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Visible Light Driven Bromide Oxidation and Ligand Substitution Photochemistry of a Ru Diimine Complex

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Abstract: The complex $[Ru(deeb)(bpz)_2]^{2+}$ (RuBPZ²⁺, deeb = 4.4'-diethylester-2.2'-bipyridine, bpz = 2.2'bipyrazine) forms a single ion pair with bromide, [**RuBPZ**²⁺, Br⁻]⁺, with $K_{eq} = 8400 \pm 200 \text{ M}^{-1}$ in acetone. The **RuBPZ**²⁺ displayed photoluminescence (PL) at room temperature with a lifetime of 1.75 μ s. The addition of bromide to a RuBPZ²⁺ acetone solution led to significant PL quenching and Stern-Volmer plots showed upward curvature. Time-resolved PL measurements identified two excited state quenching pathways, static and dynamic, which were operative towards [RuBPZ²⁺, Br⁻]⁺ and free RuBPZ²⁺, respectively. The single ion-pair [**RuBPZ**²⁺, Br⁻]^{+*} had a lifetime of 45 ± 5 ns, consistent with an electron transfer rate constant, $k_{\text{et}} = (2.2 \pm 0.3) \times 10^7 \text{ s}^{-1}$. In contrast, **RuBPZ**^{2+*} was dynamically quenched by bromide with a quenching rate constant, $k_q = (8.1 \pm 0.1) \times 10^{10} \text{ M}^{-1} \text{s}^{-1}$. Nano-second transient absorption revealed that both the static and dynamic pathways yielded $RuBPZ^+$ and Br_2^{--} products that underwent recombination to regenerate the ground state with a second-order rate constant, $k = (2.3 \pm 0.5) \times 10^{10} \,\mathrm{M^{-1} s^{-1}}$. Kinetic analysis revealed that RuBPZ⁺ was a primary photoproduct, while Br2^{•-} was secondary product formed by the reaction of a Br[•] with Br⁻, $k = (1.1 \pm 0.2) \times 10^{10} \text{ M}^{-1} \text{s}^{-1}$. Marcus theory afforded an estimate of the formal reduction potential for E⁰(Br^{•/-}) in acetone, 1.42 V vs. NHE. A ¹H NMR analysis indicated that the ion-paired bromide was preferentially situated close to the Ru^{II} center. Prolonged steady state photolysis of **RuBPZ**²⁺ and bromide yielded two ligand-substituted photoproducts, *cis*- and *trans*-Ru(deeb)(bpz)Br₂. A photochemical intermediate, proposed to be $[Ru(deeb)(bpz)(\kappa^1-bpz)(Br)]^+$, was found to absorb a second photon to yield *cis*- and *trans*-Ru(deeb)(bpz)Br₂ photoproducts.

Introduction

Excited state electron transfer reactions are central to molecular level approaches to solar energy conversion.¹⁻⁵ Recently hydrohalic acid splitting has re-emerged as a promising target.⁶⁻¹¹ Hydrobromic acid is of particular interest in this regard,¹²⁻¹⁶ Equation 1, as the hydrogen and bromine products are solar fuels amenable to storage in flow batteries¹⁷⁻¹⁸ and fuel cells.¹⁹⁻²² Here we report bromide photo-oxidation sensitized to visible light with a Ru diimine complex.

$$2 \operatorname{HBr} + hv \rightarrow \operatorname{H}_2 + \operatorname{Br}_2 \tag{1}$$

Dye-sensitized HBr splitting provides significant challenges: 1) Bromide oxidation requires a strong photo-oxidant;²³ 2) Dye excited states generally provide one-electron transfer chemistry that in this case yields reactive Br atom;²⁴⁻²⁵ 3) Bromide is a coordinating ligand that may deactivate transition metal complexes that serve as dyes;²⁶⁻²⁷ and 4) Bromine is reactive and may oxidatively add to transition metals or undergo other unwanted reactions.



This report provides new insights into the first three of these challenges. A potent photo-oxidant $\operatorname{Ru}(\operatorname{deeb})(\operatorname{bpz})_2^{2^+}$ (**RuBPZ**²⁺), where bpz is 2,2'-bipyrazine and deeb is 4,4'-diethylester-2,2'-bipyridine shown above, was synthesized and reacted with bromide in acetone. Lever has previously shown that Ru^{II} bipyrazine complexes are strong photo-oxidants,²⁸⁻²⁹ and bromide oxidation has been found to be more facile in organic solvents than in water.²⁴⁻²⁵ Clear evidence for excited state bromide oxidation was provided by photoluminescence and absorption spectroscopies. Both static and dynamic excited state electron transfer pathways were identified with compelling evidence of a bromine atom intermediate. Finally, prolonged steady state photolysis led to the formation of both *cis*- and *trans*-Ru(deeb)(bpz)Br₂, which stands in contrast to a vast literature where only one isomer was formed. A photochemical intermediate, tentatively assigned as [Ru(deeb)(bpz)(κ^4 -bpz)(Br)]⁺, was found to absorb a second photon and yielded the isomers. The observation of two isomer provided new insights into ligand loss photochemistry mechanism(s) that may be exploited for synthetic chemistry.

RESULTS

To our knowledge the photochemistry of the tri-bromide ion in non-aqueous solution has not been previously reported and was investigated here to provide insights into the dye-sensitized bromide oxidation reactions. The absorption spectra of tetrabutylammonium (TBA) salts of bromide and tri-bromide in acetonitrile are shown in Figure 1a. Tri-bromide absorbs only weakly in the visible region with a strong absorption in the ultraviolet region centered at 270 nm. Acetonitrile (CH₃CN) was utilized here as it provided a wider ultraviolet spectral window than did acetone, which was the solvent utilized for all the dye-sensitized studies.

Nanosecond transient absorption spectroscopy was used to study the intermediates after pulsed 355 nm laser excitation of tri-bromide in acetonitrile. The kinetics and spectra were dependent on the bromide concentration. In the absence of bromide irreversible photochemistry was observed that precluded signal

averaging, which was absent when bromide was intentionally added to the solution. Pulsed laser excitation of 50 μ M tri-bromide and 50 μ M bromide in acetonitrile produced an intermediate consisting of two positive absorptions centered at 370 nm and 770 nm, along with a tri-bromide ground state bleach below 340 nm (Figure 1b). The positive absorption bands were consistent with previous reports of Br₂^{•-} in aqueous solutions.³⁰ Representative kinetic data monitored at 770 nm (Figure 1b inset) revealed a biphasic feature, a growth that could not be time resolved (> 10⁸ s⁻¹), and a slower growth that reached maximum in several microseconds. The amplitudes of both features were equal.



Figure 1. (a) Molar extinction coefficient of bromide (red), tri-bromide (green) and dibromide (blue) in acetonitrile. Note the dibromide extinction coefficients were estimated from transient absorption experiments. (b) Transient absorption spectra at indicated time delay after 355-nm pulsed laser excitation of an argon purged acetonitrile solution containing 50 μ M TBABr₃ and 50 μ M TBABr. Inset: absorption change at 770 nm after pulsed light excitation. (c) Absorption change at 370 nm after 355-nm pulsed laser excitation of 50 μ M TBABr₃ and X μ M TBABr in acetonitrile. X = 50 (black), 100 (orange), 150 (blue), 200 (magenta), 1000 (green). Overlaid in red are the mono-exponential fits. Inset: k_{obs} as a function of bromide concentration.

The slow component appeared more quickly when the bromide concentration was increased. The data were fit to an exponential function that provided k_{obs} . Plots of k_{obs} versus the bromide concentration afford a second-order rate constant, $k_{CH3CN} = (1.7 \pm 0.1) \times 10^{10} \text{ M}^{-1} \text{s}^{-1}$ (Figure 1 c inset). The corresponding data measured in acetone is given in Figure S1, with $k_{acetone} = (9.2 \pm 0.7) \times 10^9 \text{ M}^{-1} \text{s}^{-1}$. On a longer timescale than is shown, this feature returned cleanly to baseline with a second-order equal concentration kinetics, $k = (5.0 \pm 0.1) \times 10^8 \text{ M}^{-1} \text{s}^{-1}$ and $(2.3 \pm 0.2) \times 10^8 \text{ M}^{-1} \text{s}^{-1}$, in CH₃CN and acetone, respectively (Figure S2). Based on the initial and final growth amplitudes and the tri-bromide bleach, the molar extinction coefficient of this species assigned as Br₂^{•-} was estimated (Figure 1a).

The absorption of **RuBPZ**²⁺ in acetone displayed two overlapping metal-to-ligand charge transfer (MLCT) bands centered at 425 and 450 nm with an absorption onset around 600 nm (Figure 2). Bromide addition led to significant changes in the **RuBPZ**²⁺ absorption spectra indicative of a ground state ion pair, Figure 2. A substantial growth appeared around 360 nm, accompanied by slight suppression and red-shift of the MLCT bands. Isosbestic points were preserved at 420 and 460 nm throughout the titration, consistent with the formation of a single ion pair, denoted as [**RuBPZ**²⁺, Br⁻]⁺. A Benesi-Hildebrand analysis of the absorption change at 360 nm afforded an equilibrium constant, $K_{eq} = 8400 \pm 200 \text{ M}^{-1}$, for the formation of the ion pair.



Figure 2. UV-Vis absorption of 55 μ M RuBPZ²⁺ in acetone with increasing bromide concentration (0 – 1 mM).

To gain more insights into the ground state ion pair, ¹H NMR spectroscopy was utilized in deuterated acetone. Nine aromatic hydrogen atoms in **RuBPZ**²⁺ are labeled in Figure 3 due to the intrinsic C_2 symmetry. A set of seven peaks were observed beyond 8.0 ppm that were assigned by analysis of peak position, peak multiplicity and 2-dimensional COSY NMR spectra (Figure S3). In the presence of bromide, **a**, **a'**, **b**, and **f**, shifted downfield, while **d**, **c**, and **c'** shifted in the opposite direction. Negligible shifts were observed for **b'** and **e**. The hydrogen atoms that associate with bromide were expected to shift downfield due to deshielding that occurs as the carbon-hydrogen bond is lengthened. At the same time, other protons may shift upfield as they gain electron density from the bromide. In this sense, bromide preferentially associated with **a**, **a'**, **b**, and **f**. Note that **a** and **a'** are the most electron deficient and hence acidic protons in the complex. The presence of bromide near **b** and **f** may be due to enhanced Coulombic attraction to the formally dicationic Ru^{II} center. In the presence of four equivalents of bromide, a notably larger shift was observed for proton **b** and **f**, 0.09 and 0.12 ppm respectively, relative to 0.03 ppm for **a** and **a'**, providing compelling evidence that bromide was preferentially located near the Ru^{II} center rather than on the exterior of the diimine ligands.





10.2 10.0 9.8 9.6 9.4 9.2 9.0 8.8 8.6 8.4 8.2 8.0

Figure 3. Upper: Molecular structure of **RuBPZ**²⁺ with the aromatic hydrogen atoms labeled. Bottom: NMR spectra of **RuBPZ**²⁺ in the presence of indicated equiv of bromide in deuterated acetone, [**RuBPZ**²⁺] = 200 μ M.

Visible light excitation of **RuBPZ**²⁺ resulted in orange photoluminescence (PL) centered at 622 nm with a quantum yield of 0.09. The PL intensity was greatly attenuated when bromide was titrated into the solution (Figure 4). Care was taken to excite at an isosbestic point so that the number of absorbed photons remained unchanged throughout the titration. At high enough bromide concentrations, a red shift in the PL spectrum was observed with a maximum at 635 nm that was largely unaffected by further addition of bromide. The red shift was correlated with the low energy absorption change. At low bromide concentrations, the Stern-Volmer plot was linear with $K_{SV} = (1.8 \pm 0.1) \times 10^5 \text{ M}^{-1}$. At higher bromide concentrations, upward curvature was apparent. A Franck-Condon line-shape analysis of the **RuBPZ**²⁺ and [**RuBPZ**²⁺, Br⁻]⁺ PL spectra afforded estimates of the free energies stored in the excited states, $\Delta G_{ES} = 2.17$ eV for both species (Figure S4). The photophysical properties of **RuBPZ**²⁺ and [**RuBPZ**²⁺, Br⁻]⁺ in acetone are summarized in Table 1.



Figure 4. Steady state photoluminescence spectra of **RuBPZ**²⁺ as bromide was titrated into a 10 μ M acetone solution. The inset shows a Stern-Volmer plot of this same data.

Compound	PL _{max} (nm)	фрі (%)	τ (ns)	kr (10 ⁴ s ⁻¹)	k _{nr} (10 ⁵ s ⁻¹)	$\Delta G_{\rm ES}$ (eV)
RuBPZ ²⁺	622	9.0	1750	5.1	5.2	2.17
[RuBPZ ²⁺ , Br ⁻] ⁺	635	0.3	45	6.7	220	2.17

Table 1. Photophysical Properties of RuBPZ²⁺ and [RuBPZ²⁺, Br⁻]⁺ in Acetone.

To better understand the upward curvature in the Stern-Volmer plots of the steady-state PL spectra, excited state relaxation was quantified on a nanosecond timescale after pulsed laser excitation. In neat acetone first-order relaxation was observed with a lifetime of 1.75 μ s. Bromide addition led to the appearance of bi-exponential kinetics with a short lifetime of $\tau_s = 45 \pm 5$ ns that was independent of the bromide concentration and a longer lived component, τ_d , that was quenched by bromide (Figure 5a). The kinetic data was fit to Equation 2 where A_s and A_d represent the pre-exponential coefficients.

$$PLI(t) = A_{s}exp(-t/45 \text{ ns}) + A_{d}exp(-t/\tau_{d})$$
(2)

At low bromide concentration, the PL decay was dominated by τ_d . As more bromide was added, τ_s became dominant and eventually at very high bromide concentration (> 100-fold), the excited state decay returned to mono-exponential with a lifetime that was consistent with $\tau_s = 45$ ns. Significantly, the ratio of A_s/A_d agreed well with the relative concentration of [**RuBPZ**²⁺, Br⁻]⁺/**RuBPZ**²⁺ calculated based on $K_{eq} = 8400$ M⁻¹ (Figure 5b). These results provided compelling evidence that τ_s and τ_d represent the lifetimes of [**RuBPZ**²⁺, Br⁻]⁺ and **RuBPZ**²⁺, respectively and that the ground and excited state equilibrium constants for ion-pairing are very similar. A linear Stern-Volmer plot was produced based on τ_d (Figure 5a inset), which afforded a $K_{SV} = (1.41 \pm 0.01) \times 10^5$ M⁻¹, corresponding to a dynamic quenching rate constant, $k_q = (8.1 \pm 0.1) \times 10^{10}$ M⁻¹s⁻¹ based on $k_q = K_{SV}/\tau_0$.



Figure 5. (a) Time-resolved PL decays measured after pulsed light excitation of **RuBPZ**²⁺ in acetone with added bromide. Overlaid in red are the bi-exponential fits to the data based on eq 2. The inset shows a Stern-Volmer plot based on dynamic quenching, with an overlaid best fit line. (b) The pre-exponential coefficient ratio A_s/A_d with respect to the calculated concentration ratio [**RuBPZ**²⁺, Br⁻]⁺/**RuBPZ**²⁺ based on $K_{eq} = 8400 \text{ M}^{-1}$.

Nanosecond transient absorption was employed to elucidate the reaction mechanism. Pulsed 532 nm laser excitation of **RuBPZ**²⁺ in acetone resulted in the prompt appearance of a transient absorption spectrum consistent with formation of MLCT excited state. At low bromide concentrations, the MLCT absorption spectrum was observed at early observation times with the appearance of new absorption features centered at 370 and 500 nm that lived for hundreds of microseconds (Figure 6a). When the bromide concentration was four times greater than the **RuBPZ**²⁺ concentration, this long-lived absorption was well modeled by equal concentration of Br₂^{•-} and **RuBPZ**⁺ (Figure 6b). At lower bromide concentration, the long-lived absorption around 370 nm (Figure 6b). This discrepancy was consistent with less than 1 eq Br₂^{•-} per **RuBPZ**⁺ at low [Br⁻], suggested Br₂^{•-} was not a direct photoproduct of excited state electron transfer reactions.

The formation of **RuBPZ**⁺ was monitored at 500 nm, where it absorbs strongly relative to $Br_2^{\bullet-}$, which also represents a wavelength where a ground state bleach is observed. The absorption change was biexponential and modelled with a fixed lifetime of $\tau_s = 45$ ns and a lifetime, τ_d , that was bromide concentration dependent (Figure 6c). At high bromide concentrations (≥ 1 mM), the absorption signal at 500 nm became mono-exponential with $\tau_s = 45$ ns (Figure 6a inset), which represents the excited state lifetime of [**RuBPZ**²⁺, Br⁻]^{+*}. Plots of $1/\tau_d$ with the free bromide concentration were linear affording a second order rate constant of $(8.6 \pm 0.7) \times 10^{10} \text{ M}^{-1} \text{s}^{-1}$ (Figure 6c inset), that agreed with k_q values extracted from time-resolved PL experiment, indicating τ_d was the lifetime of **RuBPZ**^{2+*}. Hence **RuBPZ**⁺ was a direct product of excited state electron transfer in both static and dynamic reactions. Cage escape yields measured based on the concentration of **RuBPZ**⁺ remained at 0.055 ± 0.005 over a wide range of bromide concentration, 10 µM to 5 mM, indicating the same cage escape yield for both static and dynamic reactions.

The formation of $Br_2^{\bullet-}$ was monitored at 400 nm, which represented an isosbestic point between the **RuBPZ**²⁺ ground and excited state. As shown in Figure 6d, the appearance of $Br_2^{\bullet-}$ was delayed relative to **RuBPZ**⁺, providing strong evidence that $Br_2^{\bullet-}$ was not a primary photochemical product of the excited

state reaction. Indeed, the formation of $Br_2^{\bullet-}$ was bromide concentration dependent. Varying bromide concentration allowed to abstract the second order rate constant for the formation of $Br_2^{\bullet-}$, $(1.1 \pm 0.2) \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$ (Figure 6d inset), which was 8 times smaller than that of **RuBPZ**⁺. At long time delay, $Br_2^{\bullet-}$ and **RuBPZ**⁺ were found to recombine to yield ground state products with a second-order rate constant, $k = (2.3 \pm 0.5) \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$.



Figure 6. (a) Transient absorption spectra measured at the indicated time delays after pulsed 532 nm light excitation of a 50 μ M **RuBPZ**²⁺ and 1 mM bromide acetone solution. The inset shows the absorption change monitored at 500 nm with an overlaid mono-exponential fit, $\tau = 45$ ns. (b) Absorption spectra measured 5 μ s after pulsed light excitation of 50 μ M **RuBPZ**²⁺ and the indicated bromide concentrations. Overlaid as solid lines are simulated spectra based on equal concentration of **RuBPZ**⁺ and Br₂⁻⁻. (c) The absorption change monitored at 500 nm after pulsed light excitation of a 50 μ M **RuBPZ**²⁺ bromide acetone solution. Overlaid in red are fits to a bi-exponential kinetic model with one time constant fixed at 45 ns. The inset shows k_{obs} as a function of the free bromide concentration with an overlaid best fit line, $k = (8.6 \pm 0.7) \times 10^{10}$ M⁻¹s⁻¹. (d) The absorption change monitored at 400 nm (black) and at 500 nm (red) after pulsed 532 nm laser excitation of 50 μ M **RuBPZ**²⁺ and 300 μ M bromide solution. The inset shows k_{obs} as a function of the free bromide concentration with an overlaid best fit line, $k = (1.1 \pm 0.2) \times 10^{10}$ M⁻¹s⁻¹.

Prolonged 460 nm steady-state photolysis of \mathbf{RuBPZ}^{2+} bromide acetone solutions led to significant changes in the ground state absorption spectra (Figure 7a). In the first 10 minutes, a set of clean isosbestic points at 357, 407, and 474 nm were preserved, consistent with the formation of a single photoproduct that had two absorption bands centered at 380 and 510 nm. After 10 minutes, these isosbestic points were lost and a new set of absorption bands appeared at 585, 670, and 870 nm. The initially formed photoproduct at 380 nm and 510 nm reached the maximum after 2 h, and further irradiation led to a decrease. After 20 h of irradiation, the absorption spectra became time independent and three photoproducts were isolated, free bpz

ligand and two isomeric Ru complexes, *cis*-Ru(deeb)(bpz)Br₂ (purple), and *trans*-Ru(deeb)(bpz)Br₂ (dark green). A quantum yield of 0.4% was measured for the ligand loss reaction. The identity of these two isomers was confirmed by ¹H NMR (Figure 7b). In acetone, *cis*-Ru(deeb)(bpz)Br₂ shows two absorption peaks at 410 and 572 nm, while *trans*-Ru(deeb)(bpz)Br₂ displays multiple absorption peaks at 400, 440, 490, 588, 670, and 870 nm (Figure 7c). It is worth noting the absorption onset of *trans*-Ru(deeb)(bpz)Br₂ is 950 nm, one of the longest for reported Ru^{II} diimine complexes.⁴ The photo and thermal stability of these two isomers were investigated, while *cis*-Ru(deeb)(bpz)Br₂ showed remarkable photo and thermal stability, *trans*-Ru(deeb)(bpz)Br₂ slowly converted to *cis*-Ru(deeb)(bpz)Br₂ under prolonged light irradiation or thermal heating (Figure S5).

When the photolysis was terminated prior to complete conversion, a dark orange intermediate was identified and isolated by column chromatography. The UV-vis maxima of this orange intermediate at 382 and 504 nm (Figure 7c) were consistent with the absorption maxima of the intermediate observed in steady state photolysis of \mathbf{RuBPZ}^{2+} bromide acetone solutions with 380 and 510 nm absorption maxima. They were also consistent with a mono-bromo-bound Ru complex.^{29, 31} The electrospray ionization mass spectrum ((ESI-MS) of this intermediate in methanol solution revealed a peak at m/z = 798.0 (Figure S6), consistent with chemical composition of [Ru(deeb)(bpz)(bpz)Br]⁺. The theoretical mass spectrum of [Ru(deeb)(bpz)(bpz)Br]⁺ with natural isotope distributions agreed well with the experimental data (Figure S6 inset). The ¹H NMR spectrum of the intermediate showed aromatic resonances associated with the dimine ligands with the ethyl ester groups below 5 ppm (Figure 7b). Integration in the aromatic region gave a total of 18 aromatic hydrogen atoms, indicating that all three diimine ligands were still bound to Ru center (Figure S7). The ethyl resonances showed two multiplets, which would be expected for a *cis*configuration rather than trans, Figure 7b. As continued light excitation resulted in loss of a bpz ligand, we suspect that this intermediate is cis-[Ru(deeb)(bpz)(κ^1 -bpz)(Br)]⁺. However, the stereochemistry is uncertain and an ion-paired species may have been observed in the ESI-MS. Therefore, the intermediate is referred to as [Ru(deeb)(bpz)(bpz)(Br)]+.



Figure 7. (a) UV-Vis absorption of 55 μ M **RuBPZ**²⁺ and 110 μ M TBABr in acetone under irradiation of a blue light laser (460 nm, power = 3.36 mW) at selected time delay. Inset: absorption change spectra during photolysis. (b) NMR of *cis*-Ru(deeb)(bpz)Br₂ in CD₃CN (purple), *trans*-Ru(deeb)(bpz)Br₂ in CD₂Cl₂ (green), and the intermediate [Ru(deeb)(bpz)(bpz)(Br)]⁺ (orange) in CDCl₃. (c) Molar extinction coefficients of *cis*-Ru(deeb)(bpz)Br₂ (purple), *trans*-Ru(deeb)(bpz)(bpz)(Br)2⁺ (green), and [Ru(deeb)(bpz)(Br)2⁺)⁺ in acetone.

To verify the orange product was indeed a photochemical intermediate, it was irradiated in a bromide acetone solution. As shown in Figure 8a, steady state photolysis led to significant suppression of $[Ru(deeb)(bpz)(bpz)(Br)]^+$ absorptions, with concomitant formation of new absorption bands at long wavelengths that were consistent with the formation of *cis*- and *trans*-Ru(deeb)(bpz)Br₂. Standard addition of the authentic absorption spectra of $[Ru(deeb)(bpz)(Br)]^+$, *cis*- and *trans*-Ru(deeb)(bpz)Br₂ modelled the absorption data accurately and showed that as the $[Ru(deeb)(bpz)(bpz)(Br)]^+$ disappeared, the yield of

cis- and *trans*-Ru(deeb)(bpz)Br₂ increased cleanly with no evidence of other photoproducts (Figure 8b). There was no evidence of a thermal reaction for 3 hours at room temperature (Figure 8c) or for 30 minutes at 50 °C in the dark (Figure S8).



Figure 8. a) UV-vis of an acetone solution of $[Ru(deeb)(bpz)(\kappa^1-bpz)Br]^+$ and bromide after irradiated with white light using a Xenon lamp (150 W), the UV part of which was filtered off using a GG-420 filter. Overlaid in red represent the modeled spectra based on standard addition of the authentic spectra of $[Ru(deeb)(bpz)(bpz)Br]^+$, *cis*- and *trans*-Ru(deeb)(bpz)Br₂. b) The concentration of each species during photolysis based on spectra modeling. c) UVvis of an acetone solution of $[Ru(deeb)(bpz)(bpz)Br]^+$ and bromide before (black) and after (red) storing in the dark for 3 h. Inset: UV-vis of the same solution after irradiated with a Xenon lamp.

To test generality, photolysis of bromide acetone solutions of $[Ru(deeb)_2(bpz)]^{2+}$, $[Ru(bpy)_3]^{2+}$ or $[Ru(deeb)_3]^{2+}$ were conducted. For $[Ru(bpy)_3]^{2+}$ only the *cis*-Ru(bpy)_2Br₂ product was observed while the other two complexes yielded both *cis*- and *trans*-isomers. Relative to bpy, both deeb and bpz are weaker σ -donors, which may facilitate cleavage of the second Ru–N bond in the *trans*-position to form the *trans*-isomer.

Discussion

A mechanistic study of dye-sensitized bromide oxidation is reported in acetone solutions and revealed two reaction pathways that enabled the bromine formal reduction potential in acetone to be approximated. Ligand loss photochemistry produced both *cis* and *trans* isomers, behavior that we are unaware of in the vast literature of Ru^{II} diimine compounds. Before discussion of this excited state reactivity, the photochemistry of tri-bromide is first presented.

Tri-bromide Photochemistry

The direct excitation of tri-bromide, Br_3^- , was investigated in CH₃CN solution as it provided a better spectroscopic window than did acetone in the ultraviolet region. Pulsed 355 nm light excitation of $Br_3^$ led to the prompt formation of a transient spectra consistent with the formation of the bromine radical anion, often called dibromide $Br_2^{\bullet-}$. Mass balance implies that a bromine atom, Br^{\bullet} (eq 3), whose presence was indicated by bromide titration that yielded a second equivalent of $Br_2^{\bullet-}$ with a rate constant, $(1.7 \pm 0.1) \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$, that was within a factor of two of that measured in acetone, $(9.2 \pm 0.7) \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ (eq 4), but was significantly larger than that reported in dichloromethane, $(5.4 \pm 1.0) \times 10^8 \text{ M}^{-1}\text{s}^{-1}$.²⁵ The $Br_2^{\bullet-}$ underwent disproportionation to reset the ground state (eq 5).

$$Br_{3}^{-} \xrightarrow{\mu \to} [Br_{3}^{-}]^{*} \to Br_{2}^{\bullet-} + Br^{\bullet} \qquad \qquad k_{3} > 10^{8} \text{ s}^{-1} \qquad (3)$$

$$Br^{\bullet} + Br^{-} \to Br_{2}^{\bullet-} \qquad \qquad k_{4} = (1.7 \pm 0.1) \times 10^{10} \text{ M}^{-1} \text{s}^{-1} \qquad (4)$$

$$Br_2^{\bullet-} + Br_2^{\bullet-} \rightarrow Br_3^- + Br^ k_5 = (5.0 \pm 0.1) \times 10^8 \text{ M}^{-1} \text{s}^{-1}$$
 (5)

Excited State Electron Transfer

The spectroscopic data provided compelling evidence for the ground state ion-pair equilibrium shown in Scheme 1. Metal-to-ligand charge transfer excitation of bromide solutions of **RuBPZ**²⁺, or [**RuBPZ**²⁺, Br⁻]⁺ formed identical products suggesting that the excited state solvent cage [**RuBPZ**^{2+*}, Br⁻] formed by diffusional interactions of $RuBPZ^{2+*}$ and Br^- are similar to that formed when the ion-paired complex was directly excited. Excited state quenching formally involved electron transfer from bromide to the Ru^{III} excited state to yield a bromine atom and the reduced ruthenium complex. This reaction was quantitative, yet the yield of products measured was only about 6%, $\phi_{ce} = 0.055$. In the presence of excess Br⁻ the cage escaped bromine atoms reacted quantitatively to yield dibromide whereas in the absence of excess Br- some irreversible photochemistry occurred. Dibromide and the reduced Ru complex returned to ground state products with second-order equal concentration kinetics.

Scheme 1. Summary for Excited State Electron Transfer Reactions of RuBPZ²⁺ and [RuBPZ²⁺, Br⁻]⁺.



The quenching rate constant extracted from Stern-Volmer analysis, k_q , is related to the true electron transfer rate constant k_{et} through eq 6,³² in which k_{diff} is the diffusion rate constant and K_A is the association constant. The value of k_{diff} has been calculated through eq 7, in which D_{Ru} and D_{Br} represent the diffusion coefficient of **RuBPZ**^{2+*} and Br⁻ in acetone, respectively. Based on a 7.0 and 1.96 Å radii for **RuBPZ**^{2+*} and Br⁻,³³ D_{Ru} and D_{Br} were found to be 9.75×10^{-10} and 3.48×10^{-9} m²s⁻¹, respectively, through the Einstein-Stokes equation. The parameter β is the effective reaction radius described by $R_c \exp(Rc^*\kappa)/[\exp(R_c/R)-1]$, in which R is the sum of the radii of **RuBPZ**²⁺ and of Br⁻. The Onsager radius R_c is $Z_{Ru}Z_{Br}e^2/4\pi\epsilon_r\epsilon_0k_bT$, and κ^{-1} is the Debye length, $(\epsilon_r\epsilon_0k_bT/2000e^2N_AI)^{1/2}$.³⁴ Based on an ionic strength I = 2.5 × 10⁻⁴ M⁻¹ and K_A = 8400 M⁻¹, an estimated electron transfer rate from Br⁻ to **RuBPZ**^{2+*} was calculated to be $k_{\rm et} = 4.1 \times 10^7 \, {\rm s}^{-1}$, which is within a factor of two of that measured for the ion-paired complex.

$$\frac{1}{k_{obs}} = \frac{1}{k_{diff}} + \frac{1}{K_A k_{et}} \tag{6}$$

$$k_{diff} = 4\pi N_A (D_{Ru} + D_{Br})\beta \tag{7}$$

$$k_{et} = \frac{2\pi}{\hbar} \frac{|H_{AB}|^2}{\sqrt{4\pi\lambda k_b T}} \exp(-\frac{(\lambda + \Delta G^o)^2}{4\lambda k_b T})$$
(8)

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When typical values for a pre-exponential factor, 10^{11} s⁻¹, and a reorganization energy $\lambda = 1$ eV are assumed, Marcus theory and eq. 8 indicate that $\Delta G^{\circ} = -0.11$ eV. The free energy change associated with electron transfer reaction is given by eq 9. In this equation E(Br^{•/-}) is the bromine formal reduction potential and E(Ru^{2+*/+}) is the excited state reduction potential of **RuBPZ**²⁺, calculated to be 1.68 V vs NHE with a previously reported ground state reduction potential of -0.49 V vs. NHE,²⁴ and the free energy stored in the excited state ΔG_{ES} is 2.17 eV. The work term, ΔG_w , accounts for the Coulombic energy associated with electron transfer, and is defined in eq 10, where k_e is Coulomb's constant, ε is the relative permittivity of acetone (20.7), Z_{Br} is the charge of bromide, Z_i is the partial charge of atom i in **RuBPZ**²⁺, and r_i is the distance between bromide and atom i in **RuBPZ**^{2+,35} Since the bromine atom is uncharged, the Coulombic potential energy after electron transfer is zero. For the reactants, ΔG_w was approximated by assuming point charges in the center of mass for **RuBPZ**²⁺ and Br⁻ with a sum of the ionic radii as 8.96 Å, from which ΔG_w was calculated to be 0.15 eV. This afforded an estimate of E(Br^{•/-}) = 1.42 V vs. NHE, which is substantially more negative that the accepted value in water of 1.92 V vs. NHE.²³

$$\Delta G_{\rm rxn} = [E(Br^{\bullet/-}) - E(Ru^{2+*/+})] \mathscr{F} + \Delta G_{\rm w}$$
⁽⁹⁾

$$\Delta G_{\rm w} = \frac{\rm k_e}{\epsilon} \Delta \sum_{i=1}^{2} \frac{\rm Z_{\rm Br} Z_i}{\rm r_i} \tag{10}$$

Ligand Exchange Mechanism

An Achilles heel of Ru diimine complexes is their susceptibility to ligand loss photochemistry, especially in the presence of halides. To our knowledge, in all such previously reported reactions one isomeric photoproduct of the form Ru(LL)₂X₂, where X stands for halides, were formed.³⁶ The vast majority of studies reported the cis-product,^{26-27, 29, 31, 37-53} while [Ru(bpy')(btz)₂]²⁺ (btz=1,1'-dibenzyl-4,4'-bi-1,2,3-triazolyl) yielded the *trans*-[Ru(bpy')(btz)(CH₃CN)₂]²⁺ isomer as the only photoproduct.⁵⁴⁻⁵⁶ Recently unprecedent ligand loss photochemistry was reported for an Os^{II} compound, [Os(btz)₃]²⁺, that yielded both *cis*- and *trans*-[Os(btz)₂(CH₃CN)₂]²⁺ photoproducts.⁵⁷ It was therefore of interest to understand the reaction mechanism in the present ligand loss photochemistry, a reaction that is unwanted for HBr splitting but, may have synthetic utility for preparing *trans*-Ru complexes.

To identify the photochemical reaction mechanism(s), acetone solutions of bromide and **RuBPZ**²⁺ were photolyzed and the reaction products were separated chromatographically and were characterized. This provided authentic samples of $[Ru(deeb)(bpz)(bpz)(Br)]^+$, *cis*- and *trans*-Ru(deeb)(bpz)Br₂ that were used as reference spectra for global analysis of the photolysis mixtures. It is notable that the trans isomer has significant absorption beyond 900 nm.

Figure 9 shows the visible absorption spectra of a 460-nm light illuminated bromide and **RuBPZ**²⁺ solution measured from 10 minutes to 20 hours. Note that the initial spectrum was used as a reference such that these represent difference spectra. It was not possible to simulate these spectra with standard addition of *cis*- and *trans*- Ru(deeb)(bpz)Br₂ and the spectra of [Ru(deeb)(bpz)(bpz)(Br)]⁺ was therefore included. Remarkably, standard addition of these three spectra afforded very good agreement with the experimental spectra throughout the entire photolysis experiment, suggesting these three species were the only visible light absorbing photoproducts involved. As shown in Figure 9b, the concentration of [Ru(deeb)(bpz)(bpz)(Br)]⁺ first increased and then decreased, consistent with its intermediate nature. Although ligand photosubstitution chemistry of Ru tris-diimine complexes has been known for several decades, the reaction mechanism is still unclear. Therefore, the present work represents one of the very few examples that enable isolation and direct observation of the photosubstitution intermediate. To the best of our knowledge, the only other reports managing to isolate the intermediate were the CH₃CN-substituted photochemistry of a series of [Ru(bpy')(btz)₂]²⁺ complexes.⁵⁴⁻⁵⁵



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Figure 9. a) Absorption changes measured from 10 min to 20 h during the 460-nm photolysis of a 55 μ M **RuBPZ**²⁺ and 110 μ M TBABr acetone solution. Overlaid on the data in red are modeled spectra. b) The concentration of each species as a function of time based on spectra modeling.

It was a surprise to find that *trans*-Ru(deeb)(bpz)Br₂ was the dominant photoproduct, particularly because thermal experiments indicated that *cis*-Ru(deeb)(bpz)Br₂ was the thermodynamically more stable isomer. Furthermore, only *cis*-photoproducts have been reported for the prototypical Ru(bpy)₃²⁺, consistent with these studies where *cis*-Ru(bpy)₂Br₂ was the only photoproduct observed. However, photolysis of acetone bromide solutions of [Ru(deeb)₂(bpz)]²⁺ or [Ru(deeb)₃]²⁺ revealed that both *cis*- and *trans*-dibromo isomers were formed. Therefore, the presence of the electron withdrawing ethyl ester or nitrogen groups appears to influence this photochemistry and prompted a closer investigation.

To rationalize the photochemistry, a mechanism wherein light absorption forms the MLCT excited state that undergoes activated crossing to a dissociative ligand field excited state³⁹ that dissociates a N from a bpz ligand followed by Br⁻ coordination to yield [Ru(deeb)(κ^1 -bpz)(bpz)Br]⁺, Scheme 2. This intermediate was isolated yet characterization failed to provide a conclusive stereochemistry. The inequivalence of the resonances associated with the ethyl esters and the large number of aromatic resonances associated with the diimmine ligands, suggests a *cis*-geometry, but this could also be a result of the lower symmetry of the κ^1 -bpz ligand and/or a mixture of both isomers which precludes a definitive assignment. The coordination of Br⁻ to Ru will weaken the Ru-N bond *trans*- to Br⁻ and as a weaker σ -donor the bpz ligand would be preferentially released. Full release of the bpz ligand required a second photon. If the intermediate was the *cis* isomer, a *cis*- product would be expected followed by isomerization to yield the *trans*-product. The proposed kinetic competition between Br⁻ coordination and isomerization implies that a higher yield Br⁻ concentration would yield more *cis*-isomer which was consistent with experimental findings (Figure S9).

Scheme 2. Proposed Mechanism for Ligand Substitution Photochemistry Between RuBPZ²⁺ And Br⁻.



Conclusion

In summary, visible light driven bromide oxidation by **RuBPZ**^{2+*} in acetone was investigated comprehensively by UV-vis, NMR, steady-state/time-resolved photoluminescence, and nanosecond transient absorption techniques. A ground state equilibrium between **RuBPZ**²⁺ and a single bromide ion pair [**RuBPZ**²⁺, Br⁻]⁺ was evident. Static and dynamic excited state electron transfer pathways were identified for [**RuBPZ**²⁺, Br⁻]⁺ and **RuBPZ**²⁺, respectively. Transient absorption spectroscopy revealed two photo-products: the reduced ruthenium complex, **RuBPZ**⁺, and Br₂^{•-}. The **RuBPZ**⁺ was a primary photochemical product while an intermediate Br[•] was involved in the formation of Br₂^{•-}. Prolonged laser irradiation afforded *cis*- and *trans*-Ru(deeb)(bpz)Br₂. A tentatively assigned [Ru(deeb)(bpz)(κ^{1} -bpz)Br]⁺ intermediate was proposed in the photochemical ligand loss mechanism. This study provides new insights into visible light driven halide oxidation and halide substitution reactions of coordination compounds in fluid solution.

Experimental

Materials. Tetrabutylammonium bromide (TBABr, Sigma-Aldrich, $\geq 99.0\%$), tetrabutylammonium tribromide (TBABr₃, Sigma-Aldrich, 98%), acetone (Burdick & Jackson, HPLC grade, >99.9%), acetonitrile (Burdick & Jackson, HPLC grade, >99.9%) and deuterated acetone (Cambridge Isotope Laboratories) were used as received. Argon gas (Airgas, 99.998%) was passed through a Drierite drying tube prior to use. [Ru(deeb)(bpz)₂](PF₆)₂ was prepared following literature procedure.⁵⁸

Preparation of *cis-* **and** *trans-***Ru(deeb)(bpz)Br₂.** A mixture of **RuBPZ**²⁺ (50 mg, 0.05 mmol) and TBABr (32 mg, 0.1 mmol) were dissolved in 100 mL of acetone in a round bottom flask sealed with a rubber septum. The solution was purged with argon for 20 min and illuminated with a white light lamp for 4 hours. The solvent was removed on rotary evaporator and the crude was loaded onto a silica gel column using DCM:MeOH = 20:1 (v: v) as eluent. After collecting a fast-moving green and purple bands, the eluent was changed to DCM:MeOH = 10: 1 (v: v), and the following orange band was collected. After removing the solvent on rotary evaporator, the three fractions were recrystallized in DCM/Hexane to afford the *trans*-Ru(deeb)(bpz)Br₂ (green), *cis*-Ru(deeb)(bpz)Br₂ (purple), and the intermediate [Ru(deeb)(bpz)(bpz)Br]⁺, respectively.

Characterization. NMR spectra were measured on a Bruker Avance III 600 MHz spectrometer at room temperature. NMR spectra were processed using MNOVA software. UV–Vis absorption spectra were recorded on a Varian Cary 60 spectrophotometer in a quartz cuvette with a 1.0 cm pathlength. Mass spectrometry was performed on a Shimadzu LCMS and an LTQ VELOS Thermo LCMS (positive mode).

Photoluminescence and Transient Absorption. Solutions were sparged with argon for at least 20 min prior to steady-state, time-resolved PL, and transient absorption experiments.

Steady-state PL spectra were obtained on a HORIBA Fluorolog 3 spectrofluorometer equipped with a 450 W Xe arc lamp as the excitation source. Samples were excited at 460 nm, which is the isosbestic point of **RuBPZ**²⁺ and [**RuBPZ**²⁺, Br⁻]⁺. The intensity was integrated for 0.1 s at 1 nm resolution and averaged over 3 scans. Quantum yields were measured using [Ru(bpy)₃](PF₆)₂ in dichloromethane as the standard ($\phi_{PL} = 0.029$) with the optically dilute method.⁵⁹

Time-resolved PL data were acquired with pulsed laser excitation at 500 nm (time resolution: 10 ns) by pumping a dye laser with a PTI GL-3300 nitrogen laser. The PL was detected by a Hamamatsu R928 PMT optically coupled to a ScienceTech Model 9010 monochromator terminated into a LeCroy Waverunner LT322 oscilloscope. PL decays were monitored at 630 nm and averaged over 180 scans.

For nanosecond transient absorption, a Q-switched, pulsed Nd:YAG laser (BigSky Brilliant B 5–6 ns fwhm, 1 Hz, \sim 1 cm in diameter) was doubled to 532 nm and served as the excitation light source. A 150 W xenon arc lamp (Applied Physics) pulsed at 1 Hz with 70 V was used as the probe at a right angle. The

light from the lamp was collected by a monochromator (SPEX 1702/04) optically coupled to an R928 photomultiplier tube (Hamamatsu). The signal from the PMT was sent to a digital oscilloscope (LeCroy 9450, Dual 330 MHz) and averaged 30 times to acquire the kinetic data.

Bromide Titration Experiments. Acetone solution of 4 mL 50 μ M **RuBPZ**²⁺ in a quartz cuvette was sparged with argon for 20 min. Argon was passed through acetone prior to the sample to minimize solvent evaporation. 5 mM argon-purged TBABr acetone solution was added to the **RuBPZ**²⁺ solution using a micro-syringe at an interval of 10 μ L until UV-Vis absorption/time-resolved PL became unchanged. The solution volume change was less than 5% throughout the titration. Note that in the UV-Vis titration experiments, argon purge was not performed.

Spectral Modeling. Franck-Condon lineshape analysis was performed following a published procedure.⁵⁸ The absorption of the photolysis solution was globally modelled using the molar extinction coefficient of the intermediate, *cis*-isomer, and *trans*-isomer as key spectra in a self-written Mathematica program, which afforded the concentration of each species.

Determination of the Extinction Coefficient of RuBPZ⁺. Acetone solution of 4 mL 50 μ M **RuBPZ**²⁺ was sparged with argon for 20 min in a quartz cuvette. Argon was passed through acetone prior to the sample to minimize solvent evaporation. 10 μ L argon-purged triethanolamine was added to the **RuBPZ**²⁺ solution using a micro-syringe and the mixture was irradiated with a lamp. The UV-Vis absorption of the solution was intermittently recorded until no further change, at which point the solution turned from orange to purple. The newly formed solution was the one-electron reduced product, **RuBPZ**⁺.

Determination of the Extinction Coefficient of Dibromide. Nanosecond transient absorption (TA) spectra of 50 μ M TBABr and 50 μ M TBABr₃ in CH₃CN was collected by pulsed excitation at 355 nm. The 50 ns and 10 μ s TA spectra, Δ Abs (50 ns) and Δ Abs (10 μ s), corresponds to reaction in eq 3 and eq 11, respectively, which gives rise to eq 12 and 13, in which C(Br₂^{•-}) represents the concentration of Br₂^{•-} at 50 ns after laser excitation and ϵ represents molar extinction coefficient.

$$Br_3^- + Br^- \to 2Br_2^{\bullet-} \tag{11}$$

 $\Delta Abs (50 \text{ ns}) = C(Br_2^{\bullet-}) * \varepsilon(Br_2^{\bullet-}) - C(Br_2^{\bullet-}) * \varepsilon(Br_3^{-})$ (12)

 $\Delta Abs (10 \ \mu s) = 2*C(Br_2^{\bullet-})*\varepsilon(Br_2^{\bullet-}) - C(Br_2^{\bullet-})*\varepsilon(Br_3^{-})$ (13)

Based on eq 12 and 13, $C(Br_2^{\bullet-})$ was calculated in eq 14.

$$C(Br_2^{\bullet-}) = [\Delta Abs (10 \ \mu s) - 2*\Delta Abs (50 \ ns)]/\epsilon(Br_3^{-})$$
(14)

 $\epsilon(Br_2^{\bullet-})$ was therefore calculated using eq 15.

$$\epsilon(Br_2^{\bullet-}) = [\Delta Abs \ (10 \ \mu s) - \Delta Abs \ (50 \ ns)] / \ C(Br_2^{\bullet-})$$
(15)

Photolysis Experiment. Acetone solutions containing 55 μ M **RuBPZ**²⁺ and 110 μ M or 1 mM TBABr in a quartz cuvette were sparged with argon gas for 20 mins in the dark prior to photolysis and sealed under positive pressure. Argon was passed through acetone prior to the sample to minimize solvent evaporation. The solutions were illuminated using a Coherent Genesis MX 460 nm solid state laser (power = 3.36 mW) and were stirred constantly during photolysis. The UV-Vis absorption of the solution was intermittently recorded on a Varian Cary 60 spectrophotometer with 1 nm resolution.

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Supporting Information. Nanosecond transient absorption spectra of TBABr₃ in acetone; disappearance kinetics of dibromide in acetone and CH₃CN; COSY NMR of **RuBPZ**²⁺ in acetone; steady-state PL of **RuBPZ**²⁺ and [**RuBPZ**²⁺, Br⁻]⁺ and overlaid Franck-Condon line-shape analysis; photo- and thermostability of *cis*- and *trans*- Ru(deeb)(bpz)Br₂ in acetone; mass spectrometry of [Ru(deeb)(bpz)(bpz)Br]⁺; NMR of [Ru(deeb)(bpz)(bpz)Br]⁺ in CDCl₃ with integration; thermal stability test of [Ru(deeb)(bpz)(bpz)Br]⁺ at 50 °C for 30 min in the dark; concentration of each species during 460-nm photolysis of 50 µM **RuBPZ**²⁺ and 1 mM TBABr acetone solution.

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Notes

The authors declare no competing financial interest.

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Visible Light Driven Bromide Oxidation and Ligand Substitution Photochemistry of a Ru Diimine Complex

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