_6)_4$ standard. The solution was deoxygenated by sonicating and bubbling with argon and the absorbance was measured just prior to collection of the emission spectrum. Emission quantum yield was measured relative to $[(bpy)_2Ru(dpp)Ru(bpy)_2](PF_6)_4$ in deoxygenated acetonitrile at room temperature using $\Phi^{em} = 1.38 \times 10^{-3}$ [10].

2.6. Photochemistry

The photolysis solutions consisted of $[\{(bpy)_2Ru(dpp)\}_2RhBr_2](PF_6)_5$ (65 μM), water (0.62 M) acidified to pH 2 with triflic acid, and dimethylaniline (1.5 M) in a solution of acetonitrile (4.46 mL) to provide an effective pH ≈ 9.1, assuming the pKa of dimethylaniline is not greatly perturbed relative to aqueous conditions. All solutions were deoxygenated before photolysis. Hydrogen quantification entailed headspace analysis using gas chromatography. Samples of headspace (100 μL) were injected into a GOW-MAC gas chromatograph series 580 equipped with a 5 Å molecular sieves column using argon as the carrier gas, purchased from Airgas Inc. (Radnor, PA), equipped with a rhenium tungsten thermal conductivity detector. The signal due to hydrogen was amplified with a Vernier Software instrument amplifier and recorded with Logger Pro 3.4.5 software. The system was calibrated for hydrogen quantization by three sets of triplicate measurements of hydrogen standards.

Photolyses were conducted using a light emitting diode (LED) array constructed locally with flat optical bottom cells [9,15]. Validation of the LED array was achieved using a series of potassium tris(oxalato)ferrate(II) actinometry [16] and



Scheme 1. Synthetic scheme outlining the building block approach to $[\{(bpy)_2Ru(dpp)\}_2RhBr_2](PF_6)_5$ (bpy = 2,2′-bipyridine, dpp = 2,3-bis(2-pyridyl)pyrazine).

statistical treatments and analysis of variance (ANOVA) were used to evaluate the LED array photolysis systems. ANOVA calculations confirmed that there is no statistically significant difference between the actinometry results of the LEDs evaluated. The LEDs were all set to the same power output prior to the experiment using a Scientech, Inc. (Boulder, CO) Mentor MA10 power meter with a MC 2501 calorimeter head unit [9].

3. Results and discussion

3.1. Synthesis of $[\{(bpy)_2Ru(dpp)\}_2RhBr_2](PF_6)_5$

The complex $[\{(bpy)_2Ru(dpp)\}_2RhBr_2](PF_6)_5$ was prepared using a building block approach by heating at reflux for 1 h $[(bpy)_2Ru(dpp)](PF_6)_2$ and $RhBr_3·3H_2O$, in ~2:1 stoichiometry in a EtOH:H_2O mixture, followed by metathesis of the $C1^-$ salt with KPF_6 in aqueous solution to afford the $PF_6{}^-$ salt (77%), Scheme 1. This results in a product of sufficient purity as assayed by typical methods. The high purity of the complex needed for emission spectroscopy (>99.5%) was achieved via reprecipitation in hot ethanol to afford $[\{(bpy)_2Ru(dpp)\}_2RhBr_2](PF_6)_5$ as a deep red solid in moderate yield (46%). ESI mass spectrometry analysis of $[\{(bpy)_2Ru(dpp)\}_2RhBr_2](PF_6)_5$ was consistent with its formulation.

3.2. Electrochemistry

The electrochemical data for $[\{(bpy)_2Ru(dpp)\}_2RhBr_2](PF_6)_5$ were recorded in 0.1 M solution of tetrabutylammonium hexafluorophosphate in acetonitrile under an argon atmosphere. Fig. 1 illustrates the cyclic voltammogram of $[\{(bpy)_2Ru(dpp)\}_2RhBr_2](PF_6)_5$. Table 1 summarizes the electrochemical data for $[\{(bpy)_2Ru(dpp)\}_2RhBr_2](PF_6)_5$ and $[\{(bpy)_2Ru(dpp)\}_2RhCl_2](PF_6)_5$. The oxidative electrochemistry of $[\{(bpy)_2Ru(dpp)\}_2RhBr_2](PF_6)_5$ is ruthenium based and shows overlapping $Ru^{II/III}$ oxidations at 1.60 V. The overlapping $Ru^{II/III}$ oxidations indicate the absence of significant intercomponent coupling between the two ruthenium subunits. The reductive electrochemistry shows an irreversible $Rh^{III/II/I}$ based reduction at −0.33 V followed by two reversible $dpp^{0/-}$ reductions at −0.72 and −1.02 V. The observed irreversible $Rh^{III/II/I}$ reduction is consistent with the reductive electrochemistry observed for $[Rh(bpy)_2Cl_2]^+$ in which the $Rh^{III/II/I}$ reduction occurs with the loss of two chloride ligands [17]. The $Rh^{III/II/I}$ reduction in $[\{(bpy)_2Ru(dpp)\}_2RhBr_2](PF_6)_5$ occurs at a slightly more positive potential (~40 mV) relative to the corresponding reduction for $[\{(bpy)_2Ru(dpp)\}_2RhCl_2](PF_6)_5$ [10]. The positive shift in the $Rh^{III/II/I}$ reduction compares well with the observed shift in the $Rh^{III/II/I}$ reduction in $[Rh(bpy)_2X_2](PF_6)$ from X = Cl to I [18]. The electrochemistry of $[\{(bpy)_2Ru(dpp)\}_2RhBr_2](PF_6)_5$ predicts the Ru(dπ) nature of the highest occupied molecular orbital (HOMO) and the Rh(dσ*) nature of the lowest unoccupied molecular orbital (LUMO). Similar to $[\{(bpy)_2Ru(dpp)\}_2RhCl_2](PF_6)_5$, such an orbital arrangement allows the Rh to function as an electron acceptor affording a lowest lying Ru → Rh metal-to-metal charge transfer (^{3}MMCT) excited state in this structural motif [10].

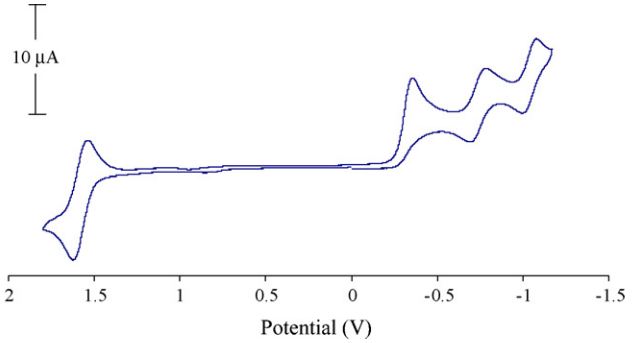


Fig. 1. Cyclic voltammogram of $[\{(bpy)_2Ru(dpp)\}_2RhBr_2](PF_6)_5$ (bpy = 2,2′-bipyridine, dpp = 2,3-bis(2-pyridyl)pyrazine) in 0.1 M n-Bu_4NPF_6 in CH_3CN using a platinum working electrode and a Ag/AgCl reference electrode.

Table 1
Electrochemical data for $[\{(bpy)_2Ru(dpp)\}_2RhBr_2](PF_6)_5$ and $[\{(bpy)_2Ru(dpp)\}_2RhCl_2](PF_6)_5$ (bpy = 2,2’-bipyridine, dpp = 2,3-bis(2-pyridyl)pyrazine)[a]

Complex	$E_{1/2}$ (V)	Assignments
$[\{(bpy)_2Ru(dpp)\}_2RhBr_2](PF_6)_5$	1.60	$2Ru^{II/III}$
	−0.33[b]	$Rh^{III/II/I}$
	−0.72	dpp,dpp/dpp,dpp$^-$
	−1.02	dpp,dpp$^-$/dpp$^-$,dpp$^-$
$[\{(bpy)_2Ru(dpp)\}_2RhCl_2](PF_6)_5$	1.60	$2Ru^{II/III}$
	−0.37[b]	$Rh^{III/II/I}$
	−0.76	dpp,dpp/dpp,dpp$^-$
	−1.02	dpp,dpp$^-$/dpp$^-$,dpp$^-$

[a] Potentials reported versus the Ag/AgCl reference electrode in 0.1 M Bu_4NPF_6 in CH_3CN.

[b] E_p value.

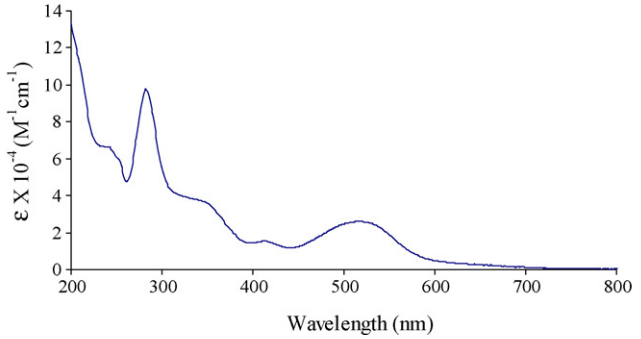


Fig. 2. The electronic absorption spectrum of $[\{(bpy)_2Ru(dpp)\}_2RhBr_2](PF_6)_5$ (bpy = 2,2′-bipyridine, dpp = 2,3-bis(2-pyridyl)pyrazine) in deoxygenated acetonitrile solution at room temperature.

3.3. Electronic absorption spectroscopy

The electronic absorption spectrum of $[\{(bpy)_2Ru(dpp)\}_2RhBr_2](PF_6)_5$ is shown in Fig. 2. The electronic absorption spectra for $[\{(bpy)_2Ru(dpp)\}_2RhBr_2](PF_6)_5$ and $[\{(bpy)_2Ru(dpp)\}_2RhCl_2](PF_6)_5$ are virtually identical with the UV regions dominated by dpp and bpy $\pi \rightarrow \pi^*$ transitions and the visible regions dominated by $Ru(d\pi) \rightarrow dpp(\pi^*)$ metal-to-ligand charge transfer (MLCT) transitions. The dpp-based transitions occur as low energy shoulders at 344 nm on the more intense higher energy bpy-based transitions that occur at 284 nm in the UV region. The $Ru(d\pi) \rightarrow bpy(\pi^*)$ and $Ru(d\pi) \rightarrow dpp(\pi^*)$ MLCT transitions occur in the visible region with the lowest energy transition being Ru → dpp in nature ($\lambda_{max}{}^{abs} = 520$ nm, $\varepsilon = 2.61 \times 10^4$ M^{-1}cm^{-1}). The electronic absorption spectra of $[\{(bpy)_2Ru(dpp)\}_2RhCl_2](PF_6)_5$ and $[\{(bpy)_2Ru(dpp)\}_2RhBr_2](PF_6)_5$ suggest that modification of the halide on the Rh center from chloride to bromide does not have a significant impact on the light absorption properties.

3.4. Emission spectroscopy

Emission spectroscopy was used to probe the excited state properties of $[\{(bpy)_2Ru(dpp)\}_2RhBr_2](PF_6)_5$. This complex displays a weak emission from the $Ru(d\pi) \rightarrow dpp(\pi^*)$ ^{3}MLCT state, $\lambda^{em}{}_{max} = 760$ nm, emission quantum yield, $\Phi^{em} = 1.5 \times 10^{-4}$ [19]; at room temperature in deoxygenated acetonitrile solution. Compared to the model system $[(bpy)_2Ru(dpp)Ru(bpy)_2](PF_6)_4$ which lacks a rhodium electron acceptor, $\lambda^{em}{}_{max} = 744$ nm, emission quantum yield $\Phi^{em} = 1.38 \times 10^{-3}$; the emission from the $Ru(d\pi) \rightarrow dpp(\pi^*)$ ^{3}MLCT state of $[\{(bpy)_2Ru(dpp)\}_2RhBr_2](PF_6)_5$ is reduced by 89% due to intramolecular electron transfer leading to the population of the lower lying $Ru(d\pi) \rightarrow Rh(d\sigma^*)$ ^{3}MMCT state, Fig. 3. Based on the assumption that k_r and k_{nr} (k_r and k_{nr} are radiative and non-radiative rate constants, respectively) are the same for $[\{(bpy)_2Ru(dpp)\}_2RhBr_2](PF_6)_5$ and $[(bpy)_2Ru(dpp)Ru(bpy)_2](PF_6)_4$, efficient intramolecular electron transfer is predicted for population of the $Ru(d\pi) \rightarrow Rh(d\sigma^*)$ ^{3}MMCT state with the rate of electron transfer, $k_{et} = 5.2 \times 10^7$ s^{-1}. The excited state properties of the $[\{(bpy)_2Ru(dpp)\}_2RhBr_2](PF_6)_5$ compares well with those observed for $[\{(bpy)_2Ru(dpp)\}_2RhCl_2](PF_6)_5$, $\lambda^{em}{}_{max} = 760$ nm, emission quantum yield, $\Phi^{em} = 7.3 \times 10^{-5}$, $k_{et} = 1.2 \times 10^8$ s^{-1} [10].

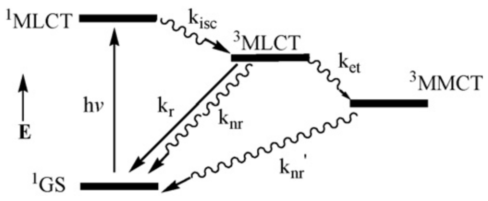


Fig. 3. Energy state diagram for $[\{(bpy)_2Ru(dpp)\}_2RhBr_2](PF_6)_5$ (bpy = 2,2′-bipyridine, dpp = 2,3-bis(2-pyridyl)pyrazine); GS: ground state; MLCT: metal-to-ligand charge-transfer; MMCT: metal-to-metal charge-transfer; k_r: rate of radiative decay; k_{nr}: rate of non-radiative decay; k_{isc}: rate of inter-system crossing; k_{et}: rate of electron transfer.

3.5. Photochemistry

The electrochemical and photochemical data suggest that similar to $[\{(bpy)_2Ru(dpp)\}_2RhCl_2](PF_6)_5$, the complex $[\{(bpy)_2Ru(dpp)\}_2RhBr_2](PF_6)_5$ can undergo photoinitiated electron collection to generate a coordinatively unsaturated Rh^I species which can interact with substrates. Photolysis of a solution of $[\{(bpy)_2Ru(dpp)\}_2RhBr_2](PF_6)_5$ (470 nm, 65 μM) in the presence of the electron donor dimethylaniline (DMA, 1.5 M) and water acidified to pH = 2 using triflic acid (0.62 M), results in the production of hydrogen with a $\Phi \approx 0.01$. The large excess of DMA in this solution leads to a basic effective pH of 9.1. Similar to the $[\{(bpy)_2Ru(dpp)\}_2RhCl_2](PF_6)_5$ system, photolysis of $[\{(bpy)_2Ru(dpp)\}_2RhBr_2](PF_6)_5$ in the presence of the electron donor affords a color change that is expected for the formation of the Rh^I species, $[\{(bpy)_2Ru(dpp)\}_2Rh^I](PF_6)_5$ [9]. Photochemical hydrogen production appears to be linear within the 4 h of photolysis, Fig. 4. The photocatalytic efficiency of the two catalysts $[\{(bpy)_2Ru(dpp)\}_2RhBr_2](PF_6)_5$ and $[\{(bpy)_2Ru(dpp)\}_2RhCl_2](PF_6)_5$ are similar with the $[\{(bpy)_2Ru(dpp)\}_2RhBr_2](PF_6)_5$ system generating larger amounts of hydrogen. Photolysis of $[\{(bpy)_2Ru(dpp)\}_2RhBr_2](PF_6)_5$ under the specified conditions for 4 h, affords 10.9 μmol of hydrogen representing a

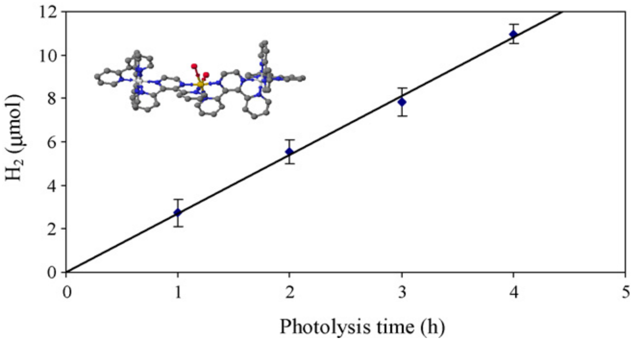


Fig. 4. Photocatalytic hydrogen production by $[\{(bpy)_2Ru(dpp)\}_2RhBr_2](PF_6)_5$ (bpy = 2,2′-bipyridine, dpp = 2,3-bis(2-pyridyl)pyrazine) (65 μM) in CH_3CN/H_2O solution using dimethylaniline (DMA, 1.5 M) as an electron donor. The photolysis was conducted using a 5 W LED having an excitation wavelength of 470 nm.

turnover of 38 compared to 8.2 μmol of hydrogen representing 30 turnovers for the $[\{(bpy)_2Ru(dpp)\}_2RhCl_2](PF_6)_5$ system.

The ability of the title $[\{(bpy)_2Ru(dpp)\}_2RhBr_2](PF_6)_5$ complex to produce higher amounts of hydrogen relative to the previously reported $[\{(bpy)_2Ru(dpp)\}_2RhCl_2](PF_6)_5$ given the similar spectroscopic properties is somewhat surprising. The substitution of the Br in place of the Cl on the Rh center does lead to a stabilization of the Rh(dσ*) orbital evidenced in the electrochemistry. This stabilization should also lead to a lower energy MMCT state in this complex relative to the Cl analog which may facilitate formation of this excited state. The photoreduction of the complex to the Rh^I state leads to loss of the two halides and formation of the same $[\{(bpy)_2Ru(dpp)\}_2Rh^I]^{5+}$ species. The identity of the halide may impact the rate of formation of this species, leading to the observed variation in photocatalysis. The details of the photocatalysis of water reduction to hydrogen by this class of complexes are an active area of our current work.

4. Conclusion

Photochemical hydrogen production from water using the new catalyst $[\{(bpy)_2Ru(dpp)\}_2RhBr_2](PF_6)_5$ has been achieved. The electrochemical and photochemical properties of the new complex suggest its ability to undergo photoinitiated electron collection at a metal center facilitating photoreduction of water to produce hydrogen. Our studies suggest that coordination of the weakly σ donating bromide ligand to Rh in $[\{(bpy)_2Ru(dpp)\}_2RhBr_2](PF_6)_5$, has little impact on its electronic and photochemical properties compared to $[\{(bpy)_2Ru(dpp)\}_2RhCl_2](PF_6)_5$ with enhancement of photocatalytic yield. The preparation of the bromide analog proceeds with somewhat higher yields and improved catalyst purity which will be advantages in further studies.

Acknowledgments

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