Electronic Energy Transfer and Collection in Luminescent Molecular Rods Containing Ruthenium(II) and Osmium(II) 2,2′:6′,2″-Terpyridine Complexes Linked by Thiophene-2,5-diyl Spacers

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Abstract: The electronic absorption spectra, luminescence spectra and lifetimes (in MeCN at room temperature and in frozen n-C_3H_7CN at 77 K), and electrochemical potentials (in MeCN) of the novel dinuclear $[(tpy)Ru(\mathbf{3})Os(tpy)]^{4+}$ and trinuclear $[(tpy)Ru(\mathbf{3})Os(\mathbf{3})Ru(tpy)]^{6+}$ complexes ($\mathbf{3}$ = 2,5-bis(2,2′:6′,2″-terpyridin-4-yl)thiophene) have been obtained and are compared with those of model mononuclear complexes and homometallic $[(tpy)Ru(\mathbf{3})Ru(tpy)]^{4+}$, $[(tpy)Os(\mathbf{3})Os(tpy)]^{4+}$ and $[(tpy)Ru(\mathbf{3})Ru(\mathbf{3})Ru(tpy)]^{6+}$ complexes. The bridging ligand **3** is nearly planar in the complexes, as seen from a preliminary X-ray determination of $[(tpy)Ru(\mathbf{3})Ru(tpy)][PF_6]_4$, and confers a high degree of rigidity upon the polynuclear species. The trinuclear species are rod-shaped with a distance of about 3 nm between the terminal metal centres. For the polynuclear complexes, the spectroscopic and electrochemical data are in accord with a significant intermetal interaction. All of the complexes are luminescent (Φ in the range 10^{-4}–10^{-2} and τ in the range 6–340 ns, at room temperature), and ruthenium- or osmium-based luminescence properties can be identified. Due to the excited state properties of the various components and to the geometric and electronic properties of the bridge, Ru → Os directional transfer of excitation energy takes place in the complexes $[(tpy)Ru(\mathbf{3})Os(tpy)]^{4+}$ (end-to-end) and $[(tpy)Ru(\mathbf{3})Os(\mathbf{3})Ru(tpy)]^{6+}$ (periphery-to-centre). With respect to the homometallic case, for $[(tpy)Ru(\mathbf{3})Os(\mathbf{3})Ru(tpy)]^{6+}$ excitation trapping at the central position is accompanied by a fivefold enhancement of luminescence intensity.

Keywords: luminescence · molecular devices · N ligands · ruthenium

Introduction

The development of specific and efficient synthetic methodologies for the assembly of large photoactive multicomponent systems has led to numerous advances in the field of photoinduced electron and energy transfer.[1] In such multicomponent systems, elaborate multiple functionality has been incorporated, allowing, inter alia, the stabilization of photoinduced charge separation,[2] multi-electron collection,[3] harvesting of excitation energy in artificial antennae,[4] and logical and switching functions[5] of interest in the developing area of molecular electronics.

The assembly of ruthenium(II) and osmium(II) polypyridine complexes, which possess valuable electrochemical, photophysical and photochemical properties[6] has led to various topographically interesting species, such as rods or wires,[7] helicates[8] and dendrimers.[9] These polynuclear species may prove to be useful both for improving fundamental knowledge of interactions within such systems and as practical components of photoconversion systems.[10, 11] A fundamental requirement is that good control can be achieved over the geometric relationships between the various components. For instance, the study of photoinduced processes in several dinuclear systems has proven useful in understanding the role of the electronic and nuclear factors in governing these key phenomena.[7, 12, 13] A rapidly expanding area in which such complexes are proving to be of use is that of energy

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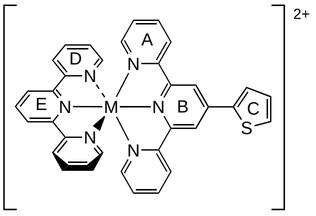
transduction and signal processing over distances of nanometres or greater. In this case, single or multi-step approaches can be envisaged,[14] and recent results based upon complexes containing modular phenylene-bridged ligands have described the transfer of excitation energy from a donor to an acceptor over a distance of at least 4 nm.[13] The spectroscopic properties of such complexes (and in this context, luminescence proves to be very advantageous) may be exploited for the sensing of protons or other cations,[11] and anions[15] leading to the development of signal-processing capacity.

From a geometrical viewpoint, suitable building blocks for the construction of topographically linear polynuclear species (molecular rods) are $\{Ru(tpy)_2\}^{2+}$ and $\{Os(tpy)_2\}^{2+}$ motifs (tpy is 2,2′:6′,2″-terpyridine).[7, 16, 17] The luminescence properties of $[Ru(tpy)_2]^{2+}$ salts are, however, not ideally suited to such applications; the room temperature luminescence efficiency and lifetime in acetonitrile are $\phi \sim 10^{-5}$ and $\tau \leq 0.3 \times 10^{-9}$ s, respectively,[16, 17] although significant luminescence improvements can be achieved by attaching suitable functionality to the tpy, extending its electronic conjugation.[18, 19]

We have prepared and studied a series of nine ruthenium and osmium complexes.[20] All of the complexes contain a thiophene ring, which of interest because of the known photoactivity of oligothiophenes.[21] In the polynuclear complexes, the 2,5-thiophenediyl spacer in bridging ligand **3** (2,5-bis(2,2′:6′,2″-terpyridin-4-yl)thiophene) provides a structurally rigid connection between photo- and electroactive centres. The molecular subunits of the bridging ligand are, at least in the solid state, coplanar as revealed by a preliminary X-ray structure determination. From an electronic viewpoint, ligand **3** provides effective communication between photoactive centres; this results in the ruthenium-based complexes being luminescent in fluid solution, in contrast to parent $[Ru(tpy)_2]^{2+}$ complexes. By using stationary and time-resolved luminescence spectroscopy, we have investigated the transport of excitation energy within the heterometallic rods $[(tpy)Ru(\mathbf{3})Os(tpy)]^{4+}$ and $[(tpy)Ru(\mathbf{3})Os(\mathbf{3})Ru(tpy)]^{6+}$.

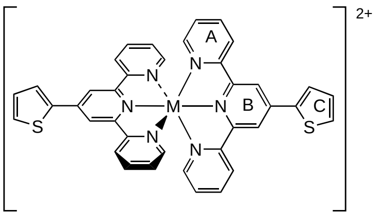
Results and Discussion

Ligand synthesis and characterization: As a part of a systematic study of the effects of substituents upon the electronic and spectroscopic properties of 2,2′:6′,2″-terpyridine complexes, we prepared a series of thienyl-functionalized ligands. Initial approaches to the parent ligand **1** were unsuccessful and resulted in the formation primarily 3:1 condensation products,[22] and we eventually adopted a convenient one-pot synthesis. Two equivalents of 2-acetylpyridine were treated with 2-thiophenecarbaldehyde at room temperature over 24 h to give an intermediate diketone (Scheme 1). The crude reaction mixture was then heated with NH_4OAc in EtOH to give **1** in 40 % yield as a white powder. Spectroscopic and physicochemical data are all in accord with the proposed formulation of the new ligand and are presented in the Experimental Section. Following our initial report,[20] an alternative synthesis of **1** has been described.[23]



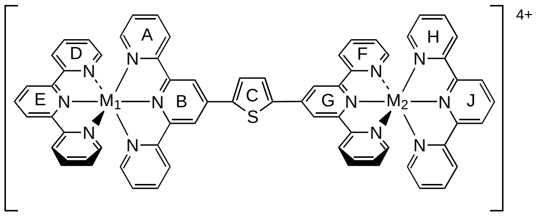
$[M(tpy)(\mathbf{1})]^{2+}$

M = Ru, Os



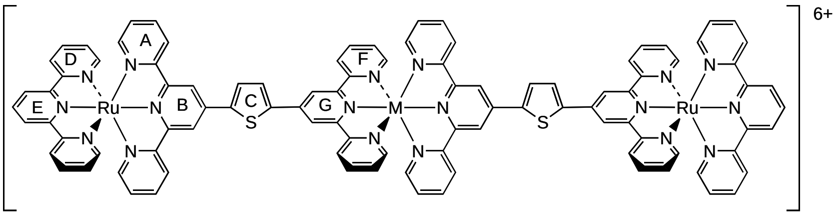
$[M(\mathbf{1})_2]^{2+}$

M = Ru, Os



$[(tpy)M_1(\mathbf{3})M_2(tpy)]^{4+}$

M_1, M_2 = Ru, Os

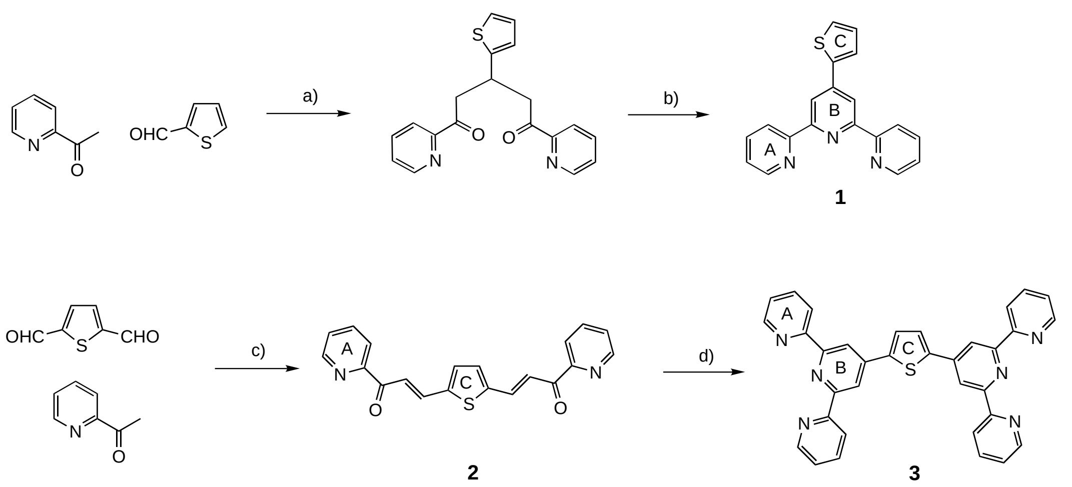


$[(tpy)Ru(\mathbf{3})M(\mathbf{3})Ru(tpy)]^{6+}$

M = Ru, Os

The bridging ligand **3** was prepared as indicated in Scheme 1. The bisenone **2**[24] was obtained in 72 % yield from the condensation of 2-acetylpyridine with 2,5-thiophenedicarbaldehyde. Reaction with *N*-[2-oxo-2(2-pyridyl)ethyl]-pyridinium iodide[25] and ammonium acetate gave the **3** in 32 % yield as an off-white solid.

Spectroscopic and physicochemical data are all in accord with the formulation of the new ligands and are presented in the Experimental Section. The absorption spectra of solutions of the ligands **1** and **3** in MeCN both show three ^{1}LC transitions ($\pi^* \leftarrow \pi$ and $\pi^* \leftarrow n$) in the region 230–290 nm, of which the lowest energy is the most intense. The



Scheme 1. a) 2.0 equiv of 2-acetylpyridine, 1.0 equiv of 2-thiophenecarbaldehyde, 7 equiv NaOH, EtOH, room temperature; 20 h; b) 2.0 equiv NH$_4$OAc, EtOH, reflux, 4 h (40 %); c) 2.0 equiv of 2-acetylpyridine, 1.0 equiv of 2,5-thiophenedicarbaldehyde, KOH, EtOH, 0 °C; 85 min (72 %); d) 1.0 equiv **2**, 2.1 equiv pyridacylpyridinium iodide, NH$_4$OAc, EtOH, reflux, 12 h (32 %).

absorption spectrum of **3** shows an additional low-energy absorption at 344 nm. Like other thienyloligopyridines,[26] the compounds are luminescent, and solutions of **1** show an emission at 360 nm arising from the 284 nm absorption, while those of **3** show a more structured emission with maxima at 400 and 384 nm.

Protonation has a similar effect to coordination on ligand-centred absorption processes, but without transitions due to metal – ligand and metal – metal interactions, and such spectra are valuable when assigning the electronic spectra of complexes. Excess HPF$_6$ was added to a solution of **1** in MeCN to generate $[H_2\mathbf{1}]^{2+}$[27] with the resultant loss of the 253 nm transition. The absorption at 284 nm is red-shifted by 6 nm and the emission is now very broad with a maximum at 494 nm. Similar changes occur upon the addition of HPF$_6$ to **3**, red-shifting the 283 nm absorption to 291 nm. These changes reflect the stabilization of the ligand π^* orbitals on protonation and are in agreement with results for 4′-(9-anthryl)-2,2′:6′,2″-terpyridine.[28]

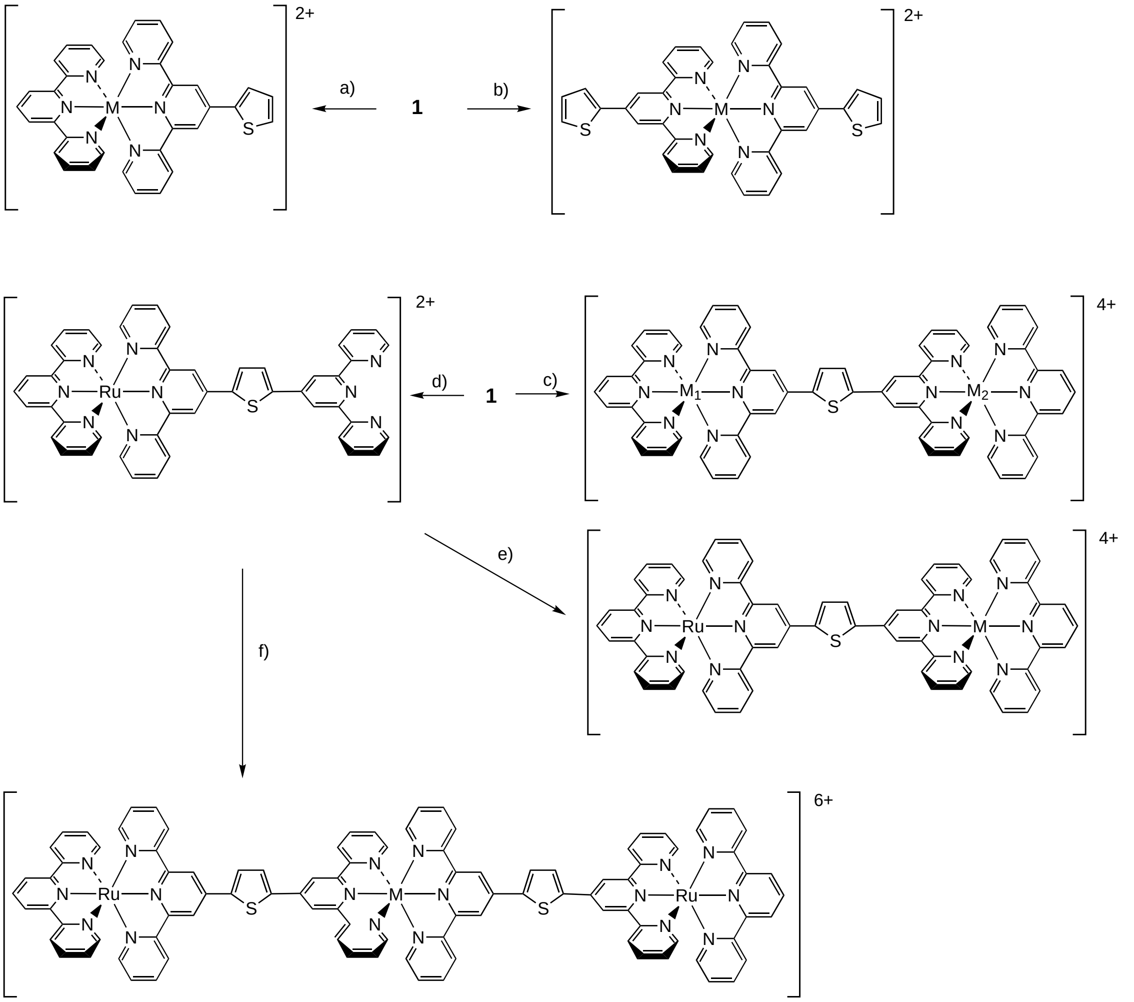
Complex synthesis: The homonuclear complexes $[Ru(\mathbf{1})_2][PF_6]_2$ and $[Os(\mathbf{1})_2][PF_6]_2$ were prepared in 70 % and 80 % yield, respectively, by the direct reaction of $RuCl_3 \cdot 3H_2O$ or $[NH_4]_2[OsCl_6]$ with **1** in ethane-1,2-diol that contained a small amount of *N*-ethylmorpholine as a reducing agent in a modified domestic microwave oven; this was followed by precipitation of the hexafluorophosphate salts and chromatographic purification. The heteroleptic species $[Ru(tpy)(\mathbf{1})][PF_6]_2$ and $[Os(tpy)(\mathbf{1})][PF_6]_2$ were prepared similarly from the reaction of **1** with $[Ru(tpy)Cl_3]$ or $[Os(tpy)(H_2O)_3][PF_6]_3$,[29] respectively (Scheme 2). The ^1H NMR spectra of the heteroleptic complexes were essentially a superposition of the spectra of the homoleptic $[M(tpy)_2]^{2+}$ and $[M(\mathbf{1})_2]^{2+}$ compounds and data are presented in the Experimental Section. All of these mononuclear complexes exhibited $[M - 2PF_6]^+$ peaks in their MALDI-TOF mass spectra.

The multinuclear complexes were prepared by the "complexes as metals/complexes as ligands" strategy.[30] The mononuclear ruthenium building block $[Ru(tpy)(\mathbf{3})][PF_6]_2$ contains a non-coordinated tpy metal-binding domain and was prepared in satisfactory yield from the reaction of $[Ru(tpy)Cl_3]$ with **3**. The osmium(II) analogue $[Os(tpy)(\mathbf{3})][PF_6]_2$ was prepared from the reaction of **3** with $[Os(tpy)(H_2O)_3][PF_6]_3$ under microwave conditions. The ruthenium and osmium complexes were obtained as orange and brown solids, respectively, and relevant spectroscopic data for these and the species that follow are presented in the Experimental Section.

The dinuclear complexes were prepared by the direct reaction of **3** with an excess of appropriate metal complex. Treatment of **3** with an excess of $[Ru(tpy)Cl_3]$ in EtOH under reducing conditions resulted in the formation of the bright red symmetric, dinuclear complex $[(tpy)Ru(\mathbf{3})Ru(tpy)][PF_6]_4$ in near quantitative yield. The purple heterodinuclear analogue $[(tpy)Ru(\mathbf{3})Os(tpy)][PF_6]_4$ was prepared from the reaction of $[(tpy)Ru(\mathbf{3})][PF_6]_2$ with $[Os(tpy)(H_2O)_3][PF_6]_3$ in ethane-1,2-diol in a microwave oven under reducing conditions. The final dinuclear complex, $[(tpy)Os(\mathbf{3})Os(tpy)][PF_6]_4$, was obtained as a deep purple solid from the direct reaction of **3** with two equivalents of $[Os(tpy)(H_2O)_3][PF_6]_3$ under forcing reducing conditions.

For the trinuclear complexes, the only sensible synthetic strategy is the building block approach outlined above. The two complementary complexes $[(tpy)Ru(\mathbf{3})M(\mathbf{3})Ru(tpy)][PF_6]_6$ (M = Ru or Os) could be prepared in principle by the reaction of $[M(\mathbf{3})_2][PF_6]_2$ with $[Ru(tpy)Cl_3]$ or by the reaction of $[Ru(tpy)(\mathbf{3})][PF_6]_2$ with appropriate labile mononuclear species. We have only investigated the latter route, and the desired trinuclear compounds were obtained in satisfactory yields as pink or purple solids from the reaction of $[Ru(tpy)(\mathbf{3})][PF_6]_2$ with $RuCl_3 \cdot 3H_2O$ or $K_2[OsCl_6]$, respectively. These synthetic routes are summarized in Scheme 2.

The complexes all exhibit well-resolved ^1H NMR spectra and a number of characteristic features are present. In general, the spectra are sufficiently well resolved that all of the individual tpy and thienyl domains may be fully eluci-



Scheme 2. a) M = Ru: 1.0 equiv of [Ru(tpy)Cl$_3$], HOCH$_2$CH$_2$OH, *N*-ethylmorpholine, 600 W microwave, 4 min (79%); M = Os: 1.2 equiv of [Os(tpy)(H$_2$O)$_3$][PF$_6$]$_3$, HOCH$_2$CH$_2$OH, *N*-ethylmorpholine, 600 W microwave, 4 min (78%); b) M = Ru: 0.5 equiv of RuCl$_3\cdot$3H$_2$O, HOCH$_2$CH$_2$OH, *N*-ethylmorpholine, 600 W microwave, 4 min (70%); M = Os: 0.49 equiv of [NH$_4$]$_2$[OsCl$_6$], HOCH$_2$CH$_2$OH, *N*-ethylmorpholine, 600 W microwave, 4 min (80%); c) M = Ru: 3 equiv of [Ru(tpy)Cl$_3$], EtOH, *N*-ethylmorpholine, reflux, 3 h (95%); M = Os: 2 equiv of [Os(tpy)(H$_2$O)$_3$][PF$_6$]$_3$, HOCH$_2$CH$_2$OH, *N*-ethylmorpholine, 600 W microwave, 4 min.(60%); d) 1.0 equiv of [Ru(tpy)Cl$_3$], EtOH, *N*-ethylmorpholine, reflux, 90 min (60%); e) M = Os: 1.1 equiv of [Os(tpy)(H$_2$O)$_3$][PF$_6$]$_3$, HOCH$_2$CH$_2$OH, *N*-ethylmorpholine, 600 W microwave, 4 min (47%); f) M = Ru: 0.5 equiv of RuCl$_3\cdot$3H$_2$O, HOCH$_2$CH$_2$OH, *N*-ethylmorpholine, 600W microwave, 4 min. (48%); M = Os: 0.49 equiv of K$_2$[OsCl$_6$], HOCH$_2$CH$_2$OH, *N*-ethylmorpholine, 600 W microwave, 4 min (46%).

dated. As an example, the one-dimensional and COSY ^{1}H NMR spectra of [(tpy)Ru(**3**)Os(tpy)][PF$_6$]$_4$ are presented in Figure 1. The individual {Ru(tpy)} and {Os(tpy)} domains may be distinguished and unambiguously assigned by comparison with the model complexes [Ru(tpy)$_2$][PF$_6$]$_2$, [Ru(tpy)(**1**)][PF$_6$]$_2$, [Os(tpy)$_2$][PF$_6$]$_2$ and [Os(tpy)(**1**)][PF$_6$]$_2$. The chemical shifts of the Xtpy and Ytpy domains in [M(Xtpy)(Ytpy)]$^{2+}$ (M = Ru, Os) complexes have been shown to be almost invariant and independent of the partner ligand.[31]

Structural characterization: In order to better understand the photophysical properties of the polynuclear complexes, we have made a number of structural studies. A full structural determination of the complex [Ru(**1**)$_2$][PF$_6$][NO$_3$]$\cdot$2CH$_3$CN is reported in this paper, together with preliminary data for [(tpy)Ru(**3**)Ru(tpy)][PF$_6$]$_4$. The mixed anions in [Ru(**1**)$_2$][PF$_6$][NO$_3$]$\cdot$2CH$_3$CN arise from the chromatographic work-up which involves a mobile phase containing KNO$_3$; the crystals were obtained by the MeCN recrystallization of the product obtained by adding ammonium hexafluorophosphate to the fraction collected from the column. The two thienyl substituents were disordered in approximately 3:1 ratios corresponding to the orientation of the sulfur with respect to the central tpy ring. A similar disorder is found in the complex [Ru(tpy)(**1**)][PF$_6$]$_2$.[32] The angles between least-squares planes of the thienyl rings and directly bonded pyridine rings lie in the range 5.06–16.43° and only the major occupancy is shown in the representation of the cation in Figure 2.

The Ru–N distances show the typical trend for tpy complexes[33] with the bonds to the central tpy ring (1.973(4), 1.978(5) Å) being significantly shorter than those to the terminal rings (2.043(5)–2.082(5) Å). All bond lengths and angles within the {Ru(tpy)$_2$} moiety are normal[31, 34] and there are no short contacts between the cation, the anions and the lattice solvent molecules, although we note that the nitrate ion and one of the central rings of the tpy are close to planar

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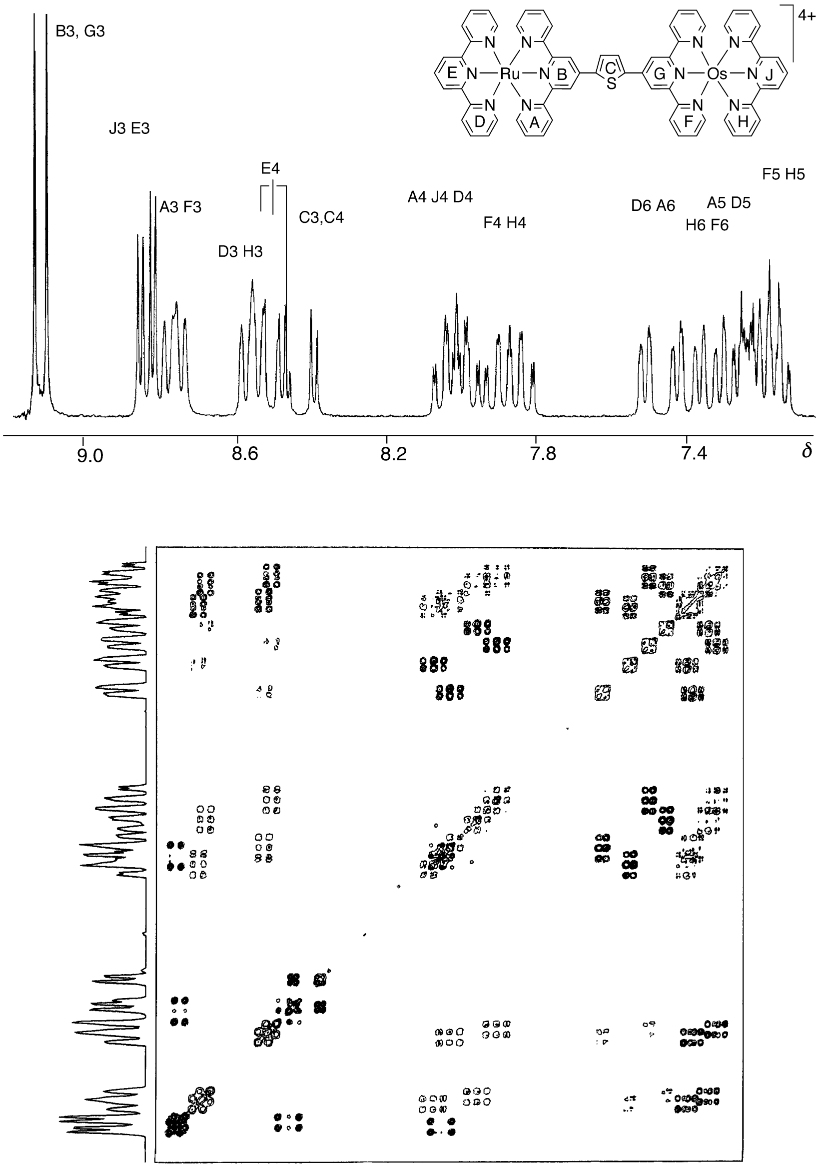

Figure 1. One-dimensional and COSY ^1H NMR spectra of $[(tpy)Ru(\mathbf{3})Os(tpy)][PF_6]_4$ (CD_3CN, 298 K, 250 MHz).

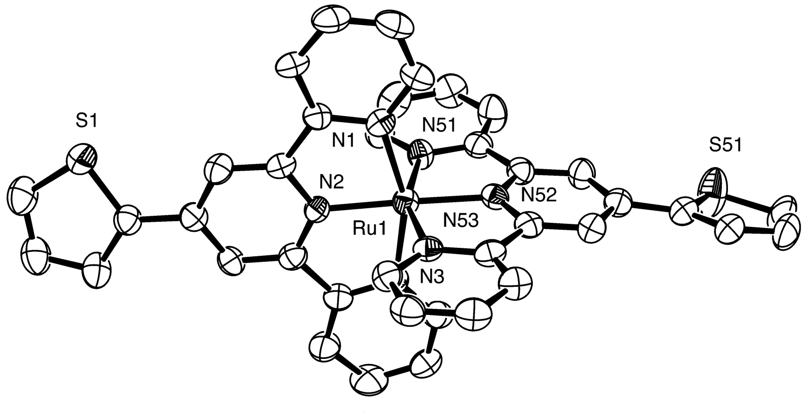

Figure 2. ORTEP representation of the $[Ru(\mathbf{1})_2]^{2+}$ ion in $[Ru(\mathbf{1})_2][PF_6]_2\cdot 2CH_3CN$ showing the numbering scheme adopted for non-carbon atoms; hydrogen atoms have been omitted for clarity and only the major thienyl occupancies are shown.

(least squares planes, 16.9°) with O13 lying ≈3.5 Å above the centroid of the ring. The tpy units are approximately planar (angles between least-squares-planes of directly bonded rings 3.05–7.58°) and the thienyl rings are conjugated with the tpy, although interactions between the tpy H3′ and H5′ with thienyl H4 result in a twisting about the interannular C–C bond (all such interannular angles are below 17°).

We have also made numerous attempts to obtain good quality data sets for the three complexes $[(tpy)M(\mathbf{3})M(tpy)][PF_6]_4$ (M = Ru, Os); on every occasion small but well-formed crystals were obtained that decompose rapidly upon irradiation or removal from the mother liquor. The data sets obtained indicate that the three compounds are isostructural and we report the data for $[(tpy)Ru(\mathbf{3})Ru(tpy)][PF_6]_4\cdot 2MeCN$. Extensive disorder of some of the anions and unrefined solvent resulted in high *R* and w*R* values. However, the chemically interesting dinuclear cation (Figure 3) may be discussed with confidence. The two $\{Ru(tpy)_2\}$ domains possess typical bond lengths and angles, closely resembling those for the $[Ru(\mathbf{1})_2]^{2+}$ cation. The terminal tpy ligands are essentially planar (angles between least-squares planes 2.34–3.67°) as are the tpy domains of the **3** ligand (angles between least-squares planes 2.08–3.97°). A most interesting observation is that the central rings of the tpy domains and the thienyl moiety of the **3** ligand are also nearly coplanar (angles between least-squares planes 5.30–6.07°). The consequence is reasonably short contacts between the thienyl protons and the tpy H3′ protons (2.214, 2.253 Å). The two metal centres are 14.395 Å apart. The thienyl spacer results in a topographically nonlinear arrangement of

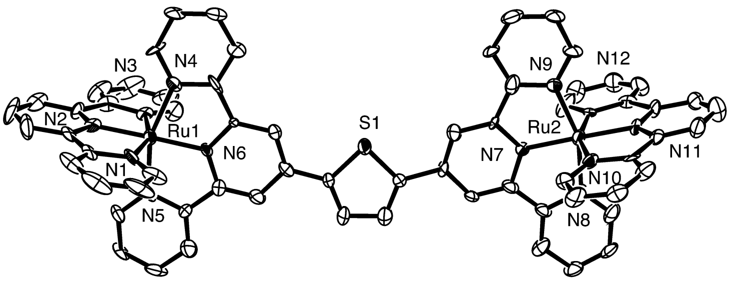

Figure 3. ORTEP representation of the $[(tpy)Ru(\mathbf{3})Ru(tpy)]^{4+}$ ion in $[(tpy)Ru(\mathbf{3})Ru(tpy)][PF_6]_4 \cdot 2CH_3CN$ showing the numbering scheme adopted; hydrogen atoms have been omitted for clarity.

the Ru1 and Ru2, such that an angle Ru1-X-Ru2 of 14.0° is described, where X is the weighted centre of the thiophene ring. Adjacent cations exhibit stacking interactions between terminal pyridine rings of the tpy ligands (centroid – centroid, 3.6 Å, angle between least-squares planes, 5°) which result in intermolecular Ru ··· Ru distances of 8.85 Å, which are shorter than the intramolecular distances.

Absorption spectra: Table 1 reports absorption maxima and intensities for solutions of the complexes in MeCN, all of which display intense UV absorption bands (307 – 316 nm, $\log \varepsilon = 3.70 - 5.20$), corresponding to ligand-centred (^{1}LC) transitions,[7] and less intense bands in the visible region

Table 1. Absorption spectra of complexes in acetonitrile.

	λ_{max} [nm] ($\varepsilon \times 10^4$ [M^{-1} cm^{-1}])			
	ligand-centered		^{1}MLCT	^{3}MLCT
$[(tpy)_2Ru]^{2+}$[a]	307 (5.2)		475 (1.26)	
$[(tpy)Ru(\mathbf{1})]^{2+}$	307 (6.5)		486 (2.4)	
$[Ru(\mathbf{1})_2]^{2+}$	316 (5.5)		498 (2.9)	
$[(tpy)_2Os]^{2+}$[a]	310 (7.4)		475 (1.5)	656 (0.42)
$[(tpy)Os(\mathbf{1})]^{2+}$	311 (6.3)		486 (2.1)	663 (0.53)
$[Os(\mathbf{1})_2]^{2+}$	316 (5.4)		498 (2.6)	673 (0.69)
$[(tpy)Ru(\mathbf{3})Ru(tpy)]^{4+}$	307 (10.6)	370 (2.9)	517 (5.8)	
$[(tpy)Os(\mathbf{3})Os(tpy)]^{4+}$	311 (11.7)		486 (3.9)	664 (0.99)
$[(tpy)Ru(\mathbf{3})Os(tpy)]^{4+}$	309 (9.4)	376 (2.4)	519 (4.9)	672 (0.89)
$[(tpy)Ru(\mathbf{3})Ru(\mathbf{3})Ru(tpy)]^{6+}$	308 (15.1)	372 (5.6)	532 (10.8)	
$[(tpy)Ru(\mathbf{3})Os(\mathbf{3})Ru(tpy)]^{6+}$	309 (9.7)	376 (3.3)	533 (7.1)	688 (1.48)

[a] Refs. [17a, 18].

(486 – 533 nm, $\log \varepsilon = 4.31 - 5.04$). In the polynuclear ruthenium complexes, a band centred around 370 nm is also present. The bands in the visible region are due to metal-to-ligand charge-transfer (^{1}MLCT) transitions.[6] The osmium-containing complexes display an additional tail with a weak absorption ($\lambda_{max} \sim 670$ nm, $\log \varepsilon = 3.60 - 4.17$) corresponding to direct, spin-forbidden population of Os → L charge transfer (CT) triplet excited states.[6]

Comparison of the absorption data for the homometallic ruthenium complexes presented in Table 1 reveals that the MLCT bands are displaced towards longer wavelengths and become more intense on passing from the mononuclear to the dinuclear and trinuclear species. This indicates that the ^{1}MLCT levels for the dinuclear and trinuclear compounds are lower in energy than for the mononuclear complex. This trend is also present for the homometallic osmium complexes.

For the heterometallic complexes, the shape and intensity of the MLCT absorption bands (which consist of overlapping contributions of Ru → L and Os → L origin) are not a superimposition of those of the mononuclear component moieties. Figure 4 provides an illustration for the case of $[(tpy)Ru(\mathbf{3})Os(tpy)]^{4+}$ and the comparison with 1) the sum of the spectra of $[(tpy)Ru(\mathbf{1})]^{2+}$ and $[(tpy)Os(\mathbf{1})]^{2+}$, and 2) the average spectrum from those of $[(tpy)Ru(\mathbf{3})Ru(tpy)]^{4+}$ and $[(tpy)Os(\mathbf{3})Os(tpy)]^{4+}$. These results indicate that the $\{Ru(tpy)_2\}$ and $\{Os(tpy)_2\}$ units cannot be described in terms of electronically isolated chromophores, at least from a spectroscopic point of view,[35] and that the increase in size of the rods is accompanied by some delocalization of the MLCT states populated by light absorption.

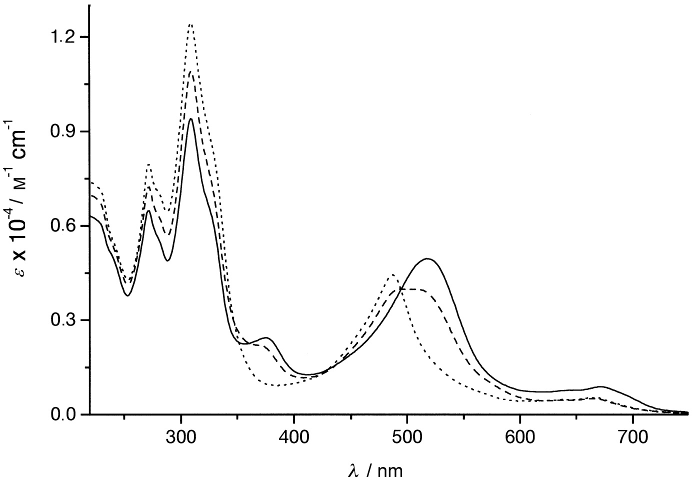

Figure 4. Ground state absorption spectra for $[(tpy)Ru(\mathbf{3})Os(tpy)]^{4+}$ (——), the sum of $[(tpy)Ru(\mathbf{1})]^{2+}$ and $[(tpy)Os(\mathbf{1})]^{2+}$ (····) and the average from $[(tpy)Ru(\mathbf{3})Ru(tpy)]^{4+}$ and $[(tpy)Os(\mathbf{3})Os(tpy)]^{4+}$ (– – –), see text. All solutions 1×10^{-5} M^{-1}.

Electrochemistry: Electrochemical data are listed in Table 2. For mononuclear ruthenium and osmium complexes, the behaviour is well documented and explained in terms of localized metal- and ligand-centred processes.[6] One can also make use of this simple approach in the present cases, although some caution is advisable (see below).

The electrochemical behaviour can be summarized as follows (Table 2, potentials vs Fc^+/Fc): 1) ruthenium-containing complexes exhibit a single oxidation step in the range +0.83 to +0.92 V, 2) osmium-containing complexes are characterized by a single oxidation step occurring in the range +0.49 to +0.58 V and 3) a series of ligand-centred reductions are observed. The reductive behaviour is complicated by irreproducible processes between −1.23 and

Table 2. Electrochemical data for complexes in acetonitrile, $[N(nBu)_4][BF_4]$ supporting electrolyte; potentials in V vs Fc^+/Fc, peak separations were in the range 60 to 100 mV.

	$Ru^{2+/3+}$	$Os^{2+/3+}$	Reductions				
$[(tpy)_2Ru]^{2+}$[a]	$+0.92$				-1.58	-1.82	-1.90
$[(tpy)Ru(\mathbf{1})]^{2+}$	$+0.88$			-1.38	-1.54	-1.85	-2.32
$[Ru(\mathbf{1})_2]^{2+}$	$+0.83$				-1.61	-1.82	-2.24
$[(tpy)_2Os]^{2+}$[a]		$+0.58$			-1.63	-1.95	
$[(tpy)Os(\mathbf{1})]^{2+}$		$+0.52$			-1.62	-1.85	-2.22
$[Os(\mathbf{1})_2]^{2+}$		$+0.49$			-1.56	-1.86	-2.27
$[(tpy)Ru(\mathbf{3})Ru(tpy)]^{4+}$	$+0.88$			-1.46	-1.62	-1.88	
$[(tpy)Os(\mathbf{3})Os(tpy)]^{4+}$		$+0.56$		-1.38	-1.70	-1.90	-2.31
$[(tpy)Ru(\mathbf{3})Os(tpy)]^{4+}$	$+0.90$	$+0.54$	-1.23	-1.48	-1.62	-2.04	
$[(tpy)Ru(\mathbf{3})Ru(\mathbf{3})Ru(tpy)]^{6+}$	$+0.87$			-1.48			
$[(tpy)Ru(\mathbf{3})Os(\mathbf{3})Ru(tpy)]^{6+}$	$+0.89$	$+0.50$	-1.25			-2.05	

[a] Refs. [17a, 18]; literature data in V vs SCE have been converted by subtracting 0.38 V.

-1.48 V associated with surface binding to the electrodes. The data are consistent with the thienyl and thiophenediyl groups possessing slight electron-releasing character.[26, 36]

The observed potentials for the metal-centred oxidation do not change significantly on passing from mononuclear to dinuclear species;[37] for instance, the potentials for $[(tpy)Ru(\mathbf{3})Os(tpy)]^{4+}$ are $+0.90$ and $+0.54$ V as compared to $+0.88$ and $+0.52$ V for $[(tpy)Ru(\mathbf{1})]^{2+}$ and $[(tpy)Os(\mathbf{1})]^{2+}$. This indicates weakly interacting centres,[38] although the interaction is not sufficiently strong to be detected spectroscopically. Single multielectron metal-centred oxidation processes were observed for $[(tpy)Ru(\mathbf{3})Ru(tpy)]^{4+}$, $[(tpy)Os(\mathbf{3})Os(tpy)]^{4+}$ and $[(tpy)Ru(\mathbf{3})Ru(\mathbf{3})Ru(tpy)]^{4+}$ and a single ruthenium-based process was observed for $[(tpy)Ru(\mathbf{3})Os(\mathbf{3})Ru(tpy)]^{4+}$. No resolution of these processes (all values accurate to ±20 mV) was observed at various scan rates. To further investigate the intermetallic interaction, we performed spectroelectrochemical experiments on $[(tpy)Ru(\mathbf{3})Os(tpy)]^{4+}$ and $[(tpy)Ru(\mathbf{3})Ru(tpy)]^{4+}$ (Figure 5). In $[(tpy)Ru(\mathbf{3})Os(tpy)]^{4+}$, the osmium centre was selectively oxidized at $+0.70$ V (vs Fc^+/Fc) and subsequent oxidation of the ruthenium occurred at $+1.0$ V (Figure 5 a). After exhaustive oxidation at $> +1$ V, the MLCT band, to which both divalent metals make approximately equal contributions, diminishes in intensity but does not collapse to zero and a new band grows in at 430 nm, possibly due to $L \rightarrow Os^{III}$ transitions. In addition, the 376 nm band disappears, which suggests that it has some CT character.[39]

A similar spectroelectrochemical experiment is shown in Figure 5 b for $[(tpy)Ru(\mathbf{3})Ru(tpy)]^{4+}$. For this complex, the applied voltage was 1.0 V. Although the two oxidation steps occur simultaneously within the experimental errors (±20 mV),[37, 38] the MLCT absorption only reduces to approximately 20% of the initial value (Figure 5 b), paralleling the behaviour of $[(tpy)Ru(\mathbf{3})Os(tpy)]^{4+}$. The residual absorption is assigned to $L \rightarrow Ru^{III}$ CT transitions, which are expected to occur with $\lambda_{max} \sim 440$ nm and $\log \varepsilon = 3.00-3.30$.[6]

The first reduction step of ruthenium(II) and osmium(II) oligopyridine complexes involves the LUMO,[6] which for dinuclear species may be localized on the bridging or on a

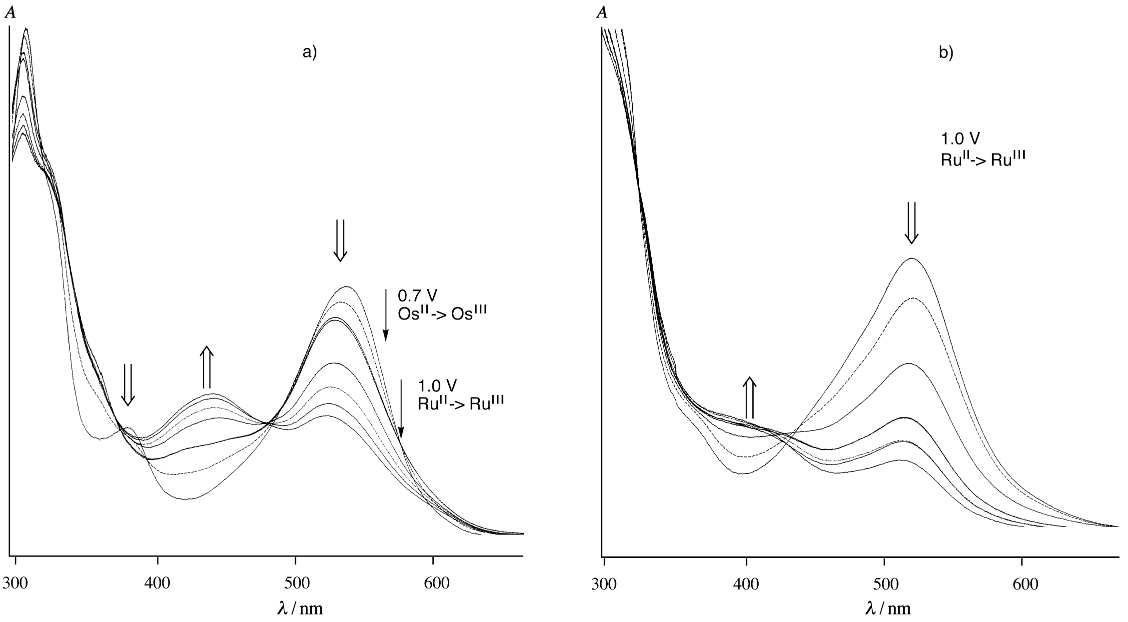

Figure 5. Spectroelectrochemistry of a) $[(tpy)Ru(\mathbf{3})Os(tpy)][PF_6]_4$ (applied potentials, 0.7, 1.0 V) and b) $[(tpy)Ru(\mathbf{3})Ru(tpy)][PF_6]_4$ (applied potentials, 0.7, 1.0 V) (Ag/AgCl *vs.* Pt in CH_3CN, $NaClO_4$ supporting electrolyte, corrected to Fc/Fc^+ reference).

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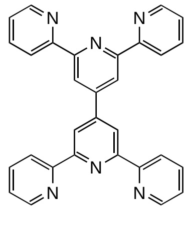
terminal ligand. In the former case, the LUMO may become energetically stabilized (for electrostatic reasons) and the first reduction step becomes less negative with respect to related mononuclear complexes. MO calculations on the free ligands are of help in determining the orbital localization of the added electron after the first reduction.[6b, 40] Using an extended Hückel molecular orbital (EHMO) approach,[41a,b] the LUMO for tpy and for the extended ligand **4** are evaluated at -4.71 and -8.22 eV, respectively, consistent with the first reduction



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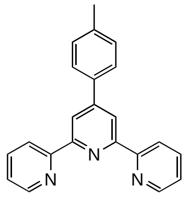

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occurring at -1.58 and -1.31 V vs Fc+/Fc for $[Ru(tpy)_2]^{2+}$ and $[(\mathbf{5})Ru(\mathbf{4})Ru(\mathbf{5})]^{2+}$, respectively. For the free **3** ligand, the LUMO is calculated to be -3.85 eV, slightly higher in energy than that for tpy. However, for the polynuclear complexes, the MOs of the bridging ligand **3** undergo a significantly larger energetic stabilization than those of the terminal tpy ligand. This is confirmed by calculations at the PM3 and HF STO-3G levels[41c] on the complexes, which show a cluster of near-degenerate orbitals (LUMO, LUMO+1, LUMO+2, LUMO+3) centred on **3**.

In conclusion, a localized description of the oxidized and reduced species can be adopted with the proviso that 1) there is significant interaction between the metal centres of the polynuclear complexes in the excited state and 2) the electron-donating properties of the spacer in the **3** ligand may influence the redox processes. For these reasons, we do not make use of commonly employed arguments based on a strict correlation between redox and spectroscopic data concerned with MLCT levels in the following discussion.[6, 42]

Luminescence properties: Table 3 lists luminescence band maxima, quantum yields and lifetimes obtained for the complexes in dilute (10^{-5} M) air-equilibrated MeCN at room temperature and in frozen n-C_3H_7CN at 77 K. Figure 6 shows luminescence spectra obtained at room temperature for the heterometallic complex $[(tpy)Ru(\mathbf{3})Os(\mathbf{3})Ru(tpy)]^{6+}$; those of of $[(tpy)Ru(\mathbf{1})]^{2+}$ and $[(tpy)Os(\mathbf{1})]^{2+}$ are shown for comparison.

The excited states responsible for the luminescence are ^{3}MLCT levels[6] and the trend of emission band maxima (at room temperature) for the homometallic ruthenium complexes indicates that they are stabilized with increasing nuclearity; $\lambda_{max}^{em} = 664$, 738 and 736 nm, for $[(tpy)Ru(\mathbf{1})]^{2+}$, $[(tpy)Ru(\mathbf{3})Ru(tpy)]^{4+}$ and $[(tpy)Ru(\mathbf{3})Ru(\mathbf{3})Ru(tpy)]^{6+}$, respectively. For the polynuclear complexes, the luminescence lifetime and quantum yield increase by two and one orders of magnitude, respectively, with respect to the mononuclear

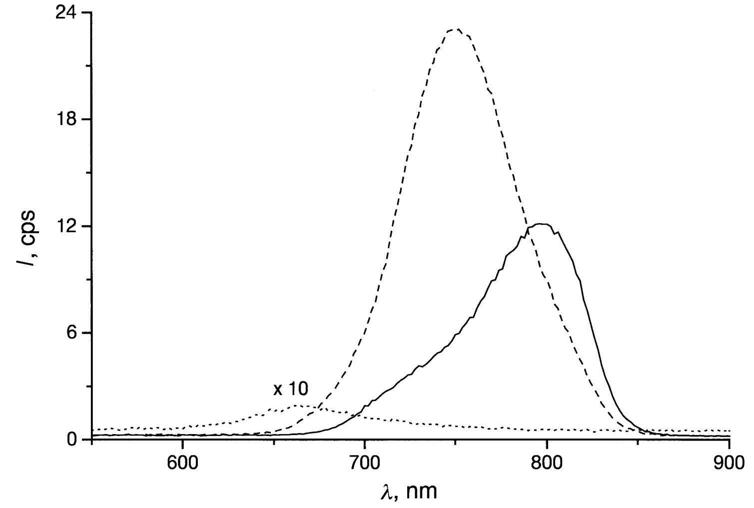

Figure 6. Luminescence spectra of $[(tpy)Ru(\mathbf{3})Os(\mathbf{3})Ru(tpy)]^{6+}$ (——), $[(tpy)Ru(\mathbf{1})]^{2+}$ (····) and $[(tpy)Os(\mathbf{1})]^{2+}$ (– – –) obtained for isoabsorbing MeCN solutions at λ_{exc} 480 nm.

Table 3. Luminescence data in CH_3CN (room temperature) or nC_3H_7CN (77 K).

	293 K						77 K			
	Ru-based			Os-based			Ru-based		Os-based	
	λ_{max} [nm]	$\Phi \times 10^{-4}$	τ [ns]	λ_{max} [nm]	$\Phi \times 10^{-3}$	τ [ns]	λ_{max} [nm]	τ [μs]	λ_{max} [nm]	τ [μs]
$[(tpy)_2Ru]^{2+}$[a]	~640	≤0.3	0.25				598	11		
$[(tpy)Ru(\mathbf{1})]^{2+}$	664	0.53	5.9				650	17		
$[Ru(\mathbf{1})_2]^{2+}$	664	0.88	8.5				656	16		
$[(tpy)_2Os]^{2+}$[a]				718	14.0	270			689	3.9
$[(tpy)Os(\mathbf{1})]^{2+}$				750	7.8	120			734	2.3
$[Os(\mathbf{1})_2]^{2+}$				756	8.4	120			744	1.9
$[(tpy)Ru(\mathbf{3})Ru(tpy)]^{4+}$	738	6.9	340				726	10		
$[(tpy)Os(\mathbf{3})Os(tpy)]^{4+}$				750	7.5	120			734	2.4
$[(tpy)Ru(\mathbf{3})Os(tpy)]^{4+}$			≤0.03[b]	802	2.1	120			784	2.1
$[(tpy)Ru(\mathbf{3})Ru(\mathbf{3})Ru(tpy)]^{6+}$	736	6.8	330				730	9		
$[(tpy)Ru(\mathbf{3})Os(\mathbf{3})Ru(tpy)]^{6+}$				796	3.7	125			794	1.5

[a] Refs. [17a, 18]. [b] From streak camera time resolved experiments, see text.

complexes (Table 3). This effect is likely to be related to the energetic stabilization of the cluster of ^{3}MLCT levels responsible for luminescence, which leads to a large energy gap between these levels and upper lying ^{3}MC levels known to offer very effective pathways for nonradiative processes.[6, 43]

Inspection of the luminescence data allows us to identify the nature of the luminescent centres in the mixed-metal complexes. The complexes [(tpy)Ru(**3**)Os(tpy)]$^{4+}$ ($\lambda_{\mathrm{max}}^{\mathrm{em}} = 802$ nm) and [(tpy)Ru(**3**)Os(**3**)Ru(tpy)]$^{6+}$ ($\lambda_{\mathrm{max}}^{\mathrm{em}} = 796$ nm) feature luminescence quantum yields $\Phi = 2.1\mathrm{y} \times 10^{-3}$ and 3.7×10^{-3} and lifetimes $\tau = 120$ and 125 ns, respectively. These values are similar to those for [(tpy)Os(**3**)Os(tpy)]$^{4+}$ ($\lambda_{\mathrm{max}}^{\mathrm{em}} = 750$ nm), $\Phi = 7.5 \times 10^{-3}$ and $\tau = 120$ ns. For the homometallic complexes [(tpy)Ru(**3**)Ru(tpy)]$^{4+}$ ($\lambda_{\mathrm{max}}^{\mathrm{em}} = 738$ nm) and [(tpy)Ru(**3**)Ru(**3**)Ru(tpy)]$^{6+}$ ($\lambda_{\mathrm{max}}^{\mathrm{em}} = 736$ nm) the luminescence quantum yield ($\Phi \sim 7 \times 10^{-4}$) is an order of magnitude smaller and the lifetime is substantially larger ($\tau = 340$ and 330 ns respectively) than the heterometallic cases. On this basis we conclude that in [(tpy)Ru(**3**)Os(tpy)]$^{4+}$ and [(tpy)Ru(**3**)Os(**3**)Ru(tpy)]$^{6+}$, the ruthenium-based emission is practically extinguished and a dominant osmium-based luminescence is observed (see below for a more detailed discussion on this point). The same conclusions can be reached from the luminescence results obtained at 77 K.

The room temperature intensity of the osmium-based luminescence for [(tpy)Ru(**3**)Os(**3**)Ru(tpy)]$^{6+}$ is about twice that of [(tpy)Ru(**3**)Os(tpy)]$^{4+}$, $\Phi = 3.7 \times 10^{-3}$ and 2.1×10^{-3}, respectively. For [(tpy)Ru(**3**)Os(**3**)Ru(tpy)]$^{6+}$, this corresponds to an effective transfer of excitation energy from the peripheral ruthenium chromophores to the central osmium-based position. By comparing the luminescence quantum yields of [(tpy)Ru(**3**)Ru(**3**)Ru(tpy)]$^{6+}$ ($\Phi = 6.8 \times 10^{-4}$) and of [(tpy)Ru(**3**)Os(**3**)Ru(tpy)]$^{6+}$ ($\Phi = 3.7 \times 10^{-3}$) it is evident that this excitation trapping effect is accompanied by a fivefold enhancement of the luminescence intensity.

Intramolecular energy transfer: From the band maxima at 77 K of the model complexes [(tpy)Ru(**1**)]$^{2+}$ and [(tpy)Os(**1**)]$^{2+}$ (Table 3), the energy difference between their triplet levels is calculated to be ≈0.2 eV. The same value can be obtained from the luminescence data for [Ru(**1**)$_2$]$^{2+}$ and [Os(**1**)$_2$]$^{2+}$. For the dinuclear and trinuclear complexes (provided the component domains retain their electronic identity—which is a rough approximation, as seen above) this energy gap might be taken as the driving force for the intramolecular Ru → Os energy transfer.

In principle, in order to monitor a donor (D) → acceptor (A) energy transfer, one should selectively excite D and observe the photophysics of both D and A partners.[44] We could not follow this approach because the absorption spectra of the ruthenium and osmium mononuclear reference complexes [(tpy)Ru(**1**)]$^{2+}$ and [(tpy)Os(**1**)]$^{2+}$ overlap extensively (Table 1). In order to obtain luminescence spectra, we employed 480 nm (MLCT absorption band) as the excitation wavelength. At this wavelength the extinction coefficients for the reference mononuclear species are practically equal (Table 1), and it may be assumed that 1) in [(tpy)Ru(**3**)Os(tpy)]$^{4+}$ excitation is equally partitioned between the two components and 2) in [(tpy)Ru(**3**)Os(**3**)Ru(tpy)]$^{6+}$ the excitation energy is partitioned 66% and 33% between ruthenium and osmium centres.

The emission spectra for the heteronuclear species do not exhibit residual Ru-based emission (Figure 6 shows the spectrum of [(tpy)Ru(**3**)Os(**3**)Ru(tpy)]$^{6+}$), suggesting that the Ru → Os energy transfer is a rather fast process. Figure 7 compares the results of time-resolved experiments (Streak camera, see Experimental Section) for [(tpy)Ru(**3**)Ru(tpy)]$^{4+}$ and [(tpy)Ru(**3**)Os(tpy)]$^{4+}$. For the latter complex, a very fast decay ($\tau \leq 30$ ps) is observed at 715 nm, that is, in the ruthenium-based spectral region. This decay corresponds to a rise observed in the osmium-based spectral portion at 820 nm (Figure 7). On the basis of $k_{\mathrm{en}} = 1/\tau - 1/\tau_{\mathrm{o}}$ one can estimate $k_{\mathrm{en}} \geq 3.3 \times 10^{10}$ s^{-1} (within this approach, a limiting value of $\tau = 30$ ps was taken for the lifetime of the quenched ruthenium-based emission in the heterometallic species; τ_{o} is the lifetime of the selected donor model, either [(tpy)Ru(**1**)]$^{2+}$ or [(tpy)Ru(**3**)Ru(tpy)]$^{4+}$). This fast rate is clearly due to the good intercentre communication provided by the geometric and electronic properties of the bridging ligand, **3**. Thus, while one useful result obtained with this family of complexes relates to the good luminescence properties of the homometallic ruthenium-based complexes,[12, 16–19] (Table 3) another is concerned with the practically quantitative Ru → Os energy transfer. It should be recalled that for polymetallic complexes in which {Ru(tpy)$_2$}$^{2+}$ moieties are expected to function as energy donors, the energy transfer step is scarcely competitive against intrinsic deactivation at {Ru(tpy)$_2$}^{2}, $k_{\mathrm{d}} = \tau^{-1}$ with $\tau = 0.25$ ns.[16, 17]

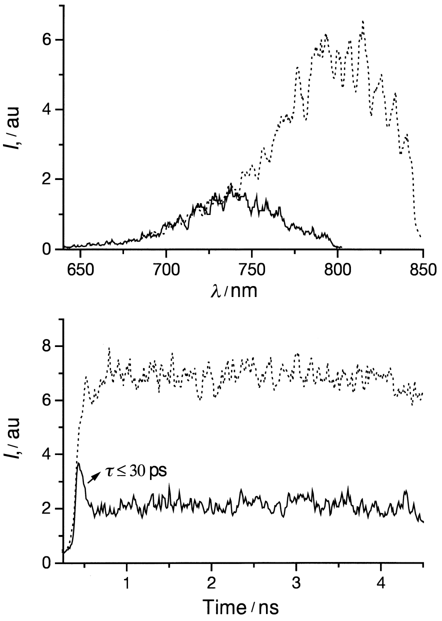

Figure 7. Top: Time-resolved luminescence spectra detected by streak camera (temporal range 0–4 ns) for [(tpy)Ru(**3**)Ru(tpy)]$^{4+}$ (——) and [(tpy)Ru(**3**)Os(tpy)]$^{4+}$ (– – –), $\lambda_{\mathrm{exc}} = 532$ nm. Bottom: Decay of the luminescence for [(tpy)Ru(**3**)Os(tpy)]$^{4+}$ as measured at 715 nm (——) and 820 nm (– – –).

By using the available spectroscopic results we can draw some conclusions regarding the energy transfer mechanism that is operative. For $[(\text{tpy})\text{Ru}(\mathbf{3})\text{Os}(\text{tpy})]^{4+}$, an estimate of the contribution of the dipole-dipole Förster mechanism was made on the basis of Equation (1).[45]

$$k_{\text{en}}^{\text{F}} = \frac{8.8 \times 10^{-25}\, K^2 \Phi}{n^4 \tau d_{\text{MM}}^6} J^{\text{F}} \tag{1}$$

Here, Φ and τ are the luminescence quantum yield and lifetime of $[(\text{tpy})\text{Ru}(\mathbf{1})]^{2+}$, (taken as the reference donor), J^{F} is the integral overlap [Eq. (2)] (J^F was 7.6×10^{-14} cm^{6}mol^{-1}) between the normalized luminescence spectrum of the donor and the absorption spectrum of the acceptor $[(\text{tpy})\text{Os}(\mathbf{1})]^{2+}$; K^2 is a geometric factor ($K^2 = 2/3$), and n is the refractive index of the solvent.

$$J^{\text{F}} = \frac{\int F(\theta)\varepsilon(\theta)/\theta\, \mathrm{d}\theta}{\int F(\theta)\mathrm{d}\theta} \tag{2}$$

For $[(\text{tpy})\text{Ru}(\mathbf{3})\text{Os}(\text{tpy})]^{4+}$, the structural analysis provides $d_{\text{MM}} = 14.4$ Å, and k_{en}^{F} is evaluated to be 1.4×10^8 s^{-1}. On this basis, the Förster mechanism cannot be responsible for the energy transfer from ruthenium to osmium that is experimentally observed with $k_{\text{en}} \geq 3.3 \times 10^{10}$ s^{-1}. It should be pointed out that the above estimate is obtained by considering a dinuclear system whose donating and accepting components retain their electronic identity, shown to be a rough approximation for the present cases. The alternative mechanism is a double-electron exchange Dexter-type transfer.[46] This latter requires good electronic mediation by the bridge between the metal centres, which in **3** is supported by the MO calculations discussed above.

Conclusion

The multinuclear complexes described in this paper all feature well-defined spatial properties, owing to the rigidity exhibited by the **3** bridging ligand; for the trinuclear species the separation between the peripheral metal centres is ~3 nm. The homometallic $[(\text{tpy})\text{Ru}(\mathbf{3})\text{Ru}(\text{tpy})]^{4+}$ and $[(\text{tpy})\text{Ru}(\mathbf{3})\text{Ru}(\mathbf{3})\text{Ru}(\text{tpy})]^{6+}$ rigid rods display interesting luminescence properties, ($\Phi \sim 10^{-3}$, $\tau \sim 330$ ns), which favourably contrast with the practically nonluminescent behaviour of the prototype $[\text{Ru}(\text{tpy})_2]^{2+}$ complex.[16, 17]

For the heterometallic complexes $[(\text{tpy})\text{Ru}(\mathbf{3})\text{Os}(\text{tpy})]^{4+}$ and $[(\text{tpy})\text{Ru}(\mathbf{3})\text{Os}(\mathbf{3})\text{Ru}(\text{tpy})]^{6+}$, an effective Ru → Os energy transfer takes place. This process is facilitated by the good conductive properties of the thiophenediyl bridge in **3**. Thus, the thiophenediyl group promises to be a valuable component for the modular development of bridges capable of transporting excitation energy over large distances on a molecular scale.

For the trinuclear $[(\text{tpy})\text{Ru}(\mathbf{3})\text{Os}(\mathbf{3})\text{Ru}(\text{tpy})]^{6+}$ complex, most of the excitation energy is transferred from the peripheral ruthenium centres to the central osmium centre. By comparing the luminescence quantum yields of $[(\text{tpy})\text{Ru}(\mathbf{3})\text{Ru}(\mathbf{3})\text{Ru}(\text{tpy})]^{6+}$ ($\Phi = 6.8 \times 10^{-4}$) and of $[(\text{tpy})\text{Ru}(\mathbf{3})\text{Os}(\mathbf{3})\text{Ru}(\text{tpy})]^{6+}$ ($\Phi = 3.7 \times 10^{-3}$) one notices that this excitation trapping effect is accompanied by a fivefold enhancement of the luminescence intensity.

Experimental Section

General: Melting points were determined on a Büchi melting-point apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AM 250 MHz, Varian Gemini 300 MHz and Bruker Avance 600 MHz spectrometers; chemical shifts were measured relative to residual non-deuterated solvent resonances. Matrix-assisted laser desorption/ionization mass spectrometry experiments were performed on a PerSeptive Biosystems Voyager-RPBiospectrometry Workstation. Fast-atom bombardment (FAB) and electron impact (EI) mass spectra were recorded on Kratos MS-50, Kratos MS-890, VG 70-250 or Kratos MS 902 mass spectrometers, with 3-nitrobenzyl alcohol as matrix for the FAB experiments. Electrospray (ES) mass spectra were recorded on a Finnigan MAT LC$_q$ mass spectrometer. FTIR spectra were recorded on a Mattson Genesis Fourier-transform spectrophotometer with samples in compressed KBr discs.

4′-(2-Thienyl)-2,2′:6′,2′′-terpyridine (1): A solution of 2-acetylpyridine (3.34 mL, 0.03 mol) in EtOH (250 mL) was added over 2 h to a stirred solution of 2-thiophenecarbaldehyde (1.4 mL, 0.015 mol) and NaOH (4.0 g) in H_2O (25 mL) and EtOH (250 mL). Stirring was continued for 20 h, and then the solvent removed in vacuo. The residue was redissolved in CH_2Cl_2 (300 mL) and was washed with H_2O (3 × 250 mL) and dried over $MgSO_4$, and the remaining solvent removed to give an orange oil. This was dissolved in EtOH (100 mL), NH_4OAc (2.00 g, 0.03 mol) was added and the mixture refluxed for 4 h. The solvent was removed in vacuo and the residue dissolved in toluene (250 mL) and was then washed with water (3 × 100 mL). The toluene was then removed and the residue dissolved in HCl (150 mL, 0.5 M) and was then washed with CH_2Cl_2 (5 × 100 mL). Neutralization of the aqueous layer with NaOH caused precipitation of **1** as an off-white solid (1.9 g, 40%). M.p. 185 °C (decomp); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 8.73$ (dd, $J = 2.0, 4.9$ Hz, 2H; A6), 8.70 (s, 2H; B3), 8.64 (d, $J =$ 7.8 Hz, 2H; A3), 7.87 (dd, $J = 7.8, 8.0$ Hz, 2H; A4), 7.78 (dd, $J = 1.2, 3.6$ Hz, 1H; C3), 7.44 (dd, $J = 1.2, 5.1$ Hz, 1H; C5), 7.35 (ddd, $J = 1.0, 2.0, 7.8$ Hz, 2H; A5), 7.16 (dd, $J = 3.6, 5.1$ Hz, 1H; C4); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 156.1$ (B2/A2), 156.0 (A2/B2), 149.1 (A6), 143.4 (B4), 141.9 (C2), 136.8 (A4), 128.2 (C4), 127.1 (C5), 125.8 (C3), 123.9 (A3), 121.3 (A5), 117.1 (B3); MALDI-TOF MS: m/z: 315 $[M]^+$, 338 $[M+\text{Na}]^+$, 630 $[2M]^+$; HRMS-EI: m/z calcd for $C_{18}H_{13}N_3S$ 315.0830; found: 315.0829; FTIR (KBr): $\tilde{\nu} = 3331$, 3112, 2957, 1722, 1613, 1603, 1573, 1553, 1477, 1428, 1374, 1251, 1165, 1054, 1028, 1016, 843, 793, 723, 558, 411 cm^{-1}; UV/Vis: $\lambda_{\max}$ ($\varepsilon_{\max}$) = 231 (19100), 253 (22400), 284 nm (34900).

2,5-Bis[3-oxo-3-(2-pyridyl)prop-2-enyl]thiophene (2): A solution of thiophene-2,5-dicarbaldehyde (0.20 g, 1.43 mmol) in EtOH (30 mL) and aqueous KOH (10%, 6 mL) was cooled in an ice bath and 2-acetylpyridine (0.34 mL, 3 mmol) added dropwise over 10 min; the resulting solution stirred for 1.25 h. The yellow precipitate was collected on Celite, washed with water, dissolved in CH_2Cl_2 and dried over $MgSO_4$, and recovered by removal of the solvent in vacuo. Purification by column chromatography (1% CH_3OH/CH_2Cl_2, SiO_2) yielded **2** as a bright yellow solid (0.35 g, 72%). M.p. 180 °C (decomp); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.77$ (dm, $J = 4.8$ Hz, 2H; A6), 8.19 (d, $J = 7.8$ Hz, 2H; A3), 8.09 (AB, $J = 56.1$, 15.9 Hz, 4H; CH=CH), 7.89 (ddd, $J = 7.8, 8.0, 1.5$ Hz, 2H; A4), 7.45 (ddd, J = 7.8, 4.8, 1.0 Hz, 2H; A5), 7.38 (s, 2H; C3); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 188.9$ (CO), 153.9, 148.9, 143.8, 137.0, 136.1, 132.9, 127.0, 122.8, 121.7; MALDI-TOF MS: m/z: 346 $[M]^+$; HRMS-EI: m/z calcd for $C_{20}H_{14}N_2O_2S$: 346.0776; found: 346.0768; FTIR (KBr): $\tilde{\nu} = 3058$, 1668, 1590, 1579, 1513, 1463, 1435, 1364, 1328, 1304, 1285, 1239, 1214, 1173, 1022, 995, 973, 786, 740, 680, 653, 618, 512 cm^{-1}.

2,5-Bis(2,2′:6′,2′′-terpyridine-4′-yl)thiophene (3): A mixture of **2** (1.00 g, 2.89 mmol), *N*-[2-oxo-2(2-pyridyl)ethyl]pyridinium iodide[25] (2.00 g, 6.13 mmol) and NH_4OAc (10.0 g, 0.05 mol) was heated to reflux in dry EtOH (300 mL) for 12 h. The solvent was removed in vacuo, and the residue was dissolved in CH_2Cl_2 and washed with water. Following drying over $MgSO_4$, the product was purified by column chromatography (3% Et_2NH, toluene, Al_2O_3) followed by recrystallization from CH_2Cl_2 to give **3** as an off-white solid (0.5 g, 32%). M.p. >250 °C; ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 8.76$ (d, $J = 4.8$ Hz, 4H; A6), 8.75 (s, 4H; B3), 8.65 (d, $J =$ 7.8 Hz, 4H; A3), 7.87 (ddd, J = 7.8, 8.0, 1.8 Hz, 4H; A4), 7.84 (s, 2H; C3), 7.36 (ddd, J = 7.3, 4.9, 1.0 Hz, 4H; A5); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta =$ 156.2 (B2), 155.9 (A2), 149.2 (A6), 143.2 (B4), 142.8 (C2), 136.9 (A4), 126.9

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(C3), 124.0 (A3), 121.3 (A5), 116.9 (B3); MALDI-TOF MS: *m/z*: 546 $[M]^+$, 570, $[M{+}Na]^+$, 1093 $[2M{+}H]^+$; HRMS-EI: *m/z* calcd for $C_{34}H_{22}N_6S$: 546.1627; found 546.1628; FTIR (KBr): $\tilde{\nu} = 3060$, 3012, 2923, 2851, 1599, 1583, 1568, 1550, 1467, 1438, 1401, 1363, 1266, 1234, 1094, 1073, 1023, 990, 884, 790, 742, 731, 676, 659, 622, 506 cm^{-1}; UV/Vis: λ_{max} (ε_{max}) = 240 (9400), 252 (9800), 283 (11800), 344 (11200).

$[Ru(1)_2][PF_6]_2$: $RuCl_3 \cdot 3H_2O$ (8.0 mg, 0.031 mmol) and **1** (20.0 mg, 0.063 mmol) were heated to reflux in ethane-1,2-diol (25 mL) containing six drops of *N*-ethylmorpholine in a microwave oven (600 W, 4 min). After cooling, aqueous NH_4PF_6 was added and the precipitate purified by column chromatography (CH_3CN/sat. aqueous KNO_3/H_2O 10:0.5:1.5, SiO_2). The major red fraction was collected and reduced to half its volume in vacuo and treated with aqueous NH_4PF_6; the precipitate collected by filtration on Celite. The solid was redissolved in CH_3CN, to which water was added until a precipitate was obtained. The precipitate was collected by filtration and dried under high vacuum to give an orange-red solid (22.0 mg, 70%). Elemental analysis calcd (%) for $C_{38}H_{26}F_{12}N_6P_2RuS_2 \cdot 2CH_3CN$: C 45.70, H 2.92, N 10.15; found: C 45.61, H 3.08, N 9.86; ^1H NMR (250 MHz, CD_3CN): $\delta = 8.94$ (s, 4H; B3), 8.66 (d, $J = 7.8$ Hz, 4H; A3), 8.19 (dd, $J = 1.2$, 3.6 Hz, 2H; C3), 7.94 (dd, $J = 7.8$, 8.0 Hz, 4H; A4), 7.83 (dd, $J = 1.2$, 5.1 Hz, 2H; C5), 7.43 (m, 6H; A6, C4), 7.18 (ddd, $J = 1.0$, 2.0, 7.8 Hz, 2H; A5); MALDI-TOF MS: *m/z*: 733 $[M - 2PF_6]^+$, 415 $[M - \mathbf{1} - 2PF_6]^+$); FTIR (KBr): $\tilde{\nu} = 1609$, 1467, 1429, 1397, 1079, 838, 787, 752, 718, 557 cm^{-1}.

$[Os(1)_2][PF_6]_2$: $[NH_4]_2[OsCl_6]$ (10.0 mg, 0.023 mmol) and **1** (15 mg, 0.048 mmol) were treated as decribed above and the product was isolated as a purple solid (20.0 mg, 80%). Elemental analysis calcd (%) for $C_{38}H_{26}F_{12}N_6P_2OsS_2 \cdot 2H_2O$: C 39.79, H 2.64, N 7.33; found: C 40.17, H 2.69, N 7.45; ^1H NMR (250 MHz, CD_3CN): $\delta = 8.96$ (s, 4H; B3), 8.64 (d, $J = 7.8$ Hz, 4H; A3), 8.10 (dd, $J = 1.2$, 3.6 Hz, 2H; C3), 7.81 (dd, $J = 7.8$, 8.0 Hz, 4H; A4), 7.73 (dd, $J = 1.2$, 5.1 Hz, 2H; C5), 7.42 (dd, $J = 3.6$, 5.1 Hz, 2H; C4), 7.31 (dd, $J = 2.0$, 4.9 Hz, 4H; A6), 7.12 (ddd, $J = 1.0$, 2.0, 7.8 Hz, 2H; A5); MALDI-TOF MS: *m/z*: 820 $[M - 2PF_6]^+$; FTIR (KBr): $\tilde{\nu} = 1665$, 1612, 1476, 1430, 1395, 1360, 1336, 1244, 1076, 1026, 836, 784, 752, 714, 557, 506 cm^{-1}.

$[Ru(tpy)(1)][PF_6]_2$: A mixture of $[Ru(tpy)Cl_3]$[31] (25.0 mg, 0.051 mmol) and **1** (16.0 mg, 0.051 mmol) were treated as described above and the product was isolated as a red-orange solid (41.0 mg, 79%). Elemental analysis calcd (%) for $C_{34}H_{24}F_{12}N_6P_2RuS$: C 43.46, H 2.57, N 8.94; found: C 43.53, H 2.82, N 8.63; ^1H NMR (250 MHz, CD_3CN): $\delta = 8.92$ (s, 2H; B3), 8.75 (m, 4H; A3, E3), 8.49 (d, $J = 7.8$ Hz, 2H; D3), 8.18 (dd, $J = 1.2$, 3.6 Hz, 1H; C3), 7.92 (dd, $J = 7.8$, 8.0 Hz, 2H; A4), 7.90 (dd, $J = 7.8$, 8.0 Hz, 2H; D4), 7.83 (dd, $J = 1.2$, 5.1 Hz, 1H; C5), 7.43 (dd, $J = 2.0$, 4.9 Hz, 2H; A6), 7.41 (dd, $J = 3.6$, 5.1 Hz, 1H; C4), 7.34 (dd, $J = 2.0$, 4.9 Hz, 2H; D6), 7.17 (m, 4H; A5, D5); MALDI-TOF MS: *m/z*: 650 $[M - 2PF_6]^+$, 334 $[(tpy)Ru]^+$, 416 $[M - \mathbf{1} - 2PF_6]^+$; FTIR (KBr): $\tilde{\nu} = 1609$, 1466, 1449, 1430, 1387, 1244, 839, 784, 767, 723, 558 cm^{-1}.

$[Os(tpy)(1)][PF_6]_2$: $[Os(tpy)(H_2O)_3][PF_6]_3$[29] (70.0 mg, 0.077 mmol) and **1** (20.0 mg, 0.063 mmol) were treated as described above and the product was isolated as a brown powder (51.0 mg, 78%). Elemental analysis calcd (%) for $C_{34}H_{24}F_{12}N_6P_2OsS.H_2O$: C 39.01, H 2.50, N 8.03; found: C 39.02, H 2.66, N 8.18; ^1H NMR (250 MHz, CD_3CN): $\delta = 8.95$ (s, 2H; B3), 8.75 (d, $J = 7.8$ Hz, 2H; D3), 8.61 (dd, $J = 7.8$, 1.2, 2H; A3), 8.46 (d, $J = 7.8$ Hz, 2H; E3), 8.01 (dd, $J = 1.2$, 3.6 Hz, 1H; C3), 7.92 (t, $J = 7.8$ Hz, 1H; E4), 7.78 (m, 4H; A4, D4), 7.70 (dd, $J = 1.2$, 5.1 Hz, 1H; C5), 7.42 (dd, $J = 3.6$, 5.1 Hz, 1H; C4), 7.29 (dd, $J = 2.0$, 4.9 Hz, 2H; A6), 7.21 (dd, $J = 2.0$, 4.9 Hz, 2H; D6), 7.13 (m, 4H; A5, D5); MALDI-TOF MS: *m/z*: 738 $[M - 2PF_6]^+$, 1479 $[2M]^+$).

$[Ru(tpy)(3)][PF_6]_2$: A mixture of $[Ru(tpy)Cl_3]$ (160.0 mg, 0.37 mmol) and **3** (200 mg, 0.37 mmol) was heated to reflux in EtOH (150 mL) with 10 drops of *N*-ethylmorpholine for 90 min. Following addition of aqueous NH_4PF_6, the salts precipitated from the mixture were purified by column chromatography (CH_3CN/sat. aqueous KNO_3/H_2O 7:1:0.5, SiO_2). The first orange-red band was collected, concentrated in vacuo and treated with alkaline aqueous NH_4PF_6 to precipitate $[Ru(tpy)(\mathbf{3})][PF_6]_2$ as an orange-red solid (257 mg, 60%). Elemental analysis calcd (%) for $C_{49}H_{33}F_{12}N_9P_2RuS \cdot CH_3CN \cdot 0.75PF_6$: C 46.35, H 2.80, N 10.60; found: C 46.25, H 2.75, N 10.60; ^1H NMR (250 MHz, CD_3COCD_3): $\delta = 9.51$ (s, 2H; B3), 9.17 (dd, $J = 7.8$, 1.2, 2H; A3), 9.10 (d, $J = 7.8$ Hz, 2H; E3), 8.93 (s, 2H; G3), 8.84 (dd, $J = 2.0$, 4.9 Hz, 2H; F6), 8.83 (dd, $J = 7.8$, 1.2 Hz, 2H; F3), 8.81 (d, $J = 7.8$ Hz, 2H; D3), 8.60 (t, $J = 7.8$ Hz, 1H; E4), 8.52 (d, $J = 3.9$ Hz, 1H; C4), 8.29 (d, $J = 3.9$ Hz, 1H; C3), 8.12 (dd, $J = 7.8$, 8.0 Hz, 2H; F4), 8.10 (m, 4H; A4, D4), 7.89 (dd, $J = 2.0$, 4.9 Hz, 2H; D6), 7.74 (dd, $J = 2.0$, 4.9 Hz, 2H; A6), 7.57 (dd, $J = 4.9$, 7.8 Hz, 2H; F5), 7.38 (dd, $J = 4.9$, 7.8 Hz, 2H; A5), 7.34 (dd, $J = 4.9$, 7.8 Hz, 2H; D5); MALDI-TOF MS: *m/z*: 1194 $[M{+}Na]^+$, 1024 $[M - PF_6]^+$, 880 $[M - 2PF_6]^+$; FTIR (KBr): $\tilde{\nu} = 1601$, 1584, 1569, 1466, 1448, 1384, 839, 798, 792, 558 cm^{-1}.

$[(tpy)Ru(3)Ru(tpy)][PF_6]_4$: A suspension of $[Ru(tpy)Cl_3]$[31] (41.0 mg, 0.09 mmol) and **3** (15.0 mg, 0.03 mmol) was heated to reflux in EtOH (50 mL) containing six drops of *N*-ethylmorpholine for 3 h. The reaction mixture was poured into aqueous NH_4PF_6, and the precipitated solid purified by column chromatography (CH_3CN/sat. aqueous KNO_3/H_2O 7:1:0.5, SiO_2). The major fraction was concentrated in vacuo and treated with aqueous NH_4PF_6 to precipitate the product as a bright red solid (48 mg, 95%). Elemental analysis calcd (%) for $C_{64}H_{44}F_{24}N_{12}P_4Ru_2S \cdot 2CH_3CN$: C 43.51, H 2.68, N 10.45; found: C 43.86, H 3.01, N 10.12; ^1H NMR (250 MHz, CD_3CN): $\delta = 9.11$ (s, 4H; B3), 8.78 (m, 8H; A3, E3), 8.52 (d, $J = 7.8$ Hz, 4H; D3), 8.44 (t, $J = 7.8$ Hz, 2H; E4), 8.43 (s, 2H; C3), 8.00 (dd, $J = 7.8$, 8.0 Hz, 4H; A4), 7.94 (dd, $J = 7.8$, 8.0 Hz, 4H; D4), 7.49 (dd, $J = 2.0$, 4.9 Hz, 4H; D6), 7.40 (dd, $J = 2.0$, 4.9 Hz, 4H; A6), 7.22 (dd, $J = 4.9$, 7.8 Hz, 4H; A5), 7.20 (dd, $J = 4.9$, 7.8 Hz, 4H; D5); MALDI-TOF MS: *m/z*: 1214 $[M - 4PF_6]^+$, 1362 $[M - 3PF_6]^+$; FTIR (KBr): $\tilde{\nu} = 1610$, 1449, 1431, 1403, 1386, 1245, 840, 789, 766, 558 cm^{-1}.

$[(tpy)Ru(3)Os(tpy)][PF_6]_4$: A suspension of $[Os(tpy)(H_2O)_3][PF_6]_3$[29] (60.0 mg, 0.066 mmol) and $[Ru(tpy)(\mathbf{3})][PF_6]_2$ (70.0 mg, 0.060 mmol) was heated in a microwave oven (600 W) in ethane-1,2-diol (50 mL) containing a few drops of *N*-ethylmorpholine for 4 min after which aqueous NH_4PF_6 was added. The precipitated residue was worked up as above to give $[(tpy)Ru(\mathbf{3})Os(tpy)][PF_6]_4$ as a red-purple solid (53 mg, 47%). Elemental analysis calcd (%) for $C_{64}H_{44}F_{24}N_{12}OsP_4RuS \cdot 2CH_3CN \cdot 3H_2O$: C 40.78, H 2.88, N 10.10; found: C 40.74, H 3.29, N 10.04; ^1H NMR (250 MHz, CD_3CN): $\delta = 9.10$ (s, 2H; B3), 9.05 (s, 2H; G3), 8.79 (d, $J = 7.8$ Hz, 2H; J3), 8.78 (d, $J = 7.8$ Hz, 2H; E3), 8.72 (dd, $J = 7.8$, 1.2 Hz, 2H; A3), 8.70 (d, $J = 7.8$ Hz, 2H; F3), 8.52 (d, $J = 7.8$ Hz, 2H; D3), 8.46 (dd, $J = 7.8$, 1.2 Hz, 2H; H3), 8.44 (t, $J = 7.8$ Hz, 1H; E4), 8.43 (d, $J = 3.9$ Hz, 1H; C3), 8.34 (d, $J = 3.9$ Hz, 1H; C4), 8.00 (dd, $J = 7.8$, 8.0 Hz, 2H; A4), 7.97 (t, $J = 7.8$ Hz, 1H; J4), 7.95 (dd, $J = 7.8$, 8.0 Hz, 2H; D4), 7.89 (dd, $J = 7.8$, 8.0 Hz, 2H; F4), 7.81 (dd, $J = 7.8$, 8.0 Hz, 2H; H4), 7.48 (dd, $J = 2.0$, 4.9 Hz, 2H; D6), 7.39 (dd, $J = 2.0$, 4.9 Hz, 2H; A6), 7.34 (dd, $J = 2.0$, 4.9 Hz, 2H; H6), 7.28 (dd, $J = 2.0$, 4.9 Hz, 2H; F6), 7.22 (dd, $J = 4.9$, 7.8 Hz, 2H; A5), 7.19 (dd, $J = 4.9$, 7.8 Hz, 2H; D5), 7.16 (dd, $J = 4.9$, 7.8 Hz, 2H; F5), 7.12 (dd, $J = 4.9$, 7.8 Hz, 2H; H5); MALDI-TOF MS: *m/z*: 1454 $[M - 3PF_6]^+$, 1306 $[M - 4PF_6]^+$, 969 $[(\mathbf{3})Os(tpy)]^+$, 882 $[(\mathbf{3})Ru(tpy)]^+$; ES MS: *m/z*: 326.2 $[M - 4PF_6]^{4+}$, 483.8 $[M - 3PF_6]^{3+}$, 798.1 $[M - PF_6]^{2+}$, 1739.1 $[M - PF_6]^+$; FTIR (KBr): $\tilde{\nu} = 1637$, 1610, 1476, 1449, 1431, 1403, 1388, 1246, 1028, 838, 787, 765, 558 cm^{-1}.

$[Os(tpy)(3)][PF_6]_2$: A suspension of $[Os(tpy)(H_2O)_3][PF_6]_3$[29] (50.0 mg, 0.05 mmol) and **3** (40.0 mg, 0.07 mmol) was heated in a microwave oven (600 W) for 6 min in ethane-1,2-diol (40 mL) with 10 drops of *N*-ethylmorpholine. The brown solution was poured into aqueous NH_4PF_6, and the precipitated solid purified by column chromatography (CH_3CN/sat. aqueous KNO_3/H_2O 7:2:2, SiO_2). The first, brown fraction was made basic by the addition of $NaHCO_3$, and the product precipitated by addition of aqueous NH_4PF_6. After washing with water, the mononuclear complex was recovered as a brown powder: ^1H NMR (250 MHz, CD_3COCD_3): $\delta = 9.52$ (s, 2H; B3), 9.14 (dd, $J = 7.8$, 1.2 Hz, 2H; A3), 9.10 (d, $J = 7.8$ Hz, 2H; E3), 8.93 (s, 2H; G3), 8.84 (dd, $J = 2.0$, 4.9 Hz, 2H; F6), 8.83 (dd, $J = 7.8$, 1.2 Hz, 2H; F3), 8.82 (d, $J = 7.8$ Hz, 2H; D3), 8.43 (d, $J = 3.9$ Hz, 1H; C4), 8.28 (d, $J = 3.9$ Hz, 1H; C3), 8.11 (t, $J = 7.8$ Hz, 1H; E4), 8.08 (dd, $J = 7.8$, 8.0 Hz, 2H; F4), 7.96 (m, 4H; A4, D4), 7.76 (dd, $J = 2.0$, 4.9 Hz, 2H; D6), 7.63 (dd, $J = 2.0$, 4.9 Hz, 2H; A6), 7.57 (dd, $J = 4.9$, 7.8 Hz, 2H; F5), 7.28 (m, 4H; A5, D5); MALDI-TOF MS: *m/z*: 970 $[M - 2PF_6]^+$; FTIR (KBr): $\tilde{\nu} = 1600$, 1570, 1533, 1476, 1450, 1429, 1399, 1384, 1317, 1283, 1152, 1027, 839, 786, 768, 601, 558 cm^{-1}.

$[(tpy)Os(3)Os(tpy)][PF_6]_4$: A suspension of $[Os(tpy)(H_2O)_3][PF_6]_3$[29] (84.0 mg, 9.21 mmol) and **3** (25.0 mg, 4.67 mmol) was heated in a microwave oven (600 W) in ethane-1,2-diol (50 mL) containing a few drops of *N*-ethylmorpholine for 4 min. An aqueous solution of NH_4PF_6 was added, and the precipitated residue was purified by column chromatography (CH_3CN:sat. aqueous KNO_3:H_2O 10:0.5:1.5, SiO_2). The product was the third fraction eluted from the column and was concentrated in vacuo and treated with aqueous NH_4PF_6 to precipitate $[(tpy)Os(\mathbf{3})Os(tpy)][PF_6]_4$ as a dark purple solid (54.0 mg, 60%). elemental analysis calcd (%) for

$C_{64}H_{44}F_{24}N_{12}Os_2P_4S \cdot 7\,H_2O$: C 36.61, H 2.78, N 8.01; found: C 36.73, H 3.00, N 8.27; ^{1}H NMR (250 MHz, CD_3CN): $\delta = 9.06$ (s, 4H; B3), 8.79 (d, $J = 7.8$ Hz, 4H; E3), 8.71 (dd, $J = 7.8$, 1.2 Hz, 4H; A3), 8.50 (d, $J = 7.8$ Hz, 4H; D3), 7.97 (t, $J = 7.8$ Hz, 2H; E4), 8.35 (s, 2H; C3), 7.83 (dd, $J = 7.8$, 8.0 Hz, 4H; A4), 7.80 (dd, $J = 7.8$, 8.0 Hz, 4H; D4), 7.33 (dd, $J = 2.0$, 4.9 Hz, 2H; D6), 7.28 (dd, $J = 4.9$, 7.8 Hz, 4H; A6), 7.15 (dd, $J = 4.9$, 7.8 Hz, 4H; A5), 7.13 (dd, $J = 4.9$, 7.8 Hz, 4H; D5); MALDI-TOF MS: m/z: 1449 $[M - 3\,PF_6]^+$, 1305 $[M - 4\,PF_6]^+$, 970 [(**3**)Os(tpy)]$^+$, 882 [(**3**)Ru(tpy)]$^+$; ES MS: m/z: 326 $[M - 4\,PF_6]^{4+}$, 483 $[M - 3\,PF_6]^{3+}$, 797 $[M - 2\,PF_6]^{2+}$, 1739 $[M - PF_6]^+$.

[(tpy)Ru(3)Ru(3)Ru(tpy)][PF$_6$]$_6$: A mixture of $RuCl_3 \cdot 3\,H_2O$ (4.0 mg, 0.015 mmol) and [Ru(tpy)(**3**)][PF$_6$]$_2$ (36.0 mg, 0.030 mmol) was heated in a microwave oven (600 W) in ethane-1,2-diol (20 mL) with 10 drops of *N*-ethylmorpholine for 4 min. Following addition of aqueous NH_4PF_6, the salts precipitated from the mixture were purified by column chromatography (CH_3CN/sat. aqueous KNO_3/H_2O 10:0.5:1.5, SiO_2). The product was concentrated in vacuo and treated with aqueous NH_4PF_6 to precipitate the product as a pink solid (20.0 mg, 48%). Elemental analysis calcd (%) for $C_{98}H_{66}F_{36}N_{18}P_6Ru_3S_2 \cdot 12\,H_2O$: C 39.91, H 3.08, N 8.55; found: C 39.67, H 3.04, N 8.59; ^{1}H NMR (250 MHz, CD_3CN): $\delta = 9.15$ (s, 4H; B3), 9.10 (s, 4H; G3), 8.79 (m, 8H; A3, E3), 8.76 (d, $J = 7.8$ Hz, 4H; F3), 8.53 (d, $J = 7.8$ Hz, 4H; D3), 8.44 (t, $J = 7.8$ Hz, 2H; E4), 8.44 (s, 4H; C3, C4), 8.04 (dd, $J = 7.8$, 8.0 Hz, 4H; F4), 8.01 (dd, $J = 7.8$, 8.0 Hz, 4H; A4), 7.96 (dd, $J = 7.8$, 8.0 Hz, 4H; D4), 7.55 (dd, $J = 2.0$, 4.9 Hz, 4H; F6), 7.48 (dd, $J = 2.0$, 4.9 Hz, 4H; D6), 7.40 (dd, $J = 2.0$, 4.9 Hz, 4H; A6), 7.27 (dd, $J = 4.9$, 7.8 Hz, 4H; F5), 7.23 (dd, $J = 4.9$, 7.8 Hz, 4H; A5), 7.21 (dd, $J = 4.9$, 7.8 Hz, 4H; D5); MALDI-TOF MS: m/z: 881 [(tpy)Ru(**3**)]$^+$; ES MS: m/z: 310.6 $[M - 6\,PF_6]^{6+}$, 401.6 $[M - 5\,PF_6]^{5+}$, 538.3 $[M - 4\,PF_6]^{4+}$, 766.1 $[M - 3\,PF_6]^{3+}$, 1221.5 $[M - 2\,PF_6]^{2+}$; FTIR (KBr): $\tilde{\nu} = 1608$, 1466, 1449, 1429, 1402, 1387, 1246, 838, 787, 769, 754, 558 cm^{-1}.

[(tpy)Ru(3)Os(3)Ru(tpy)][PF$_6$]$_6$: This complex was prepared by following the procedure described for [(tpy)Ru(**3**)Ru(**3**)Ru(tpy)][PF$_6$]$_6$, but with $K_2[OsCl_6]$ (4.0 mg, 0.008 mmol) and [Ru(tpy)(**3**)][PF$_6$]$_2$ (18.0 mg, 0.015 mmol) to give a purple solid (10.0 mg, 46%). ^{1}H NMR (250 MHz, CD_3CN): $\delta = 9.14$ (s, 4H; B3), 9.07 (s, 4H; G3), 8.78 (d, $J = 7.8$ Hz, 4H; E3), 8.75 (d, $J = 7.8$ Hz, 4H; F3), 8.74 (dd, $J = 7.8$, 1.2 Hz, 4H; A3), 8.53 (d, $J = 7.8$ Hz, 4H; D3), 8.44 (t, $J = 7.8$ Hz, 2H; E4), 8.44 (d, $J = 3.9$ Hz, 2H; C3), 8.37 (d, $J = 3.9$ Hz, 2H; C4), 8.00 (dd, $J = 7.8$, 8.0 Hz, 4H; A4), 7.96 (dd, $J = 7.8$, 8.0 Hz, 4H; D4), 7.90 (dd, $J = 7.8$, 8.0 Hz, 4H; F4), 7.49 (dd, $J = 2.0$, 4.9 Hz, 4H; D6), 7.41 (dd, $J = 2.0$, 4.9 Hz, 4H; F6), 7.40 (dd, $J = 2.0$, 4.9 Hz, 4H; A6), 7.23 (dd, $J = 4.9$, 7.8 Hz, 4H; A5), 7.20 (m, 8H; D5, F5); MALDI-TOF MS: m/z: 881 [(tpy)Ru(**3**)]$^+$; ES MS: m/z: 325.3 $[M - 6\,PF_6]^{6+}$, 419.5 $[M - 5\,PF_6]^{5+}$, 560.6 $[M - 4\,PF_6]^{4+}$, 795.7 $[M - 3\,PF_6]^{3+}$, 1267 $[M - 2\,PF_6]^{2+}$; FTIR (KBr): $\tilde{\nu} = 1607$, 1476, 1465, 1449, 1429, 1400, 1385, 1285, 1246, 1162, 1080, 1026, 838, 785, 768, 754, 558 cm^{-1}.

Crystallographic analysis: Diisopropyl ether vapor was allowed to diffuse into a solution of the mixture of nitrate and hexafluorophosphate salts of [Ru(**1**)$_2$]$^{2+}$ in CH_3CN obtained after chromatographic purification as described above to give dark red crystals of [Ru(**1**)$_2$][PF$_6$][NO$_3$]$\cdot 2\,CH_3CN$. X-ray crystallographic analysis was performed on an Enraf-Nonius CAD4 diffractometer with monochromated $Cu_{K\alpha}$ radiation ($\lambda = 1.54180$ Å). DIFABS was employed for the absorption correction.[47] The crystal structure was solved by using SIR92[48] and refined by using CRYSTALS.[49] Non-H atoms were refined anisotropically. All H atoms with isotropic thermal parameters were located on the calculated positions. A model was adopted in which the two rotationally disordered thienyl substituents occupied two sites with approximately 3:1 occupancies. Crystal and experimental data: dark red-brown cube ($0.46 \times 0.48 \times 0.77$ mm), $C_{42}H_{32}F_6N_9O_3PRuS_2$ (1020.93) monoclinic $P2_1/c$, $a = 16.913(2)$, $b = 14.741(3)$, $c = 17.048(3)$ Å, $\beta = 96.8(1)^\circ$, $V = 4220.5(1.0)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.61$ g cm^{-3}, $F_{000} = 2064$, $\mu(Cu_{K\alpha}) = 5.04$ mm^{-1}; $T = 293$ K, $\theta_{max} = 77.5^\circ$, 7357 reflections measured, 6978 unique, 4155 with $I > 4.0\sigma(I)$, 670 variables, $R = 0.0518$, $R_w = 0.0602$, GOF = 1.028, $\rho_{max} = 0.86$ e Å^{-3}, $\rho_{min} = -0.50$ e Å^{-3}.

Benzene vapor was diffused into a solution of the salt [(tpy)Ru(**3**)Ru(tpy)][PF$_6$]$_4$ in acetonitrile to give dark red crystals of [(tpy)Ru(**3**)Ru(tpy)][PF$_6$]$_4 \cdot 2\,CH_3CN$. Data collection was performed on a STOE IPDS with monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). The crystal structure was solved by using SHELXS 86[50] and refined by using SHELXL 93.[51] Non-H atoms were refined anisotropically and all H atoms with isotropic thermal parameters were located on the calculated positions. Although two of the PF_6^- counterions were refined well, the remaining two were disordered over four sites with occupancies 0.57:0.43 and 0.59:0.41. An additional rotational disorder was associated with the equatorial F atoms of the lower occupancy sites. There is clearly additional disordered solvent in the lattice ($\rho_{max/min} = 1.703/-1.265$ e Å^{-3}, solvent accessible voids, 132 Å^3, 1.6%) although no satisfactory model was found. Crystal and experimental data: dark red block ($0.31 \times 0.25 \times 0.33$ mm), $C_{68}H_{50}F_{24}N_{14}P_4Ru_2S$ (1877.30), monoclinic $P2_1/n$, $a = 12.185(2)$, $b = 52.352(11)$, $c = 12.665(3)$ Å, $\beta = 90.12(3)^\circ$, $V = 8079.1(1.0)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.54$ g cm^{-3}, $F_{000} = 3744$, $\mu(Mo_{K\alpha}) = 0.583$ mm^{-1}; $T = 293$ K, $\theta_{max} = 22.47^\circ$, 23878 reflections measured, 10117 unique, 8939 with $I > 2.0\sigma(I)$, 1094 variables, 62 restraints, $R = 0.1588$ (all), 0.1517 (obs), $R_w = 0.3838$ (all), 0.3761 (all), GOF = 1.146 (all), 1.216 (obs), $\rho_{max} = 1.703$ e Å^{-3}, $\rho_{min} = -1.265$ e Å^{-3}. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-163154 and CCDC-163155. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Electrochemistry and spectroelectrochemistry: Routine electrochemical measurements were performed with an Eco Chemie Autolab PGSTAT 20 system by using platinum or glassy carbon working and auxiliary electrodes with an Ag/AgCl reference using purified acetonitrile as solvent and 0.1M [nBu$_4$N][BF$_4$] as supporting electrolyte; ferrocene was added at the end of each experiment as an internal reference. Spectroelectrochemistry was performed using a Shimadzu 3100 UV/Vis/NIR double-beam spectrophotometer interfaced with an Elonex PC-433. The required potentials were applied by using an EG&G PAR 273 potentiostat/galvanostat and a conventional three electrode cell with a BAS Ag/AgCl electrode and platinum meshes acting as the working and auxiliary electrode, respectively. The substances were solved in purified MeCN with added $LiClO_4$ as electrolyte.

Spectroscopy: Absorption spectra of dilute solutions (10^{-5}M) of the investigated complexes were measured in acetonitrile at room temperature with Perkin–Elmer Lambda 5, Lambda 9 or Lambda 19 UV/Vis spectrophotometers. For the luminescence experiments, air-equilibrated acetonitrile (room temperature) or butyronitrile (77 K) solutions of the samples were used. Luminescence spectra were obtained from solutions whose absorbance values were ≤ 0.2 at the employed excitation wavelength (480 nm) by using Perkin–Elmer LS50B or Spex Fluorolog II spectrofluorimeters. While uncorrected band maxima are used throughout the text, for the determination of the luminescence quantum yields we have employed corrected spectra.[52] The correction procedure takes care of the wavelength dependent phototube response, and from the area of the corrected luminescence spectra on an energy scale (cm^{-1}), we obtained luminescence quantum yields for the samples with reference to $[Ru(bpy)_3]^{2+}$ ($\Phi = 0.028$ in air-equilibrated water) and $[Os(phen)_3]^{2+}$ ($\Phi = 0.005$ in degassed acetonitrile) as standards.[53] Band maxima and relative luminescence intensities were affected by an uncertainty of 2 nm and ~20%, respectively. Luminescence lifetimes were obtained by using $\lambda_{exc} = 337$ nm from IBH single-photon counting equipment or 532 nm from a picosecond fluorescence spectrometer based on a Nd:YAG laser (Continuum PY62–10) and a Hamamatsu C1587 streak camera. The uncertainty in the lifetime values is within 8%. Further details of luminescence measurements are reported elsewhere.[52]

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