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Intramolecular, Photoinduced Electron Transfer in Ruthenium(II) Bipyridine−Quinone Complexes

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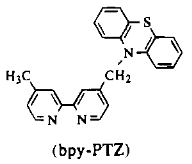
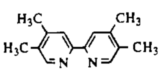
Intramolecular electron transfer quenching following metal-to-ligand charge transfer (MLCT) excitation of complexes of Ru^{II} containing the ligand *N*-((4′-methyl-2,2′-bipyridyl)-4-methyl)-9,10-anthraquinone-2-carboxamide (bpy-AQ) have been investigated by transient emission and absorption measurements. For $[Ru^{II}(bpy)_2(bpy\text{-}AQ)]^{2+}$ (bpy is 2,2′-bipyridine) in acetonitrile at room temperature, partial quenching of the initial ($Ru^{III}bpy^{\bullet-}$) excited state occurs as evidenced by decreased emission quantum yields (0.062 vs 0.011) and lifetimes (980 vs 158 ns) relative to $[Ru^{III}(bpy^{\bullet-})(bpy)(dmb)]^{2+*}$ (dmb is 4,4′-dimethyl-2,2′-bipyridine). In $[Ru^{II}(tmb)_2(bpy\text{-}AQ)]^{2+}$ (tmb is 4,4′,5,5′-tetramethyl-2,2′-bipyridine), electron transfer quenching is nearly complete ($\Phi_{em} = 0.002$, $\tau = 6$ ns). In neither case is there evidence for $AQ^{\bullet-}$ ($\lambda_{max} = 590$ nm) by transient absorption measurements, and it is concluded that the expected redox-separated states, e.g., $[Ru^{III}(bpy)_2(bpy\text{-}AQ^{\bullet-})]^{2+}$, undergo rapid back electron transfer to return to the ground states. MLCT excitation of the donor-chromophore-acceptor complex $[Ru^{II}(bpy\text{-}AQ)_2(bpy\text{-}PTZ)]^{2+}$ [bpy-PTZ is {10−[(4′-methyl-2,2′-bipyridin-4-yl)methyl]phenothiazine}] leads to formation of the redox-separated state $[Ru^{II}(bpy\text{-}AQ)(bpy\text{-}AQ^{\bullet-})(bpy\text{-}PTZ^{\bullet+})]^{2+}$ ($\lambda_{max}(-PTZ^{\bullet+}) = 510$ nm) in approximately 40% yield. It undergoes back-electron-transfer to give the ground state with $k(25\ °C, CH_3CN) = 6.7 \times 10^6\ s^{-1}$.

Introduction

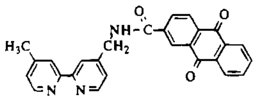
Chromophore−quencher complexes based on polypyridyl complexes of Ru^{II}, Os^{II}, and Re^{I} have proven valuable in the study of photoinduced electron and energy transfer.[1−4] In these studies a variety of oxidative and reductive quenchers have been linked chemically to complexes containing metal-to-ligand charge transfer (MLCT) chromophores. In many of these studies pyridiniums have been utilized as the electron acceptor.[5] We report here an extension of this chemistry in which a quinone acceptor is employed. Quinones play an important role in the natural photosynthetic apparatus[6] and have been used extensively as electron acceptors in electron transfer studies involving organic donors and porphyrins.[7] There is an extensive background synthetic chemistry,[7,8] and redox potentials can be varied systematically by altering the substituents on the quinone.[8] Recently Lehn et al. reported data on a bipyridine−quinone ligand in a polypyridyl complex of Ru^{II}.[7a] In our studies we have prepared a series of chromophore-quencher complexes that incorporate the anthraquinone-based acceptor ligand bpy-AQ (*N*-(4′-methyl-2,2′-bipyridyl)-4-methyl)-9,10-anthraquinone-2-carboxamide), the donor bpy-PTZ {10-[(4′-methyl-2,2′-bipyridin-4-yl)methyl]phenothiazine}, and the ancillary ligands bpy (2,2′-bipyridine), dmb (4,4′-dimethyl-2,2′-bipyridine), and tmb (4,4′,5,5′-tetramethyl-2,2′-bipyridine. We report here that MLCT excitation of these complexes leads to photoinduced electron transfer. In the donor−chromophore−acceptor complex $[Ru^{II}(bpy\text{-}AQ)_2(bpy\text{-}PTZ)]^{2+}$, one isomer of which is illustrated below, excitation gives rise to the redox-separated state $[Ru^{II}(bpy\text{-}AQ^{\bullet-})(bpy\text{-}AQ)(bpy\text{-}PTZ^{\bullet+})]^{2+}$.



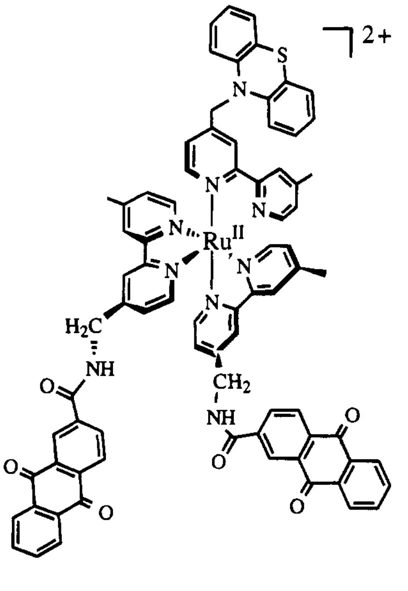
(bpy-PTZ)



(tmb)



(bpy-AQ)



$[Ru^{II}(bpy\text{-}AQ)_2(bpy\text{-}PTZ)]^{2+}$

Experimental Section

Materials. The ligands 4,4′,5,5′-tetramethyl-2,2′-bipyridine[9] and bpy-PTZ[10] and the complexes $[Ru^{II}(bpy)_2Cl_2{\cdot}2H_2O]$[11] and $[Ru^{II}(dmb)_2Cl_2]$[12] were prepared according to published procedures. The complex $[Ru^{II}(tmb)_2Cl_2]$ was prepared by using the same method as for $[Ru^{II}(dmb)_2Cl_2]$. The compounds 2,2′-bipyridine, 4,4′-dimethyl-2,2′-bipyridine, anthraquinone-2-carboxylic acid, Proton Sponge, and $RuCl_3{\cdot}3H_2O$ were obtained from Aldrich and used as supplied. Thionyl chloride was obtained from Aldrich and distilled before use. All

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solvents used in the preparations were reagent grade and used as supplied except where specified. Spectrophotometric grade acetonitrile (Burdick and Jackson) was used for all spectroscopic and electrochemical measurements. The electrolyte $[N(n\text{-}C_4H_9)_4]PF_6$ (TBAH) was obtained from Aldrich and recrystallized from hot EtOH. Chemical analyses were performed by Oneida Research Services, Inc.

N-(4′-methyl-2,2′-bipyridyl-4-methylene)-9,10-anthraquinone-2-carboxamide (bpy-AQ). Approximately 0.460 g (0.0023 mol) of 4-aminomethyl-4′-methyl-2,2′-bipyridine[10] and 0.495 g (0.0023 mol) of Proton Sponge were placed in a reaction flask along with 50 mL of distilled THF. The solution was allowed to stir at room temperature for 5 min, and 0.625 g (0.0023 mol) of 2-(chlorocarboxy)anthraquinone were added to the stirring solution. The mixture was allowed to stir overnight. The solution was filtered, and the solvent removed by rotary evaporation. The solid was purified on a silica gel column by using 8:2 toluene/acetonitrile as the eluent (350 mg, 85% yield). Anal. Calcd for $C_{27}H_{19}N_3O_3$: C, 74.81; H, 4.42; N, 9.69. Found: C, 74.49; H, 4.37; N, 8.97. ^1H NMR ($CDCl_3$): δ 2.50 (3H, s), 4.80 (2H, d), 7.30 (1H, d), 7.41 (1H, d), 7.63 (1H, b), 7.80 (2H, m), 8.30 (3H, m), 8.40 (2H, m), 8.53 (1H, d), 8.65 (2H, m), 8.73 ppm (1H, s).

$[Ru(bpy)_2(bpy\text{-}AQ)](PF_6)_2$. The complex $[Ru(bpy)_2Cl_2]\cdot 2H_2O$ (0.200 g, 3.84×10^{-4} mol) was added to 25 mL of 95% EtOH and allowed to stir for 10 min under Ar. To the stirring reaction mixture was added bpy-AQ, (0.250 g, 5.76×10^{-4} mol). The mixture was heated to reflux and maintained at reflux for 2.25 h. The reaction mixture was allowed to cool to room temperature. A saturated aqueous solution of NH_4PF_6 was added to the reaction flask. The resulting orange precipitate was filtered and washed with EtOH and diethyl ether (429 mg, 92% yield). Anal. Calcd for $C_{47}H_{35}N_7O_3F_{12}P_6Ru$: C, 49.66; H, 3.10; N, 8.62. Found: C, 49.15; H, 2.94; N, 8.41. ^1H NMR (CD_3CN): δ 2.50 (3H, s), 4.74 (2H, d), 7.23 (1H, d), 7.37 (5H, m), 7.53 (1H, d), 7.64 (1H, d), 7.70 (5H, m), 7.91 (2H, m), 8.02 (4H, m), 8.15 (1H, t), 8.30 (3, m), 8.39 (1H, s), 8.47 (5H, m), 8.70 ppm (1H, s).

$[Ru(tmb)_2(bpy\text{-}AQ)](PF_6)_2\cdot 2H_2O$. The complex $Ru(tmb)_2Cl_2$ (0.200 g, 3.35×10^{-4} mol) and bpy-AQ (0.145 g, 3.35×10^{-4} mol) were mixed in 95% EtOH and heated at reflux for 2.5 h under Ar. The reaction was allowed to cool and rotary evaporated almost to dryness. A saturated aqueous solution of NH_4PF_6 was added to obtain the PF_6^- salt. The resulting orange precipitate was filtered and washed with EtOH and diethyl ether (325 mg, 69% yield). Anal. Calcd for $C_{55}H_{51}N_7O_5P_2F_{12}Ru$: C, 51.40; H, 4.28; N, 7.63. Found: C, 51.44; H, 4.06; N, 7.63 ^1H NMR (acetone-d_6): δ 2.53 (3H, s), 2.81 (12H, s), 2.84 (12H, s), 4.89 (2H, d), 7.37 (1H, d), 7.54 (1H, s), 7.65 (4H, m), 7.84 (1H, d), 7.91 (1H, d), 7.98 (2H, m), 8.31 (2H, m), 8.40 (2H, d), 8.53 (4H, s), 8.63 (1H, s), 8.73 (1H, s), 8.81 (1H, s), 9.01 ppm (1H, t).

$[Ru(bpy\text{-}AQ)_2Cl_2]$. The compound $Ru(DMSO)_4Cl_2$ (0.056 g, 1.16 $\times 10^{-4}$ mol) was dissolved in 5 mL of ethylene glycol under Ar. To this solution was added bpy-AQ (0.100 g, 2.31×10^{-4} mol) and LiCl (0.049 g, 1.16×10^{-3} mol). The reaction mixture was allowed to heat at reflux for 15 min and cooled to room temperature. The mixture was poured into 5 mL of distilled water and 10 mL of CH_2Cl_2. The purple organic layer was removed and the water layer was further extracted with CH_2Cl_2 (4 × 10 mL). The organic layers were combined and dried over Na_2SO_4 for 2 h. The Na_2SO_4 was filtered off and the filtrate rotary evaporated to dryness. The solid obtained was not further purified (187 mg, 53% yield).

$[Ru(bpy\text{-}AQ)_2(bpy\text{-}PTZ)](PF_6)_2\cdot 3H_2O$. The complex $Ru(bpy\text{-}AQ)_2Cl_2$ (0.100 g, 9.63×10^{-5} mol) and bpy-PTZ (0.055 g, 1.44×10^{-4} mol) were dissolved in 20 mL of EtOH and heated at reflux for 2 h under Ar. The reaction mixture was cooled to room temperature and rotary evaporated almost to dryness. A saturated aqueous solution of NH_4PF_6 was added to the solution to precipitate the PF_6^- salt. The resulting orange precipitate was filtered and washed with EtOH and

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Table 1. Spectral and Electrochemical Data in Acetonitrile at 23 ± 2 °C

	$E_{1/2}$, V (vs SSCE)[b]					
complex[a]	PTZ$^{0/+}$	AQ$^{0/-}$	L$^{0/-}$ [c]	Ru$^{III/II}$	λ_{max}, nm[d]	ϵ[e]
$[Ru^{II}(dmb)_3]^{2+}$			−1.47	+1.09	250, π → π*	18 200
					288, π → π*	58 100
					458, dπ → π*	10 200
$[Ru^{II}(bpy)_2(dmb)]^{2+}$			−1.40	+1.27	246, π → π*	25 200
					286, π → π*	75 600
					454, dπ → π*	13 100
$[Ru^{II}(tmb)_2(dmb)]^{2+}$			−1.49	+1.07	208, π → π*	72 400
					258, π → π*	26 500
					290, π → π*	77 200
					450, π → π*	13 300
$[Ru^{II}(bpy)_2(bpy\text{-}AQ)]^{2+}$		−0.79	−1.38	+1.26	212, π → π*	99 500
					258, π → π*	96 200
					288, π → π*	114 000
					326, π → π*	23 400
					456, dπ → π*	20 800
$[Ru^{II}(tmb)_2(bpy\text{-}AQ)]^{2+}$		−0.85	−1.55	+1.09	210, π → π*	96 500
					258, π → π*	80 100
					290, π → π*	93 500
					326, π → π*	19 800
					450, dπ → π*	14 800
$[Ru^{II}(bpy\text{-}AQ)_2(bpy\text{-}PTZ)]^{2+}$	+0.80	−0.76	−1.72	+1.18	216, π → π*	132 000
					248, π → π*	147 000
					256, π → π*	147 000
					288, π → π*	134 000
					326, π → π*	42 800
					460, dπ → π*	25 100

[a] As PF_6^- salts. [b] Volts vs (SSCE) in CH_3CN solution with 0.1 M tetra-*n*-butylammonium hexafluorophosphate, $[N(n\text{-}C_4H_9)_4]PF_6$, as supporting electrolyte, ± 0.02 V. [c] $E_{1/2}$ for the first polypyridyl-based reductions. [d] Absorption λ_{max} ± 2 nm and band assignments. [e] ϵ values in L mol^{-1} cm^{-1}.

Table 2. Emission Energies, Quantum Yields, and Lifetimes in Acetonitrile at 23 ± 2 °C

complex[a]	λ_{max}, nm (E_{em}, eV)[b]	Φ_{em}[c]	τ, ns[d]	τ_{rs}, ns[e]
$[Ru^{II}(bpy)_3]^{2+}$	626 (1.98)	0.062	920	
$[Ru^{II}(dmb)_3]^{2+}$	642 (1.93)	0.100	950	
$[Ru^{II}(bpy)_2(dmb)]^{2+}$	640 (1.94)	0.07	980	
$[Ru^{II}(tmb)_2(dmb)]^{2+}$	642 (1.93)	0.062	708	
$[Ru^{II}(bpy)_2(bpy\text{-}AQ)]^{2+}$	634 (1.96)	0.011	158	<20
$[Ru^{II}(tmb)_2(bpy\text{-}AQ)]^{2+}$	680 (1.82)	0.002	<6	<2
$[Ru^{II}(bpy\text{-}AQ)_2(bpy\text{-}PTZ)]^{2+}$	670 (1.85)	0.003	17	150

[a] As PF_6^- salts. [b] Emission band maxima in nm (±2) and in eV. [c] Emission quantum yields, ±10%. [d] Emission lifetimes (±5%) at the emission maxima following laser excitation at 460 nm. [e] Redox separated state lifetime measured by transient absorption measurements.

diethyl ether (70 mg, 44% yield). Anal. Calcd for $C_{78}H_{63}N_9O_9F_{12}P_2SRu$: C, 57.15; H, 3.50; N, 7.69. Found: C, 55.32; H, 3.75, N, 7.45. ^1H NMR (CD_3CN): δ 2.37 (3H, s), 2.48 (6H, s), 4.71 (4H, s), 5.27 (2H, d), 6.75 (2H, d), 6.91−7.64 (15H, m), 7.87 (4H, m), 8.04−8.60 ppm (19H, m).

General Methods. Uncorrected melting points were obtained with a Fisher-Johns apparatus. UV−vis spectra were recorded on a Hewlett-Packard 8452A photodiode-array spectrophotometer. Infrared spectra were recorded on a Nicolet DX20 FT-IR spectrophotometer. ^1H NMR spectra were recorded at 200 MHz on a Bruker AC 200 spectrometer. Cation-exchange HPLC was performed with an Aquapore CX-300 column (1.0 cm × 10 cm) of poly(DL-Asp)silica (Brownlee) with a gradient of 0−400 mM KBr in 2:3 (v/v) CH_3CN/0.6 mM phosphate buffer (pH 7.2). Thin-layer chromatograms were performed on Bakerflex silica gel plates.

Electrochemistry. Tetra-1-butylammonium hexafluorophosphate (TBAH), $[(n\text{-}C_4H_9)_4N]PF_6$, was twice recrystallized from ethanol and vacuum dried for 10 h. UV-grade CH_3CN (Burdick and Jackson) was used as received. Cyclic voltammograms were obtained in 0.1 M TBAH/CH_3CN solutions with a Princeton Applied Research 273 potentiostat/galvanostat, a silver/silver nitrate (0.1 M) reference electrode, a platinum-wire auxiliary electrode, and a BAS MF-2013 platinum-disk working electrode (0.31 cm^2 electrode area) at a scan rate of 100 mV/s. All half-wave potentials are reported vs. SSCE.

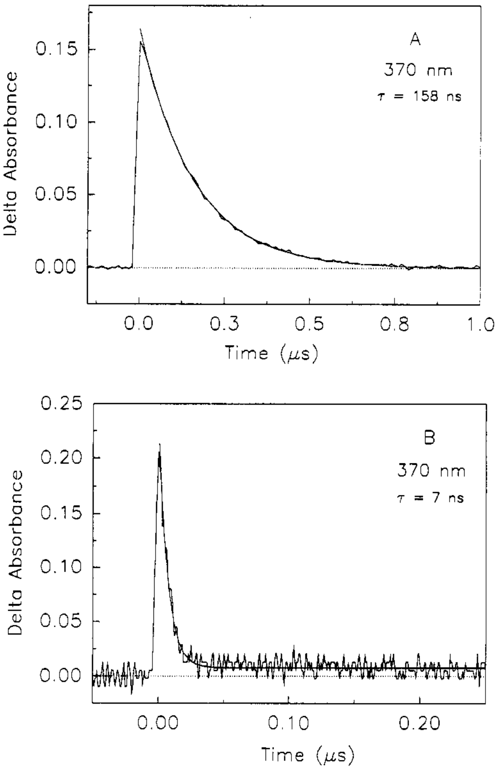

Figure 1. Transient absorption decay at 370 nm at 298 K following 420-nm excitation (1.2 mJ/pulse) of an CH_3CN solution: (a) $[Ru^{II}(bpy)_2(bpy\text{-}AQ)](PF_6)_2$ (A_{420} ~ 0.2); $[Ru^{II}(tmb)_2(bpy\text{-}AQ)](PF_6)_2$ (A_{420} ~ 0.2). The smooth curve is a single-exponential fit to the experimental data.

Photophysical Measurements. Luminescence spectra were obtained with a SPEX Fluorolog 212 photon-counting spectrofluorimeter with 460-nm excitation and a 2-mm slit width and are corrected for the instrument response by the procedure supplied by the manufacturer. Emission quantum yields, Φ_{em}, were measured in optically dilute CH_3CN solutions (A_{460} = 0.09−0.13) relative to $[Ru^{II}(bpy)_3](PF_6)_2$ for which

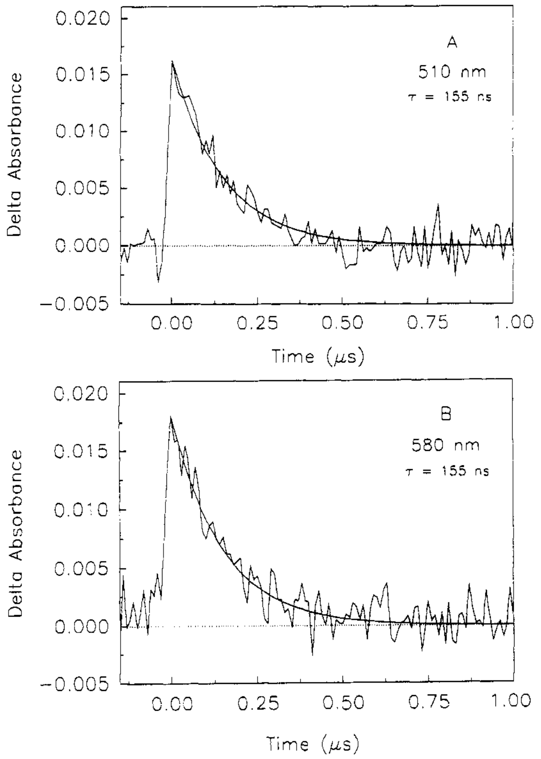

Figure 2. Transient absorption decay traces at 298 K following 420-nm excitation of an CH_3CN solution (A_{420} ~ 0.2) of $[Ru^{II}(bpy\text{-}AQ)_2(bpy\text{-}PTZ)](PF_6)_2$: (a) at 510 nm ($-PTZ^{\bullet+}$); (b) at 580 nm ($-AQ^{\bullet-}$). The smooth curve is a single-exponential fit to the experimental data.

Φ_{em} = 0.062 in CH_3CN at 295 K.[13] The quantum yields were calculated as reported previously.[14]

Emission lifetimes were measured with a PRA LN1000/LN 102 nitrogen laser/dye laser combination operated at 460 nm for sample excitation. Emission was monitored at 90° to the excitation with a PRA B204-3 monochromator and a cooled 10-stage Hammamatsu R928 PMT coupled to either a LeCroy 9400 digital oscilloscope or a LeCroy 6880/6010 transient digitizer interfaced to an IBM PC. Samples dissolved in UV-grade CH_3CN (Burdick and Jackson) had an absorbance of ~0.1 at 460 nm in a 1-cm quartz cuvette and were bubble-deoxygenated with high-purity argon for at least 10 min. This instrumentation and procedures used for treatment of data have been described previously.[14]

Nanosecond transient absorption spectra and kinetics were also obtained by means of previously described methods and instrumentation.[14,15] The third harmonic (354.7 nm) of a Quanta Ray DCR-2A Nd:YAG laser was used to pump a Quanta Ray PDL-2 dye laser to produce 420-nm excitation pulses with energy of <2 mJ/pulse, which was used to excite the samples. The excitation beam was coincident at the sample and colinear with the monitoring beam provided by an Applied Photophysics laser kinetic spectrometer, which utilized, a 300-W pulsed Xe arc lamp probe source, an *f*/3.4 grating monochromator, and a five-stage PMT. The resulting output was collected with the use of a LeCroy 6880/6010 transient digitizer interfaced to an IBM PC. Electronic control and synchronization of the laser, probe, and transient digitizer were provided by electronics of our own design. Appropriate Oriel or Corning cutoff filters were used to exclude high-energy probe light and minimize direct irradiation of PTZ. UV-grade CH_3CN (Burdick and Jackson) solutions with absorbances of 0.09–0.13 were bubble-deoxygenated with high-purity argon for at least 10 min.

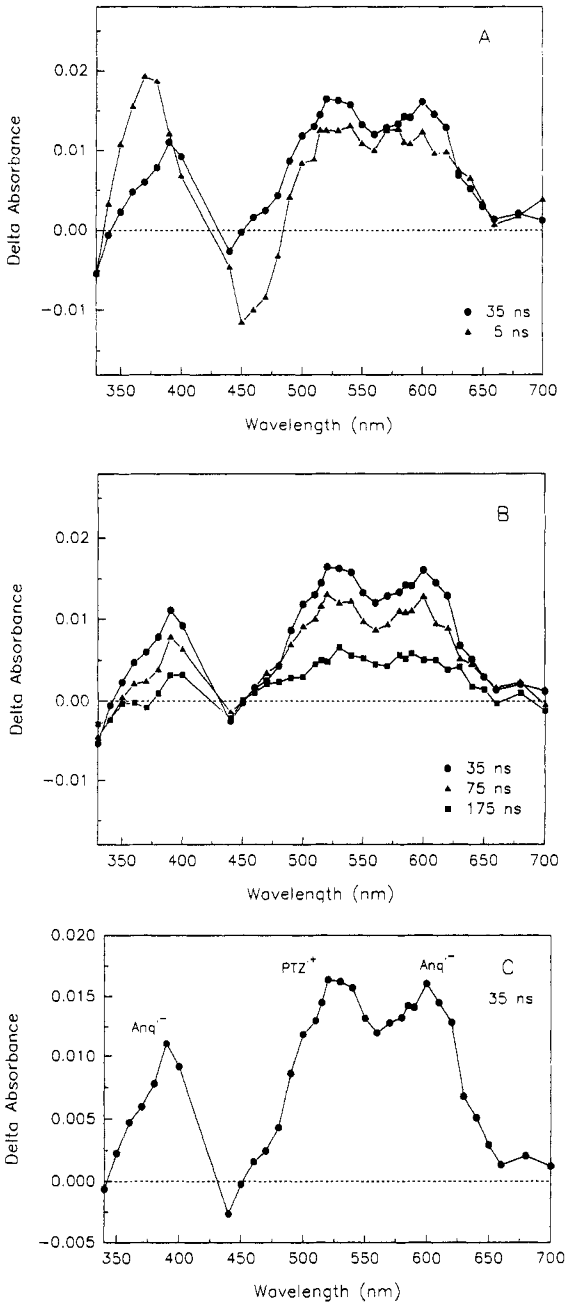

Figure 3. Nanosecond transient absorption difference spectra obtained following 420-nm, 4-ns pulsed (1.2 mJ/pulse) excitation of $[Ru^{II}(bpy\text{-}AQ)_2(bpy\text{-}PTZ)](PF_6)_2$ in CH_3CN at 25 °C: (a) rise of the transient spectrum; (b) decay; (c) transient spectrum of $[Ru^{II}(bpy\text{-}AQ^{\bullet-})(bpy\text{-}AQ)(bpy\text{-}PTZ^{\bullet+})]^{2+}$ at its maximum concentration 35 ns after excitation.

For full-spectrum transient absorption measurements, a 20 mL sample was freeze–pump–thaw degassed to ~10^{-6} Torr in a "tipsy" cell, which was then sealed. Use of this cell provided a renewable supply of unirradiated sample during the experiment.

Both emission and transient absorption decay profiles followed simple first order kinetics.

Results

UV–Visible Absorption Spectra. UV–visible absorption maxima and electrochemical data are given in Table 1. Spectra in the visible region are dominated by MLCT bands of high absorptivity arising from $d\pi(Ru^{II}) \rightarrow \pi^*(bpy)$ transitions and in the UV region by ligand-based $\pi \rightarrow \pi^*$ bands. The latter include bpy-based bands and bands arising from the phenothiazine and/or anthraquinone derivatives.

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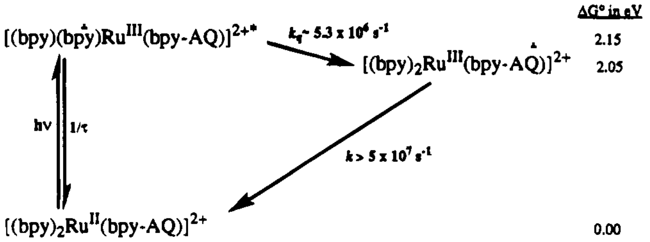
(13) Boyde, S.; Strouse, G. F.; Jones, W. E., Jr.; Meyer, T. J. *J. Am. Chem. Soc.* **1989**, *111*, 7448.

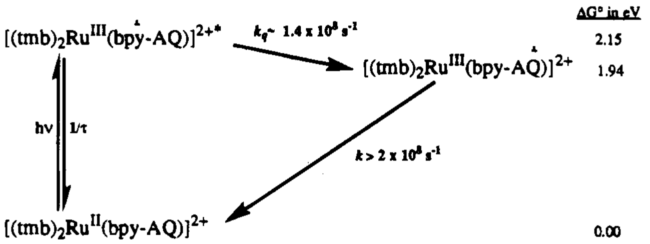
(14) Chen, P.; Duesing, R.; Graff, D. K.; Meyer, T. J. *J. Phys. Chem.* **1991**, *95*, 5850.

(15) (a) Younathan, J.; Jones, W. E.; Meyer, T. J. *J. Phys. Chem.* **1991**, *95*, 488. (b) Duesing, R.; Tapolsky, G.; Meyer, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 5378.

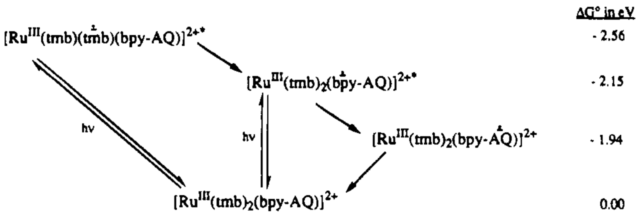
Scheme 1



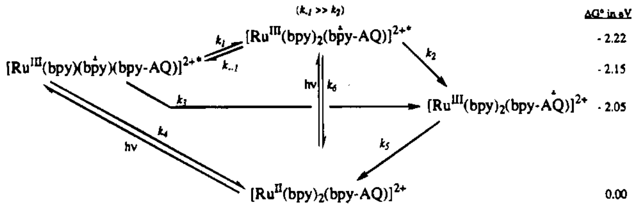
Scheme 2



Scheme 3



Scheme 4



Electrochemistry. $E_{1/2}$ values were obtained by cyclic voltammetry in 0.1M TBAH in acetonitrile vs SSCE and are listed in Table 1. In all of the complexes, the first polypyridyl-based reductions were observed from −1.29 to −1.72 V, and the $Ru^{III/II}$ couples from +1.09 to +1.26 V. For $[Ru^{II}(bpy\text{-}AQ)_2(bpy\text{-}PTZ)]^{2+}$ the $PTZ^{+/0}$ couple appears at $E_{1/2} = +0.80$ V and the second, irreversible PTZ-based oxidation at $E_{1/2} = +1.56$ V. Reduction of bound bpy-AQ occurs in the range $E_{1/2} = -0.76$ to -0.85 V.

Emission. Emission energies, quantum yields (Φ_{em}), and lifetimes (τ) for the MLCT-based emissions are given in Table 2 and are compared with those of $[Ru^{II}(dmb)_3]^{2+}$, $[Ru^{II}(bpy)_2(dmb)]^{2+}$, and $[Ru^{II}(tmb)_2(dmb)]^{2+}$. Emission from $[Ru^{II}(bpy\text{-}AQ)_2(bpy\text{-}PTZ)]^{2+}$ occurred with $\Phi_{em} = 0.003$ and $\tau = 17$ ns with a small fraction (≤5%) of a long-lived component ($\tau \sim 1$ μs) that was due to an impurity.

Transient Absorption. Laser flash excitation of CH_3CN solutions containing $[Ru^{II}(bpy)_2(bpy\text{-}AQ)]^{2+}$ with a 420-nm, 4-ns laser pulse resulted in the appearance of typical transient absorption features, $\lambda_{max} = 370$ nm ($\pi \rightarrow \pi^*$, $bpy^{\bullet-}$), and a bleach at 460 nm (loss of $d\pi \rightarrow \pi^*$). They decay to the ground state with $\tau = 158$ ns, Figure 1a. There were no absorption features in the 590-nm region for $AQ^{\bullet-}$.[16] The same spectral changes were observed for $[Ru^{II}(tmb)_2(bpy\text{-}AQ)](PF_6)_2$ but with $\tau < 6$ ns, Figure 1b, with no evidence for $-AQ^{\bullet-}$.

Laser flash excitation of $[Ru^{II}(bpy\text{-}AQ)_2(bpy\text{-}PTZ)](PF_6)_2$ in CH_3CN gave the positive and negative absorptions at 370 and 460 nm for an MLCT excitated state with $\tau = 19$ ns and a long-lived component attributable to the emitting impurity seen in the emission data. Decay of the MLCT absorption features was accompanied by the appearance of new bands at 510 and 590 nm, consistent with $-PTZ^{\bullet+}$ and $-AQ^{\bullet-}$ in the redox-separated state $[Ru^{II}(bpy\text{-}AQ^{\bullet-})(bpy\text{-}AQ)(bpy\text{-}PTZ^{\bullet+})]^{2+}$ (Figure 3). They decayed with $\tau = 155$ ns at both 510 and 580 nm, Figure 2. The decay was monitored at 580 nm to obtain less noise in the signal. The assignment of $-AQ^{\bullet-}$ at $\lambda_{max} = 590$ nm was confirmed by comparison with the spectrum obtained by a spectroelectrochemical study of Anq-$NHCH_3$ (*N*-methyl-9,10-anthraquinone-2-carboxamide), as described elsewhere.[16] The relative absorption changes associated with the redox-separated state were of comparable intensity and reached their maximum ~35 ns after laser flash excitation. At this point, the redox-separated state had formed in ~40% yield relative to the known efficiency of cage escape of the paraquat radical cation ($PQ^{\bullet+}$, $\lambda_{max} = 610$ nm) following oxidative quenching of $[Ru^{II}(bpy)_3]^{2+*}$ in CH_3CN formed by 420-nm excitation.[17] For $AQ^{\bullet-}$, $\epsilon = 4000 \pm 100$ L mol^{-1} cm^{-1} at $\lambda_{max} = 592$ nm, from the spectroelectrochemical experiment.[16]

All samples were purified by ion-exchange HPLC prior to photophysical measurements. They were stable toward photo-induced decomposition under the conditions used as judged before and after photolysis by UV–visible absorption measurements.

Discussion

The results of the emission experiments provide clear evidence that the presence of the attached quinone group in the bpy-AQ ligand leads to a significant level of quenching of MLCT emission. Compared to the electronically related, parent complex, $[Ru^{II}(bpy)_2(dmb)]^{2+}$ with $\tau_{em} = 980$ ns, emission from $[Ru^{II}(bpy)_2(bpy\text{-}AQ)]^{2+}$ was quenched by ~84% with $\tau_{em} = 158$ ns ($k_q = 5.3 \times 10^6$ s^{-1}). Quenching in $[Ru^{II}(tmb)_2(bpy\text{-}AQ)]^{2+}$ relative to $[Ru^{II}(tmb)_2(dmb)]^{2+}$ with $\tau_{em} < 6$ ns ($k_q > 1.7 \times 10^8$ s^{-1}) was even greater, ~99%. These observations are consistent with Schemes 1 and 2 and electron transfer quenching. Because of the electronic substituent effect of the alkyl groups, the lowest MLCT state in $[Ru^{II}(bpy)_2(bpy\text{-}AQ)]^{2+}$ is at bpy and in $[Ru^{II}(tmb)_2(bpy\text{-}AQ)]^{2+}$ at the bpy of bpy-AQ.

There is no evidence from the transient absorption measurements for the buildup of the expected $-AQ^{\bullet-}$-based redox-separated states, and we conclude that subsequent $-AQ^{\bullet-} \rightarrow Ru^{III}$ back-electron-transfer is more rapid than initial quenching. The quenching rate constants (k_q) in these schemes were estimated from the experimental lifetimes (τ) and the lifetime for the model (τ_o) by

$$1/\tau - 1/\tau_o \sim k_q \tag{1}$$

The energies of the MLCT excited states ($\Delta G°_{ES}$) were estimated from parameters derived from emission spectral fitting[18] of the emission profiles of $[Ru^{II}(dmb)_3]^{2+}$, $[Ru^{II}(bpy)_2(bpy\text{-}AQ)]^{2+}$, and $[Ru^{II}(tmb)_2(bpy\text{-}AQ)]^{2+}$ in CH_3CN at 29.7 °C. The energies of the redox-separated states were estimated

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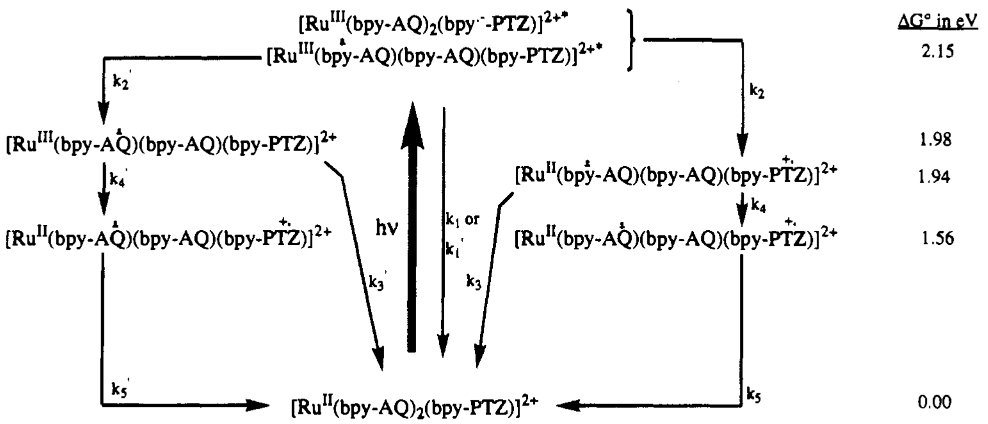
(16) (a) Nakayama, T.; Ushida, K.; Hamanoue, K.; Washio, M.; Tagawa, S.; Tabata, Y. *J. Chem. Soc., Faraday Trans. 1* **1990**, *86*, 95. (b) Mecklenburg, S. L.; McCafferty, D.; Peek, B. M.; Erickson, B. W.; Meyer, T. J. *Inorg. Chem.*, in press.

(17) Olmstead, J., III; Meyer, T. J. *J. Phys. Chem.* **1987**, *91*, 1649.

Scheme 5



from the electrochemical measurements by using eq 2 and the $E_{1/2}$ values in Table 1.

$$\Delta G^\circ_{\mathrm{ES}} = E_{1/2}(\mathrm{Ru}^{\mathrm{III/II}}) - E_{1/2}(\text{-AQ}^{0/-}) \tag{2}$$

The analysis of excited state energetics suggests that electron transfer quenching is only slightly spontaneous in either case. However, there is no evidence for nonexponentiality in the decay data, and it appears that dynamic coupling with the equilibrium ($\mathrm{bpy}^{\bullet-}$-AQ) $\rightleftharpoons$ (bpy-$\mathrm{AQ}^{\bullet-}$), Schemes 1 and 2, does not play an important role. Intramolecular electron transfer is irreversible.

The energy analysis predicts ligand-based, intramolecular kinetic effects. In $[\mathrm{Ru^{II}(tmb)_2(bpy\text{-}AQ)}]^{2+}$ the bpy of bpy-AQ is a lower energy MLCT acceptor than tmb. Intramolecular electron transfer by the sequence, $\mathrm{tmb}^{\bullet-} \rightarrow \mathrm{bpy}^{\bullet-}\text{-AQ} \rightarrow \text{bpy-AQ}^{\bullet-}$, is rapid because there is a free energy gradient, Scheme 3.

For $[\mathrm{Ru^{II}(bpy)_2(bpy\text{-}AQ)}]^{2+}$, bpy is the lower energy MLCT acceptor and $\mathrm{bpy}^{\bullet-} \rightarrow \mathrm{bpy}^{\bullet-}\text{-AQ} \rightarrow \text{bpy-AQ}^{\bullet-}$ electron transfer involves an initial uphill step, Scheme 4. In this case there are three pathways for $\mathrm{bpy}^{\bullet-}\text{-AQ} \rightarrow \text{bpy-AQ}^{\bullet-}$ electron transfer. In *pathway 1*, $\mathrm{Ru^{II}} \rightarrow$ bpy excitation is followed by sequential $\mathrm{bpy}^{\bullet-} \rightarrow \mathrm{bpy}^{\bullet-}\text{-AQ}$ (k_1, $\Delta G^\circ \sim +0.07$ eV) and $\mathrm{bpy}^{\bullet-}\text{-AQ} \rightarrow \text{bpy-AQ}^{\bullet-}$ (k_2, $\Delta G^\circ \sim -0.17$ eV) electron transfers. In *pathway 2*, $\mathrm{Ru^{II}} \rightarrow$ bpy excitation is followed by direct, through space $\mathrm{bpy}^{\bullet-} \rightarrow \text{bpy-AQ}^{\bullet-}$ electron transfer (k_3, $\Delta G^\circ \sim -0.10$ eV). In *pathway 3*, initial $\mathrm{Ru^{II}} \rightarrow$ bpy-AQ excitation is followed by $\mathrm{bpy}^{\bullet-}\text{-AQ} \rightarrow \mathrm{bpy}^{\bullet-}$ electron transfer (k_{-1}, $\Delta G^\circ \sim -0.07$ eV) to give $[\mathrm{Ru^{III}(bpy)(bpy^{\bullet-})(bpy\text{-}AQ)}]^{2+*}$, followed by pathways 1 and/or 2.

Electron transfer quenching by pathway 1, 2, or 3 could be relatively slow. For pathway 1 this is because of the uphill nature of the first step. For pathway 2 it is because of the outer-sphere nature of the electron transfer over a distance of ~3–4 Å. If pathway 1 dominates, k_q is the rate constant for electron hopping between the bpy ligands.

Pathway 3 occurs in competition with $\mathrm{bpy}^{\bullet-}\text{-AQ} \rightarrow \text{bpy-AQ}^{\bullet-}$ electron transfer to give the redox-separated state. If this pathway were an important competitior, the ratio of emission quantum yields for $[\mathrm{Ru(bpy)_2(dmb)}]^{2+}$ and $[\mathrm{Ru(bpy)_2(bpy\text{-}AQ)}]^{2+}$, $\Phi_0/\Phi \sim 6$, should have been greater than τ_0/τ. Since these values are comparable, $\tau_0/\tau \sim 6$, $k_2 \ll k_{-1}$ in Scheme 4. This observation also rules out a significant contribution from direct $\mathrm{Ru^{II}} \rightarrow$ -AQ excitation which is expected since there is no electronic basis for significant coupling between the donor and acceptor.

For both $[\mathrm{Ru^{III}(bpy)_2(bpy\text{-}AQ^{\bullet-})}]^{2+}$ and $[\mathrm{Ru^{III}(tmb)_2(bpy\text{-}AQ^{\bullet-})}]^{2+}$, back electron transfer is rapid as evidenced by the absence of evidence for the -$\mathrm{AQ}^{\bullet-}$-based electron transfer intermediates. On the basis of the experimental data, $k_q > 5 \times 10^7\ \mathrm{s^{-1}}$ for $[\mathrm{Ru^{III}(bpy)_2(bpy\text{-}AQ^{\bullet-})}]^{2+}$ and $k_q > 2 \times 10^8\ \mathrm{s^{-1}}$ for $[\mathrm{Ru^{III}(tmb)_2(bpy\text{-}AQ^{\bullet-})}]^{2+}$. This is true even though driving forces are large, ~2 eV, and the reactions occur in the inverted region.[19,20] There is sufficient flexibility in the amide link to bring $-\mathrm{AQ}^{\bullet-}$ in relatively close proximity to $\mathrm{Ru^{III}}$. The resulting electronic coupling may contribute to rapid back electron transfer.[21]

Transient absorption measurements provide direct evidence for intramolecular electron transfer quenching in $[\mathrm{Ru^{II}(bpy\text{-}AQ)_2(bpy\text{-}PTZ)}]^{2+}$. Emission was ~97% quenched relative to $[\mathrm{Ru(dmb)_3}]^{2+}$ with $\tau = 17$ ns ($k = 5.6 \times 10^7\ \mathrm{s^{-1}}$). The redox-separated state $[\mathrm{Ru^{II}(bpy\text{-}AQ)(bpy\text{-}AQ^{\bullet-})(bpy\text{-}PTZ^{\bullet+})}]^{2+}$ was observed following laser flash photolysis by the appearance of bands for $-\mathrm{PTZ}^{\bullet+}$ (510 nm) and $-\mathrm{AQ}^{\bullet-}$ (590 nm). It appeared within the laser pulse, continued to grow at the expense of MLCT emission, and reached a maximum, $\Phi_{\mathrm{rs}} \sim 40\%$, approximately 35 ns after the laser flash. It decayed with $\tau = 150$ ns ($k = 6.7 \times 10^6\ \mathrm{s^{-1}}$).

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(18) (a) In this procedure, emission spectra at 303 K in $\mathrm{CH_3CN}$ were fit by using one quantum mode and the solvent. The parameters were as follows: E_0, the energy gap; S, the electron–vibrational coupling constant (Huang–Rhys factor) for the acceptor mode; $\hbar\omega$, the quantum spacing; and $\Delta\bar{\nu}_{0,1/2}$, the full width at half-maximum for a single vibronic component. The parameters obtained for $[\mathrm{Ru(tmb)_2(bpy\text{-}AQ)}]^{2+}$ were $S = 0.83$, $\hbar\omega = 1350\ \mathrm{cm^{-1}}$, $E_0 = 14\,700\ \mathrm{cm^{-1}}$, and $\Delta\bar{\nu}_{0,1/2} = 2560\ \mathrm{cm^{-1}}$. The quantity $\Delta\bar{\nu}_{0,1/2}$ is related to the sum of the solvent reorganizational energy (χ_o) and the contribution from low-frequency modes treated classically[20b,c] (χ_L') by $\chi' = \chi_o + \chi_L' = (\Delta\bar{\nu}_{0,1/2})^2(16k_BT \ln 2)^{-1} = 1660\ \mathrm{cm^{-1}}$. With these definitions, the free energy content of the excited state above the ground state ($\Delta G^\circ_{\mathrm{es}}$), excluding the electronic entropic change which is expected to be small,[18e] is given by $\Delta G^\circ_{\mathrm{es}} = E_0 + \chi' = 2.15$ eV.[18b,d] (b) Hupp, J. T.; Neyhart, G. A.; Meyer, T. J.; Kober, E. M. *J. Phys. Chem.* **1993**, *97*, 10820. (c) Kober, E. M.; Caspar, J. V.; Lumpkin, R. S.; Meyer, T. J. *J. Phys. Chem.* **1986**, *90*, 3722. (d) Worl, L. A.; Duesing, R.; Chen, P.; Della Ciana, L.; Meyer, T. J. *J. Chem. Soc., Dalton Trans.* **1991**, 849. (e) Claude, J. P.; Meyer, T. J. Manuscript in preparation.

(19) (a) The Marcus inverted region is defined[19b–f] by $|\Delta G^\circ| > \lambda$, where λ is the reorganizational energy.[20] (b) Marcus, R. A. *J. Phys. Chem.* **1989**, *93*, 3078. (c) Brunschwig, B. S.; Sutin, N. *Comments Inorg. Chem.* **1987**, *6*, 209. (d) Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265. (e) Sutin, N. *Prog. Inorg. Chem.* **1983**, *30*, 441. (f) Siders, P.; Marcus, R. A. *J. Am. Chem. Soc.* **1981**, *103*, 748.

(20) (a) The sum of the intramolecular (λ_i) and solvent (λ_o) reorganizational energies ($\lambda = \lambda_i + \lambda_o$) can be estimated from self-exchange rate constant data, k_{ex}, by

$$\lambda = 4k_BT \ln(\nu_{\mathrm{et}}\mathrm{K_A}/k_{\mathrm{ex}}) \tag{3}$$

K_A is the equilibrium constant for formation of the association complex between reactants, and ν_{et} is the frequency factor for electron transfer. From $k_{\mathrm{ex}} \sim 1.0 \times 10^8\ \mathrm{s^{-1}}$ for anthraquinone$^{0/-}$ self-exchange,[20b] $\lambda(\mathrm{AQ}^{0/-}) \sim 7600\ \mathrm{cm^{-1}}$ (0.94 eV) if it is assumed that $(\nu_{\mathrm{et}}K_A) = 10^{12}\ \mathrm{s^{-1}}$. For bpy$^{0/-}$ self-exchange in $[\mathrm{Ru^{II}(bpy)_3}]^{2+/+}$ in $\mathrm{CH_3CN}$ at 298 K, $\lambda(\mathrm{Ru}^{2+/+}) \sim 7300\ \mathrm{cm^{-1}}$ (0.91 eV).[20c] From these values, $\lambda \sim [\lambda(\mathrm{Ru^{II/III}}) + \lambda(\mathrm{AQ}^{0/-})]/2 = 0.93$ eV and $-\Delta G^\circ > \lambda$. (b) Meisel, D.; Fessenden, R. W. *J. Am. Chem. Soc.* **1976**, *98*, 7505. (c) Chan, M.-S.; Wahl, A. C. *J. Phys. Chem.* **1978**, *82*, 2542.

The mechanism in Scheme 5 is consistent with schemes proposed earlier for related donor-chromophore-acceptor complexes.[1a,5a,16b] In the scheme, initial excitation produces MLCT excited states based either on Ru^{II} → bpy-PTZ or Ru^{II} → bpy-AQ excitation. They undergo electron transfer quenching by $(k_1 + k_2 + k'_2)$ or $(k_1' + k_2 + k'_2) \sim \tau_{em}^{-1} = 5.9 \times 10^7$ s^{-1} which is within an order of magnitude of k_q for the bpy-AQ complexes in Schemes 1 and 2. The simultaneous appearance of $-$AQ$^{\bullet-}$ and $-$PTZ$^{\bullet+}$ implies that initial quenching is followed by a second, rapid electron transfer. In either case the second electron transfer is favored by ~0.6 eV.

Given the results for [Ru(bpy)$_2$(bpy-AQ)]$^{2+}$ and [Ru(tmb)$_2$(bpy-AQ)]$^{2+}$ and the evidence for rapid back electron transfer between Ru^{III} and $-$AQ$^{\bullet-}$, the appearance of the redox-separated state may rely on the fraction of events occurring by the k_2 branch in Scheme 5 with initial-PTZ → Ru^{III} electron transfer. The equivalent reaction for [Ru^{III}(bpy)(bpy$^{\bullet-}$)(bpy-CH$_2$-PTZ)]$^{2+*}$ is known to be rapid[22] with $k \geq 2.5 \times 10^8$ s^{-1}; [Ru(bpy)(bpy$^{\bullet-}$)(bpy-CH$_2$-PTZ$^{\bullet+}$)]$^{2+}$, which results, returns to the ground state with $k = 8 \times 10^6$ s^{-1} ($\tau = 125$ ns). This path avoids formation of Ru^{III}(bpy-AQ$^{\bullet-}$) and rapid back-electron-transfer to the ground state (k_3'). Back-electron-transfer in [Ru^{II}(bpy-AQ$^{\bullet-}$)(bpy-AQ)(bpy-PTZ$^{\bullet+}$)]$^{2+}$ to give the ground state, k_5 in Scheme 3, occurs with $k = 6.7 \times 10^6$ s^{-1} and $\Delta G° = 1.56$ eV which is also in the inverted region. The mechanism does not proceed by reversal of the electron transfer chains, e.g., [Ru^{II}(bpy-AQ$^{\bullet-}$)(bpy-AQ)(bpy-PTZ$^{\bullet+}$)]$^{2+}$ → [Ru^{III}(bpy-AQ$^{\bullet-}$)(bpy-AQ)(bpy-PTZ)]$^{2+}$, because of the uphill nature of the initial steps. There may be contributions from a combination of through-bond and through-space electronic coupling.

The photophysical properties of the bis- and tris-substituted complexes could be complicated by positional isomerization arising from the unsymmetrical derivatization of the ligands.[23] The various isomers of [Ru^{II}(bpy-AQ)$_2$(bpy-PTZ)]$^{2+}$ are illustrated by the stick diagrams in Figure 4. For each isomer there is a *d,l* optical isomer pair. The sample used in this study was purified by ion-exchange HPLC and the major band collected was a single peak with no evidence for multiple components. There was no evidence for multiple isomers in the photophysical data in that transient absorption decay traces for return of the redox-separated state to the ground state were monoexponential.

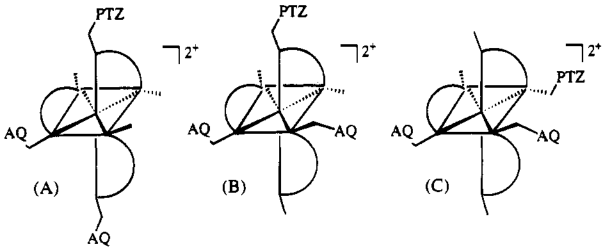

Figure 4. Positional isomers for [Ru^{II}(bpy-AQ)$_2$(bpy-PTZ)]$^{2+}$. The chelate rings are shown as arcs.

From these observations we conclude that either there is one dominant isomer in the sample or that a mixture of isomers exists which is not separable by ion-exchange HPLC. If there is more than one isomer, each has a comparable rate of back electron transfer, k_5 in Scheme 5. This may not be unreasonable since in all three isomers the $-$AQ$^{\bullet-}$/$-$PTZ$^{\bullet+}$ donor-acceptor pairs have the *cis* geometry relative to each other.

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