Building Block Approach to the Construction of Long-Lived Osmium(II) and Ruthenium(II) Multimetallic Complexes Incorporating the Tridentate Bridging Ligand 2,3,5,6-Tetrakis(2-pyridyl)pyrazine

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Two classes of synthetically useful bimetallic complexes of the form [(tpy)M(tpp)RuCl$_3$](PF$_6$) and [(tpy)M(tpp)-Ru(tpp)](PF$_6$)$_4$ have been prepared and their spectroscopic and electrochemical properties investigated (tpy = 2,2′:6′,2″-terpyridine, tpp = 2,3,5,6-tetrakis(2-pyridyl)pyrazine, and M = Ru^{II} or Os^{II}). Synthetic methods have been developed for the stepwise construction of tpp-bridged systems using a building block approach. In all four complexes, the tpp that serves as the bridging ligand is the site of localization of the lowest unoccupied molecular orbital (LUMO). The nature of the HOMO (highest occupied molecular orbital) varies depending upon the components present. In the systems of the type [(tpy)M(tpp)RuCl$_3$](PF$_6$), the ruthenium metal coordinated to tpp and three chlorides is the easiest to oxidize and is the site of localization of the HOMO. In contrast, for the [(tpy)M(tpp)Ru(tpp)](PF$_6$)$_4$ systems, the HOMO is based on the metal, M, that is varied, either Ru or Os. This gives rise to systems which possess a lowest lying excited state that is always a metal-to-ligand charge transfer state involving tpp but can be tuned to involve Os or Ru metal centers in a variety of coordination environments. The synthetic variation of the components within this framework has allowed for understanding the spectroscopic and electrochemical properties. Bimetallic systems incorporating this tpp ligand have long-lived excited states at room temperature (lifetimes of ca. 100 ns). The bimetallic system [(tpy)Ru(tpp)Ru(tpp)](PF$_6$)$_4$ has a longer excited state lifetime than the monometallic system from which it was constructed, [(tpy)Ru(tpp)](PF$_6$)$_2$. Details of the spectroscopic and electrochemical studies are reported herein.

Introduction

Since the discovery of [Ru(bpy)$_3$]$^{2+}$, many studies have concentrated on the utilization of its long-lived metal-to-ligand charge transfer (MLCT) excited state in photochemical energy conversion schemes.[1] Ruthenium and osmium polypyridine complexes have been of interest due to their ability to undergo MLCT excitation.[1−3] These MLCT states have been shown to undergo intermolecular electron transfer and can be prepared using a variety of ligands providing easily tunable ground state redox properties and excited state energies.[1−3] The introduction of polyazine bridging ligands has resulted in the study of supramolecular compounds which incorporate ruthenium and osmium polypyridine complexes covalently linked to other components through the utilization of the bridging capability of these ligands.[4−17] The nature of these excited states has led to a series of studies investigating the light-absorbing and photochemical reaction properties of such systems. These systems often utilize tris-chelated complexes which are covalently linked through a bridging ligand to other parts of the supramolecular architecture. These tris-chelated species have the possibility of existing as Δ or Λ stereoisomers.[4−10] Upon

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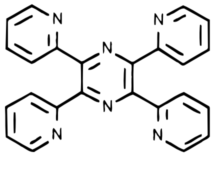
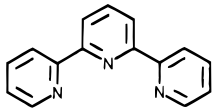
incorporation into supramolecular complexes, this yields a mixture of stereoisomers that are typically not separated. In addition, these systems often have short excited state lifetimes.[4−10]

One approach to the elimination of the multiple stereoisomers found in supramolecular complexes built using tris-chelated complexes is to incorporate tridentate ligands such as tpy or tpp (tpy = 2,2′:6′,2″-terpyridine or tpp = 2,3,5,6-tetrakis(2-pyridyl)pyrazine).[14−18] These ligands will eliminate the Δ and Λ isomers possible when using bidentate ligands. Interest in this area has been hindered by the short excited state lifetime and absence of a room temperature emission for $[Ru(tpy)_2]^{2+}$.[18] It has been concluded that this behavior is due to the thermal population of a ligand field state giving rise to rapid nonradiative deactivation of the MLCT excited state.[18]



tpp



tpy

Incorporation of a polyazine bridging ligand into this framework to form $[Ru(tpy)(tpp)]^{2+}$ has been reported in the literature.[14,15,17] This ruthenium complex is emissive in fluid solution at room temperature.[14,17] The emission from $[Ru(tpy)(tpp)]^{2+}$, in contrast to $[Ru(tpy)_2]^{2+}$, is the result of a stabilization of the MLCT state relative to the ligand field state, hindering thermal population of the latter. This allows the MLCT state to be longer lived than $[Ru(tpy)_2]^{2+}$ and emissive at room temperature. An osmium analog, $[Os(tpy)(tpp)]^{2+}$, has been synthesized which is also emissive at room temperature.[14,16] For both the ruthenium and osmium complexes, the lowest energy absorbance is a $M(d\pi) \rightarrow tpp(\pi^*)$ MLCT excited state, centered at 474 and 468 nm, respectively, in the electronic absorption spectra.[14−17] The emission from this excited state occurs at 665 and 775 nm with an excited state lifetime of 27 and 260 ns for $[Ru(tpy)(tpp)]^{2+}$ and $[Os(tpy)(tpp)]^{2+}$, respectively.[14,16,17] This is quite similar to the $[M(tpy)_2]^{2+}$ series in which the excited state lifetime of the osmium system is far in excess of that of the ruthenium complex, 270 ns (Os) vs <1 ns (Ru), when measured in fluid solution at room temperature.[3d,18]

The lifetime of the osmium excited state would be expected to be slightly shorter than that of the ruthenium complex due to the decreased energy gap between the ground and excited states.[19] Because the emissive MLCT state is lower in energy for the osmium complex, nonradiative decay to the ground state should be more efficient. However, the osmium analog has a much longer lifetime than the ruthenium analog. This is due to the much higher energy ligand field state for Os relative to Ru. This results in the LF excited state being much higher in energy than the MLCT state, eliminating thermal population of the LF state in the osmium-based systems. This indicates that the MLCT excited state of $[Ru(tpy)(tpp)]^{2+}$ does still undergo thermal population of the ligand field state at room temperature and that this process is competitive with relaxation of the MLCT excited state to the ground state. This would indicate that for the ruthenium complexes of this type, further stabilization of the MLCT state might lead to the lifetime of the chromophore being enhanced since this will result in a loss of thermal population of the deactivating LF state. A stabilization of the Ru → tpp CT state is expected upon formation of bimetallic complexes using this chromophore. Hence, $[Ru(tpy)(tpp)]^{2+}$ and $[Os(tpy)(tpp)]^{2+}$ can both serve as efficient chromophores in supramolecular complexes.

In a series of elegant reports, Sauvage and co-workers have prepared and characterized homo- and heterobimetallic systems using both tpy and ttpy (4′-*p*-tolyl-2,2′:6′,2″-terpyridine) as the terminal ligands.[21] The bridging ligand used in these studies is two tpy ligands linked back-to-back via the 4′ position (tpy−tpy) as well as ones using phenyl spacers allowing the bridging ligand length to vary, tpy−ph−tpy and $tpy-ph_2-tpy$. Recently they utilized tpp as a bridging ligand to prepare $[(ttpy)Ru(tpp)Ru(ttpy)]^{4+}$; however, no excited state properties are given.[21]

In a very interesting study, Abruña et al. reported on the preparation and characterization of numerous osmium and ruthenium tpp-bridged bi- and trimetallic complexes.[16] Systems that relate to this study were of the type $[(tpp)Os(tpp)Os(tpp)]^{4+}$, $[(tpy)Ru(tpp)Ru(tpp)]^{4+}$, $[(tpy)Ru(tpp)Ru(tpy)]^{4+}$, and $[(tpy)Os(tpp)Ru(tpy)]^{4+}$. In this study, both the electrochemistry and electronic absorption spectroscopy were investigated. No excited state properties of their polymetallic complexes were reported.

Reported herein is the synthesis of two series of synthetically useful bimetallic complexes incorporating the two monometallic fragments discussed above: $[(tpy)Ru(tpp)RuCl_3](PF_6)$, $[(tpy)Os(tpp)RuCl_3](PF_6)$, $[(tpy)Ru(tpp)Ru(tpp)](PF_6)_4$, and $[(tpy)Os(tpp)Ru(tpp)](PF_6)_4$. These complexes have been synthesized and characterized by electronic absorption spectroscopy, emission spectroscopy, excited state lifetime measurements, and electrochemistry. They represent a unique series of stereochemically defined, long-lived polymetallic complexes.

Experimental Section

Materials used were Fisher reagent grade and used without further purification. The tetrabutylammonium hexafluorophosphate (TBAH) used in this study was prepared by the metathesis of tetrabutylammonium bromide with potassium hexafluorophosphate. The acetonitrile used in the spectroscopic and electrochemical studies was Burdick and Jackson UV grade. The ligand tpy was purchased from Aldrich Chemical Co. The ligand tpp was first prepared by Goodwin and Lions

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but can be purchased from GFS Chemical.[20] Ru(tpy)Cl$_3$,[3g] [Ru(tpy)(tpp)](PF$_6$)$_2$,[14,15,17] and Os(tpy)Cl$_3$[2c] were prepared as previously reported.

Triaquo(2,2′:6′,2″-terpyridine)osmium(II) Hexafluorophosphate. Preparation of [Os(tpy)(H$_2$O)$_3$](PF$_6$)$_3$ was achieved by reacting [Os(tpy)Cl$_3$] (0.079 g, 0.149 mmol) with AgCF$_3$SO$_3$ (0.386 g, 1.50 mmol) in 50 mL of deionized water. The solution was heated at reflux under argon for ca. 48 h. The solution volume was decreased to 25 mL by rotary evaporation. The resulting solution was added to a saturated aqueous solution of KPF$_6$ to induce precipitation and then was separated by vacuum filtration. A typical yield for this reaction was 63%.

(2,2′:6′,2″-Terpyridine)[2,3,5,6-tetrakis(2-pyridyl)pyrazine]osmium(II) Hexafluorophosphate. To alleviate purification problems encountered through the previously published syntheses,[14b,16] [Os(tpy)(tpp)]$^{2+}$ was synthesized using [Os(tpy)(H$_2$O)$_3$]$^{3+}$ (0.106 g, 0.138 mmol) and tpp (0.065 g, 0.168 mmol). These were reacted in 30 mL of ethylene glycol at reflux for 30 min under argon. The resulting solution was removed from heat, a saturated solution of KPF$_6$ was added to induce precipitation, and the precipitate was separated by vacuum filtration. Purification of the product was achieved by column chromatography on adsorption alumina using 2:1 (v/v) toluene/acetonitrile solution. The brown band, the product of interest, was collected. Concentration of this solution was achieved by rotary evaporation. Under these conditions ligand scrambling is not observed. A typical yield for this reaction was 75%.

(2,2′:6′,2″-Terpyridine)ruthenium(II)[*μ*-2,3,5,6-tetrakis(2-pyridyl)pyrazine]trichlororuthenium(II) Hexafluorophosphate. [(tpy)Ru(tpp)RuCl$_3$](PF$_6$) was prepared by using our building block approach by reacting [Ru(tpy)(tpp)]$^{2+}$ (0.069 g, 0.068 mmol) with RuCl$_3$·3H$_2$O (0.127 g, 0.490 mmol). The RuCl$_3$·3H$_2$O was heated in ca. 30 mL of ethanol to reflux under argon. The [Ru(tpy)(tpp)]$^{2+}$ was heated in ca. 15 mL of hot absolute ethanol with 5 mL of acetonitrile to allow it to go completely into solution. The [Ru(tpy)(tpp)]$^{2+}$ solution was added to the RuCl$_3$. The solution went from an orange/brown to a green color. This was heated at reflux for 1.5 h, and no color changes occurred. The flask was then removed from the heat, and the volume was reduced to ca. 20 mL. To this was added a saturated solution of aqueous KPF$_6$ (50 mL) with stirring to induce precipitation. This precipitate was dissolved in a minimum amount of acetonitrile, precipitated in ether, and filtered by vacuum filtration. Purification was achieved by absorption chromatography on alumina eluting with acetonitrile and monitoring the separation of UV/vis electronic absorption spectroscopy. A typical field for this reaction was 88%.

(2,2′:6′,2″-Terpyridine)osmium(II)[*μ*-2,3,5,6-tetrakis(2-pyridyl)pyrazine]trichlororuthenium(II) Hexafluorophosphate. [(tpy)Os(tpp)RuCl$_3$](PF$_6$) was prepared as above substituting [Os(tpy)(tpp)]$^{2+}$ (0.078 g, 0.070 mmol) for [Ru(tpy)(tpp)]$^{2+}$ giving a blue/green complex. A typical yield for this reaction was 77%.

(2,2′:6′,2″-Terpyridine)ruthenium(II)[*μ*-2,3,5,6-tetrakis(2-pyridyl)pyrazine]ruthenium(II)[2,3,5,6-tetrakis(2-pyridyl)pyrazine] Hexafluorophosphate. [(tpy)Ru(tpp)Ru(tpp)]$^{4+}$ has been prepared previously by Abruña et al. following a different synthetic procedure.[16] Using the building block approach developed in this laboratory, [(tpy)Ru(tpp)Ru(tpp)]$^{4+}$ was prepared by reacting 1 equiv of [(tpy)Ru(tpp)RuCl$_3$]$^+$ (0.027 g, 0.025 mmol) and 7 equiv of tpp (0.068 g, 0.175 mmol) in 50 mL of absolute ethanol. The solution was heated at reflux under argon for 1.5 h. The solution volume was reduced by rotary evaporation to ca. 20 mL. Precipitation was induced when the reaction solution was added dropwise to a stirring, saturated, aqueous solution of KPF$_6$. The precipitate was then collected using vacuum filtration. The product was isolated using column chromatography on adsorption alumina using 3:2 (v/v) toluene/acetonitrile solution. The product of interest, the purple band, was isolated when the solvent solution was switched to a 2:3 (v/v) toluene/acetonitrile solution. The purification process was monitored by UV/vis electronic absorption spectroscopy. A typical yield for this reaction was 86%.

(2,2′:6′,2″-Terpyridine)osmium(II)[*μ*-2,3,5,6-tetrakis(2-pyridyl)pyrazine]ruthenium(II)[2,3,5,6-tetrakis(2-pyridyl)pyrazine] Hexafluorophosphate. [(tpy)Os(tpp)Ru(tpp)](PF$_6$)$_4$ was prepared as above substituting [(tpy)Os(tpp)RuCl$_3$]$^+$ (0.080 g, 0.068 mmol) for [(tpy)Ru(tpp)RuCl$_3$]$^+$ and reacting this with tpp (0.199 g, 0.513 mmol) in 50 mL of absolute ethanol. Purification was performed by column chromatography on adsorption alumina in 3:2 (v/v) acetonitrile/toluene solution monitoring by UV/vis electronic absorption spectroscopy. The purple band was the desired product. A typical yield for this reaction was 83%.

Table 1. FAB Mass Spectral Data for a Series of Ruthenium(II) and Osmium(II) Complexes Incorporating the Tridentate Bridging Ligand tpp[a]

compound	*m*/*z*	rel abund	assignment
[(tpy)Ru(tpp)RuCl$_3$]$^+$	722	100	[(tpy)Ru(tpp)]$^+$
	894	95	[(tpy)Ru(tpp)RuCl$_2$]$^+$
	1039	26	[(tpy)Ru(tpp)RuCl$_2$](PF$_6$)$^+$
[tpy)Os(tpp)RuCl$_3$]$^+$	811	85	[(tpy)Os(tpp)]$^+$
	825	28	[Os(tpp)Ru](PF$_6$)$^+$
	956	43	[(tpy)Os(tpp)](PF$_6$)$^+$
	983	22	[(tpy)Os(tpp)RuCl$_2$]$^+$
	1128	12	[(tpy)Os(tpp)RuCl$_2$](PF$_6$)$^+$
[(tpy)Ru(tpp)Ru(tpp)]$^{4+}$	722	95	[(tpy)Ru(tpp)]$^+$
	877	57	[(tpp)Ru(tpp)]$^+$
	1212	27	[(tpy)Ru(tpp)Ru(tpp)]$^+$
	1357	30	[(tpy)Ru(tpp)Ru(tpp)](PF$_6$)$^+$
	1502	25	[(tpy)Ru(tpp)Ru(tpp)](PF$_6$)$_2$$^+$
[(tpy)Os(tpp)Ru(tpp)]$^{4+}$	811	53	[(tpy)Os(tpp)]$^+$
	877	95	[(tpp)Ru(tpp)]$^+$
	1022	45	[(tpp)Ru(tpp)](PF$_6$)$^+$
	1301	17	[(tpy)Os(tpp)Ru(tpp)]$^+$
	1446	20	[(tpy)Os(tpp)Ru(tpp)](PF$_6$)$^+$
	1591	17	[(tpy)Os(tpp)Ru(tpp)](PF$_6$)$_2$$^+$
	1736	4	[(tpy)Os(tpp)Ru(tpp)](PF$_6$)$_3$$^+$

[a] tpp = 2,3,5,6-(2′-pyridyl)pyrazine and tpy = 2,2′:6′,2″-terpyridine.

Spectroscopy. Absorption spectra were recorded at room temperature in acetonitrile on a Hewlett Packard 8452A diode array spectrophotometer (resolution 2 nm).

Emission spectra were recorded at room temperature in deoxygenated acetonitrile solution and obtained on a PTI Alphascan fluorimeter modified to detect red-shifted emissions using a thermoelectrically cooled Hamamatsu R666S photomultiplier tube.[14]

Emission lifetimes were determined using a PTI PL 2300 nitrogen laser; the details of the configuration of these measurements have been reported elsewhere.[14] Deoxygenated acetonitrile solutions were prepared utilizing the freeze−pump−thaw degassing method, repeating the process four times. The glass cells were then sealed under vacuum. Lifetime measurements were performed when the cells returned to room temperature; 77 K lifetimes were measured in ethanolic glasses in a liquid nitrogen finger Dewar.

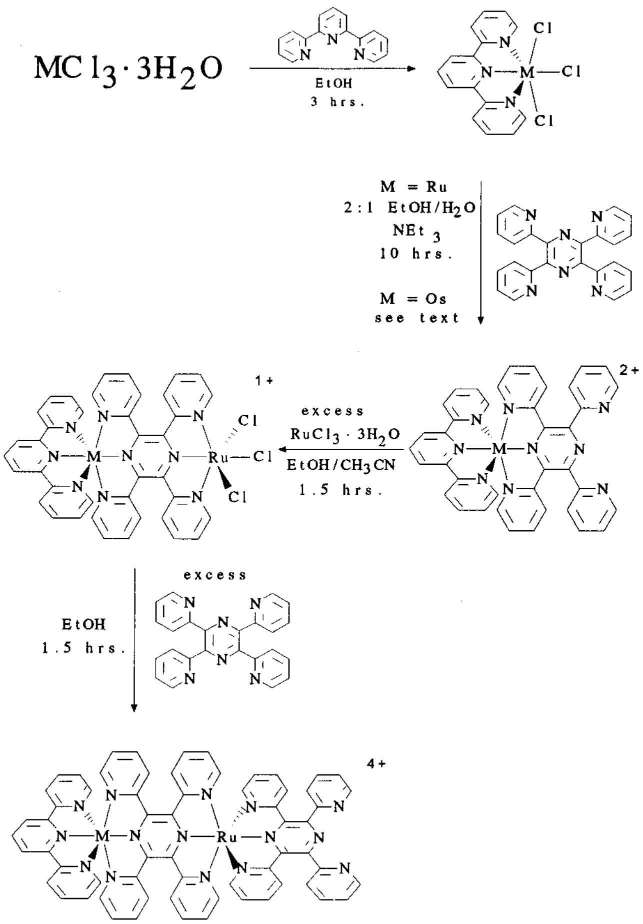
Electrochemistry. Cyclic voltammograms were performed on a BioAnalytical Systems 100W electrochemical analyzer. The solvent used in these studies was high-purity acetonitrile, Burdick and Jackson, dried over molecular sieves. The supporting electrolyte was TBAH. The solutions were bubbled with argon for 20 min prior to each scan and blanketed with argon during each scan. The three-electrode system used in these measurements consisted of a platinum auxiliary electrode, a platinum disk working electrode, and a Ag/AgCl reference electrode (0.29 V versus NHE).

FAB Mass Spectral Analysis. FAB mass spectral analysis were conducted on a Fisons VG Quattro triple-stage quadrupole mass spectrophotometer using *m*-nitrobenzyl alcohol as a matrix. For systems of this type which are composed of repeating units, elemental analysis is not particularly valuable. Systems incorporating the tpp bridging ligand have been shown to be relatively stable under FAB mass spectral analysis[16] giving fragments that often leave the ligands intact. The highest *m*/*z* peaks for each of the complexes are given in Table 1 along with the fragment corresponding to this mass. Full mass spectral data are included as supporting information. Fragmentation patterns were consistent with the proposed molecular structures.

Results and Discussion

Synthetic Route. The series of bimetallic complexes has been prepared using the building block approach outlined in Scheme 1. A new method for the preparation of [Os(tpy)(tpp)]$^{2+}$ is outlined in the Experimental Section which circumvents the ligand scrambling observed in the past preparations.[14b]

Scheme 1



The illustrated stepwise approach to the construction of these molecules allows further extension of the molecular design using these methodologies. This will allow for the systematic construction of a wide variety of mixed metal systems of variable but known length and composition.

FAB Mass Spectral Analysis. A summary of the highest mass peaks from the FAB mass spectral analysis of the title trimetallics is given in Table 1. Under the conditions used in this study, the metal complexes gave easily interpretable fragmentation patterns with the tpy and tpp ligands remaining intact. This is quite similar to an elegant study by Abruna et al.[16] on a large series of tpp-bridged systems. Full mass spectral data for our complexes are available as Supporting Information.

Electrochemistry. The electrochemical properties of ruthenium and osmium polypyridine complexes typically show metal-based oxidations and reductions based on each ligand. The ligands tpy and tpp used in this study have been characterized previously.[14−18] The ligand tpp is easier to reduce than tpy. This gives rise to mixed ligand tpy and tpp complexes in which the lowest unoccupied molecular orbital (LUMO) will be localized on the tpp ligand. In ruthenium and osmium polypyridyl complexes, the highest occupied molecular orbital (HOMO), will be based on the metal center and oxidative processes are metal based. Table 2 shows the electrochemical data for the monometallic precursor complexes $[Ru(tpy)(tpp)](PF_6)_2$[14,15,17] and $[Os(tpy)(tpp)](PF_6)_2$[14,16] as well as the bimetallic complexes $[(tpy)Ru(tpp)RuCl_3]^+$, $[(tpy)Ru(tpp)Ru(tpp)]^{4+}$, $[(tpy)Os(tpp)RuCl_3]^+$, and $[(tpy)Os(tpp)Ru(tpp)]^{4+}$.

Table 2. Cyclic Voltammetric Data for a Series of Ruthenium(II) and Osmium(II) Complexes Incorporating the Tridentate Bridging Ligand tpp[a]

compound	$E_{1/2}$ (V)	assignment
$[Ru(tpy)(tpp)]^{2+}$ [b]	+1.40	Ru(II)/Ru(III)
	−0.97	tpp/tpp$^-$
	−1.38	tpy/tpy$^-$
$[Os(tpy)(tpp)]^{2+}$ [c]	+1.06	Os(II)/Os(III)
	−0.97	tpp/tpp$^-$
	−1.39	tpy/tpy$^-$
$[(tpy)Ru(tpp)RuCl_3]^+$	+1.61	Ru(II)/Ru(III)
	+0.73	Ru(II)/Ru(III)
	−0.60	tpp/tpp$^-$
	−1.10	tpp$^-$/tpp^{2-}
$[(tpy)Os(tpp)RuCl_3]^+$	+1.32	Os(II)/Os(III)
	+0.66	Ru(II)/Ru(III)
	−0.59	tpp/tpp$^-$
	−1.07	tpp$^-$/tpp^{2-}
$[(tpy)Ru(tpp)Ru(tpp)]^{4+}$ [c]	+1.86	Ru(II)/Ru(III)
	+1.51	Ru(II)/Ru(III)
	−0.30	tpp/tpp$^-$
	−0.82	tpp$^-$/tpp^{2-}
$[(tpy)Os(tpp)Ru(tpp)]^{4+}$	+1.81	Ru(II)/Ru(III)
	+1.17	Os(II)/Os(III)
	−0.36	tpp/tpp$^-$
	−0.81	tpp$^-$/tpp^{2-}

[a] Potentials reported in CH_3CN solution with 0.1 M TBAH and reported vs Ag/AgCl (0.29 V vs NHE). [b] Although this system has been previously reported (refs 14 and 15), the numbers reported are for our system prepared from our synthetic methodology and studied under our conditions to make comparisons more valid. [c] Although this system has been previously reported (refs 14 and 16), the numbers reported are for our system prepared from our sythetic methodology and studied under our conditions to make comparisons more valid.

The electrochemical properties of the mixed ligand ruthenium and osmium complexes $[M(tpy)(tpp)]^{2+}$ have been previously studied.[14−17] In the monometallic $[Ru(tpy)(tpp)]^{2+}$, the oxidation at +1.40 V has been assigned as a Ru(II)/Ru(III) metal-centered oxidation with the reductions being assigned as tpp/tpp$^-$ and tpy/tpy$^-$ ligand-centered processes at −0.97 and −1.38 V, respectively.[14,15,17] In the monometallic $[Os(tpy)(tpp)]^{2+}$, the metal-based oxidation occurs at +1.06 V and the ligand-localized reductions occur at −0.97 and −1.39 V.[14,16] Osmium is expected to have dπ orbitals higher in energy than ruthenium leading to a metal that is more easily oxidized. The tpp and tpy reductions in these two complexes appear to be insensitive to the nature of the coordinated metal leading to the conclusion that the reductions are largely ligand localized.[14−17]

Upon attachment of a $RuCl_3$ moiety to $[Ru(tpy)(tpp)]^{2+}$ to produce $[(tpy)Ru(tpp)RuCl_3]^+$, an additional oxidation is observed and the first reduction is shifted to more positive potentials. The first oxidation at +0.73 V is assigned as being the ruthenium that is coordinated to tpp and three chloride ligands. This metal would be more electron rich since chloride is a π donor while tpy is a π acceptor. The second oxidation at +1.61 V is assigned as the ruthenium coordinated to tpy and tpp which becomes harder to oxidize relative to the monometallic analog due to the enhanced π backbonding to the tpp upon bimetallic formation. The two reductions at −0.60 and −1.10 V are assigned as being sequential tpp reductions which is typical for polyazine-bridged systems of this type.[14,15,17] These reductions occur at more positive potentials than in $[Ru(tpy)(tpp)]^{2+}$ due to the stabilization of the tpp π* orbitals upon addition of a second metal center as the tpp acts as a bridging ligand. This yields a complex, $[(tpy)Ru(tpp)RuCl_3]^+$, in which the HOMO is based on the ruthenium bound to the three chlorides and the LUMO is based on the bridging tpp ligand.

Upon incorporation of $RuCl_3$ to the remote nitrogens on the tpp ligand of $[Os(tpy)(tpp)]^{2+}$ to produce $[(tpy)Os(tpp)RuCl_3]^+$, an additional oxidation is observed and the first reduction shifts to more positive potentials. The first oxidation for $[(tpy)Os(tpp)RuCl_3]^+$ at +0.66 V is assigned as the Ru(II)/Ru(III) oxidation. The ruthenium metal will be more electron rich than the osmium due to its coordination environment. Interestingly, this ruthenium-based oxidation occurs at a less positive potential in this heterobimetallic complexes relative to the all-ruthenium analog. This likely is a consequence of the enhanced π-backbonding ability of the Os metal center giving rise to a decreased π-accepting ability of the tpp ligand. This gives a more electron rich (tpp)RuCl$_3$ moiety in the heterobimetallic complex relative to the all-ruthenium analog. The second oxidation in [(tpy)Os(tpp)RuCl$_3$]$^+$ at $+1.32$ V is assigned as an Os(II)/Os(III) metal-based process. This metal is harder to oxidize than the analogous monometallic complex [Os(tpy)(tpp)]$^{2+}$. This is a consequence of the increased π acceptor ability of the bridging tpp ligand leading to a less electron rich metal. As predicted by the electrochemical properties of the monometallic fragments, the osmium oxidation in [(tpy)Os(tpp)RuCl$_3$]$^+$ occurs at a lower potential than the similarly coordinated ruthenium in the Ru/Ru bimetallic system. The first two reductions at -0.59 and -1.07 V are assigned as sequential tpp reductions. This system, [(tpy)Os(tpp)RuCl$_3$]$^+$, has a ruthenium-based HOMO and a tpp-based LUMO.

Substitution of the chlorides on [(tpy)Ru(tpp)RuCl$_3$]$^+$ by tpp produces [(tpy)Ru(tpp)Ru(tpp)]$^{4+}$. The first oxidation of this complex is shifted to more positive potentials relative to the [(tpy)Ru(tpp)RuCl$_3$]$^+$ starting material. It has been shown previously that [Ru(tpp)$_2$]$^{2+}$ has a Ru(II)/Ru(III) oxidation at $+1.57$ V[5d,16] and thus is harder to oxidize than [Ru(tpy)(tpp)]$^{2+}$ by 170 mV.[14−17] This is consistent with tpp having an increased π acidity relative to tpy leaving the metal center less electron rich. Consequently, the first oxidation at $+1.51$ V in [(tpy)Ru(tpp)Ru(tpp)]$^{4+}$ represents the Ru(II)/Ru(III) processes that is centered on the ruthenium coordinated to both tpp and tpy, whereas the second oxidation at $+1.86$ V is the Ru(II)/Ru(III) couple for the ruthenium coordinated to two tpp ligands. The two reductions at -0.30 and -0.82 V correspond to the expected sequential reduction of the bridging tpp ligand. This electrochemical behavior is in agreement with that reported by Abruña et al. on a sample of this complex prepared by a different method.[16] This yields a complex in which the HOMO is based on the ruthenium site bound to tpy and the LUMO is based on the bridging tpp ligand.

Substitution of the chlorides in [(tpy)Os(tpp)RuCl$_3$]$^+$ by tpp to form [(tpy)Os(tpp)Ru(tpp)]$^{4+}$ leads to a reversal in the order of the metal-centered oxidations. The first oxidation at $+1.17$ V is assigned as being an Os(II)/Os(III) oxidation with the second oxidation at $+1.81$ V being a Ru(II)/Ru(III) metal-based oxidation. The osmium oxidation is slightly shifted relative to the monometallic one due to the electron-withdrawing effect of the additional ruthenium center and the enhanced π-backbonding ability of the bridging tpp. As expected, the osmium oxidation occurs at a lower potential than the similarly coordinated ruthenium in [(tpy)Ru(tpp)Ru(tpp)]$^{4+}$. The second oxidation in [(tpy)Os(tpp)Ru(tpp)]$^{4+}$ corresponds to the Ru(II)/Ru(III) couple and occurs at a slightly less positive potential in [(tpy)Os(tpp)Ru(tpp)]$^{4+}$ than in the Ru/Ru bimetallic system. This more electron rich ruthenium site is a consequence of an enhanced π backbonding of the osmium metal to the tpp ligand relative to the ruthenium analog. This gives rise to a lower degree of π backbonding from the ruthenium site making it more electron rich. The ligand reductions at -0.36 and -0.81 V are assigned as tpp/tpp$^-$ and tpp$^-$/tpp^{2-} reductive processes consistent with a bridging tpp ligand. This results in a complex with an osmium-based HOMO and a bridging tpp-based LUMO.

Electronic Absorption Spectroscopy. The electronic absorption spectra for the title bimetallics are shown in Figures 1 and 2. The free ligand spectra for tpy and tpp have been previously reported and contain intense $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions in the ultraviolet region of the spectrum.[14−17,20] The electronic absorption spectroscopy for ruthenium and osmium polypyridyl complexes typically contains $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ bands in the ultraviolet and MLCT transitions terminating on each acceptor ligand in the visible. The lowest energy transition at 474 nm in [Ru(tpy)(tpp)]$^{2+}$ has been assigned as overlapping Ru(dπ) → tpp(π^*) and Ru(dπ) → tpy(π^*) MLCT transitions with the latter occurring at slightly higher energy.[14,15,17] The lowest energy transition at 468 nm is [Os(tpy)(tpp)]$^{2+}$ has been assigned as overlapping Os(dπ) → tpp(π^*) and Os(dπ) → tpy(π^*) MLCT transitions with the tpp-based transition at lower energy.[14−16] The spectroscopy of this osmium-based system is remarkably similar to that of the ruthenium analog.

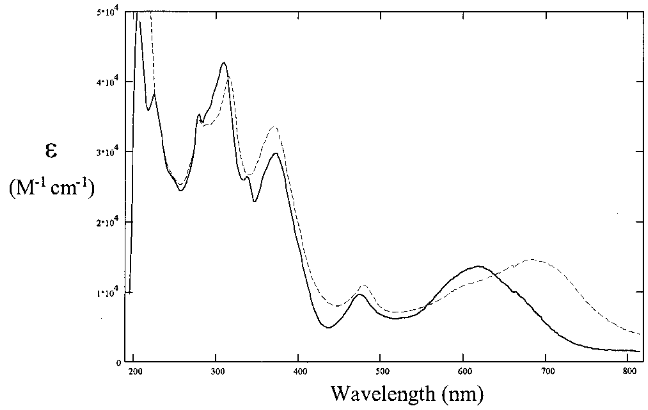


Figure 1. Electronic absorption spectra in acetonitrile for ruthenium(II) bimetallic complexes incorporating the tridentate polypyridyl bridging ligand tpp: (— — —) [(tpy)Ru(tpp)RuCl$_3$]$^+$ and (—) [(tpy)Os(tpp)RuCl$_3$]$^+$.

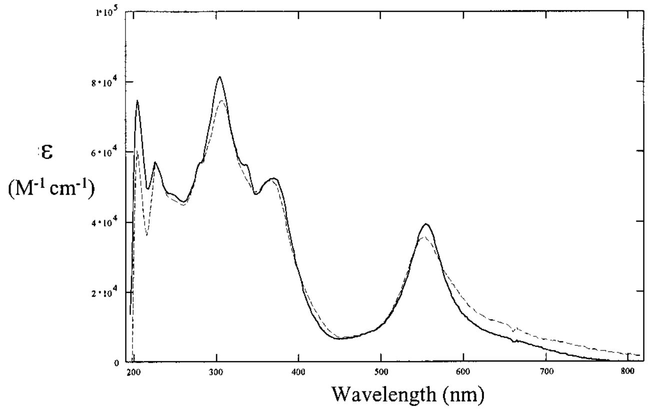


Figure 2. Electronic absorption spectra in acetonitrile for mixed metal ruthenium(II) and osmium(II) bimetallic complexes incorporating the tridentate polypyridyl bridging ligand tpp: (— — —) [(tpy)Ru(tpp)Ru(tpp)]$^{4+}$ and (—) [(tpy)Os(tpp)Ru(tpp)]$^{4+}$.

Figure 1 contains the electronic absorption spectra of the bimetallic complexes [(tpy)Ru(tpp)RuCl$_3$]$^+$ and [(tpy)Os(tpp)RuCl$_3$]$^+$. The addition of RuCl$_3$ to the three vacant sites on tpp of [Ru(tpy)(tpp)]$^{2+}$ to form [(tpy)Ru(tpp)RuCl$_3$]$^+$ results in two major bands appearing in the visible, one at 470 nm and another at 612 nm. The band at 470 nm is assigned as a Ru(dπ) → tpy(π^*) MLCT centered on the ruthenium coordinated to tpy and tpp and is relatively unchanged by bimetallic formation. The Ru(dπ) → tpp(π^*) MLCT transition centered on the ruthenium coordinated to tpy and tpp is at ca. 525 nm. This peak is shifted to lower energy compared to the monometallic [Ru(tpy)(tpp)]$^{2+}$ as a consequence of the stabilization of the tpp π^* orbitals. The broad transition at 612 nm is assigned as a Ru(dπ) → tpp(π^*) MLCT transition centered on the ruthenium metal coordinated to tpp and three chlorides. This transition is expected to occur at lower energy than the analogous transition from the ruthenium coordinated to a tpy and tpp ligand since the electrochemical data indicate that the Ru(dπ) orbitals on the (tpp)Ru^{II}Cl$_3$ moiety are significantly higher in energy than those of the (tpy)Ru^{II}(tpp) moiety. This [(tpy)Ru(tpp)RuCl$_3$]$^+$ has a lowest lying excited state that is Ru → tpp MLCT in nature, consistent with the electrochemical properties. The intense peaks in the ultraviolet are assigned as ligand-based n → π* and π → π* transitions for both tpp and tpy.

The spectrum of [(tpy)Os(tpp)RuCl$_3$]$^+$ is similar to [(tpy)Ru(tpp)RuCl$_3$]$^+$ in the ultraviolet with some differences in the visible. The coordination of RuCl$_3$ to the vacant sites on tpp to form [(tpy)Os(tpp)RuCl$_3$]$^+$ results in three bands in the visible at 474, 606, and 678 nm. The band at 474 nm is assigned as an Os(dπ) → tpy(π*) MLCT transition. The band at 606 nm is assigned as the Os(dπ) → tpp(π*) MLCT transition. The band at 678 nm represents the Ru(dπ) → tpp(π*) CT transition as well as some contributions from the Os → tpp ^{3}MLCT. One might expect the spectrum of the Os/Ru system to look like its Ru/Ru analog with minor changes due to the ^{3}MLCT states. The shift in the Ru → tpp CT transition is quite unusual. The electrochemically measured HOMO−LUMO gap for the two complexes [(tpy)Ru(tpp)RuCl$_3$]$^+$ and [(tpy)Os(tpp)RuCl$_3$]$^+$ is 1.33 and 1.25 V, respectively. This would predict a red-shifted lowest lying MLCT for [(tpy)Os(tpp)RuCl$_3$]$^+$ versus the all-ruthenium analog. The degree of red shift of this transition is somewhat surprising. The Os(II)/Os(III) oxidation occurs at a lower potential than the analogous Ru(II)/Ru(III) oxidation (1.32 versus 1.61 V, respectively). Thus, the presence of the Os-based dπ orbitals in close proximity to the Ru-based dπ orbitals (the ruthenium coordinated to tpp and three chlorides) may result in an interaction between the two which could lead to the observed red shift of the Ru → tpp CT transition. This mixing may also result in increased intensity to the ^{3}MLCT band associated with this ruthenium metal center.[22] As expected, the intense peaks in the UV are n → π and π → π* transitions for both tpy and tpp.

Figure 2 contains the electronic absorption spectra of the bimetallic complexes [(tpy)Ru(tpp)Ru(tpp)]$^{4+}$ and [(tpy)Os(tpp)Ru(tpp)]$^{4+}$. Our electronic absorption spectroscopy of [(tpy)Ru(tpp)Ru(tpp)]$^{4+}$ is in agreement with that reported by Abruña et al.[16] Substitution of the chlorides on [(tpy)Ru(tpp)RuCl$_3$]$^+$ with tpp to form [(tpy)Ru(tpp)Ru(tpp)]$^{4+}$ results in a major band at 548 nm. This band is assigned as two overlapping Ru(dπ) → tpp(π*) MLCT transitions involving the bridging tpp. The Ru(dπ) → tpp(π*) CT based on the (tpy)Ru^{II}(tpp) moiety should occur at slightly lower energy than the similar transition for the (tpp)Ru^{II}(tpp) moiety. The band at 360 nm is assigned as a Ru(dπ) → tpy(π*) transition overlapping with a Ru(dπ) → tpp(π*) transition involving the terminal tpp ligand. The ultraviolet consists of π → π* transitions that are tpp and tpy based.

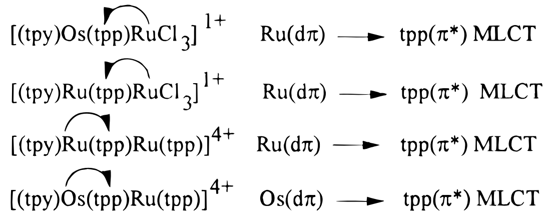
Substitution of the chlorides on [(tpy)Os(tpp)RuCl$_3$]$^+$ with tpp to form [(tpy)Os(tpp)Ru(tpp)]$^{4+}$ results in a major band at 546 nm with a tail at lower energy and a peak at ca. 360 nm. The band at 546 nm is assigned as overlapping Ru(dπ) → tpp(π*) and Os(dπ) → tpp(π*) MLCT transitions based on the bridging tpp with the Os(dπ) → tpp(π*) MLCT being the lower energy component. The tailing at lower energy can be assigned as Os(dπ) → tpp(π*) ^{3}MLCT transition due to the high degree of spin−orbit coupling in osmium. The peak at 360 nm can be assigned as the Os(dπ) → tpy(π*) MLCT transition overlapping with the Ru(dπ) → tpp(π*) MLCT transition involving the terminal tpp ligand. Interestingly, the spectra for [(tpy)Ru(tpp)Ru(tpp)]$^{4+}$ and [(tpy)Os(tpp)Ru(tpp)]$^{4+}$ are almost identical except for the ^{3}MLCT transitions that occur at lower energy than the ^{1}MLCT in the Os/Ru bimetallic complex. This would be as expected since the spectra of the monometallic fragments that compose these complexes, i.e., [Ru(tpy)(tpp)]$^{2+}$ and [Os(tpy)(tpp)]$^{2+}$, are quite similar. This similarity in the electronic absorption spectroscopy of osmium- and ruthenium-based systems of these tridentate ligands is somewhat surprising due to the much smaller electrochemical energy gap between the HOMO and LUMO for the osmium-based systems.

Table 3. Electronic Absorption Spectroscopy and Photophysical Data for a Series of Ruthenium(II) and Osmium(II) Complexes Containing the Tridentate Bridging Ligand tpp[a]

complex	λ_{max}^{abs} (nm)[b] (ϵ, M^{-1} cm^{-1})	λ_{max}^{em} (nm)[c]	τ (ns)[c]
[Ru(tpy)(tpp)]$^{2+}$ [d]	474 (1.6×10^4)	665	30
[Os(tpy)(tpp)]$^{2+}$ [e]	468 (1.5×10^4)	775	260
[(tpy)Ru(tpp)RuCl$_3$]$^+$	612 (1.4×10^4)	*g*	*g*
[(tpy)Os(tpp)RuCl$_3$]$^+$	678 (1.5×10^4)	*g*	*g*
[(tpy)Ru(tpp)Ru(tpp)]$^{4+}$ [f]	548 (4.0×10^4)	833	100
[(tpy)Os(tpp)Ru(tpp)]$^{4+}$	546 (3.6×10^4)	820	120

[a] tpp = 2,3,5,6-(2′-pyridyl)pyrazine and tpy = 2,2′:6′,2″-terpyridine. [b] Reported for the lowest energy ^{1}MLCT in acetonitrile solution at room temperature. [c] Measured in deoxygenated acetonitrile solution at room temperature. [d] Although this system has bee previously reported,[14,15] the numbers reported are for the systems synthesized for this study and under our conditions to make valid comparisons. [e] Although this system has been previously reported,[14,16] the numbers reported are for the systems synthesized for this study and under our conditions to make valid comparisons. [f] Although the sythesis of this system has been reported previously,[16] no excited state properties were given. [g] No emission was observed on our system.

The photochemistry of these types of polypyridyl complexes is dominated by the nature of the lowest lying excited state. Thus, the ability to synthetically manipulate the nature of this state is very important in molecular design. The nature of this state in our series of complexes is illustrated below



In the [(tpy)M(tpp)Ru(tpp)]$^{4+}$ series the HOMO is always located on the terminal metal that is coordinated to a tpy and tpp. This is useful; in theory, one can attach an acceptor to the other tpp sites and get charge separation over a long distance in a stereochemically defined multimetallic system.[23]

Emission Spectroscopy and Excited State Lifetimes. One way to probe the lowest lying excited state is through emission spectroscopy and excited state lifetime measurements. Both [(tpy)Ru(tpp)Ru(tpp)]$^{4+}$ and [(tpy)Os(tpp)Ru(tpp)]$^{4+}$ emit in fluid solution at room temperature. The complexes [(tpy)Ru(tpp)Cl$_3$]$^+$ and [(tpy)Os(tpp)RuCl$_3$]$^+$ may display red-shifted emissions beyond the detection limits of our system. The lack of an emission from the (tpy)M^{II}(tpp) unit in these [(tpy)M(tpp)RuCl$_3$]$^+$ systems indicates efficient quenching of this M → tpp charge transfer state by the (tpp)Ru^{II}Cl$_3$ moiety. This indicates a relatively strong coupling through the tpp bridge. The emission maxima and excited state lifetimes of the [(tpy)M(tpp)Ru(tpp)]$^{4+}$ systems are reported in Table 3.

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(22) Lumpkin, R. S. Private communication.

(23) Vogler, L. M.; Lee, J. D.; Brewer, K. J. Work in progress.

It has been reported that in polypyridyl complexes, visible light absorption is generally into a ^{1}MLCT state whereas emission occurs from the ^{3}MLCT state.[1−3] The emission spectra for both $[\mathrm{Ru(tpy)(tpp)}]^{2+}$ and $[\mathrm{Os(tpy)(tpp)}]^{2+}$ have been published previously with emission at 665 nm (27 ns) and 775 nm (260 ns) assigned as arising from the ^{3}MLCT excited states.[14−17] A comparison of these systems has not been made. The energy gap decreases in the osmium system relative to the ruthenium complex. This typically results in significantly shorter excited state lifetimes in osmium versus ruthenium systems of analogous polypyridine ligands.[1−17] The much shorter lifetime of $[\mathrm{Ru(tpy)(tpp)}]^{2+}$ relative to the Os analog is a consequence of the low-lying LF state in ruthenium that can be thermally populated at room temperature from the emissive MLCT state. The osmium system, $[\mathrm{Os(tpy)(tpp)}]^{2+}$, does not possess this low-lying LF state, and hence deactivation is only from the ^{3}MLCT state leading to the observed longer excited state lifetime. This point is verified by the analysis of the 77 K excited state lifetimes of these complexes. At 77 K, the lifetimes are 7.1 and 3.8 μs for $[\mathrm{Ru(tpy)(tpp)}]^{2+}$ and $[\mathrm{Os(tpy)(tpp)}]^{2+}$, respectively. When thermal population of this deactivating LF state is removed by lowering the temperature to 77 K, the energy gap law is obeyed and the expected ordering of excited state lifetimes is observed, i.e., $\tau_{\mathrm{Ru}} > \tau_{\mathrm{Os}}$.

Formation of the bimetallic $[\mathrm{(tpy)Ru(tpp)Ru(tpp)}]^{4+}$ leads to a system that emits at 833 nm with a lifetime of 100 ns. This is a long excited state lifetime for a polymetallic polyazine ruthenium complex. Considering the decrease in the energy gap relative to $[\mathrm{Ru(tpy)(tpp)}]^{2+}$, one would expect that the emissive lifetime for $[\mathrm{(tpy)Ru(tpp)Ru(tpp)}]^{4+}$ to decrease relative to $[\mathrm{Ru(tpy)(tpp)}]^{2+}$. In fact, this bimetallic system has a longer lifetime than the $[\mathrm{Ru(tpy)(tpp)}]^{2+}$ monometallic one at room temperature. In the $[\mathrm{(tpy)Ru(tpp)Ru(tpp)}]^{4+}$ bimetallic system, the MLCT state is greatly stabilized relative to the ligand field state. This prevents thermal population of the LF state in the bimetallic complex at room temperature. This results in the lifetime of the chromophore in the bimetallic complex to be enhanced relative to the monometallic $[\mathrm{Ru(tpy)(tpp)}]^{2+}$ when measured at room temperature.

The osmium-based bimetallic $[\mathrm{(tpy)Os(tpp)Ru(tpp)}]^{4+}$ emits from an Os-based ^{3}MLCT state with a $\lambda_{\mathrm{max}}{}^{\mathrm{em}}$ of 820 nm and a lifetime of 120 ns. The osmium-based chromophores are not expected to have low-lying LF states. Hence formation of a bimetallic complex should result in the normal trend of a decreased lifetime due to a decrease in the energy gap between the ground and excited states.[4−17] This is observed as the excited state lifetime is decreased from 260 to 120 ns upon bimetallic formation. The 120 ns excited state lifetime for an osmium polymetallic complex is large compared to other polyazine-bridged osmium systems studied to date.[7,9,12] The similarities of the absorption and emission energies, as well as the excited state lifetimes, of the Ru/Ru and Os/Ru bimetallic complexes are unusual and seem to be unique to these tpp-bridged systems.

Conclusions

In this study two types of synthetically useful bimetallic complexes have been synthesized, $[\mathrm{(tpy)M(tpp)RuCl_3}]^{+}$ and $[\mathrm{(tpy)M(tpp)Ru(tpp)}]^{4+}$ where M = Ru or Os. In the first set of complexes, it is found that the HOMO is based on the $\mathrm{Ru^{II}}$-$\mathrm{Cl_3}$ moiety and the LUMO is tpp based. In the second set of complexes, the LUMO is still localized on the bridging tpp ligand whereas the HOMO is localized on the metal that is varied, either ruthenium or osmium that is coordinated to both tpy and tpp. The synthetic methodologies developed in this study will allow for the construction of larger polymetallic systems of this type. Both $[\mathrm{(tpy)Ru(tpp)Ru(tpp)}]^{4+}$ and $[\mathrm{(tpy)Os(tpp)Ru(tpp)}]^{4+}$ emit in fluid solution at room temperature and are quite unique in the class of polymetallic polyazine-bridged complexes in that they have lifetimes of ca. 100 ns. As a result of the thermally accessible ligand field state in $[\mathrm{Ru(tpy)(tpp)}]^{2+}$, the bimetallic complex $[\mathrm{(tpy)Ru(tpp)Ru(tpp)}]^{4+}$ has a longer excited state lifetime at room temperature than the monometallic form from which it was constructed, $[\mathrm{Ru(tpy)(tpp)}]^{2+}$. This is a rather unique result. The long lifetimes of these bimetallic chromophores make them useful components in the design of supramolecular complexes. These studies indicate that the tpp ligand holds great promise by providing efficient coupling of the bridged metal centers within a stereochemically defined framework while maintaining long-lived excited states.

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Supporting Information Available: Copies of the FAB mass spectral data (4 pages). Ordering information is given on any current masthead page.

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