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A Tridentate-Bridged Ruthenium−Rhodium Complex as a Stereochemically Defined Light-Absorber−Electron-Acceptor Dyad

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The complex $[(tpy)Ru(tpp)RhCl_3](PF_6)_2$ (tpy = 2,2′,6′,2″-terpyridine and tpp = 2,3,5,6-tetrakis(2-pyridyl)pyrazine) has been prepared and its spectroscopic, electrochemical, and photophysical properties investigated. This complex couples a ruthenium light absorber to a rhodium electron acceptor to create the first tpp-bridged light-absorber−electron-acceptor dyad. This study illustrates the applicability of this $(tpy)Ru^{II}(\mu\text{-tpp})$ chromophore in the construction of photochemical molecular devices. This system is of interest since the tpp ligand has been shown to provide stereochemically defined polymetallic complexes with reasonably long-lived metal to ligand charge transfer excited states. The complex $[(tpy)Ru(tpp)RhCl_3](PF_6)_2$ displays a Ru→tpp CT transition centered at 516 nm that is the lowest lying electronic transition. The electrochemistry of $[(tpy)Ru(tpp)RhCl_3](PF_6)_2$ shows a $Ru^{II/III}$ couple at 1.60 V vs Ag/AgCl, an irreversible $Rh^{III/I}$ reduction at −0.23 V and, a $tpp^{0/-}$ couple at −0.60 V. This illustrates that although this complex has a lowest lying spin-allowed spectroscopic transition that is Ru→tpp CT in nature, the lowest occupied molecular orbital is Rh based. Thus, following excitation of this $[(tpy)Ru(tpp)RhCl_3](PF_6)_2$ complex into the Ru→tpp CT state, electron transfer to the rhodium is thermodyamically favorable. This electron transfer leads to a quenching of the emission normally observed for this Ru→tpp CT excited state. Emission quenching for $[(tpy)Ru(tpp)RhCl_3](PF_6)_2$ via electron transfer is 80% efficient with a k_{et} of 4×10^7 s^{-1}. Details of these studies are presented herein.

Introduction

Since the discovery of $[Ru(bpy)_3]^{2+}$, there has been much research aimed at exploiting the desirable excited-state properties of this and related chromophores in light conversion schemes (bpy = 2,2′-bipyridine).[1−3] A recent trend has been in the introduction of polyazine bridging ligands into this framework to allow for covalent attachment of other metal centers and the development of supramolecular systems.[4−27] One of the most widely utilized polyazine bridging ligands within this context has been dpp (2,3-bis(2-pyridyl)pyrazine).[4−9,10a−d,11,12,14,15] Polymetallic complexes constructed with tris-diimine coordination to each metal center exist as a mixture of stereoisomers that are not typically separated. This leads to systems that are stereochemically ill-defined. This limits the ability to define and control donor−acceptor distances and orientations within

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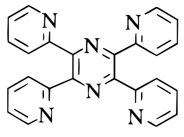
this framework. The control of such factors is important in supramolecular design.

The utilization of tridentate ligands in the construction of polymetallic systems leads to complexes that are stereochemically defined.[4,11b,16−24] The application of these bis-tridentate complexes to the construction of supramolecular systems with applications to light energy conversion schemes has been somewhat limited by the short metal to ligand charge transfer (MLCT) excited-state lifetime of $[Ru(tpy)_2]^{2+}$ (tpy = 2,2′,6′,2″-terpyridine).[28−31] This short MLCT excited-state lifetime results from the tpy ligand providing a weaker ligand field, leading to a thermally accessible ligand field (LF) state that rapidly deactivates the MLCT excited state.

Recently, we reported that the utilization of the tridentate bridging ligand tpp (2,3,5,6-tetrakis(2-pyridyl)pyrazine) as an acceptor ligand for the MLCT excited state of bis-tridentate ruthenium complexes can lead to polymetallic systems that are emissive at room temperature (RT) and exhibit reasonably long-lived excited states.[17b]



tpp

Abruna et al. reported on the synthesis, spectroscopic, and electrochemical properties of a very interesting array of tpp-bridged complexes.[18] Ruminski reported the preparation of $[Rh(tpp)Cl_3]$ and $[Cl_3Rh(tpp)RhCl_3]$.[20b] We have shown that bimetallic complexes which possess a bridging tpp ligand typically display a long-lived Ru→tpp CT excited state.[17b] For example, $[(tpy)Ru(tpp)Ru(tpp)](PF_6)_4$ exhibits an emission at 800 nm and an excited-state lifetime of 100 ns at RT in deoxygenated acetonitrile.[17b] This long-lived MLCT excited-state results from the tpp ligand possessing a π^* orbital that is significantly lower in energy than that of tpy. This stabilizes the MLCT in tpp complexes relative to bis-terpyridine systems. This prevents the tpp-based systems from undergoing thermal population to the LF state that is responsible for the rapid deactivation of the MLCT excited state of $[Ru(tpy)_2]^{2+}$.[17b,28−31] This makes tpp a promising ligand for the development of stereochemically defined supramolecular systems with interesting properties.

A number of elegant studies pioneering the application of tridentate bridging ligands to the construction of stereochemically defined systems have appeared.[4,11b,16−24] Sauvage, Balzani, Barigelletti, Collin, and co-workers have utilized linked tpy ligands for the construction of polymetallic complexes, dyads, and triads of light absorbers (LA) coupled to electron donors (ED) and/or electron acceptors (EA).[16,22] Mixed-metal Ru−Os systems were used to illustrate that facile energy transfer from the ruthenium MLCT excited state to the osmium-based MLCT excited state occurred within this framework. Of particular interest is the recent report by Indelli, Scandola, Collin, Sauvage, and Sour of the photophysical properties of $[(tpy)Ru(tpy{-}(Ph)_n{-}tpy)Rh(tpy)]^{5+}$ (n = 0, 1, or 2).[22b] In these systems they observed electron-transfer quenching of the Ru-based MLCT excited state by the Rh^{III} center at 150 K for the n = 0 but not the n = 1 or 2 complexes. They attribute this to the increased distance between the donor and the acceptor in the complexes with the phenyl spacers. The tpy−tpy-bridged complex does undergo electron-transfer quenching and, thus, represents a metal-based light-absorber−electron-acceptor dyad. One disadvantage presented in that study is the short MLCT excited-state lifetime observed for these systems at RT. This prohibits RT electron-transfer quenching within these dyads. Ziessel, Harriman et al. have presented a series of reports on very interesting ethynyl-bridged bis-terpyridine ligands and their application to the construction of polymetallic systems.[24] Ruthenium bimetallic systems are reported with long-lived MLCT excited states at RT.

A vast amount of literature exists on the construction and study of polyazine-based supramolecular systems which couple

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light absorbers, electron acceptors, and electron donors.[4,16] The majority of metal-based systems studied utilize tris-chelated metal complexes, which are often stereochemically ill-defined. These studies have lead to the construction of some very interesting complexes. In trying to understand the factors controlling electron transfer in these supramolecular systems, it is often desirable to be able to control the stereochemical arrangement of the light absorber, electron donor, and electron acceptor. This is not always possible when utilizing the tris-bidentate coordination of the metal center.

Several relevant studies on the coupling of ruthenium light absorbers to rhodium electron acceptors in supramolecular frameworks have appeared.[14,22b,25−27] Scandola, Indelli et al. reported on $Ru^{II}(Me_2phen)_2-(Mebpy-CH_2CH_2-Mebpy)-Rh^{III}(Me_2bpy)_2{}^{5+}$ (Me_2phen = 4,7-dimethyl-1,10-phenanthroline, Mebpy = 4-methyl-2,2′-bipyridine, Me_2bpy = 4,4′-dimethyl-2,2′-bipyridine).[25] Kalyanasundaram et al. reported on $[(bpy)_2Ru^{II}(dpp)Rh^{III}(bpy)_2]^{5+}$.[14] Ohna, Haga, and Nozaki reported on a series of complexes of the form $[(bpy)_2Ru^{II}(L-L)Rh^{III}(bpy)_2]^{5+}$ (L−L = 2,6-bis(2′-pyridyl)benziimidazole, 2,2′-bis-(2″-pyridyl)bibenzimidazole, 1,1′-dimethyl-2,2′-bis(2″-pyridyl)-6,6′-bibenzoimidazole, and bis[2-(2′-pyridyl)benzimidazoyl]-ethane.[26] All of these systems are reported to undergo intramolecular electron-transfer quenching of the Ru-based MLCT excited state by the rhodium center. Endicott et al. have studied Ru^{II},Rh^{III} cyanide-bridged complexes.[27] Some complexes have been designed in which direct optical excitation of the MMCT band is possible. Varying the coordination geometry on the metal centers while maintaining the cyanide bridges can produce systems in which energy transfer to the rhodium-centered LF state occurs.

Within this framework, we have prepared the complex $[(tpy)Ru(tpp)RhCl_3](PF_6)_2$. This system couples a ruthenium light absorber known to have a long-lived MLCT excited state at RT to a rhodium electron acceptor. This system is unique in that unlike the tris-bidentate complexes, the complex is stereochemically defined. In addition, it has a ruthenium chromophore that is emissive at RT. This study is aimed at establishing the utility of the $(tpy)Ru^{II}(\mu\text{-tpp})$ chromophore as a LA for the construction of supramolecular systems. The preparation and study of this LA−EA dyad is presented herein.

Experimental Section

Materials. The materials used were Fisher reagent grade and used without further purification. The tpp ligand was obtained from GFS Chemicals. $[(tpy)Ru(tpp)](PF_6)_2$[17a] and $[(tpy)Ru(tpp)Ru(tpp)](PF_6)_4$[17b] were prepared as previously described. The acetonitrile used in the electrochemical and spectroscopic studies was Burdick and Jackson UV Grade and obtained from VWR.

Synthesis of $[(tpy)Ru(tpp)RhCl_3](PF_6)_2$. The mixed-metal bimetallic complex was prepared from the reaction of 0.12 g (0.12 mmol) of $[(tpy)Ru(tpp)](PF_6)_2$ with 0.097 g (0.37 mmol) of $RhCl_3\cdot 3H_2O$ in 50 mL of 95% EtOH. This reaction mixture was heated at reflux for 4.5 h. The reaction was allowed to cool to RT and added to ca. 50 mL of saturated aqueous KPF_6 to induce precipitation. The solid was collected by vacuum filtration. The product was purified by size-exclusion chromatography on a Sephadex LH-20 resin using a 2:1 EtOH:CH_3CN mobile phase. The purple band containing the desired bimetallic was the first to elute. This band was collected, the solvent removed by rotoevaporation, and the residue dissolved in a minimal amount of acetonitrile and flash precipitated in diethyl ether. The product was separated by vacuum filtration and dried under vacuum. Yield: 70%. FAB-MS: *m*/*z* (relative abundance, ion) 1075 (10, $[(tpy)Ru(tpp)RhCl_3](PF_6)^+$), 930 (58, $[(tpy)Ru(tpp)RhCl_3]^+$), 895 (45, $[(tpy)Ru(tpp)RhCl_2]^+$), 859 (80, $[(tpy)Ru(tpp)RhCl]^+$), 824 (36, $[(tpy)Ru(tpp)Rh]^+$), 721 (100, $[(tpy)Ru(tpp)]^+$).

Electronic Absorption Spectroscopy. Electronic absorption spectra were collected at room temperature on acetonitrile solutions using a HP 8452A diode array spectrophotometer with 2 nm resolution.

Emission Spectroscopy. Emission spectra were recorded on deoxygenated, absorbance-matched acetonitrile solutions of each analyte using a modified Photon Technology Inc. Alphascan spectrofluorometer. The system was modified to use a thermoelectrically cooled Hamamatsu R666S single-photon counting detection system with 0.25 nm resolution. The acetonitrile solutions of each analyte were prepared to have a absorbance of ca. 0.4 at the wavelength of excitation (550 nm). The solutions were deoxygenated by bubbling with high-purity argon for 20 min prior to measurement of the emission spectrum, and the absorbance at 550 nm was measured just prior to collection of the emission spectrum.

Emission quantum yields were measured relative to a $[Os(bpy)_3](PF_6)_2$ reference in deoxygenated CH_3CN at RT using $\Phi^{em} = 0.00462\,(Area_{sample})(Abs_{ref})/(Area_{ref})(Abs_{sample})$.[32] The emission spectra were corrected for PMT response prior to integration. The bimetallic systems studied emit at relatively low energy, 830 nm. The Hamamatsu R666S PMT response in this region is relatively weak and makes the absolute values of the emission quantum yields for these two systems lower estimates. The primary information for this study is the relative intensity of the emission of absorbance-matched samples of the two bimetallic complexes. Since these two systems emit at the same energy, these relative values are much more accurate, ±5%.

Emission Lifetime Measurements. Laser-induced emission lifetime measurements were obtained on a system that utilizes a Photon Technology Inc. PL-2300 nitrogen laser equipped with a PL-201 continuously tunable dye laser (360−900 nm) excitation source. The emission was passed through a monochromator and detected at a right angle to the excitation by a Hamamatsu R928 photomultiplier tube. The RT samples were acetonitrile solutions prepared to have an absorbance at 550 nm of 0.4. These solutions were deoxygenated by bubbling with high-purity argon for 20 min. The 77 K measurements were made on ethanolic solutions of the analyte contained in NMR tubes using a finger Dewar of local design and construction. The samples were sonicated for 20 min and then immediately frozen at 77 K. The signal was recorded on a LeCroy 6880 digitizer with 800 ps resolution and the data transferred to a computer for analysis. The raw data, which is an average of 500 traces, was fit to a single-exponential function of the form $Y = A + B(\exp(-X/c))$, where $c = \tau = 1/k$ (in s), after discarding the initial segment of the data containing the laser pulse.

Electrochemistry. Cyclic voltammetry was performed using a BAS 100W electrochemical analyzer. The measurements used a three-electrode system that consisted of a Pt disk working electrode, Pt wire auxiliary electrode, and a Ag/AgCl reference electrode (0.29 V vs NHE). The reference electrode was calibrated using the $Fe(C_5H_5)_2/Fe(C_5H_5)_2{}^+$ couple (0.665 V vs NHE).[33] Cyclic voltammograms were recorded at a scan rate of 200 mV/s, and the working electrode was manually cleaned by polishing with alumina prior to each scan. The supporting electrolyte was 0.1 M Bu_4NPF_6, and the measurements were made in Burdick and Jackson UV-grade acetonitrile.

FAB Mass Spectral Analysis. FAB mass spectral analyses of tpp-bridged complexes been reported by Abruna et al.[18] and by our group.[17c] Our system was analyzed using a Fisons VG Quattro triple-stage quadrupole mass spectrophotometer using *m*-nitrobenzyl alcohol as the matrix. The bimetallic gave a nice fragmentation pattern with sequential loss of the hexafluorophosphate counterions and coordinated chlorides.

Results and Discussion

The complex $[(tpy)Ru(tpp)RhCl_3](PF_6)_2$ is prepared with a typical purified yield of 70% by the reaction of $RhCl_3\cdot 3H_2O$ with $[(tpy)Ru(tpp)](PF_6)_2$ in 2:1 EtOH/H_2O.

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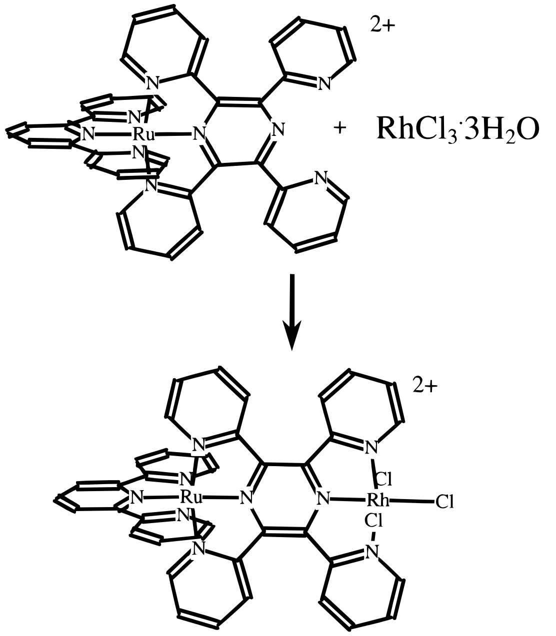


Size-exclusion chromatography is used to remove minor amounts of ruthenium monometallic impurity. This mixed-metal bimetallic system has been analyzed by FAB mass spectral analysis. The complex shows a nice fragmentation pattern with sequential loss of PF$_6^-$ counterions and chloride ligands.

Ruthenium polyazine complexes of this type typically display ligand-based $\pi \rightarrow \pi^*$ transitions from each polyazine ligand in the ultraviolet region of the spectrum and MLCT transitions for each acceptor ligand in the visible.[4,16] The electronic absorption spectroscopy of [(tpy)Ru(tpp)RhCl$_3$](PF$_6$)$_2$ in acetonitrile at room temperature is shown in Figure 1. The ruthenium monometallic [(tpy)Ru(tpp)](PF$_6$)$_2$ from which this system was constructed displays an electronic absorption spectrum that has been previously reported as containing tpp $\pi \rightarrow \pi^*$ transitions at 328 and 354 nm and overlapping Ru→tpy and Ru→tpp CT transitions at 472 nm.[11b,17−19] The Ru→tpp CT component is expected to occur at lower energy due to the more stabilized π^* orbital on the tpp ligand relative to tpy. When this chromophore is coupled to another metal center through bridge formation on the tpp ligand, the Ru→tpp CT transition shifts to lower energy.[11b,17−19] For example, previously studied [(tpy)Ru(tpp)Ru(tpp)](PF$_6$)$_4$ displays overlapping Ru→tpp CT bands for each ruthenium metal center at 548 nm.[17b,18] This shift of the Ru→tpp CT band results from the stabilization of the tpp π^* orbital upon coordination of the second metal center. This stabilized tpp π^* orbital also leads to a red shift of the tpp-based $\pi \rightarrow \pi^*$ transitions that now occur at 380 and 368 nm for [(tpy)Ru(tpp)Ru(tpp)](PF$_6$)$_4$.[17]

The mixed-metal bimetallic complex [(tpy)Ru(tpp)RhCl$_3$](PF$_6$)$_2$ displays intense peaks throughout most of the ultraviolet and visible region of the spectrum. The lowest energy peak at 516 nm represents the Ru→tpp CT transition. This transition is red-shifted relative to the ruthenium monometallic complex [(tpy)Ru(tpp)](PF$_6$)$_2$, indicative of the stabilization of the tpp π^* orbital upon coordination of the rhodium metal center. This stabilization is slightly less than that imparted by coordination of another ruthenium metal center observed for the bimetallic system [(tpy)Ru(tpp)Ru(tpp)](PF$_6$)$_4$ described above. This likely results from the rhodium metal center having three chloride ligands, which makes it somewhat more electron rich. [(tpy)Ru(tpp)RhCl$_3$](PF$_6$)$_2$ displays a set of two peaks at 372 and 380 nm that represent the tpp $\pi \rightarrow \pi^*$ transitions typically seen in this region for complexes with bridging tpp ligands.[17b,d] A shoulder at 460 nm is seen, and this complex would be expected to possess a Ru→tpy CT band in this region. The ultraviolet region of the spectrum displays the very characteristic pattern of peaks at 272, 298, and 330 nm. Peaks at these locations in other complexes containing the [(tpy)Ru^{II}(μ-tpp)] unit have been shown via spectroelectrochemistry to be tpy $\pi \rightarrow \pi^*$, overlapping tpp $\pi \rightarrow \pi^*$ and higher energy Ru→tpy CT, and tpy $\pi \rightarrow \pi^*$ transitions, respectively.[17d]

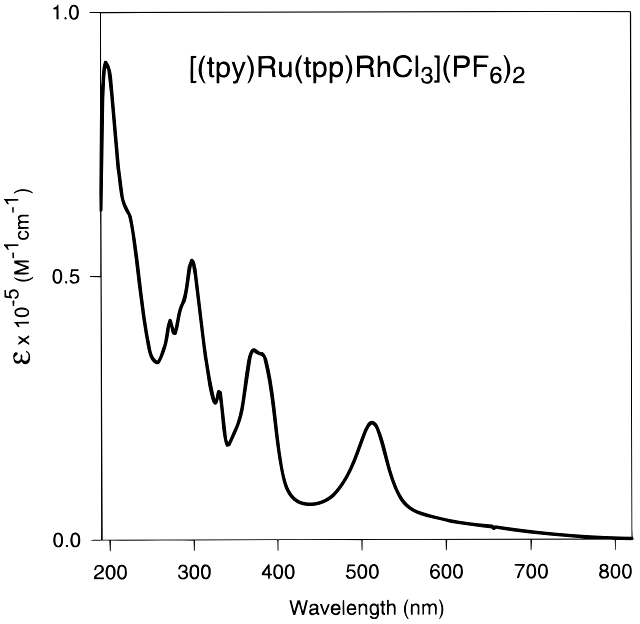


Figure 1. Electronic absorption spectroscopy of [(tpy)Ru(tpp)RhCl$_3$](PF$_6$)$_2$ in acetonitrile at room temperature.

Table 1. Electrochemical Data for a Series of 2,3,5,6-Tetrakis(2-pyridyl)pyrazine Complexes of Ruthenium(II) and Rhodium(III)[a]

	$E_{1/2}$ (V)[b]		
complex	oxidations	reductions	
[(tpy)Ru(tpp)RhCl$_3$](PF$_6$)$_2$	1.60 Ru$^{II/III}$	−0.23 Rh$^{III/I}$	−0.60 tpp$^{0/-}$
		−0.98 tpp$^{-/2-}$	−1.40 tpy$^{0/-}$
[(tpy)Ru(tpp)](PF$_6$)$_2$[c]	1.40 Ru$^{II/III}$	−0.97 tpp$^{0/-}$	−139 tpy$^{0/-}$
[(tpy)**Ru**(**tpp**)Ru(tpp)](PF$_6$)$_4$[c]	1.51 **Ru**$^{II/III}$	−0.30 **tpp**$^{0/-}$	−0.82 **tpp**$^{-/2-}$
	1.86 Ru$^{II/III}$	−1.10 tpp$^{0/-}$	

[a] tpp = 2,3,5,6-tetrakis(2-pyridyl)pyrazine, tpy = 2,2′,6′,2″-terpyridine. [b] Potentials reported in 0.1 M Bu$_4$NPF$_6$ CH$_3$CN versus Ag/AgCl (0.29 V vs NHE). [c] Reference 17b.

The electrochemistry of [(tpy)Ru(tpp)RhCl$_3$](PF$_6$)$_2$, the previously reported monometallic precursor [(tpy)Ru(tpp)](PF$_6$)$_2$, and model bimetallic system [(tpy)Ru(tpp)Ru(tpp)](PF$_6$)$_4$ are summarized in Table 1.[11b,17−19] Ruthenium polyazine complexes typically possess metal-based oxidations and ligand-based reductions. The tpp ligand has a more stabilized π^* orbital than tpy and thus is expected to undergo reduction at a more positive potential. It has been shown that bridging tpp ligands undergo two sequential reductions, tpp$^{0/-}$ and tpp$^{-/2-}$, prior to reduction of the tpy ligands in polymetallic ruthenium complexes of these ligands.[11b,17−19] The previously studied [(tpy)Ru(tpp)](PF$_6$)$_2$ has a reversible Ru$^{II/III}$ couple at 1.40 V vs Ag/AgCl. Reductively, it displays two reversible couples, tpp$^{0/-}$ at −0.97 V and tpy$^{0/-}$ at −1.39 V.[17a,b] When the tpp ligand is coordinated to another metal center to form polymetallic complexes, a stabilization of the tpp π^* orbital is observed. This leads to a shift to more positive potential of the tpp$^{0/-}$ couple and the appearance of the tpp$^{-/2-}$ couple prior to tpy reduction. The previously studied [(tpy)Ru(tpp)Ru(tpp)]$(PF_6)_4$ displays two reversible oxidations at 1.51 and 1.86 V with the ruthenium bound to the tpy and tpp ligand oxidizing at lower potential.[17b] Reductively, this complex displays three well-behaved reversible reductions. [(tpy)Ru(tpp)Ru(tpp)]$(PF_6)_4$ displays a tpp$^{0/-}$ couple at −0.30 V and a tpp$^{-/2-}$ couple at −0.82 V for the bridging tpp ligand. The terminal tpp ligand is subsequently reduced at −1.10 V. Further reduction leads to adsorption of the reduced complex onto the electrode surface.

The mixed-metal bimetallic complex [(tpy)Ru(tpp)$RhCl_3$]$(PF_6)_2$ displays one reversible oxidation, a quasi-reversible reduction, followed by three reversible reductions. The oxidation occurs at 1.60 V and represents the Ru$^{II/III}$ couple. The first reduction occurs at −0.23 V and is quasi-reversible. The reversibility of this couple increases as the scan rate is increased. The couple is almost totally irreversible at a scan rate of 50 mV/s, and i_p^a/i_p^c becomes 1 at a scan rate of 1000 mV/s. This irreversibility and the higher peak current for this peak relative to the ruthenium oxidation suggests that this reduction corresponds to the Rh$^{III/I}$ couple. This couple is expected to be irreversible due to the generation of the d^8, Rh^I species which would prefer to be square planar and is thus expected to undergo subsequent ligand loss. For systems of the type $[Rh(LL)_2Cl_2]^+$ (LL = bpy or dpp), the rhodium reduction is followed by loss of the two chloride ligands to form a square-planar Rh^I$(LL)_2$ species.[34,35] The [(tpy)Ru(tpp)$RhCl_3$]$(PF_6)_2$ rhodium metal center also has coordinated chloride ligands which can be lost following Rh reduction. The cyclic voltammetric analysis of [(tpy)Ru(tpp)$RhCl_3$]$(PF_6)_2$ was repeated with the addition of excess Bu_4NCl. This lead to a dramatic increase in the reversibility of this couple at −0.23 V, substantiating its assignment as a Rh$^{III/I}$ couple. [(tpy)Ru(tpp)$RhCl_3$]$(PF_6)_2$ displays a second reduction at −0.60 V, and this represents the tpp$^{0/-}$ couple. The third reduction at −0.98 V represents the tpp$^{-/2-}$ couple that is expected to occur prior to tpy reduction in polymetallic complexes. The tpy$^{0/-}$ couple follows at −1.40 V. This electrochemical data indicates that this mixed-metal system possesses a ruthenium-based highest occupied molecular orbital (HOMO) and a rhodium based lowest unoccupied molecular orbital (LUMO). This would suggest that although the lowest lying spectroscopic transition seen in the electronic absorption spectroscopy was a Ru→tpp CT transition, excitation of this molecule to this state should be followed by intramolecular electron transfer to the lower energy rhodium acceptor orbital. This makes this complex a LA−EA dyad. Since this [(tpy)Ru(tpp)$RhCl_3$]$(PF_6)_2$ system has a (tpy)Ru^{II}(μ-tpp) chromophore which has been shown to be emissive at RT, it should be possible to use emission spectroscopy and emission lifetime measurements to probe this intramolecular electron-transfer quenching of the Ru→tpp CT excited state by the rhodium-based electron acceptor.

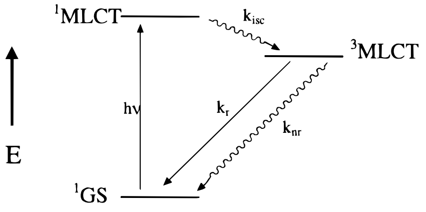
Table 2 summarizes the spectroscopic and photophysical properties of [(tpy)Ru(tpp)$RhCl_3$]$(PF_6)_2$ and the previously reported monometallic precursor [(tpy)Ru(tpp)]$(PF_6)_2$ and model bimetallic system [(tpy)Ru(tpp)Ru(tpp)]$(PF_6)_4$.[17a−c] All of these complexes have lowest lying, spin-allowed optical transitions that are Ru(dπ)→tpp(π*) CT in nature. Optical population of this state is expected to lead to rapid intersystem crossing to the emissive ^{3}MLCT state. The $[(tpy)Ru(tpp)Ru(tpp)]^{4+}$ complex was selected over a symmetric system like $[(tpy)Ru(tpp)Ru(tpy)]^{4+}$ since the introduction of the slightly varied coordination of the two ruthenium centers localizes the lowest lying Ru→tpp CT state on one (tpy)Ru^{II}(μ-tpp) metal center, making it directly analogous to [(tpy)Ru(tpp)$RhCl_3$]$(PF_6)_2$ system.

Table 2. Spectroscopic and Photophysical Data for a Series of 2,3,5,6-Tetrakis(2-pyridyl)pyrazine Complexes of Ruthenium(II) and Rhodium(III)[a,b]

complex	λ_{max}^{abs} (nm)	λ_{max}^{em} (nm)	τ (ns)	Φ^{em}
[(tpy)Ru(tpp)$RhCl_3$]$(PF_6)_2$	516	830	22	2.0×10^{-4}
[(tpy)Ru(tpp)]$(PF_6)_2$[c]	474	665	30	7.9×10^{-4}
[(tpy)Ru(tpp)Ru(tpp)]$(PF_6)_4$[c]	548	830	100	1.1×10^{-3}

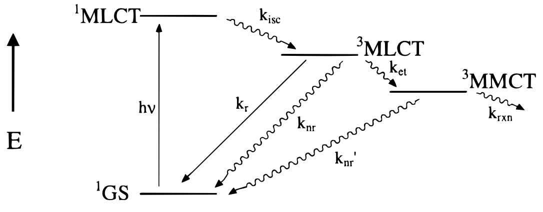
[a] tpp = 2,3,5,6-tetrakis(2-pyridyl)pyrazine, tpy = 2,2′,6′,2′′-terpyridine. [b] Recorded in deoxygenated acetonitrile solutions at RT. [c] Reference 17b,c.

The emission properties of the monometallic and all ruthenium bimetallic complexes have been previously reported. The [(tpy)Ru(tpp)]$(PF_6)_2$ system is emissive at RT and displays an emission maximum at 665 nm and a lifetime in deoxygenated acetonitrile solution of 30 ns.[17a] The Φ^{em} is 7.9×10^{-4}.[17c] The bimetallic model system [(tpy)Ru(tpp)Ru(tpp)]$(PF_6)_4$ displays a RT emission maximum at 830 nm and a lifetime of 100 ns at RT.[17b] The emission is red-shifted relative to the monometallic complex, consistent with the absorption spectroscopy and the expected stabilization of the tpp-based π* acceptor orbital upon coordination of a second metal center to the remote site of the tpp ligand. We previously reported that at RT this bimetallic complex possesses a longer excited-state lifetime than the monometallic from which it is constructed, [(tpy)Ru(tpp)]$(PF_6)_2$.[17b] This results from the fact that [(tpy)Ru(tpp)]$(PF_6)_2$ still has some thermal population of the LF state at RT, and the bimetallic, [(tpy)Ru(tpp)Ru(tpp)]$(PF_6)_4$, has a more stabilized ^{3}MLCT excited-state preventing this thermal population of the LF state. A state diagram for the [(tpy)Ru(tpp)Ru(tpp)]$(PF_6)_4$ system is shown below.



$[(tpy)Ru(tpp)Ru(tpp)]^{4+}$

The introduction of the rhodium metal center in [(tpy)Ru(tpp)$RhCl_3$]$(PF_6)_2$ allows for a new mode of deactivation of the emissive Ru(dπ)→tpp(π*) CT state of this chromophore, namely the desired intramolecular electron-transfer quenching to generate a ^{3}MMCT state. A state diagram for this LA−EA dyad is shown below.



$[(tpy)Ru(tpp)RhCl_3]^{2+}$

This complex would not be expected to have the possibility of energy-transfer quenching of the emissive ^{3}MLCT excited

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(34) Rasmussen, S. C.; Richter, M. M.; Yi, E.; Place, H.; Brewer, K. J. *Inorg. Chem.* **1990**, *29*, 3926.

(35) Kahl, J. L.; Hanck, W.; DeArmond, M. K. *J. Phys. Chem.* **1978**, *82*, 540.

state by the rhodium center. This results from the lower energy of this ^{3}MLCT excited state within this polymetallic framework, which will shift it below the energy typically expected for the rhodium LF state.[14,17,25−27] The desired intramolecular electron transfer to the rhodium acceptor should lead to an observed quenching of the emission of the Ru(dπ)→tpp(π*) CT excited state of this chromophore. This is observed as the [(tpy)Ru(tpp)RhCl$_3$](PF$_6$)$_2$ system displays a dramatically reduced quantum efficiency for emission and a shorter excited-state lifetime relative to the [(tpy)Ru(tpp)Ru(tpp)](PF$_6$)$_4$ model system. The excited-state lifetime of [(tpy)Ru(tpp)RhCl$_3$](PF$_6$)$_2$ is 22 ns compared to that of 100 ns for [(tpy)Ru(tpp)Ru(tpp)](PF$_6$)$_4$. Assuming the above diagrams and assuming the [(tpy)Ru(tpp)Ru(tpp)]$^{4+}$ is a suitable model system

$$k_{\mathrm{et}} = 1/\tau([(\mathrm{tpy})\mathrm{Ru}(\mathrm{tpp})\mathrm{RhCl}_3](\mathrm{PF}_6)_2) - 1/\tau([(\mathrm{tpy})\mathrm{Ru}(\mathrm{tpp})\mathrm{Ru}(\mathrm{tpp})](\mathrm{PF}_6)_4)$$

This allows one to calculate k_{et} for [(tpy)Ru(tpp)RhCl$_3$](PF$_6$)$_2$ to be 3.5×10^7 s^{-1}. The relative quantum efficiencies of the emission for the [(tpy)Ru(tpp)RhCl$_3$](PF$_6$)$_2$ and [(tpy)Ru(tpp)Ru(tpp)](PF$_6$)$_4$ systems have also been determined. This gives another method of evaluating k_{et} and the proposed state diagrams. Given the above state diagrams and assuming that intersystem crossing to the emissive ^{3}MLCT excited state is 100% efficient, Φ^{em} for [(tpy)Ru(tpp)RhCl$_3$](PF$_6$)$_2$ $= k_{\mathrm{r}}/(k_{\mathrm{r}} + k_{\mathrm{nr}} + k_{\mathrm{et}})$, and for the model system without the quenching from the intramolecular electron transfer Φ^{em} for [(tpy)Ru(tpp)Ru(tpp)](PF$_6$)$_4$ $= k_{\mathrm{r}}/(k_{\mathrm{r}} + k_{\mathrm{nr}})$. Assuming that k_{r} and k_{nr} do not change within these two complexes and that τ for [(tpy)Ru(tpp)Ru(tpp)](PF$_6$)$_4$ $= 1/(k_{\mathrm{r}} + k_{\mathrm{nr}})$, k_{et} for [(tpy)Ru(tpp)RhCl$_3$](PF$_6$)$_2$ is calculated to be 4.5×10^7 s^{-1}. This assumption of a constant k_{r} and k_{nr} for these two emissive states is reasonable as they are both ^{3}MLCT states based on the same Ru(dπ)→μ-tpp(π*) CT excitation and their emissions are centered at a very similar energy. These two values for k_{et} are in reasonable agreement and are consistent with the illustrated state diagrams. These values indicate that relatively rapid intramolecular electron transfer occurs to the rhodium acceptor within this framework.

These two complexes display an intense emission at 77 K. The excited-state lifetime of [(tpy)Ru(tpp)Ru(tpp)](PF$_6$)$_4$ at 77 K in a frozen ethanolic glass is 360 ns. The observed lifetime for [(tpy)Ru(tpp)RhCl$_3$](PF$_6$)$_2$ under these conditions is 330 ns. In this frozen matrix, electron-transfer quenching does not occur and these two chromophores display similar excited-state emissions and lifetimes characteristic of the Ru→(μ-tpp) CT state.

Conclusions

The (tpy)Ru$^{\mathrm{II}}$(tpp) light absorber can be easily synthetically coupled to other metal centers. This chromophore displays a RT emission that allows for a convenient handle into the excited-state properties of larger supramolecular systems constructed from this system. The coupling of a rhodium metal center to produce [(tpy)Ru(tpp)RhCl$_3$](PF$_6$)$_2$ has led to the construction of the first dyad which utilizes this (tpy)Ru$^{\mathrm{II}}$(μ-tpp) chromophore. This mixed-metal Ru−Rh, LA-EA dyad undergoes facile electron-transfer quenching of the optically populated Ru→(μ-tpp) CT excited state. This intramolecular electron transfer quenches the emission normally observed for this (tpy)Ru$^{\mathrm{II}}$(μ-tpp) chromophore and shortens the excited-state lifetime. At 77 K, this intramolecular electron-transfer quenching is not observed and [(tpy)Ru(tpp)RhCl$_3$](PF$_6$)$_2$ displays an excited-state lifetime consistent with an unquenched (tpy)Ru$^{\mathrm{II}}$(μ-tpp) chromophore. This study clearly illustrates the promise of this (tpy)Ru$^{\mathrm{II}}$(μ-tpp) chromophore in the construction of devices for photoinitiated charge separation. Our group has developed synthetic methodologies which use a building-block approach to extend polymetallic systems constructed from the (tpy)Ru$^{\mathrm{II}}$(tpp) unit one metal center at a time.[17b] This should allow for the construction of larger supramolecular systems which couple this (tpy)Ru$^{\mathrm{II}}$(μ-tpp) unit to a rhodium acceptor with intervening metal centers, i.e., [(tpy)Ru(tpp)M(tpp)RhCl$_3$]$^{n+}$. Systems of this type and more extended variations should allow for a large spatial separation between the Ru donor and the Rh acceptor. This could lead to system with long-lived charge-separated states.[36] This (tpy)Ru$^{\mathrm{II}}$(μ-tpp) chromophore holds promise as a light-absorbing unit in the construction of a wide assortment of supramolecular systems. Work in our group is aimed at exploring these systems.[36]

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