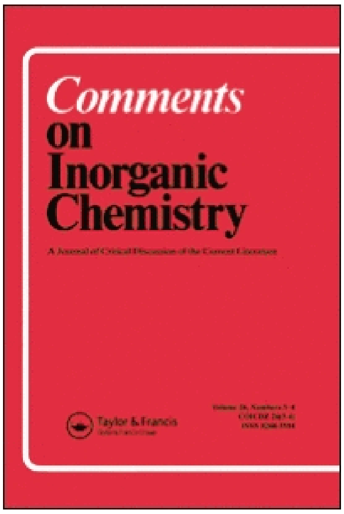

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Tridentate-Bridged Polyazine Complexes of Ruthenium(II) and Osmium(II) and their Application to the Development of Photochemical Molecular Devices

Karen J. Brewer[a]
[a] Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, Virginia

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Tridentate-Bridged Polyazine Complexes of Ruthenium(II) and Osmium(II) and their Application to the Development of Photochemical Molecular Devices

KAREN J. BREWER*

Department of Chemistry,
Virginia Polytechnic Institute and State University,
Blacksburg, Virginia 24061–0212

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The application of polymetallic complexes to photochemical energy conversion is an active area of research. The use of tridentate complexes within this context has been less well explored than the highly studied tris-bidentate structural motif. Recent interest has expanded to explore the class of tridentate bridged complexes that incorporate Ru^{II} and Os^{II} chromophores. These systems hold promise in that they give rise to polymetallic systems that are stereochemically defined. This is important in the construction of molecular devices that utilize energy or electron transfer as it will allow control of donor – acceptor distance and orientation. This article describes some of the recent research in the construction and study of polyazine-based, tridentate-bridged complexes containing Ru^{II} and Os^{II} chromophores.

Keywords: *polymetallic, bridging ligands, polyazine, polypyridyl, photochemistry, osmium, ruthenium, molecular device*

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* Correspondence Author.

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INTRODUCTION

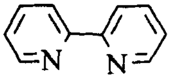
The excited state properties of $[Ru(bpy)_3]^{2+}$ sparked much interest in the utilization of this and related chromophores in energy conversion schemes (bpy= 2,2'-bipyridine).[1–6] The intense $Ru(d\pi)\rightarrow bpy(\pi^*)$ MLCT (metal-to-ligand charge transfer) absorption occurs at 450 nm in acetonitrile solution for $[Ru(bpy)_3]^{2+}$. This ^{3}MLCT excited state displays a strong emission in deoxygenated acetonitrile solution centered at 630 nm with an excited-state lifetime of 600 ns at room temperature (RT). This prototypical chromophore possesses a long-lived ^{3}MLCT excited state that undergoes facile energy and electron transfer. Since the excited state of $[Ru(bpy)_3]^{2+}$ is both a more powerful oxidizing and reducing agent than its ground state, it is capable of undergoing either oxidative or reductive electron transfer quenching (Q = quencher, EA = electron acceptor, ED = electron donor).

$[Ru(bpy)_3]^{2+} + h\nu \rightarrow {}^*[Ru(bpy)_3]^{2+}$	Excitation
${}^*[Ru(bpy)_3]^{2+} + Q \rightarrow [Ru(bpy)_3]^{2+} + {}^*Q$	Energy Transfer Quenching
${}^*[Ru(bpy)_3]^{2+} + EA \rightarrow [Ru(bpy)_3]^{3+} + EA^-$	Oxidative Electron Transfer Quenching
${}^*[Ru(bpy)_3]^{2+} + ED \rightarrow [Ru(bpy)_3]^{+} + ED^+$	Reductive Electron Transfer Quenching

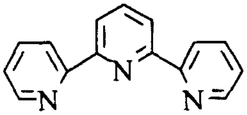
The many desirable properties of this chromophore have led to a variety of very interesting studies exploiting the properties of this system, and recent reviews have appeared.[1,2] A major drawback for the utilization of this and other related monometallic chromophores in energy conversion schemes is the need for collisional contact between the excited state of the light absorber and the quencher during the excited state lifetime of the chromophore. This limitation has stimulated active research into the modification of this $[Ru(bpy)_3]^{2+}$ system to incorporate other polyazine ligands that are capable of binding to additional metal centers, the polyazine bridging ligands.

Polyazine Bridging Ligands

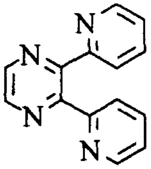
The most widely studied class contains polyazine bridging ligands which bind to both metal centers in a bidentate fashion. A comprehensive review has summarized this rapidly expanding area of polyazine chemistry.[7] One of the most highly studied polyazine bridging ligands in this class is dpp (dpp = 2,3-bis(2-pyridyl)pyrazine).[7–31]



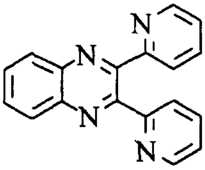
bpy



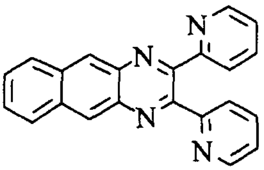
tpy



dpp



dpq

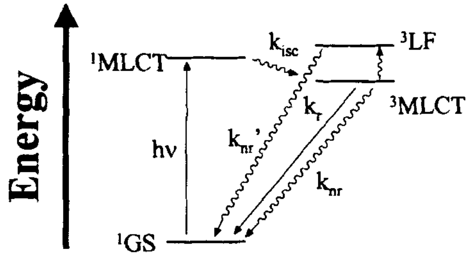


dpb

Incorporation of this polyazine bridging ligand into this $[Ru(bpy)_3]^{2+}$ chromophoric unit leads to a modification of the properties observed. For example, $[Ru(bpy)_2(dpp)]^{2+}$ displays a red-shifted absorption (λ_{max} = 463 nm) and emission (λ_{max} = 691 nm) relative to $[Ru(bpy)_3]^{2+}$ and a shortened ^{3}MLCT excited-state lifetime (τ = 240 ns).[12,24] The lower energy excited state results from the dpp ligand possessing a lower energy π^* acceptor orbital than bpy. This $[Ru(bpy)_2(dpp)]^{2+}$ chromophore does possess remote coordination sites on the dpp ligand and has been incorporated into a large number of very interesting polymetallic systems. Upon bridge formation to produce polymetallic complexes, the ^{3}MLCT excited state is further stabilized, leading to even more red-shifted absorptions and emissions for these types of polymetallic systems and further shortening of the excited state lifetimes.[7,19,24] A number of supramolecular complexes have been reported which incorporate this dpp bridging ligand.[7] These systems are quite interesting and have served to advance the understanding of the promissing properties of polymetallic, polyazine bridged ruthenium complexes. In these larger systems, the utilization of this tris-bidentate structural motif rapidly results in the possibility of large numbers of stereoisomers. The dpp ligand itself is an AB type chelate that binds to a metal through two nitrogen donor atoms that are inequivalent. This results in additional stereoisomerization in complexes of this ligand.

Supramolecular Systems and Photochemical Molecular Devices

Polyazine bridging ligand complexes of ruthenium and osmium have potential as chromophores in supramolecular systems for light-activated processes. In 1987 Balzani *et al.* presented an elegant report on a vast array of photochemical molecular devices, their design and energetic requirements.[16] His manuscript reveals some of potential applications of ruthenium and osmium polyazine bridged complexes. Reviews have appeared highlighting some of this very exciting chemistry.[7,17] Gafney *et al.*,[23,24] Rillema *et al.*[32–34] and Petersen *et al.*[18–22] also presented some of the early reports of dpp- and dpp-bridged ruthenium complexes. Balzani and co-workers, pioneers in this area of chemistry, have prepared a vast array of large ruthenium and osmium supramolecular systems of the dpp bridging ligand that display quite unique and interesting photophysical and electrochemical properties.[7-14,16,17] Our group has explored trimetallic complexes that couple two light absorbers to a central electron-collecting metal center of the form $\{[(bpy)_2Ru(dpb)]_2IrCl_2\}^{5+}$, and we have shown it to be the first molecular device for photoinitiated electron collection.[29,30] Much of the research in this area has utilized the tris-bidentate coordination geometry of the ruthenium and osmium chromophores. This approach results in complexes that are often stereochemically ill-defined. This stereochemical complexity can present some difficulties in the design of more complex supramolecular systems and in the study of factors like donor-acceptor distance and orientation that often dictate device properties. One method to eliminate the possibility of these stereoisomers is the utilization of the bis-tridentate coordination environment on the metal center using complexes such as $[Ru(tpy)_2]^{2+}$ (tpy = 2,2':6',2"-terpyridine).

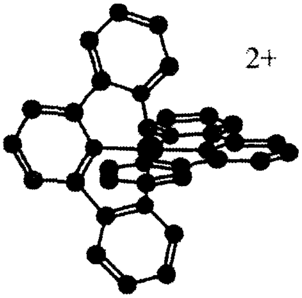


$[Ru(tpy)_2]^{2+}$

FIGURE 1 State diagram for $[Ru(tpy)_2]^{2+}$, (tpy = 2,2′,6′,2″-terpyridine GS = ground state, MLCT = metal-to-ligand charge transfer state, LF = ligand field state, k_{isc} = rate constant for intersystem crossing, k_{nr} = rate constant for non-radiative decay, k_r = rate constant for radiative decay, wavy arrows represent non-radiative processes and straight arrows radiative processes)

Bis(2,2′,6′,2″-terpyridine)ruthenium(II) and Related Chromophores

Some of the properties of $[Ru(tpy)_2]^{2+}$ have limited its application in solar energy conversion schemes.[35–38] (see Fig. 1)



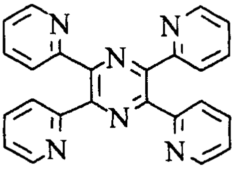
This simple bis-tridentate polyazine complex of ruthenium possesses an intense Ru(dπ)→tpy(π*) CT absorption in the visible centered at 476 nm, which is slightly red-shifted relative to $[Ru(bpy)_3]^{2+}$ due to the expected stabilization of the tpy π^* acceptor orbitals relative to bpy. Unlike $[Ru(bpy)_3)]^{2+}$, $[Ru(tpy)_2]^{2+}$ does not display an easily detectable emission at RT. The excited state lifetime of the ^{3}MLCT state of $[Ru(tpy)_2]^{2+}$ is reported to be 0.25 ns, in contrast to the long-lived ^{3}MLCT excited state of $[Ru(bpy)_3]^{2+}$.[36] The short ^{3}MLCT excited state lifetime for $[Ru(tpy)_2]^{2+}$ has been attributed to a facile thermal population of the low-lying ^{3}LF state.[35–38] This ^{3}LF state rapidly deactivates to the ground state (k_{nr}'), The presence of this lower lying, thermally accessible LF state in $[Ru(tpy)_2]^{2+}$ likely results from the weaker ligand field of the two tpy ligands relative to the three bpy ligands due to the poor bite angle of the tpy ligand, which is not ideally suited to the octahedral coordination of the ruthenium metal center. This short excited state lifetime of the $[Ru(tpy)_2]^{2+}$ chromophore resulted in far less research into the properties of bis-tridentate complexes of ruthenium relative to the vast amount of literature covering the tris-bidentate area of ruthenium polyazine chemistry.

Modification of the terpyridine ligand is possible and can lead to complexes that display more desirable photophysical properties while still maintaining the stereochemical integrity obtained through this bis-tridentate coordination.[35,39–41] A variety of substituted tpy complexes have been reported, and many display an observable emission at RT. $[Ru(tptpy)_2]^{2+}$ displays an emission at 650 nm with a lifetime of 3.8 ns at RT (tptpy = 4,4′,4″-triphenyl-2,2′:6′,2″-terpyridine).[41] $[Ru(MeSO_2\text{-}tpy)_2]^{2+}$ displays an emission centered at 666 nm with a lifetime of 25 ns at RT ($MeSO_2$-tpy = 4′-methylsulfonyl-2,2′:6′,2″-terpyridine).[40] The presence of a RT emission in these complexes is a result of the stabilization of the ^{3}MLCT state relative to the ^{3}LF state limiting the thermal population of the latter. A recent report by Maestri, Balzani, Constable *et. al.* studied a series of substituted tpy complexes of ruthenium using temperature-dependent lifetime data to probe the thermal population of the deactivating LF state.[40] They found that the energy of the emission decreased for both electron-donating and electron-accepting substituents relative to $[Ru(tpy)_2]^{2+}$. They concluded that this results from the electron-accepting substituents giving a larger stabilization of the LUMO than the HOMO and the electron-donating substituents giving a larger destablization of the HOMO than the LUMO in these complexes. This leads to the observed unique property of both types of substituents giving rise to a red-shifted emission relative to the unsubstituted $[Ru(tpy)_2]^{2+}$.

The use of osmium in place of ruthenium within this bis-tridentate coordination geometry leads to some interesting changes in the properties of these chromophores. Osmium has a larger ligand field splitting than ruthenium in analogous systems. This will lead to an increase in the energy of the LF state in the Os based complexes and thus is expected to eliminate the thermal population of this state observed for many of the ruthenium systems. Osmium possesses higher energy dπ orbitals that typically lead to complexes with red-shifted absorptions and emissions relative to their ruthenium analogs. $[Os(tpy)_2]^{2+}$ displays an intense ^{1}MLCT absorption at 477 nm which is at an energy quite similar to the ruthenium analog. This has been attributed to the more covalent character of the osmium systems relative to the ruthenium analogs. The ^{3}MLCT absorption is quite intense in $[Os(tpy)_2]^{2+}$ at 657 nm with $\varepsilon = 3.7 \times 10^4\ M^{-1}\ cm^{-1}$.[41,42] This ^{3}MLCT state displays an emission at 718 nm at RT.[41,42] Elimination of the thermal population of the ^{3}LF state leads to a dramatic increase in the lifetime of $[Os(tpy)_2]^{2+}$ relative to $[Ru(tpy)_2]^{2+}$. The ^{3}MLCT state of $[Os(tpy)_2]^{2+}$ has a lifetime of 270 ns at RT.[41,42] There are many advantages to the use of bis-tridentate complexes as chromophores in the construction of larger polymetallic systems if the shorter MLCT excited state lifetimes of the ruthenium-based systems can be overcome. This coordination geometry gives rise to stereochemically defined complexes. This is a very attractive feature in the design of molecular devices for functions like photoinitiated charge separation or directed energy transfer as donor-acceptor distance and orientation can be controlled. The ability to control these factors makes the design, construction and study of supramolecular complexes with tridentate bridging ligands an exciting new area of coordination chemistry research. These tridentate ligands have already been used to fix the geometry of appended donors and acceptors in systems containing single metal centers. This has allowed for the construction of stereochemically defined systems for photoinitiated charge separation.[43]

TRIDENTATE BRIDGED COMPLEXES

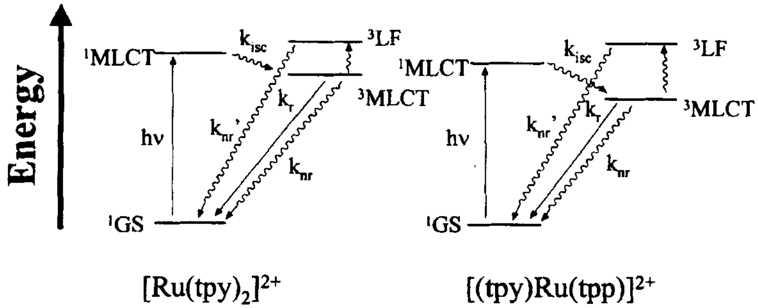
Recently various polyazine ligands have been used for the construction of polymetallic complexes of bis-tridentate systems incorporating ruthenium and osmium chromophores. One of the earliest studies of tridentate bridged polyazine ruthenium complexes with bis-tridentate coordination of the metal centers used the ligand tpp (tpp = 2,3,5,6-tetrakis(2-pyridyl)pyrazine).[7,20, 44–5]



tpp

This ligand possesses two tridentate sites for coordination to a metal center and thus is capable of bridging two metal centers, allowing for the construction of more complex supramolecular systems. The tpp ligand also possesses a stabilized π^* orbital relative to tpy which will make it the site of localization of the lowest unoccupied molecular orbital (LUMO) in mixed-ligand complexes of tpy and tpp.

In 1987 Petersen reported on the properties of $[(tpy)Ru(tpp)]^{2+}$ and $[(tpy)Ru(tpp)Ru(tpy)]^{4+}$.[20] (see Fig. 2). Both of these chromophores displayed interesting spectroscopic, photophysical and electrochemical properties. The monometallic complex $[(tpy)Ru(tpp)]^{2+}$ was reported to have a lowest-lying absorption maximum at 472 nm assigned as a Ru(dπ)$\rightarrow$tpp(π^*) CT transition. This complex was found to be emissive at RT with an emission maximum at 684 nm and an excited state lifetime of 91 ns. The intense emission from this chromophore, in marked contrast to the $[Ru(tpy)_2]^{2+}$ system, can be attributed to a stabilization of the π^* acceptor orbital on the tpp ligand leading to a stabilized ^{3}MLCT state. This stabilization will limit the thermal population of the ^{3}LF state, extending the ^{3}MCLT excited-state lifetime of this chromophore, a situation quite similar to that observed for the substituted tpy ligands discussed above. The electrochemistry reported by Petersen for $[(tpy)Ru(tpp)]^{2+}$ was typical of that observed for ruthenium polyazine complexes with a metal-based oxidation at 1.40 V vs. SCE ($Ru^{II/III}$) and a $tpp^{0/-}$-based reduction at –0.94 V. This electrochemistry is consistent with the Ru(dπ) nature of the highest occupied molecular orbital (HOMO) and the tpp (π^*) nature of the lowest unoccupied molecular orbital (LUMO) in this complex and correlates with the lowest-lying excited state being Ru→tpp CT in nature. The bimetallic system $[(tpy)Ru(tpp)Ru(tpy)]^{4+}$ was reported to have two oxidations at 1.43 and 1.72 V, indicating a coupling of the two equivalent ruthenium centers through this tpp bridging ligand. Petersen also reported a $tpp^{0/-}$ couple at –0.34 V, which indicated that the formation of the bimetallic complex through coordination of a metal to the remote site of the tpp ligand in the $[(tpy)Ru(tpp)]^{2+}$ system leads to a substantial stabilization of the π^* acceptor orbital on the tpp. $[(tpy)Ru(tpp)Ru(tpy)]^{4+}$ displays a lowest-lying absorption Ru → tpp CT at 650 nm, red-shifted relative to $[(tpy)Ru(tpp)]^{2+}$. The ^{3}MLCT state of this bimetallic chromophore was reported to be emissive at RT (λ_{max} = 826 nm) with an excited state lifetime of 100 ns. This first report of tpp-bridged chromophores of this type illustrates that this ligand can be used to prepare complexes that have many desirable properties for the subsequent construction of supramolecular systems with application to light conversion processes.

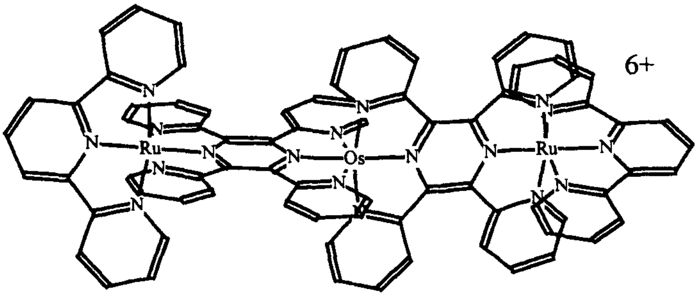


$[Ru(tpy)_2]^{2+}$ $[(tpy)Ru(tpp)]^{2+}$

FIGURE 2 Relative state diagrams for $[Ru(tpy)_2]^{2+}$ and $[(tpy)Ru(tpp)]^{2+}$, (tpy = 2,2′,6′,2″-terpyridine and tpp = 2,3,5,6-tetrakis(2-pyridyl)pyrazine)

Several other early reports of tpp bridged complexes have appeared.[45–50,54] In 1988 Thummel reported on some NMR properties and further electrochemical characterization of these $[(tpy)Ru(tpp)]^{2+}$ and $[(tpy)Ru(tpp)Ru(tpy)]^{4+}$, chromophores.[46] His NMR characterization highlights the fact that these complexes are single stereoisomers, giving clean and easily interpretable ^{1}H NMR spectra. Thummel also reported more detailed electrochemical characterization of these systems. In 1989 Ruminski reported on triammineruthenium(II) complexes of the tpp ligand, further illustrating the ability of the tpp ligand to function as a bridging ligand for ruthenium chromophores.[47]

In a very interesting manuscript, Arana and Abruna reported on a series of tpp bridged complexes of ruthenium and osmium,[48] among them the first osmium tpp complexes, which included $[(tpy)Os(tpp)Os(tpy)]^{4+}$, $[(tpy)Ru(tpp)Os(tpy)]^{4+}$ and $[(tpy)Ru(tpp)Os(tpp)Ru(tpy)]^{6+}$. This report highlighted the ability of the tpp ligand to be used to prepare a wide variety of polymetallic complexes. Abruna pointed out that in these complexes metals bridged by the tpp ligand display electrochemical properties consistent with a high degree of coupling of the two bridged metals. Remarkably even the two equivalent ruthenium centers in the $[(tpy)Ru(tpp)Os(tpp)Ru(tpy)]^{6+}$ oxidize at different potentials, 1.59 and 1.72 V vs. SSCE (both occur after the $Os^{II/III}$ couple at 1.23 V). This behavior indicates a significant degree of interaction between these two ruthenium centers that are separated by ca. 30 Å and a $(tpp)Os^{II}(tpp)$ bridge. Abruna suggested that the tpp ligand might be useful for the construction of larger complexes that, due to the strong coupling of the metal centers, might give rise to band formation and function as molecular wires.



$[(tpy)Ru(tpp)Os(tpp)Ru(tpy)]^{6+}$

A report exploring the NIR spectroscopy of tridentate bridged complexes has appeared.[49] (see Fig. 3.) This includes a tpp bridged system, $[(ttpy)Ru^{II}(tpp)Ru^{III}(ttpy)]^{5+}$, and indicates that this mixed-valence complex appears to be a class III, delocalized system (ttpy = 4′-p-tolyl-2,2′:6′,2″-terpyridine). This illustrates the strong coupling of metal centers bridged by the tpp ligand.

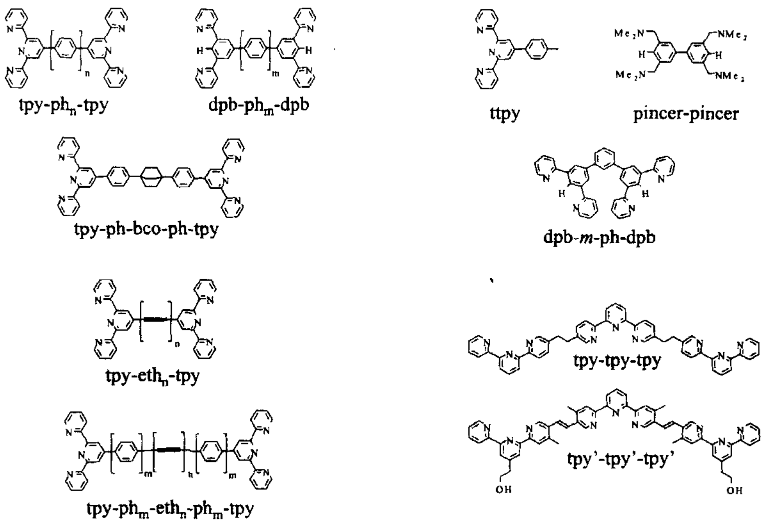


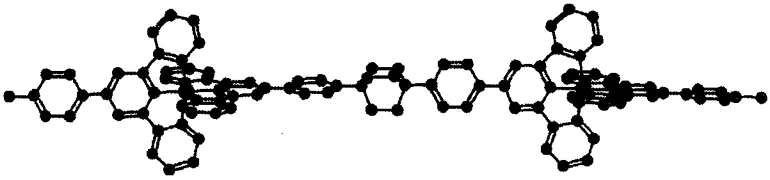
FIGURE 3 Tridentate bridging ligands

Another series of ligands was developed for use in the construction of tridentate bridged complexes. These ligands linked two terpyridine ligand through the 4′ positions through a variety of linkers to form "back-to-back" terpyridines.[7,44,49,58–80]

In 1990 Constable presented the synthesis and coordination properties of the directly linked tpy-tpy ligand, pointing out the potential of the use of this type of ligand.[58] Constable and co-workers showed that this ligand defines the stereochemistry of polymetallic complexes, allowing the assignment of the ^{1}H NMR spectra of $[(\text{tpy})\text{Ru}(\text{tpy-tpy})\text{Ru}(\text{tpy})]^{4+}$. For this complex they observed overlapping $\text{Ru}^{\text{II/III}}$ couples for both metal centers which they interpreted as the two metals being largely electronically uncoupled through this tpy-tpy bridge. Since that time other linked tridentate bridged systems have been reported.[58–63]

Some very exciting results have been presented by Sauvage and co-workers using a wide assortment of tridentate bridging ligands.[44,49,62–74] They have investigated the intervalence charge transfer bands (IT) of a wide variety of tridentate bridged complexes and found that most of these systems display intense IT bands indicative of a large degree of metal-metal coupling, often over very long metal-metal distances. In 1991 Sauvage reported on the properties of the directly linked biscyclometalating ligand dpb-dpb shown above, the complex $[(ttpy)Ru(dpb\text{-}dpb)Ru(ttpy)]^{2+}$, and its mixed-valence form.[64] The Ru^{II}, Ru^{III} form displays an intense intervalence charge transfer band $\lambda_{max} = 1820$ nm, $\varepsilon = 27{,}000\ M^{-1}\ cm^{-1}$ and $\Delta\nu_{1/2} = 2.82 \times 10^3 cm^{-1}$ which indicates significant delocalization of the mixed-valence state. A later study looked at systems with phenyl spacers, $[(ttpy)Ru(dpb\text{-}ph_m\text{-}dpb)Ru(ttpy)]^{2+}$, m = 0, 1 and 2.[68] Even the system with m = 2 displays an intense IT band, $\lambda_{max} = 1214$ nm, $\varepsilon = 2{,}200\ M^{-1}\ cm^{-1}$ and $\Delta\nu_{1/2} = 5.71 \times 10^3\ cm^{-1}$, displaying this large degree of metal-metal coupling with a 20 Å metal-metal distance. Sauvage also reported on the properties of the linked tpy-tpy systems with phenyl spacers, $[(ttpy)Ru(tpy\text{-}ph_n\text{-}tpy)Ru(ttpy)]^{4+}$, n = 0, 1 and 2.[49] These systems also showed intense IT bands, n = 0, $\lambda_{max} = 1580$ nm, $\varepsilon = 1{,}600\ M^{-1}\ cm^{-1}$ and $\Delta\nu_{1/2} = 4.01 \times 10\ cm^{-1}$. Sauvage indicates that these $tpy\text{-}ph_n\text{-}tpy$ bridged systems display significant coupling, even for the n = 2 system. They developed another interesting tridentate bridging ligand, pincer-pincer. The complex $[(tpy)Ru(pincer\text{-}pincer)\ Ru(tpy)]^{2+}$ and its mixed-valence form were studied.[81] The mixed-valence complex displays the most intense IT band of this series, $\lambda_{max} = 1875$ nm, $\varepsilon = 33{,}000\ M^{-1}\ cm^{-1}$.

Recently Sauvage has prepared many interesting mixed-metal ruthenium, osmium complexes bridged by these tridentate ligands and studied energy transfer in these supramolecular systems.[44, 62, 63, 66- 69, 71, 73, 74] Systems incorporating the tpy-tpy linked bridging ligand with varying phenyl spacers, $[(ttpy)Os(tpy\text{-}ph_n\text{-}tpy)Ru(ttpy)]^{4+}$ (n = 0, 1, 2) and $[(ttpy)Ru(tpy\text{-}ph_n\text{-}tpy)Os(tpy\text{-}ph_n\text{-}tpy)Ru(ttpy)]^{6+}$ (n = 1, 2), have been studied, varying the metal-metal distance from 11 to 20 Å.[44, 62, 63, 74] These systems all displayed quenching of the ruthenium-based MLCT state by the osmium-based MLCT state. The rate of energy transfer was larger than $10^{10}\ s^{-1}$at RT. A similar series of mixed-metal systems using the biscyclometalating bridging ligands as also been studied, $[(ttpy)Ru(dpb\text{-}ph_n\text{-}dpb)Os(ttpy)]^{2+}$, n = 0, 1, 2.[44, 66-68, 71] In the case of the biscyclometalating bridging ligand the lowest-lying excited state was postulated to involve the terminal ttpy ligands. Energy transfer quenching of the ruthenium chromophore by the osmium center was observed but with much lower rate constants, 2.6×10^9 to $< 2.2 \times 10^7 s^{-1}$ for n = 0 and 2, respectively. A complex with a 2.4 nm metal-metal distance has also been reported, $[(ttpy)Ru(tpy\text{-}ph\text{-}bco\text{-}ph\text{-}tpy)Os(ttpy)]^{4+}$.[69, 73, 74]



This system does not display energy transfer quenching of the ruthenium excited state by the osmium center at RT. Below 200 K energy transfer quenching does occur and a rate constant of $5.2 \times 10^6 s^{-1}$ is observed over the 90–200 K temperature range.

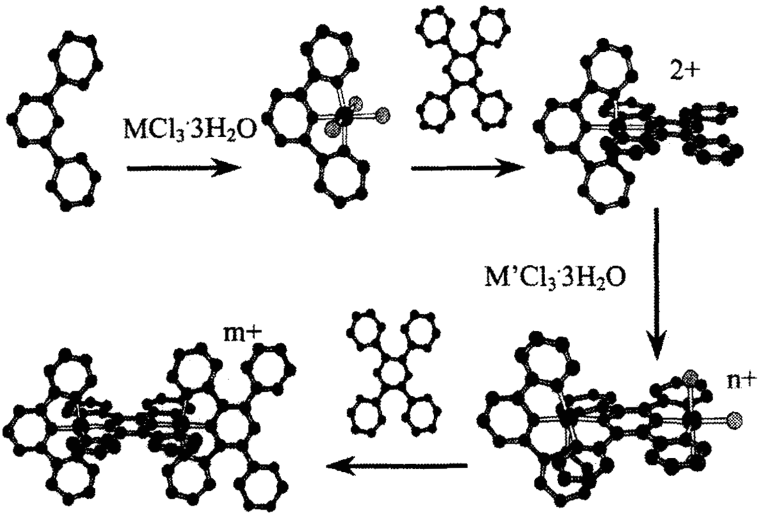
Sauvage has reported an interesting series of mixed-metal ruthenium, rhodium complexes bridged by the tpy-ph$_n$-tpy ligands and studied energy and electron transfer within this supramolecular framework.[72] Complexes of the form $[(ttpy)Ru(tpy\text{-}ph_n\text{-}tpy)Rh(ttpy)]^{5+}$, n = 0,1, 2, have been studied. At 77 K they observed energy transfer quenching of the excited rhodium by the ruthenium. No electron transfer quenching was observed at 77 K. At 150 K energy transfer of the excited rhodium by the ruthenium was still observed for all systems, and the n = 0 system displayed electron transfer quenching of the excited ruthenium to the rhodium acceptor. Sauvage has also used bis-terpyridine coordination of metals to prepare many interesting linked porphyrin and interlocking and threaded supramolecular systems.[82–85]

Ziessel and Harriman have described some very interesting ethynyl-bridged complexes.[75–80] Systems pertinent to this report with varying numbers of ethynyl (eth$_n$) linkers and mixed phenyl (ph$_m$) and ethynyl linkers have been described, $[(tpy)Ru(tpy\text{-}ph_m\text{-}eth_n\text{-}ph_m\text{-}tpy))M(tpy)]^{4+}$, M = Ru^{II} or Os^{II}. Many interesting reports on incorporation of other metal centers and organometallic platinum linkers have also appeared. A very exciting result is that the use of the ethynyl bridged complexes leads to very long-lived MLCT excited states at RT.[76, 77] The compound $[(tpy)Ru(tpy\text{-}eth\text{-}tpy)]^{2+}$ is reported to have a RT emission at 690 nm with a lifetime of 55 ns. The complex with two ethynyl units, $[(tpy)Ru(tpy\text{-}eth_2\text{-}tpy)]^{2+}$, had a RT emission at 710 nm with a lifetime of 170 ns. The bimetallic complexes, $[(tpy)Ru(tpy\text{-}eth\text{-}tpy)Ru(tpy)]^{4+}$ and $[(tpy)Ru(tpy\text{-}eth_2\text{-}tpy)Ru(tpy)]^{4+}$, had RT emissions at 722 and 735 nm with lifetimes of 565 and 720 ns, respectively. This enhanced MLCT excited state lifetime is attributed to selective population of the substituted ligand acceptor orbital. Because of the lower energy of this MLCT state, there should be less thermal population of the deactivating LF state. In addition, Ziessel comments that the delocalization of the electron over the extended π^*-orbital yields a reduced electron-electron repulsion, leading to smaller nuclear displacements and weakened overlap between the vibronic levels of the excited triplet and ground state manifolds. The study of the mixed-metal systems, $[(tpy)Ru(tpy\text{-}eth_n\text{-}tpy)Os(tpy)]^{4+}$, n = 1, 2, yields some valuable information.[77] Both of these complexes display a dramatic quenching of the ruthenium-based emission and efficient energy transfer to the osmium center at both RT and 77 K. The osmium-based emission, at 746 and 760 nm, displays a lifetime of 225 and 200 ns at RT for n = 1 or 2, respectively.

Recently Balzani, Lehn and Campagna have reported some interesting complexes which utilize three tridentate tpy coordination sites linked together, tpy-tpy-tpy and tpy'-tpy'-tpy'.[86] The ligand tpy-tpy-tpy uses two ethane spacers while tpy'-tpy'-tpy' uses two *trans*-ethylene spacers. Formation of three-metal systems with these ligands by binding of a $(tpy)Ru^{II}$ unit to each tridentate coordination site leads to complexes with interesting properties. The $\{[(tpy)Ru]_3(tpy\text{-}tpy\text{-}tpy)\}^{6+}$ system displays excited state properties similar to $[Ru(tpy)_2]^{2+}$ with no detectable RT emission. Use of the bridging ligand with the ethylene linkages to construct $\{[(tpy)Ru]_3(tpy'\text{-}tpy'\text{-}tpy')\}^{6+}$ gives rise to different properties. This complex displays a RT emission at 690 nm with a lifetime of 11 ns. These differences in properties were attributed to $\{[(tpy)Ru]_3(tpy\text{-}tpy\text{-}tpy)\}^{6+}$ having a tpy-based lowest-lying MLCT excited state and $\{[(tpy)Ru]_3(tpy'\text{-}tpy'\text{-}tpy')\}^{6+}$ having a bridging ligand based MLCT state. Balzani *et al.* postulate that the bis(pyridyl)ethylene unit dictates the properties of the chromophore in the $\{[(tpy)Ru]_3(tpy'\text{-}tpy'\text{-}tpy')\}^{6+}$ system.

Our group has concentrated on the use of the tpp ligand to construct stereochemically defined polymetallic complexes with long-lived MLCT excited states.[50–57] Our interest in these systems resulted from their potential to yield polymetallic complexes with long-lived MLCT excited states that can display detectable emissions at RT. The tpp bridging ligand also leads to the construction of systems that are stereochemically defined. The tpp ligand holds adjacent metals close together, gives rise to a large degree of metal-metal couple and could facilitate efficient intramolecular energy and electron transfer. We also believe that this bis-tridentate coordination environment would lend itself nicely to the development of a building block approach to supramolecular synthesis. This would involve starting the construction at one end of the molecule and successively adding metals or ligands to build up the rigid, linear system.

Our building block approach for the construction of these types of tpp bridged complexes is shown below. To date we have used this full methodology to produce complexes with M = Ru^{II} or Os^{II} and M′ = Ru^{II}.[51, 53, 56] We have also used the first three steps to produce systems with M′ = Ir^{III} or Rh^{III}.[50, 55, 57] Modification of the final step to yield systems with different ligands has also been accomplished; for example, $[(tpy)Ru(tpp)Ru(CH_3CN)_3](PF_6)_4$ and $[(tpy)Ru(tpp)Ru(dpq)Cl](PF_6)_3$ have been prepared.[53,56]



This class of tpp-containing ruthenium and osmium chromophores displays very intense absorbances throughout the ultraviolet and visible region of the spectrum. These compounds typically possess ligand centered $\pi \rightarrow \pi^*$ transitions in the UV and a series of MLCT transitions in the visible. The energy of the MLCT transitions can be modified by synthetic variation of the metal centers or coordinated ligands.[51,53,56] For example, $[(tpy)Os(tpp)RuCl_3](PF_6)$ has a lowest-lying MLCT transition that is Ru → μ-tpp CT in nature and occurs at 678 nm. [(tpy)Ru(tpp)Ru(tpp)]$(PF_6)_4$ has a Ru → μ-tpp CT transition that occurs at 548 nm. This transition represents overlapping bands for the two Ru centers and the bridging tpp with the lowest energy component being due to the Ru center bound to the tpy and tpp.

One of the most promising properties displayed by this class of chromophores is the excited state lifetimes and RT emission.[51,56] [(tpy)Ru(tpp)Ru(tpp)]$(PF_6)_4$ displays a RT emission at 833 nm with a lifetime of 100 ns. This wavelength is longer than the monometallic from which it was constructed, $[(tpy)Ru(tpp)]^{2+}$, which displays a RT emission at 665 nm with a lifetime of 30 ns under our conditions. This long-lived MLCT excited state of this ruthenium bimetallic system makes it an attractive chromophore for the construction of a wide assortment of supramolecular systems. The fact that the bimetallic system displays a longer excited state lifetime than the monometallic from which it is constructed is somewhat surprising. This bimetallic system displays an emission that is red-shifted relative to the monometallic synthon. This red shift in an emission typically leads to a shortening of the excited state lifetime as the rate of nonradiative decay increases as the energy gap between the ground state and emissive excited state decreases in a series of related complexes. This lengthening of the excited state lifetime in the bimetallic systems can in fact be rationalized by the lower energy of the emissive MLCT state in the bimetallic species. Within this bis-tridentate coordination environment this lowering of the MLCT state prevents thermal population of the deactivating LF state giving rise to the observed enhanced MLCT excited state lifetime. (See Fig. 4.) The study of the emission properties of these two chromophores at 77 K confirms this assertion. The [Ru(tpy)(tpp)]$(PF_6)_2$ complex displays an emission lifetime of 7.1 μs at 77 K while the bimetallic [(tpy)Ru(tpp)Ru(tpp)]$(PF_6)_4$ has an emission lifetime of 480 ns. The dramatic enhancement of the MLCT excited state lifetime of [Ru(tpy)(tpp)]$(PF_6)_2$ on going from RT to 77 K is quite similar to that observed for $[Ru(tpy)_2]^{2+}$. This is consistent with thermal population of the LF state at RT giving rise to the shortened MLCT excited state lifetime of [Ru(tpy)(tpp)]$(PF_6)_2$.

We have also studied the photophysical properties of the osmium-based systems.[51,56] Here the LF state is much higher in energy, and thermal population at RT is not possible. The [Os(tpy)(tpp)]$(PF_6)_2$ system emits at 775 nm, red-shifted relative to the ruthenium analog due

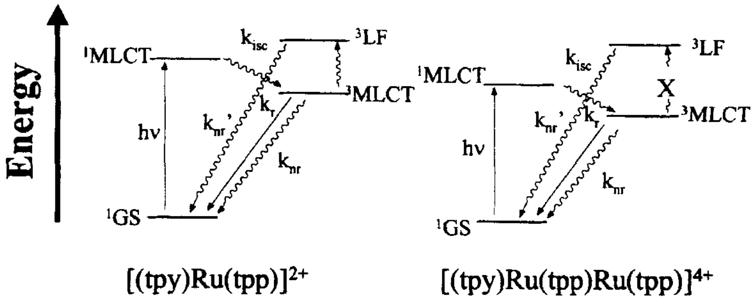


FIGURE 4 Relative state diagrams for $[(tpy)Ru(tpp)]^{2+}$ and $[(tpy)Ru(tpp)Ru(tpp)]^{4+}$, (tpy = 2,2′,6′,2″-terpyridine and tpp =2,3,5,6-tetrakis(2-pyridyl)pyrazine)

to the higher energy dπ orbitals on osmium. The emission lifetime of this chromophore is 260 ns at RT. This is longer than that of the ruthenium analog. This provides further evidence that the MLCT excited state of $[Ru(tpy)(tpp)](PF_6)_2$ does undergo deactivation via thermal population of the LF state since the osmium chromophore would normally be expected to display an excited state lifetime lower than that of the analogous ruthenium system due to energy gap considerations. The bimetallic mixed-metal system, $[(tpy)Os(tpp)Ru(tpp)](PF_6)_4$, displays an osmium-centered emission at 820 nm with a lifetime of 120 ns at RT. Excitation of the ruthenium chromophore is followed by efficient energy transfer to yield only osmium-based emission. Comparison of the excited state lifetimes of these osmium-based chromophores, $[Os(tpy)(tpp)](PF_6)_2$ and $[(tpy)Os(tpp)Ru(tpp)](PF_6)_4$, yield the expected trend with the bimetallic system having a shortened lifetime relative to the monometallic synthon. Both the osmium- and ruthenium-based bimetallic systems display excited state lifetimes of ca. 100 ns at RT. These are quite long for polymetallic complexes and make these chromophores very attractive candidates for the construction of supramolecular systems that utilize the light-absorbing properties of these chromophores.

The electrochemical properties of these tpp-bridged complexes are also very interesting.[50–57] It is possible through ligand and metal variation to tune the oxidation and reduction potentials of these complexes. Typically polyazine complexes of osmium and ruthenium display metal-centered oxidations with the osmium systems oxidizing at less positive potentials than the analogous ruthenium systems. This class of complexes displays ligand-centered reductions for each polyazine ligand with bridging tpp ligands typically displaying tpp$^{0/-}$ and tpp$^{-/2-}$ prior to reduction of terminal ligands such as tpy. We have synthetically varied the oxidation and reduction potentials in these tpp-bridged complexes as well as changed the site of localization of the HOMO and LUMO within this polymetallic architecture. For example, $[(tpy)Ru(tpp)Ru(tpp)](PF_6)_4$ has two oxidations at 1.51 and 1.86 V vs. Ag/AgCl. The first oxidation is the Ru$^{II/III}$ couple for the (tpy)Ru^{II}(μ-tpp) site. This shows that the HOMO is localized on the ruthenium center at the terminal tpy-containing end of this molecule. The second oxidation is the Ru$^{II/III}$ couple for the less electron rich (μ-tpp)Ru^{II}(tpp) center. Reductively this complex displays a μ-tpp$^{0/-}$ couple at –0.30 and μ-tpp$^{-/2-}$ at –0.82 and tpp$^{0/-}$ at -1.10 V. This shows that the LUMO is localized on the bridging tpp ligand. If one changes the coordination environment of the ruthenium center to produce $[(tpy)Ru(tpp)RuCl_3](PF_6)$, the electrochemical properties observed will be dramatically altered. This complex possesses two oxidations at 0.73 and 1.61 V. The first oxidation is the Ru$^{II/III}$ couple for the (μ-tpp)Ru^{II}Cl$_3$ center followed by the second oxidative process, the Ru$^{II/III}$ couple for the (tpy)Ru^{II}(tpp) center. By this variation of ligands bound to the ruthenium center we have significantly shifted oxidation potentials of this complex and altered the site of localization of the HOMO to the (tpp)Ru^{II}Cl$_3$ ruthenium center. This complex displays μ-tpp$^{0/-}$ and μ-tpp$^{-/2-}$ couples at-0.60 and –1.10 V. This ability to tune the oxidation and reduction potentials as well as alter the site of localization of the HOMO and LUMO within this tridentate bridged architecture is essential to controlling the direction of electron and energy transfer. This control is needed in the design of molecular devices for photoinitiated energy and electron transfer.

Recently we have explored the spectroelectrochemistry of these polymetallic systems in an effort to probe their complicated spectroscopy in more detail.[53] This approach has been very useful in the assignment of the spectroscopy and electrochemistry of these systems. One particular aspect of this study is that we were able to uncover some general spectroscopic characteristics that are very useful. The study probes a series of $[(tpy)M(tpp)Ru(LLL)]^{n+}$ (M= Ru^{II} or Os^{II}, LLL = 3Cl$^-$, 3CH$_3$CN, tpy, tpp or dpq and Cl$^-$). We found that in addition to the lowest lying M

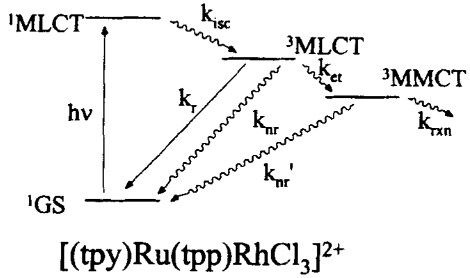


FIGURE 5 State diagram for $[(tpy)Ru(tpp)RhCl_3]^{2+}$, (tpy = 2,2′,6′,2″-terpyridine, tpp = 2,3,5,6-tetrakis(2-pyridyl)pyrazine, k_{et} = rate constant for intramolecular electron transfer and k_{rxn} = rate constant for reaction)

→ μ-tpp and Ru → μ-tpp CT bands, in the 540–650 nm region, other characteristic MLCT transitions could be found. We identified a M → tpy CT band for all complexes in the 460–480 nm region of the spectrum. Interestingly a transition was found at 300 nm for all the complexes studied that appears to represent a higher energy M → tpy CT transition. This is particularly valuable as changes in this spectral region can be used as a characteristic of oxidation of the (tpy)M(μ-tpp) center, allowing for assignment of complicated electrochemistry in some of the polymetallic complexes.

Very recently we have prepared and studied a system that couples a rhodium-based electron acceptor to this promising $(tpy)Ru^{II}(tpp)$ chromophore.[55] This $[(tpy)Ru(tpp)RhCl_3](PF_6)_2$ complex represents a light absorber – electron acceptor dyad. The electronic spectrum of this complex shows a lowest-lying transition at 516 nm that represents the Ru → μ-tpp CT transition. The electrochemistry of this complex shows a quasi-reversible $Rh^{III/I}$ couple at –0.23 V vs. Ag/AgCl followed by the $tpp^{0/-}$ and $tpp^{-/2-}$ couples at –0.60 and –0.98 V. This indicates that the LUMO is rhodium based. Therefore, excitation into the Ru → μ-tpp CT state should be followed by intramolecular electron transfer. This appears to be the case as the emission of the MLCT excited state of this $[(tpy)Ru(tpp)RhCl_3](PF_6)_2$ system is quenched relative to $[(tpy)Ru(tpp)Ru(tpp)](PF_6)_4$. This intramolecular electron transfer quenching occurs at a rate of 4×10^7 s^{-1}. The state diagram for this $[(tpy)Ru(tpp)RhCl_3](PF_6)_2$system is shown in Fig. 5. This study represents the first utilization of the tpp-based chromophore in the construction of a molecular device, here a system for photo-initiated charge separation. The use of this type of intramolecular electron transfer quenching of this chromophore holds great promise. The development of additional, larger supramolecular assemblies with this chromophore is in progress. Our building block synthetic methodology should allow us to systematically construct larger linear systems with greater donor-acceptor distances and varied spacers and light absorbers.

CONCLUSIONS

There has been a recent surge in the study of tridentate bridged chromophores of Ru^{II} and Os^{II}. These compounds offer promise in the construction of supramolecular systems applicable to a wide assortment of functions, such as photo-initiated charge separation for the construction of molecular photovoltaics and molecular switches, molecular wires, or directed energy transfer systems for light harvesting. Many systems have been studied that undergo facile energy transfer. Electron transfer and photo-initiated charge separation are also being explored. These exciting systems are stereochemically defined and thus possess known geometric arrangements of units within the supramolecular systems. This will allow for the study of the factors that influence energy and electron transfer within these supramolecular, metal-based systems. Many of these polymetallic systems have been shown to possess long-lived MLCT excited states that are emissive at RT. This property allows for a convenient probe into the excited state dynamics of these systems. This area of chemistry is rapidly advancing, and the future will uncover new more elaborate systems with interesting and useful properties for the conversion of light energy.

A number of groups have illustrated the synthetic ability to construct complex molecules with varied components. Synthetic approaches will need to be expanded to allow incorporation of more widely varied components. The molecular behavior must be carefully considered to design and produce complexes with properties useful for accomplishing specific functions. The real potential of this class of chromophores will be uncovered in the future following their incorporation into a wider array of larger, more sophisticated supramolecular systems.

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