

Synthesis, characterization, and study of the photophysics and photocatalytic properties of the photoinitiated electron collector [$\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{RhBr}_2\}(\text{PF}_6)_5$]

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ABSTRACT

The heterometallic photoinitiated electron collector [$\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{RhBr}_2\}(\text{PF}_6)_5$ (phen = 1,10-phenanthroline, dpp = 2,3-bis(2-pyridyl)pyrazine) has been synthesized and studied by spectroscopic, photophysical, electrochemical, and photochemical techniques. Substitution of chloride with bromide in the previously reported [$\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{RhCl}_2\}(\text{PF}_6)_5$ complex presents a new photoinitiated electron collector which can assist in understanding the functioning of our supramolecular systems [$\{(\text{TL})_2\text{Ru}(\text{BL})\}_2\text{RhX}_2\}(\text{PF}_6)_5$ (TL = terminal ligand, BL = bridging ligand, X = halide) in the photoinitiated electron collection and generation of hydrogen through the reduction of water and a detailed comparison is presented. Both the bromide and chloride analogues of these supramolecular complexes contain low energy, emissive metal-to-ligand charge transfer ($^3\text{MLCT}$) excited states that populate lower lying metal-to-metal charge transfer ($^3\text{MMCT}$) excited states. The electrochemistry of these complexes showed an impact on the reduction of the central Rh^{III} upon halide substitution with the bromide analogue [$\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{RhBr}_2\}(\text{PF}_6)_5$ having a slightly lower reduction potential than the corresponding chloride counterpart. The more positive reduction of Rh^{III} to generate the Rh^{I} species in the bromide analogue impacts the photocatalytic properties upon photolysis in the presence of a sacrificial electron donor. The trimetallic complex [$\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{RhBr}_2\}(\text{PF}_6)_5$ generates hydrogen through the reduction of water with higher yields than the chloride [$\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{RhCl}_2\}(\text{PF}_6)_5$ analogue under the same conditions. Despite the longer lived $^3\text{MLCT}$ state of both [$(\text{TL})_2\text{Ru}(\text{dpp})\}^{2+}$ and [$\{(\text{TL})_2\text{Ru}\}_2(\text{dpp})\}^{4+}$ when TL = phen vs. bpy (bpy = 2,2'-bipyridine), the phen trimetallics with X = Cl^- or Br^- do not display longer lived $^3\text{MLCT}$ states and show lower H_2 yields than the analogous bpy trimetallic systems.

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1. Introduction

Supramolecular complexes functioning as photoinitiated electron collectors are capable of being designed as multi-electron photocatalysts [1]. In many cases, photoinitiated electron collectors incorporate metal-based light absorbers containing polypyridyl terminal ligands, polyazine bridging ligands, and electron collecting units [2–5]. Variation of the molecular components within these complexes can influence spectroscopic, photophysical and electrochemical properties, as well as the photocatalytic properties. Polypyridyl terminal ligands and polyazine bridging ligands are shown in Fig. 1. The Brewer group reported the first photochemical molecular device that functions as a photoinitiated electron collector [6]. The trimetallic complex [$\{(\text{bpy})_2\text{Ru}(\text{dpb})\}_2\text{IrCl}_2\}(\text{PF}_6)_5$ (bpy = 2,2'-bipyridine,

dpb = 2,3-bis(2-pyridyl)benzoquinoline) has been shown to collect electrons in the bridging ligand π^* LUMO upon photoexcitation. MacDonnell and Campagna [7,8] reported bimetallic complexes [$(\text{phen})_2\text{Ru}(\text{BL})\text{Ru}(\text{phen})_2\}(\text{PF}_6)_4$ (BL = 9,11,20,22-tetraazatetrapyrido[3,2-a:2'3'-c:3'',2''-1:2''',3''''-n]pentacene (tatpp) or 9,11,20,22-tetraazatetrapyrido[3,2-a:2'3'-c:3'',2''-1:2''',3''''-n]pentacene-10,21-quinone (tatpq)) that are capable of storing up to two or four electrons in the bridging ligand π^* LUMO, respectively. The first functioning photoinitiated electron collector [$\{(\text{bpy})_2\text{Ru}(\text{dpp})\}_2\text{RhCl}_2\}(\text{PF}_6)_5$ (dpp = 2,3-bis(2-pyridyl)pyrazine) to collect electrons at a reactive metal center while remaining intact following reduction was reported by Brewer [9]. Following photoexcitation, reduction of the metal center and subsequent halide loss generates the square planar Rh^{I} species. Enhanced photocatalytic activity was observed upon varying the halide from chloride to bromide in the trimetallic complex [$\{(\text{bpy})_2\text{Ru}(\text{dpp})\}_2\text{RhBr}_2\}(\text{PF}_6)_5$ for the generation of H_2 from water in the presence of an electron donor [10]. The phen analogue [$\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{RhCl}_2\}(\text{PF}_6)_5$ of the bpy trimetallic complex

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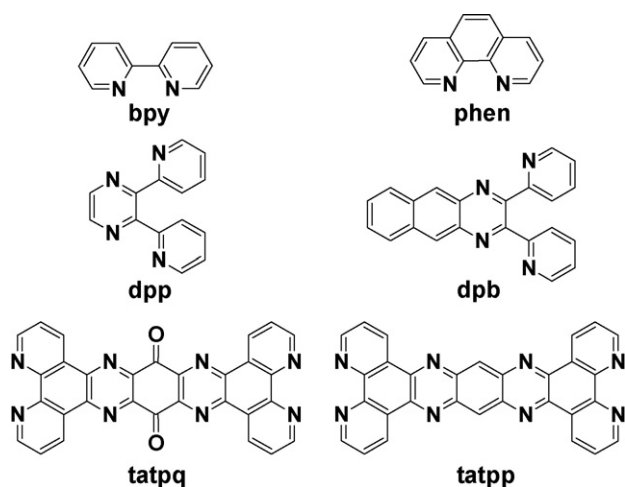


Fig. 1. Terminal and bridging ligands. bpy = 2,2'-bipyridine; phen = 1,10-phenanthroline; dpp = 2,3-bis(2-pyridyl)pyrazine; dpb = 2,3-bis(2-pyridyl)benzoquinoxaline; tatpq = 9,11,20,22-tetraazatetrapyrido[3,2-a:2'3'-c:3'',2''-1:2''',3'''-n]penta-cene-10,21-quinone; tatpp = 9,11,20,22-tetraazatetrapyrido[3,2-a:2'3'-c:3'',2''-1:2''',3'''-n]penta-cene.

has shown to function as a photoinitiated electron collector as well, indicating that other polypyridyl terminal ligands are capable of being used [11].

Reported herein are the spectroscopic, photophysical, electrochemical, and photochemical properties of the new photoinitiated electron collector $\{[(\text{phen})_2\text{Ru}(\text{dpp})]_2\text{RhBr}_2\}(\text{PF}_6)_5$ with a detailed comparison of the phen vs. bpy and bromide vs. chloride trimetallic systems. This Ru,Rh,Ru trimetallic complex is able to photocatalytically reduce water to generate hydrogen while still remaining intact after successive catalytic cycles.

2. Experimental

2.1. Materials

All solvents and chemicals were used as received unless otherwise stated. The complexes $\{[(\text{bpy})_2\text{Ru}(\text{dpp})]_2\text{RhCl}_2\}(\text{PF}_6)_5$ [9], $\{[(\text{bpy})_2\text{Ru}(\text{dpp})]_2\text{RhBr}_2\}(\text{PF}_6)_5$ [10] and $\{[(\text{phen})_2\text{Ru}(\text{dpp})]_2\text{RhCl}_2\}(\text{PF}_6)_5$ [11] were prepared as previously described.

2.2. Synthesis of $\{[(\text{phen})_2\text{Ru}(\text{dpp})]_2\text{RhBr}_2\}(\text{PF}_6)_5$

The precursor complex $[(\text{phen})_2\text{Ru}(\text{dpp})](\text{PF}_6)_2$ was synthesized by modification of a previously reported method [12,13]. Using column chromatography, purification was achieved with methanol deactivated alumina as the stationary phase and 2:3 acetonitrile:toluene as the mobile phase. ESI-MS: $[M-\text{PF}_6]^+$, $m/z = 841$. The title complex $\{[(\text{phen})_2\text{Ru}(\text{dpp})]_2\text{RhBr}_2\}(\text{PF}_6)_5$ was synthesized by heating at reflux $[(\text{phen})_2\text{Ru}(\text{dpp})](\text{PF}_6)_2$ (0.60 g, 0.60 mmol) and $\text{RhBr}_3 \cdot 3\text{H}_2\text{O}$ (0.14 g, 0.35 mmol) in a 2:1 EtOH/ H_2O solution (40 mL) for 1 h. The sample solution was allowed to cool before adding dropwise to an aqueous NH_4PF_6 solution (100 mL) to induce precipitation as a PF_6^- salt. The sample was filtered, washed with water, hot ethanol, diethyl ether and dried under vacuum in a desiccator overnight. Enhanced purity of $\{[(\text{phen})_2\text{Ru}(\text{dpp})]_2\text{RhBr}_2\}(\text{PF}_6)_5$ was achieved by recrystallization of the sample from hot ethanol to obtain a dark maroon solid (0.56 g, 0.23 mmol, yield = 73%). Electronic absorption spectroscopy in CH_3CN , λ_{max} ($\epsilon \times 10^{-4} \text{ M}^{-1} \text{ cm}^{-1}$): 224 nm (15.2), 262 nm (15.9), 346 nm (3.9), 418 nm (2.3), 520 nm (2.6). ESI-MS: $[M-\text{PF}_6]^+$, $m/z = 2235$.

2.3. Electronic absorption spectroscopy

The electronic absorption spectra were obtained using a Hewlett Packard 8452A diode array spectrophotometer. The wavelength range of measurement was 190–820 nm with a sampling interval of 2 nm and an integration time of 0.5 s. The samples were measured in UV-grade acetonitrile at room temperature using a 1 cm path length quartz cuvette (Starna Cells, Inc., Atascadero, CA). The extinction coefficient measurements were performed in triplicate.

2.4. Luminescence spectroscopy

The room temperature steady state emission spectra were collected in degassed UV-grade acetonitrile using a 1 cm path length quartz cuvette. The instrument used to record the spectra was a QuantaMaster Model QM-200-45E fluorimeter from Photon Technologies International, Inc. The source of excitation was a water-cooled 150 W Xenon arc lamp, with the corresponding emission collected at a 90° angle using a thermoelectrically cooled Hamamatsu 1527 photomultiplier tube operating in photon counting mode with 0.25 nm resolution. The emission quantum yields were measured against $[\text{Os}(\text{bpy})_3]^{2+}$ ($\Phi^{\text{em}} = 4.62 \times 10^{-3}$) with all samples studied using the same instrument settings [14]. The 77 K emission spectra were obtained using a 4:1 ethanol/methanol solution submerged in liquid N_2 in a finger dewar to form a rigid glass matrix. The emission spectra were corrected for PMT response.

2.5. Excited state lifetime measurements

The excited state lifetimes were measured using a Photon Technologies International, Inc. PL-2300 nitrogen laser with an attached PL-201 tunable dye laser as the source of excitation. The dye used was Coumarin 500 and the excitation monochromator was set to 520 nm. The emission was detected at a 90° angle from the excitation source after passing through an emission monochromator set to 746 nm using a Hamamatsu R928 photomultiplier tube operating in direct analog mode. The signal was recorded using a LeCroy 9361 oscilloscope which averaged the results of 300 sweeps. All complexes were studied with the same instrument settings.

2.6. Electrochemistry

Cyclic voltammograms were obtained using a Bioanalytical Systems (BAS) Epsilon electrochemical analyzer with a three electrode, single compartment cell. The supporting electrolyte used was a 0.1 M solution of tetrabutyl ammonium hexafluorophosphate (TBAH) in UV-grade acetonitrile. The working electrode was a platinum disk and the auxiliary electrode was a platinum wire. Ag/AgCl was used as a reference electrode and was calibrated against the ferrocene/ferrocenium ($\text{FcCp}_2/\text{FcCp}_2^+$) redox couple as an internal standard (0.43 V vs. SCE) [15]. The cyclic voltammograms were obtained at a scan rate of 100 mV/s. All electrochemical data were collected for the complexes using the same electrodes and instrument settings to allow for observation of small changes in redox potentials.

2.7. Mass spectroscopy

The electrospray ionization mass spectra were measured using an Agilent Technologies 6220 Accurate-Mass TOF LC-MS with a dual ESI source. The solvent used was HPLC grade acetonitrile.

2.8. Photochemistry

Photocatalytic hydrogen production experiments were performed using previously reported conditions [11]. The acetonitrile,

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