Synthesis of, Characterization of, and Photoinduced Processes in Polymetallic Triad Complexes Containing Fe(II), Ru(II), and Rh(III) Metal Centers

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A series of new trimetallic mixed complexes containing Fe(II), Ru(II), and Rh(III) metal centers have been prepared and characterized, and their excited-state properties in a nanosecond time domain have been investigated. These new compounds were synthesized by following a "building block" strategy from monomeric Rh(III) and Ru(II) polyazines and tetracyanoferrate(II) ions. The products generated in each synthetic step were fully characterized and their excited-state properties investigated. These new trimetallic complexes, $[(CN)_4Fe^{II}(BL(1))Ru^{II}(bpy)(BL(2))Rh^{III}(tpy)(MQ^+)](PF_6)_4$ (tpy = 2,2′:6′:2″-terpyridine; BL(1) = 2,3-bis(2-pyridyl)pyrazine (dpp) or 2,2′-bipyrimidine (bpm); BL(2) = dpp or bpm; MQ^+ = N-methyl-4,4′-bipyridinium (monoquat)), consist of three fundamental parts linked by bridging ligands (i) an electron donor group, the tetracyanoferrate(II) unit; (ii) an antenna fragment, the Ru(II) polypyridyl moiety; and (iii) an electron acceptor group. The electron acceptor group is a Rh(III) polypyridyl that contains the ligands tpy and MQ^+. No emission was observed in any of the reported complexes either in fluid solutions at room temperature or in glassy solutions at 77 K. Time-resolved experiments conducted on these triads showed formation of a transient intermediate within the laser pulse. Redox properties and transient absorption observations helped us to identify the nature of this intermediate as an Fe-(III)/Ru(II) mixed-valence species that decays exponentially by following a first-order law with a lifetime of $\tau \leq$ 70 ns in fluid solution at room temperature.

Introduction

Intramolecular electron transfer processes in supramolecular structures made of organic or inorganic sensitizers covalently linked to electron acceptor and/or electron donor groups are currently the subject of several investigations.[3−11] These systems show great promise in terms of their potential to generate relatively long-lived, charge-separated states. The role played by factors such as strength of the electronic coupling between the metal centers mediated by the bridging ligand, energetics

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of the photoinitiated electron and energy transfer processes, solvent, distance, and relative orientation of the parts has been investigated in detail.

Several homo- and heteropolynuclear complexes containing Ru(II) polypyridyl units with identical or different bridging ligands have been synthesized in our laboratory and others, and their ground- and excited-state properties have been determined.[9-11] Ru(II) polypyridyl complexes are suitable photosensitizers for such systems because of their many favorable properties. They are stable in a number of oxidation states, absorb light in a broad region of the visible spectrum, and possess relatively long-lived metal-to-ligand charge transfer states (MLCT).[3-5]

The electron transfer quenching of the excited state of a chromophore constitutes the primary step leading to energy-storing redox processes.[10,11] Creutz and Sutin measured the intermolecular reductive quenching of $[Ru(bpy)_3]^{2+*}$ by $[Fe^{II}(CN)_6]^{4-}$ ions and calculated a bimolecular rate constant of $k_q = 3.5 \times 10^9$ M$^{-1} \cdot$s^{-1}.[12]

$$[Fe^{II}(CN)_6]^{4-} + [Ru(bpy)_3]^{2+*} \rightarrow$$
$$[Fe^{III}(CN)_6]^{3-} + [Ru(bpy)_3]^{+} \quad (1)$$
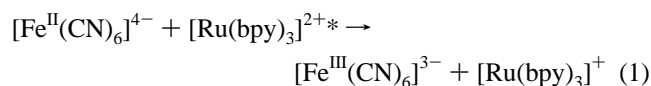
Intramolecular electron transfer quenching of Ru(II)* polypyridyl units by tetracyanoferrate(II) complexes was also investigated in our laboratories with binuclear complexes of the type $[(CN)_4Fe^{II}(BL)Ru^{II}(bpy)_2]$ (where BL = 2,3-bis(2-pyridyl)-pyrazine (dpp) or 2,2'-bipyrimidine (bpm)).[8] In these chromophore–quencher dyads, the tetracyanoferrate(II) moiety acts as an electron donor group and is bound to the Ru(II) center through a bridging ligand, bpm or dpp. The emission properties were correlated with the electronic coupling between both units and the communication ability of the bridging ligand.[8]

The work reported herein describes the design, synthesis, characterization, and excited-state properties of a series of trimetallic complexes, $[(CN)_4Fe^{II}(BL(1))Ru^{II}(bpy)(BL(2))Rh^{III}(tpy)(MQ^+)](PF_6)_4$ (bpy = 2,2'-bipyridine; tpy = 2,2':6',2''-terpyridine; MQ$^+$ = N-methyl-4,4'-bipyridinium (monoquat)). These triads contain three fundamental parts: (i) an antenna
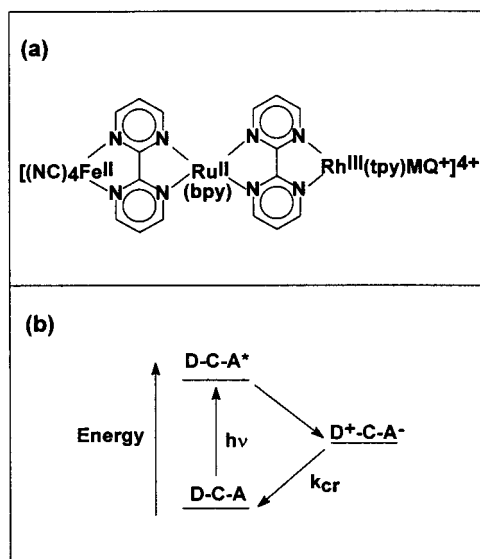
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Figure 1. Charge separation system: (a) one of four trimetallic complexes, $[(NC)_4Fe^{II}(BL(1))Ru^{II}(bpy)(BL(2))Rh^{III}(tpy)(MQ^+)]^{4+}$, when BL(1) = BL(2) = bpm; (b) typical scheme for a donor–antenna–acceptor system (D = electron donor; C = chromophore; A = electron acceptor).

fragment, the Ru(II) polyazine; (ii) an electron donor, the tetracaynoferrate unit; and (iii) an electron acceptor group, the Rh(III) mixed polyamine complex, containing the monoquat ligand. Once a d$_\pi$ electron hole is generated at the antenna fragment, there is ~+0.7 eV driving force for the Fe(II) center to reduce the antenna and form Fe^{III}BL^{-}·Ru^{II} intermediates. The electron acceptor system needs to be chosen on the basis of a sufficiently low orbital energy to accept an electron from the photoexcited ruthenium antenna (~+0.70 V vs SCE). Two of the species that proved to fit these energy requirements are monoquat, MQ$^+$, and methylated bipyrazine, dmbpz^{2+}.[13] In this work we used monoquat directly coordinated to a Rh(III) polypyridyl complex, $[Rh^{III}(tpy)(BL)(MQ^+)]^{4+}$ (BL = dpp or bpm), as the electron acceptor group. Rh(III) polypyridyl complexes were chosen because they have absorption, photophysics, and electrochemical properties thoroughly characterized and understood.[14-17] The purpose of this study was (i) to investigate the communication ability of the bridging ligands, bpm and dpp, when they are incorporated in a trimetallic structure and (ii) to assess the electron donor and acceptor capabilities of both groups, covalently attached to the chromophore through bridging ligands.

Figure 1 shows a simple scheme for a typical charge separation system, where the antenna fragment is excited upon illumination with UV or visible light. The design of each component part was based on previous studies with similar groups. It has been shown that redox and excited-state properties of polypyridyl complexes of Ru(II) and Rh(III) can be manipulated by introducing variations in the ligand composition. Surprisingly, these rhodium(III) fragments display unusual reduction potentials, where the Rh(III)/Rh(II) and tpy ligand (tpy$^{0/-}$) couples appear at more positive potentials than for

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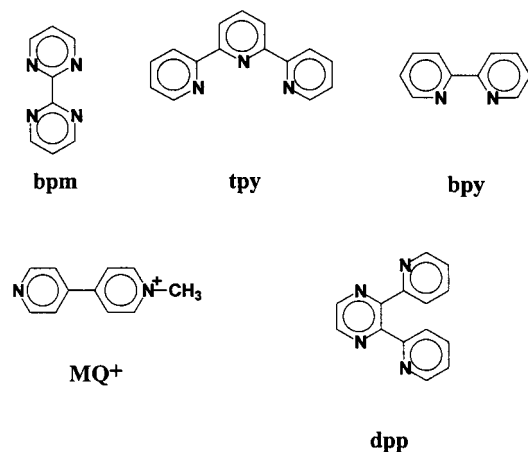
Figure 2. Structural formulas of the ligands.

similar Rh(III) moieties containing polypyridyl ligands. This fact influences the electron transfer reactions and directs the added electron toward the tpy ligand instead of the monoquat. However, the design of trimetallic systems offers a wide range of possibilities and a great deal of flexibility. Future modifications to these systems are discussed on the basis of our experimental observations.

To prepare the new series of triad complexes, we developed a sequential strategy consisting of a series of synthetic steps in which the precursor complexes, [Rh(tpy)(BL)MQ]$^{4+}$ and [Cl$_2$-Ru(bpy)(BL)Rh(tpy)MQ]$^{4+}$, are linked by bridging ligands. The synthesis and characterization of all the new materials are also reported in this paper. Figure 2 shows the structural formulas of the polypyridyl ligands used in this study.

Experimental Section

Materials. All materials were of reagent grade and were used without further purification. 2,2′-Bipyrimidine (bpm) was purchased from Lancaster Chemicals. *N*-Methyl-4,4′-bipyridinium (monoquat, MQ$^+$) was prepared by methylation of 4,4′-bipyridine with CH$_3$I and precipitated as the hexafluorophosphate salt.[18] Trichloro(terpyridine)-rhodium(III), [Rh(tpy)Cl$_3$], from RhCl$_3$·nH$_2$O (Sigma) plus terpyridine (Aldrich) was synthesized and purified by literature protocols.[17,19] Ru-(bpy)Cl$_4$ and [Ru(bpy)(bpm)$_2$](PF$_6$)$_2$ were prepared as reported previously.[20,21a] [Rh(bpy)$_2$(bpm)](PF$_6$)$_3$, [Rh(bpy)$_2$(4,4′-bpy)$_2$](PF$_6$)$_3$, and [(CN)$_4$Fe(dpp)Ru(tpy)(4,4′-bpy)] were available from previous work.[21]

[Rh(tpy)(BL)(MQ)](PF$_6$)$_4$ (BL = bpm or dpp). (i) [Rh(tpy)-(CF$_3$SO$_3$)$_3$]. Trifluoromethanesulfonic acid (CF$_3$SO$_3$H, 4 mL) was added dropwise to a stirred suspension of [Rh(tpy)Cl$_3$] (0.7 g, 2 mmol) in 1,2-dichlorobenzene (40 mL). The solution was heated at reflux under an N$_2$ atmosphere for 4 h. Cooling to room temperature, followed by addition of cold anhydrous Et$_2$O, induced precipitation of a bright yellow solid. The typical yield was 40%.

(ii) [Rh(tpy)(BL)(CF$_3$SO$_3$)](CF$_3$SO$_3$). A solution of [Rh(tpy)(CF$_3$-SO$_3$)$_3$] (0.5 g, 0.638 mmol) in acetone (20 mL) was added dropwise to an acetone solution (20 mL) containing 1.8 mmol of BL (BL = bpm, 0.285 g; BL = dpp, 0.42 g). The solution was heated at reflux for 24 h. Cooling to room temperature, followed by addition of cold anhydrous Et$_2$O, induced precipitation of a white solid. The solid was vacuum-filtered and washed several times with acetone and ether. This compound was used without further purification. The typical yield was 50%.

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(iii) [Rh(tpy)(BL)MQ](PF$_6$)$_4$. A solution of 0.3 mmol of [Rh(tpy)-(BL)(CF$_3$SO$_3$)](CF$_3$SO$_3$)$_2$ (BL = bpm, 0.282 g; BL = dpp, 0.31 g) and 0.25 g of MQ(PF$_6$) (0.8 mmol) in 40 mL of acetone was heated at reflux for 24 h. The solution was cooled to room temperature and the volume reduced to 10 mL by rotary evaporation. The solid product was obtained by addition of a saturated, aqueous solution of KPF$_6$. Purification was afforded by liquid chromatography employing alumina (Fisher, 80−200 mesh) as the stationary phase and acetonitrile/toluene (1:1) as the mobile phase. The pale yellow solid was precipitated with Et$_2$O. The typical yield was 50%.

Anal. Calcd for RhC$_{34}$H$_{29}$N$_9$P$_4$F$_{24}$: C, 32.74; H, 2.33; N, 10.11. Found: C, 32.61; H, 2.61; N, 10.00.

Anal. Calcd for RhC$_{40}$H$_{33}$N$_9$P$_4$F$_{24}$·H$_2$O: C, 35.85; H, 2.61; N, 9.41. Found: C, 35.33; H, 2.53; N, 9.39.

[Cl$_2$Ru(bpy)(BL)Rh(tpy)(MQ)](PF$_6$)$_4$ (BL = bpm or dpp). Ru-(bpy)Cl$_4$ (0.432 mmol, 0.18 g) was reduced over a Zn(Hg) amalgam under N$_2$ in EtOH/H$_2$O (50% v/v, 150 mL). During the course of the reduction, the color of the solution turned from dark brown to dark red (λ_{max} = 245, 295, 370, 520 nm). At this point, a deoxygenated solution of [Rh(tpy)(BL)(MQ)](PF$_6$)$_4$ (0.288 mmol; BL = bpm, 0.36 g; BL = dpp, 0.38 g) in a minimum amount of acetone was added with a gastight Hamilton syringe, and the mixture was stirred for 3 h. The volume was reduced to 20 mL and enough of a saturated, aqueous solution of KPF$_6$ was added to precipitate a dark-brown (BL = bpm) or dark-purple (BL = dpp) product. The solid was redissolved in acetonitrile and passed through a Sephadex LH-20 chromatographic column with EtOH/CH$_3$CN (2:1) as the mobile phase. Evaporation of the solvent led to a microcrystalline powder. The typical yield was 79%.

Anal. Calcd for RhRuC$_{44}$H$_{37}$N$_{11}$Cl$_2$P$_4$F$_{24}$·2H$_2$O: C, 32.41; N, 9.46, H, 2.51. Found: C, 32.37; N, 9.40; H, 2.56.

Anal. Calcd for RhRuC$_{50}$N$_{11}$H$_{41}$Cl$_2$P$_4$F$_{2\ 4}$·3H$_2$O: C, 33.63; N, 8.63; H, 2.63; Cl, 3.98. Found: C, 33.42; N, 8.64; H, 2.60; Cl, 3.91.

[(CN)$_4$Fe(BL)Ru(bpy)(bpm)Rh(tpy)(MQ)](PF$_6$)$_4$ (BL = bpm or dpp). A 0.15 g sample of [Cl$_2$Ru(bpy)(bpm)Rh(tpy)(MQ)](PF$_6$)$_4$·2H$_2$O (0.08 mmol) was dissolved in a minimum amount of acetone, and the solution was added to another solution containing 0.202 mmol of K$_2$-[Fe(CN)$_4$(BL)] in 100 mL of EtOH/water (3:1 v/v). After the mixture was stirred overnight at room temperature, the solvent was reduced by rotavaporation and a saturated aqueous solution of KPF$_6$ was added to induce precipitation. The dark solid was collected by vacuum filtration and washed with several portions of ethanol and then with ether. The solid was dissolved in acetonitrile and reprecipitated by slow addition of an aqueous solution of KPF$_6$. Purification of these compounds by column chromatography is very arduous, and the yield decreases drastically after each chromatographic step. Chromatography was conducted with columns containing Sephadex LH-20 as the solid phase and mixtures of EtOH/CH$_3$CN (2:1) as the mobile phase. However, it was found that the impurities come from a coprecipitation of excess KPF$_6$ and do not change the properties of the solid. Cyclic voltammetry confirmed the absence of monomeric and/or dimeric species. There is an excellent agreement between the experimental and predicted theoretical values for all the C/N ratios.

Anal. Calcd for FeRhRuC$_{56}$N$_{19}$H$_{43}$P$_4$F$_{24}$·2H$_2$O: C, 36.19; N, 14.32; H, 2.53; C/N = 2.53. Found: C, 36.18; N, 13.83; H, 2.55; C/N = 2.62. The typical yield was 20%.

Anal. Calcd for FeRhRuC$_{62}$H$_{47}$N$_{19}$P$_4$F$_{24}$·2H$_2$O·KPF$_6$: C, 35.21; N, 12.59; H, 2.22; C/N = 2.80. Found: C, 35.01; N, 12.39; H, 2.51; C/N = 2.83. The typical yield was 35%.

[(CN)$_4$Fe(BL)Ru(bpy)(dpp)Rh(tpy)(MQ)](PF6)$_4$ (BL = bpm or dpp). These compounds were prepared as described above for substituting [Cl$_2$Ru(bpy)(bpm)Rh(tpy)(MQ)](PF$_6$)$_4$·2H$_2$O (0.14 g, 0.08 mmol) for [Cl$_2$Ru(bpy)(dpp)Rh(tpy)(MQ)](PF$_6$)$_4$·3H$_2$O (0.15 g, 0.08 mmol).

Anal. Calcd for FeRhRuC$_{62}$H$_{47}$N$_{19}$P$_4$F$_{24}$: C, 39.22; N, 14.02; H, 2.48; C/N = 2.80. Found: C, 39.47; N, 13.80; H, 2.67; C/N = 2.86. The typical yield was 20%.

Anal. Calcd for FeRhRuC$_{68}$H$_{51}$N$_{19}$P$_4$F$_{24}$: C, 41.36; N, 13.48; H, 2.56; C/N = 3.07. Found: C, 41.45; N, 13.47; H, 2.59; C/N = 3.08. The typical yield was 39%.

General Methods. UV−visible spectra were obtained on a Shimadzu UV-3100 UV−vis−NIR spectrophotometer with 1-cm matched quartz cuvettes. Infrared spectra were recorded on a Nicolet 5D Fourier transform IR spectrometer. Samples were prepared as KBr pellets. Elemental analyses were performed by Atlantic Microlab, Atlanta, GA, and Midwest Microlab, Indianapolis, IN.

Electrochemistry. Tetrabutylammonium hexafluorophosphate, (n-$C_4H_9)_4N(PF_6)$ (Aldrich), was recrystallized twice from EtOH and vacuum-dried for 24 h. UV grade CH_3CN (Burdick and Jackson) was used as supplied. Cyclic voltammograms were recorded in 0.1 M (n-$C_4H_9)_4N(PF_6)/CH_3CN$ solutions with an EG&G Princeton Applied Research model 273 potentiostat/galvanostat, an IBM Instrument model 7424 MT X-Y recorder, and two 2 mm Pt disk electrodes for both working and auxiliary electrodes (Bioanalytical Sciences). All half-wave potentials were reported vs SCE at a scan rate of 200 mV·s^{-1}.

Photophysical Measurements. Luminescence spectra were obtained using a Spex Fluorolog II photon-counting spectrofluorometer equipped with a Hamamatsu R928 photomultiplier tube. Experimental control was effected by a Spex DM1B spectroscopy laboratory coordinator. The spectra were plotted on a Houston Instruments DMP-40 digital plotter and were uncorrected for instrument response.

Emission lifetimes were measured with a PRA LN 1000 nitrogen laser as an excitation source at 337 nm. Emission was monitored at 90° to the excitation beam with an ISA model H-10 F3/4 scanning monochromator and a Hamamatsu R928 photomultiplier tube powered by an EG&G Ortec 456 high-voltage power supply. The output of the detector was amplified and digitized with a Stanford Research SR250 gated integrater and a boxcar averager powered by a Stanford Research SR245 computer interface. Data manipulation was performed with the Stanford SR270 software. All decay traces were successfully fit to a single-exponential decay function.

Nanosecond laser flash photolysis measurements were conducted at the Radiation Laboratory, University of Notre Dame, Notre Dame, IN. A Quanta Ray Nd:YAG laser was employed to provide pulsed 355 nm, 10 ns, 5 mJ flash excitation. Each experimental data point and kinetic trace represents the average of at least 10 flash photolysis experiments. The samples were dissolved in CH_3CN, and the solutions were deaerated with O_2-free nitrogen for 20 min. A flow cell was employed to minimize photochemical decomposition. UV−visible spectra taken before and after each flash photolysis experiment were identical.

Results and Discussion

Synthesis and Characterization of the Compounds. A new series of monometallic, bimetallic, and trimetallic complexes were synthesized and characterized by elemental analysis, cyclic voltammetry, and infrared and electronic spectroscopies. The synthetic strategy utilized consisted of a series of steps in which the different "blocks" were linked by polyazine bridging ligands. Each step involved the synthesis and characterization of a new type of compound. Mild reaction conditions were used to prepare the triad complexes from $[Cl_2Ru(bpy)(BL)Rh(tpy)(bpm)MQ]^{4+}$ and $[Fe(CN)_4BL]^{2-}$ in order to avoid aquation of the Fe(II) moiety.[22]

Ground-State Absorption Spectra. Absorption band maxima and molar extinction coefficients for the monometallic Rh(III) polyazines are given in Table 1. A representative spectrum for $[Rh(tpy)(bpm)(4,4'-bpy)](PF_6)_3$ in CH_3CN solution is shown in Figure 3a. The UV region is dominated by intense intraligand ($\pi-\pi^*$) transitions at 270 and 325 nm, respectively.[23] These complexes display relatively intense bands ($\lambda_{max} \sim 320-360$ nm, $\epsilon \sim 4000-8000$ M^{-1}·cm^{-1}) assigned as MLCT transitions ($d\pi(Rh) \rightarrow p^*(BL)$). These transitions are less intense and occur

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Table 1. Absorption Data for Mixed Rhodium(III) Polypyridyl Complexes[a]

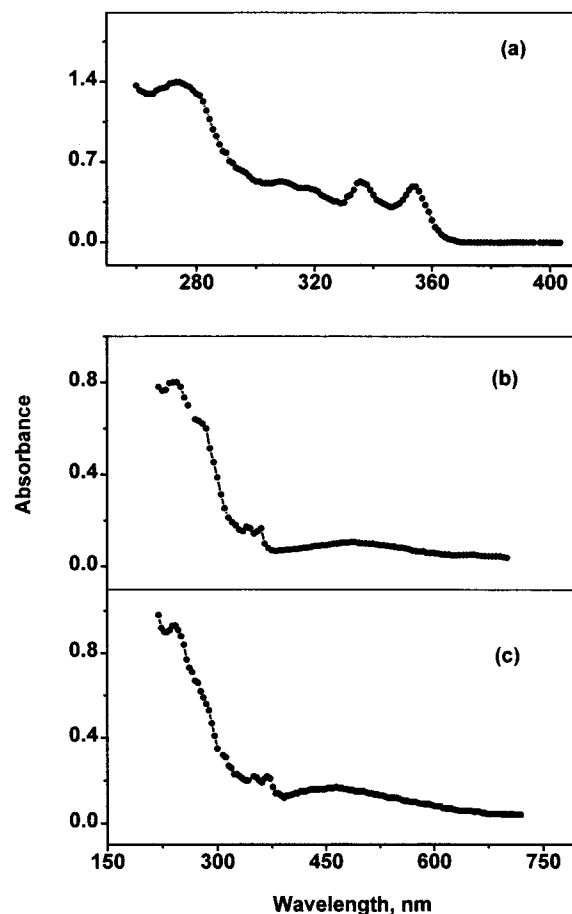| complex	λ_{max}, nm ($10^{-4}\epsilon$, M^{-1}·cm^{-1})
$[Rh(bpy)_2(bpm)](PF_6)_3$	320 (2.9), 308 (2.7), 239 (4.5), 209 (7.9)
$[Rh(bpy)_2(4,4'-bpy)_2](PF_6)_3$	321 (3.4), 308 (3.1), 256 (8.3)
$[Rh(tpy)(bpm)(4,4'-bpy)](PF_6)_3$	358 (0.80), 341 (0.79), 325 (0.67), 271 (2.9)
$[Rh(tpy)(bpm)(MQ)](PF_6)_4$	356 (0.40), 340 (0.65), 320 (0.95), 250 (5.3)
$[Rh(tpy)(dpp)(MQ)](PF_6)_4$	356 (1.25), 324 (2.45), 286 (3.73), 236 (6.91)

[a] At room temperature, in acetonitrile.

Figure 3. UV−visible spectra of 10^{-3} M acetonitrile solutions of (a) $[Rh(tpy)(bpm)(MQ)]^{4+}$, (b) $[Cl_2Ru(bpy)(bpm)Rh(tpy)MQ]^{4+}$, and (c) $[(CN)_4Fe(bpm)Ru(bpy)(bpm)Rh(tpy)MQ]^{4+}$.

at lower energy relative to the observed bands for $[Rh(bpy)_2(bpm)](PF_6)_2$ and $[Rh(bpy)_2(4,4'-bpy)_2](PF_6)_2$.

The electronic spectra of the binuclear complexes, $[Cl_2Ru(bpy)(BL)Rh(tpy)MQ](PF_6)_4$, displayed the typical features for the Rh(III) and Ru(II) polypyridyl moieties (see Figure 3b). The visible region of the spectrum is dominated by broad absorption bands centered at 487 nm (BL = bpm) and 564 nm (BL = dpp), assigned as $d\pi(Ru) \rightarrow p^*$ (BL) and $d\pi(Ru) \rightarrow p^*$ (bpy) transitions. At higher energy, the spectra feature the absorption bands corresponding to the Rh(III) polypyridine.

The UV−visible spectra of the trimetallic complexes in CH_3CN show the characteristic absorption bands of the individual components; see Table 2 and Figure 3. For all four complexes, there is an absorption band that can be assigned as a $d\pi(Ru) \rightarrow \pi^*(BL)$ MLCT transition at 521 nm for BL(1) = BL(2) = dpp and 609 nm for BL(1) = BL(2) = bpm. For the complexes

Table 2. UV−Visible Absorption Bands for Trimetallic Compounds, [(CN)$_4$Fe(BL(1))Ru(bpy)(BL(2))Rh(tpy)MQ]$^{4+}$ ^{a}

BL(1)	BL(2)	λ_{max}, nm ($10^{-4}\epsilon$, M$^{-1}\cdot$cm^{-1})
bpm	bpm	284 (2.36), 293 (2.43), 305 (2.37), 319 (2.17), 340 (0.64), 356 (0.64), 444 (0.63)
dpp	bpm	283 (1.23), 340 (1.79), 353 (1.64), 393 (1.07), 540 (0.74)
bpm	dpp	282 (3.67), 323 (2.14), 338 (2.17), 354 (2.17), 411 (0.93), 544 (0.90)
dpp	dpp	283 (3.45), 320 (2.02), 340 (1.72), 352 (1.52), 521 (0.70)

^{a} In acetonitrile.

Table 3. Redox Potentials for Rhodium(III) Polypyridyl Complexes^{a,b}

	$E_{1/2}$, V (ΔE, mV)^c	
complex	Rh(III)/Rh(II)	ligand reductions
[Rh(tpy)(bpm)(4,4'-bpy)]$^{3+}$	−0.60 (E_a)	−0.41 (E_a), −0.84 (80), −1.05 (40), −1.53 (160)
[Rh(tpy)(bpm)MQ]$^{4+}$	−0.58 (E_a)	−0.45 (100), −0.84 (30), −0.94 (100), −1.78 (40)
[Rh(tpy)(dpp)MQ]$^{4+}$	−0.63 (E_a)	−0.86 (80), −1.04 (160), −1.38 (40), −1.62 (E_a)
[Rh(tpy)Cl$_3$]	−0.73 (80)	−0.36 (80), −1.50 (60)

^{a} In acetonitrile. ^{b} TBAH as supporting electrolyte. ^{c} $E_{1/2}$ vs SCE calculated as average of anodic and cathodic peaks with peak-to-peak separation (ΔE) shown in parentheses. E_a indicates that only the anodic peak was observed.
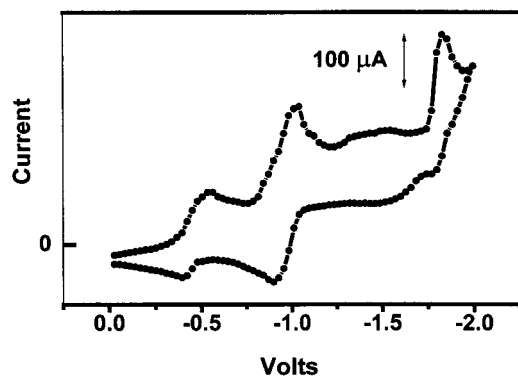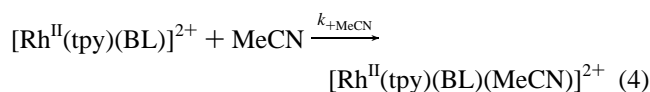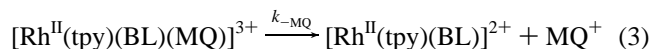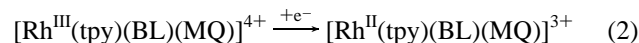

Figure 4. Cyclic voltammogram for [Rh(tpy)(bpm)(MQ)]$^{4+}$ in CH$_3$-CN. The supporting electrolyte is TBAH, and the scan rate is 100 mV/s.

with mixed bridging ligands (BL(1) ≠ BL(2)), there is a broad absorption band located at ∼540 nm, assigned as a dπ(Ru) → π*(BL) MLCT transition where the Ru(II) → dpp and Ru(II) → bpm transitions overlap. The broad absorption bands also have contributions from dπ(Ru) → π*(bpy), dπ(Fe) → π_1*-(BL), and dπ(Fe) → π_2*(BL) MLCT bands from the [Fe(CN)$_4$-(bpm)]$^{2-}$ and [Fe(CN)$_4$(dpp)]$^{2-}$ components.[9] Higher energy bands at 340 and 356 nm, assigned to dπ(Rh) → π*(BL) MLCT transitions, are clearly discernible in the UV spectra.

Electrochemistry. Half-wave reduction potentials ($E_{1/2}$) for the monomeric Rh(III) complexes were determined in CH$_3$CN solution by cyclic voltammetry; see Table 3. No electrode processes were observed on scanning anodically to the solvent limit (2.0 V vs SCE) for any of the Rh(III) complexes. Cathodic scans revealed a complex reductive pattern with a number of redox waves covering a wide potential range with varying degrees of reversibility, as illustrated for [Rh(tpy)(bpm)(MQ)]-(PF$_6$)$_4$ in Figure 4. The first wave located at approximately −0.40 V is assigned as the first reduction for the tpy ligand, tpy$^{0/-}$. The tpy-based initial reduction is supported by com-

parison of the MLCT transition energies in the UV spectra of Rh(III)−bpy and Rh(III)−tpy complexes, from which it seems that the lowest π* levels are in the order tpy < bpy. All these complexes show an irreversible metal-center reduction for the reductive couple Rh(III)/Rh(II) at ∼−0.60 V vs SCE and several ligand-based reductions, BL$^{0/-}$ (BL = bpm or dpp) and tpy$^{-/2-}$, in the −0.84 to −1.78 V range. By analogy with similar compounds, we assign the redox waves at −0.84 and −0.86 V as bridging ligand first reductions BL$^{0/-}$ (BL = bpm and dpp).[24] For [Rh(tpy)Cl$_3$], three reversible reductions at −0.36 (tpy$^{0/-}$), −0.73 (Rh$^{III/II}$), and −1.50 (tpy$^{-/2-}$) V vs SCE were observed. Rh$^{III/II}$ couples of all the complexes containing tpy are shifted to more positive potentials (∼+200 mV) than was previously observed for other Rh(III) polyamines,[25] probably due to an increase in the tpy π-accepting properties with respect to bpy.

The irreversible character of the reduction pattern can be explained in light of the loss of one of the polypyridyl ligands upon reduction of the Rh(III) metal center.[26] One-electron reduction of [Rh^{III}(LL)$_3$]$^{3+}$ gives [Rh^{II}(LL)$_3$]$^{2+}$, a d^7 metal complex that undergoes slow dissociation of one of the bidentate ligands. Monoquat as a free ligand[27] undergoes its first reduction wave at −0.94 V vs SCE in acetonitrile. On the basis of our voltammetric studies (scan rate = 50−500 mV/s) and the fact that the MQ$^{+/0}$ reduction couple in [Rh(tpy)(BL)-(MQ)]$^{4+}$ appears at −0.94 and −1.04 V for bpm and dpp, respectively, the mechanism described in eqs 2−4 is invoked to best explain the observed behavior. The complex [Rh(tpy)-(BL)MQ]$^{3+}$ is anticipated to rapidly dissociate MQ$^+$ and coordinate acetonitrile.

$$[Rh^{III}(tpy)(BL)(MQ)]^{4+} \xrightarrow{+e^-} [Rh^{II}(tpy)(BL)(MQ)]^{3+} \quad (2)$$

$$[Rh^{II}(tpy)(BL)(MQ)]^{3+} \xrightarrow{k_{-MQ}} [Rh^{II}(tpy)(BL)]^{2+} + MQ^+ \quad (3)$$

$$[Rh^{II}(tpy)(BL)]^{2+} + MeCN \xrightarrow{k_{+MeCN}} [Rh^{II}(tpy)(BL)(MeCN)]^{2+} \quad (4)$$

Electrochemical data and their assignments for [Cl$_2$Ru(bpy)-(BL)Rh(tpy)(MQ)]$^{4+}$ complexes are summarized in Table 4b. The Ru^{III}/Ru^{II} redox couple is observed at 1.21 and 1.41 V vs SCE for BL = bpm and dpp, respectively. Rh$^{III/II}$ redox couples are observed at −0.48 and −0.57 V for bpm and dpp. The small shift with respect to the redox waves for the monomeric species reveals little communication between both metal centers. Reductive waves corresponding to the first reduction of the bridging ligands are located at −0.48 V (overlapping with the Rh$^{III/II}$ couple) and −0.45 V for bpm and dpp, respectively. This assignment was made in analogy to other binuclear species in which the redox waves of the bridging ligands were shifted ∼+400 mV with respect to the same polypyridyl ligand in a nonbridging environment.[24] First reduction waves for the bridging ligands bpm and dpp were found at −0.97 and −1.01 V in the monomeric species [Ru(bpy)(BL)$_2$]$^{2+}$.[21a]

The half-wave reduction potentials for the trimetallic compounds are given in Table 4c. Redox waves for Ru$^{III/II}$ and

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Table 4. Electrochemical Data for Mono-, Bi-, and Trimetallic Complexes Containing Polypyridines[a]

	$E_{1/2}$, V (ΔE, mV)			
complex	Fe^{III}/Fe^{II}	Ru^{III}/Ru^{II}	Rh^{III}/Rh^{II}	ligand reductions
			(a) Monometallic Compounds	
[Ru(bpy)(bpm)$_2$]$^{2+}$		1.50 (80)		−0.97 (50), −1.14 (40), −1.61 (70)
[Ru(bpy)(dpp)$_2$]$^{2+}$		1.42 (50)		−1.01 (50), −1.23 (60), −1.53 (E_a)
[Fe(CN)$_4$(bpm)]$^{2-}$	0.55(60)[b]			
[Fe(CN)$_4$(dpp)]$^{2-}$	0.45(60)[b]			
			(b) Bimetallic Ru^{II}/Rh^{III} Complexes, [Cl$_2$Ru(bpy)(BL)Rh(tpy)MQ]$^{4+}$	
bpm		1.21 (50)	−0.48 (E_a)[c]	−0.85 (E_a), −1.20 (E_a), −1.36 (E_a), −1.55 (E_a)
dpp		1.14 (50)	−0.57 (E_a)	−0.45 (E_a), −1.10 (E_a), −1.25 (E_a), −1.40 (E_a), −1.63 (E_a)
			(c) Trimetallic Fe^{II}/Ru^{II}/Rh^{III} Complexes, [(CN)$_4$Fe(BL(1))Ru(bpy)(BL(2))Rh(tpy)MQ]$^{4+}$	
bpm, bpm		−0.59 (E_a)	−0.30 (E_a)	−0.84 (E_a), −1.03 (E_a), −1.33 (E_a), −1.47 (E_a), −1.57 (30), −1.67 (E_a)
bpm, dpp		−0.60 (E_a)	−0.43 (E_a)	−0.84 (E_a), −1.05 (E_a), −1.21 (E_a), −1.38 (E_a), −1.58 (E_a)
dpp, bpm		−0.63 (E_a)	−0.20 (E_a)	−1.04 (E_a), −1.13 (E_a), −1.61 (E_a)
dpp, dpp		−0.60 (E_a)	−0.20 (E_a)	−1.05 (E_a), −1.15 (E_a), −1.58 (E_a)

[a] In acetonitrile. [b] In aqueous solution at 25 °C. 2 M KCl as supporting electrolyte (from ref 32). [c] Also assigned as first bridging ligand reduction (see text).

Fe$^{III/II}$ couples were not observed in the anodic scans within the solvent window (2.0 V vs SCE). The large positive charge and extensive metal−metal communication are expected to shift the metal oxidations to higher potentials as reported for a core Ru(II) in a polymetallic structure.[28] Ru$^{III/II}$ couples are very sensitive to the average environment around the Ru center and to the overall charge of the complex.[9] An effect of the complex charge on the reductive waves was also observed for Fe(II)/Ru(II) dyads such as [(CN)$_4$Fe(BL)Ru(tpy)(4,4′-bpy)] and [(CN)$_4$Fe(BL)(tpy)(MQ)]$^+$ (BL = bpm and dpp).[21b] The dyads containing 4,4′-bpy showed two reversible oxidations located at 0.40 and 1.02 V and at 0.41 and 1.03 V for dpp and bpm, respectively. The monoquat complexes also displayed two reversible waves at 1.16 and 1.36 V (dpp) and 1.17 and 1.29 V (bpm). In all cases, the first process was assigned to the Fe^{III}/Fe^{II} couple, while the second was assigned to the Ru^{III}/Ru^{II} couple. In these cases, a change of one unit in the overall complex charge shifted the reduction potentials about +0.7 V (Fe^{III}/Fe^{II} couple) and +0.30 V (Ru^{III}/Ru^{II}). Therefore, it is not surprising that a +4 complex charge pushes the redox waves outside the solvent window (see Table 4 for data corresponding to the monomeric Ru(II) polyazine and tetracyanoferrate(II) units).

All four trimetallic complexes exhibit rich patterns of waves in the reductive scans of the cyclic voltammograms. Several reductive waves corresponding to reduction of the ligands are located in the range −0.20 to −1.67 V. As for the monomeric Rh(III) complexes, the MQ$^{+/0}$ potential is found at ∼−1.00 V vs SCE. The Rh$^{III/II}$ reductive couples are located at ∼−0.60 V.

Infrared Spectroscopy. Infrared spectra of the trimetallic complexes showed the typical features of the three different components. The tetracyanoferrate(II) moiety in the supramolecular structure can be easily identified by the characteristic cyanide stretching (ν_{CN}) around 2070 cm^{-1}.[29] The wavenumbers corresponding to the cyanide stretching modes for the triads are 2073 (BL(1) = BL(2) = bpm), 2073 (BL(1) = bpm; BL(2) = dpp), 2067 (BL(1) = dpp; BL(2) = bpm), and 2069 cm^{-1} (BL(1) = BL(2) = dpp). Low-temperature IR spectra of [(CN)$_4$Fe^{II}(dpp)Ru^{II}(bpy)(bpm)Rh^{III}(tpy)(bpy)MQ]$^{4+}$ and the corresponding Fe(II) monomer showed identical splittings of the cyanide stretching modes, with peaks located at 2067, 2076,

and 2094 cm^{-1}, for both complexes. Coordinated MQ$^+$ was identified by its characteristic stretching mode at 1653 cm^{-1}.

Excited-State Properties. No emission was observed for any of the Rh(III) monomeric complexes at room temperature in fluid solution, in agreement with the luminescent behavior of similar polypyridyl rhodium(III) compounds.[30] We observed ^{3}LC ($^3\pi-\pi^*$) luminescence with substantial vibrational structure from MeOH/EtOH (1:1) glassy solutions at 77 K (λ_{exc} = 280 or 325 nm) for [Rh(tpy)(bpm)(BL)](PF$_6$)$_n$ (BL = 4,4′-bpy, n = 3; BL = MQ$^+$, n = 4) salts with emission maxima centered at 483 and 433 nm, respectively, in analogy to other Rh(III) polyazine complexes described in the literature.[23,30−32] Ligand field (d−d*) emission was not observed at longer wavelengths, $\lambda \sim$ 730 nm, as was reported for other [Rh(tpy)(bpy)(L)]$^{3+}$ complexes.[17] No 77 K emission was observed for MeOH/EtOH glassy solutions of [Rh(tpy)(dpp)(L)](PF$_6$)$_n$ (L = 4,4′-bpy, n = 3; L = MQ$^+$, n = 4).

The photophysics of [Cl$_2$Ru(BL)Rh(tpy)(MQ)](PF$_6$)$_4$ was investigated using steady-state and time-resolved techniques. These dyads contain two fragment units that are photoexcitable, Ru(II) and Rh(III) polypyridyl complexes. As previously noted by Scandola et al.,[4i] selective excitation should lead to the same Ru(III)/Ru(II) excited state in the picosecond time domain. Selective excitation showed no observable Ru-based (λ_{exc} = 450−480 nm) or Rh-based emission (λ_{exc} = 280−320 nm) either for acetonitrile solutions at room temperature or for glassy MeOH/EtOH solutions at 77 K. Previous reports for similar Ru(II)/Rh(III) polyazines have ascribed the lack of emission to intramolecular electron transfer quenching.[4i,28] Transient absorption measurements (λ_{exc} = 355 nm) showed formation of an intermediate within the laser pulse, with spectral features that are typical for Ru(II) polypyridyl units (bleaching at ∼450 nm corresponding to ground-state absorption).[26,28]

The excited-state properties of the triads, [(CN)$_4$Fe^{II}(BL$_1$)-Ru^{II}(bpy)(BL$_2$)Rh^{III}(tpy)(bpy)MQ]$^{4+}$, were also explored. The photophysics and photochemistry of the component fragments—namely, [Fe(CN)$_4$(BL)]$^{2-}$, [(CN)$_4$Fe(BL)Ru(bpy)$_2$], and Ru(II)/Rh(III) polypyridyl dyads—have been described in detail elsewhere.[4i,8b,33] No emission was observed for these salts at

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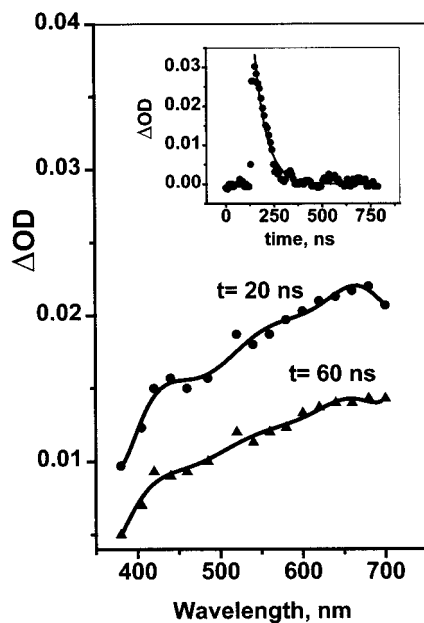(29) Nakamoto, K. *Infrared Spectra of Inorganic and Coordination Compounds*; John Wiley and Sons: New York, 1970.

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Figure 5. Transient absorption spectra for [Fe(CN)$_4$(bpm)Ru(bpy)-(dpp)Rh(tpy)(MQ)]$^{4+}$ in deoxygenated acetonitrile. The inset shows a typical decay monitored at $\lambda = 640$ nm

Figure 6. Transient absorption spectrum of an acetonitrile solution 10^{-4} M in [Fe(CN)$_4$(bpm)Ru(bpy)(dpp)Rh(tpy)(MQ)]$^{4+}$ and 10^{-2} M in MQPF$_6$ taken after 20 ns of the laser pulse.

room temperature in fluid solution or in 77 K glasses (MeOH/EtOH, 1:1 v/v) using excitation wavelengths ranging from 300 to 600 nm. The strong, long-lived luminescence of the ruthenium fragment (i.e., [Ru(bpy)(bpm)$_2$]$^{2+}$, $\tau = 870$ ns)[34] is efficiently quenched when it is covalently bound to the [Fe(CN)$_4$(BL)]$^{2-}$ and/or [Rh(tpy)(BL(MQ)]$^{4+}$ moieties. Transient absorption experiments in the nanosecond time domain showed formation of an intermediate within the laser pulse that decays back to the ground state by following a first-order law with lifetimes of $\tau < 70$ ns ($\tau = 70$ ns (BL(1) = BL(2) = bpm), 37 ns (BL(1) = BL(2) = dpp), 46 ns (BL(1) = bpm, BL(2) = dpp), 37 ns (BL(1) = dpp, BL(2) = bpm)).

The most prominent features are broad absorption bands in the visible region, centered at 420, 560, and 680 nm (see Figure 5). By analogy with previously reported transient absorbencies for [Ru(bpy)$_3$]$^{2+}$ and [Ru(tpy)$_2$]$^{2+}$, we can assign the bands located at 400 and 500 nm to the L$^-$ species present in the ^{3}-MLCT excited state.[28] In light of our cyclic voltammetry experiments, we could speculate that the ligand tpy will have the lowest π^* level and thus be the site for the electron in the lowest excited state. The reductive nature of the excited state was investigated by intermolecular electron transfer quenching with free MQ$^+$; see Figure 6. Transient absorption spectra acquired in the presence of MQ$^+$ showed the typical absorption maxima corresponding to MQ$^{\bullet}$ ($\lambda_{max} = 380$ and 550 nm).[35] This experiment ruled out the possibility of intramolecular formation of the monoquat radical and suggested the presence of the added electron in a ligand-based orbital, most likely of tpy or bridging ligand character. On the basis of our experimental observations and the absence of a bleach at ~450 nm (indicative of a Ru^{III} transient state), we assign the absorbencies at 450 and 680 nm to the formation of a mixed-valence Fe(III)−Ru(II) compound. Transient absorption measurements were also conducted on acetonitrile solutions of the dimeric species [Fe(CN)$_4$(dpp)Ru-(tpy)(4,4′-bpy)]. The results obtained in these experiments were used as a blank to help to identify the nature of the transient
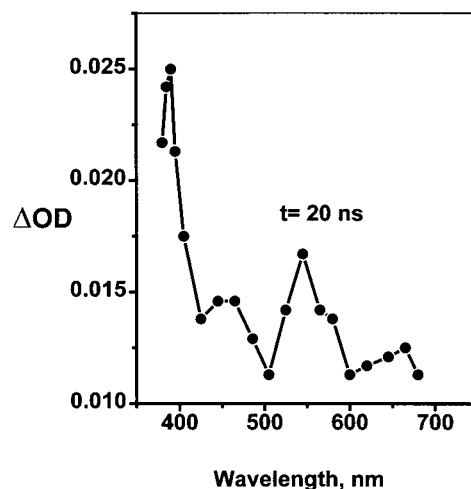
intermediates formed from the trimetallic species. Upon excitation with $\lambda = 355$ nm, an intermediate was formed within the laser pulse which displayed broad absorption bands in the visible region of the spectrum ($\lambda_{max} = 400, 540,$ and 680 nm) and disappeared by following a first-order exponential decay with a lifetime of $\tau = 52$ ns. Again, we can assign the absorbencies centered at ~450 and 680 nm to the formation of an Fe(III)-Ru(II) transient intermediate. The absorbencies centered at ~400 and 540 nm are assigned to a L$^-$ transient state. For this complex, the first reduction wave at ~−1.0 V was assigned to reduction of the bridging ligand, dpp$^{0/-}$.[21b] This intermediate displays the same spectral features observed in the experiments described above for the trimetallic species and rules out any contribution of a Rh-based excited state. For the triads, the reduction potentials of Rh(III)/Rh(II) couples are very close to the expected values for the ligand reduction potentials. Self-exchange rate constant studies of Rh(III) polyamines[25] support the hypothesis of a first reduction involving orbitals of ligand character rather than the metal center. We associate the intense visible absorptions at ~400 and ~500 nm with the polypyridyl radical anion, indicative of a L$^-$ transient state. This fact suggests that even when metal- and ligand-centered reductions are close in energy, reduction at the ligand is thermodynamically favored for the complexes under study.

From our experimental observations, we can conclude that, for the [(CN)$_4$Fe(BL(1)) Ru(bpy)(BL(2)) Rh(tpy)MQ]$^{4+}$ complexes, 355 nm laser excitation of the Ru(II) and Rh(III) units should lead to formation of an excited state, [Fe^{II}−Ru^{II}−BL−Rh^{III}*]*, that relaxes rapidly to form [Fe^{II}−Ru^{III}−L$^{-\bullet}$−Rh^{III}] or [Fe^{II}−Ru^{III}−L−Rh^{II}] charge transfer intermediates (bridging and ancillary ligands have been omitted for clarity).[36] Fast intramolecular quenching yields [Fe^{III}−Ru^{II}−L$^{-\bullet}$−Rh^{III}] within the laser pulse ($t < 8$ ns). The absence of Rh(II)- or monoquat-based excited states can be easily understood by inspection of the cyclic voltammetry data. Electrochemical observations indicate that bridging and tpy ligands are more easily reduced than Rh(III) metal centers and monoquat, favoring formation of a L$^-$ transient state.

The triads described in this paper display very interesting redox and spectroscopic properties. While the donor and chromophore groups appeared to have very good communication

(34) Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; Von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85.
(35) Watanabe, T.; Honda, K. *J. Phys. Chem.* **1982**, *86*, 2617.

(36) Rh(III) polypyridyl complexes absorb approximately 40% of the excitation light at 355 nm.

between both metal centers, the electron acceptor did not show the desired properties. As mentioned before, the redox and excited-state properties of Rh(III) polyamines can be subtly modified by introducing modifications in the ligand composition. The monomeric Rh(III) species reported herein showed the strong effect of the ligand composition on the reductive waves of the metal center and the terminal and bridging ligands. In view of our experimental observations, we suggest that an improvement to these charge separation systems requires the design of a Rh(III) fragment which displays a more negative Rh(III)/Rh(II) redox couple and is attached to an electron acceptor unit that is more easily reduced than monoquat. Surprisingly, our newly synthesized Rh(III) units containing tpy displayed fairly positive reduction potentials ($E°_{1/2} \sim -0.60$ V) by comparison with other polyazines previously reported in the literature ($E°_{1/2} \sim -0.80$ to -1.00 V).[25] To direct the electron transfer process toward the electron acceptor group (MQ$^+$), the Rh(III) fragment should also contain terminal ligands with reduction potentials more negative than those of tpy. In such a system, the Rh(III) centers would act as spacing units and display the desired effect of slowing down back electron reactions.