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Photo-induced energy transfer and its switching in dyad and triad chromophore systems composed of coumarin, Ru(II) and Os(II) terpyridine-type complexes †

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A new dyad and two triad chromophore compounds containing coumarin, Ru(II) and Os(II) terpyridine-type complexes were synthesized. The dyad is composed of coumarin and Os(II) units, while the triads are composed of coumarin, Ru(II) and Os(II) units. One of the triads has a phenylene spacer to connect the Ru(II) unit and the Os(II) unit, while the other has an azo moiety. Energy transfer in these multichromophoric systems has been probed by electronic absorption and luminescence spectroscopy. The switching behavior of photo-induced energy transfer by redox stimuli in the latter triad has been examined. Photophysical and electrochemical analysis indicates that the contribution of the energy transfer from the coumarin chromophores and the Ru(II) center to the Os(II)-centered emission in the 'switch-on state' is estimated to be about 70%. This contribution is larger than that in the previously reported Ru(II)/Os(II) dyad system, which was evaluated to be 40%. Thus, it is concluded that an improved switching of directional energy transfer has been achieved from the coumarin moiety to the Os(II) center in this new triad chromophore system.

Introduction

The development of molecule-based electronic/photonic devices performing processes including electron and energy transfer processes has attracted considerable interest over the past ten years.[1] Switching of these processes in response to external stimuli is required for processing information at the molecular level. Several molecular switches for intramolecular photo/electronic processes have been reported.[2]

We have previously shown that the Ru(II)/Os(II) tpy-type (tpy = 2,2′:6′,2″-terpyridine) heterodinuclear complex bridged by bis[2,6-bis(2-pyridyl)-4-pyridyl]diazene (**azotpy**), $[(tpy)_2Ru(azotpy)Os(tpy)_2]^{4+}$ (**Ru-azo-Os**), serves as a switch for intramolecular energy transfer.[3] When the bridging ligand is neutral, the metal-to-ligand charge-transfer (MLCT) excited state is rapidly deactivated thermally. On the other hand, when the bridging ligand is electrochemically reduced, the photo-excited state behaves more or less like the parent complexes, $[M(tpy)_2]^{2+}$, leading to intramolecular energy transfer.

In the reduced form of this dyad complex, **Ru-azo-Os**, however, the contribution of the light absorption at the Ru(II) center through the energy transfer to the Os(II)-centered emission is estimated to be 40%, and the remaining 60% of luminescence arises from the direct excitation of the Os(II) center. This is due to the fact that the Ru(II) center and the Os(II) center are excited simultaneously because of the spectral overlap of their MLCT bands. The absorption by Os(II) polypyridine complexes covers the whole range of wavelengths at which Ru(II) complexes can absorb. Hence, it is not possible to selectively excite the 'input site' (*i.e.* Ru(II) center) without exciting the 'output site' (*i.e.* Os(II) center) directly. To circumvent this problem and improve the contribution of the energy transfer, we have extended the dyad chromophore system to the triad system by introducing a light harvesting unit. We chose 7-amino-3-trifluoromethyl-coumarin (coumarin 151, **C151**) as the light harvesting unit, because **C151** (1) absorbs light around 390 nm where absorption by Ru(II) and Os(II) polypyridine complexes is relatively weak, (2) emits fluorescence in the wavelength range at which the MLCT band of Ru(II) complexes lies, and (3) has an amino group as a convenient derivatizing point for the synthesis of triad systems. The triad system composed of chromophores with relatively long excited state lifetimes[2c,d,4] will allow long range energy transfer through these chromophores, and various functional groups can be introduced in between these chromophores in order to tune or switch the energy transfer process. Two triad chromophore compounds containing coumarin, Ru(II) and Os(II) terpyridine-type complexes were synthesized. One of the compounds has a phenylene spacer to connect the Ru(II) unit and the Os(II) unit, while the other has an azo moiety. The switching behavior of photo-induced energy transfer by redox stimuli in the latter triad has been examined. A coumarin-Os(II) dyad was also prepared for comparative purposes.

Results

Synthesis

The reaction scheme is illustrated in Fig. 1. The terpyridine ligand having two coumarin chromophores (**$(C151)_2$-tpy**) was obtained in three steps starting with 3,5-bis(bromomethyl)-anisole and **C151** according to the literature procedure by Fréchet *et al.*[5] The Os(II) complex which has directly attached coumarin moieties, **$(C151)_2$-Os**, was prepared from the reaction of **$(C151)_2$-tpy** with $Os(ttpy)Cl_3$ (ttpy = 4′-tolyl-2,2′:6′,2″-terpyridine). The triad complexes were synthesized by the "complexes as metals / complexes as ligands" strategy.[6] The mononuclear Os(II) building blocks, $[Os(ttpy)(tpy\text{-}ph\text{-}tpy)][PF_6]_2$ (tpy-ph-tpy = 4,4‴′-(1,4-phenylene)bis(2,2′:6′,2″-terpyridine)) and $[Os(ttpy)(azotpy)][PF_6]_2$, containing a non-coordinated tpy metal-binding domain were prepared from the reaction of $Os(ttpy)Cl_3$ with tpy-ph-tpy and azotpy, respectively. The dinuclear Os(II) complex, $[(ttpy)Os(tpy\text{-}ph\text{-}tpy)Os(ttpy)][PF_6]_4$ (**Os-ph-Os**) was obtained as a by-product in the former

† Electronic supplementary information (ESI) available: ^{1}H NMR and ES mass spectra of the new dyad and triad coumarin-containing complexes, **$(C151)_2$-Os**, **$(C151)_2$-Ru-ph-Os** and **$(C151)_2$-Ru-azo-Os** and the emission spectra of **$(C151)_2$-tpy** and **$(C151)_2$-Os**. See http://www.rsc.org/suppdata/dt/b2/b212274j/

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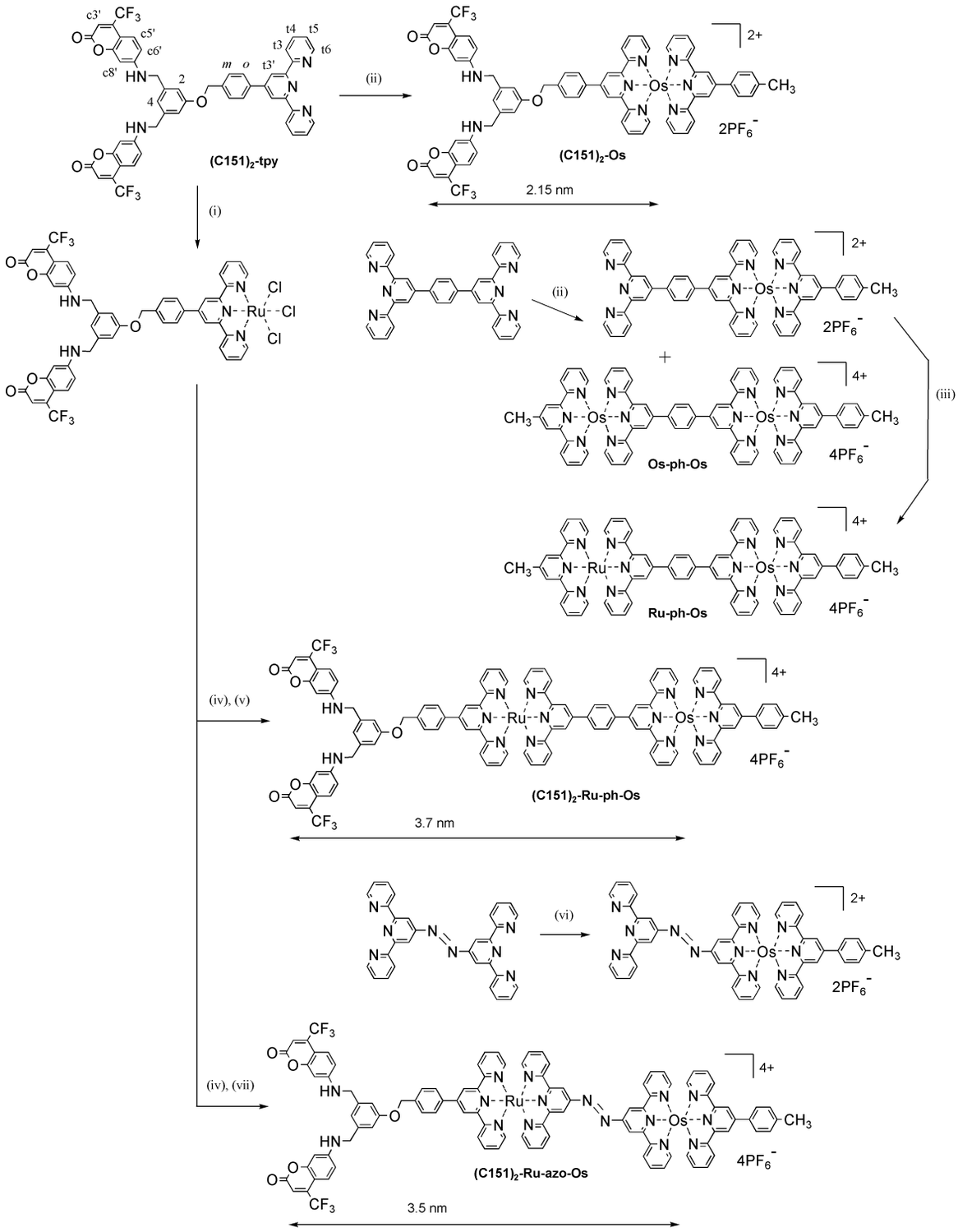

Fig. 1 Synthetic scheme for the preparation of the dyad and triad complexes. (i) $RuCl_3$ hydrate–EtOH, reflux for 3 h; (ii) $Os(ttpy)Cl_3$–ethylene glycol, reflux for 1 h, then NH_4PF_6; (iii) $Ru(ttpy)Cl_3$, *N*-ethylmorpholine–MeOH, reflux for 2 h, then NH_4PF_6; (iv) $AgBF_4$–acetone, reflux for 2 h; (v) $[(tpy\text{-}ph\text{-}tpy)Os(ttpy)][PF_6]_2$–*N,N*-dimethylacetamide, 120 °C for 3 h, then NH_4PF_6; (vi) $Os(ttpy)Cl_3$–ethylene glycol, 160 °C, 30 min, then NH_4PF_6; (vii) $[(azotpy)Os(ttpy)][PF_6]_2$–*N,N*-dimethylacetamide, 120 °C for 2 h, then NH_4PF_6.

reaction. $[Os(ttpy)(tpy\text{-}ph\text{-}tpy)][PF_6]_2$ was reacted with $[((C151)_2\text{-}tpy)Ru(acetone)_3]^{2+}$, prepared by the complexation of **$(C151)_2$-tpy** with $RuCl_3$ followed by substitution reaction of Cl atoms,[7] to yield the triad complex, **$(C151)_2$-Ru-ph-Os**. The reference dyad complex without coumarin chromophore, **Ru-ph-Os**,[8] was synthesized from the reaction of $[Os(ttpy)(tpy\text{-}ph\text{-}tpy)][PF_6]_2$ with $Ru(ttpy)Cl_3$. Finally, the triad complex containing azotpy, **$(C151)_2$-Ru-azo-Os**, was prepared by the reaction of $[Os(ttpy)(azotpy)][PF_6]_2$ with $[((C151)_2\text{-}tpy)Ru(acetone)_3]^{2+}$. Each complex was purified by column chromatography or preparative TLC on silica with CH_3CN/0.4 M aqueous KNO_3 as eluent. Purity of the complexes was carefully confirmed by TLC, and all new compounds were characterized by ^1H NMR spectroscopy and FAB or ES mass spectrometry.†

Absorption and emission spectra

The absorption spectra of the dyad and triad complexes, together with those of the reference compounds (1.00×10^{-5} M) were measured in CH_3CN at 25 °C, and are shown in Fig. 2a–c, and the data are collected in Table 1. The high-intensity absorption band at about 300 nm can be ascribed to

Table 1 Absorption and emission (λ_{ex} = 390 nm) properties at 25 °C in CH_3CN

	Absorption					Emission	
						λ_{max}/nm (rel. int.)	
Compound	λ_{max}/nm ($10^{-4}\varepsilon$/cm^{-1} M^{-1})					Coumarin	Os based
(C151)$_2$-tpy[a]	266 (4.29)	278 (4.29)	390 (3.04)			485 (≡1)	
(C151)$_2$-Os	285 (6.59)	315 (7.27)	378 (3.60)	491 (2.62)	669 (0.68)	460 (0.0054)	738 (2.92)
Os	286 (5.93)	315 (7.30)	491 (2.62)	667 (0.68)			738 (≡1)
(C151)$_2$-Ru-ph-Os	287 (12.25)	311 (15.08)	360 (5.73)	500 (7.30)	670 (0.95)	461 (0.0070)	752 (2.06)
Ru-ph-Os	287 (11.14)	312 (14.41)	500 (6.95)	672 (1.01)			757 (0.96)
Os-ph-Os	288 (10.56)	314 (14.02)	500 (6.38)	673 (1.79)			757 (1.23)
(C151)$_2$-Ru-azo-Os	287 (12.48)	469 (2.19)	625 (4.19)	773 (1.16)			

[a] In DMF.

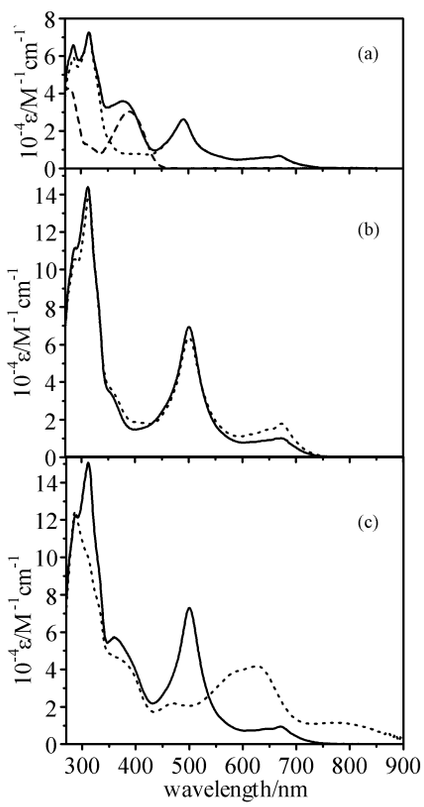

Fig. 2 Absorption spectra of (a) **(C151)$_2$-tpy** (---), **Os** (···) and **(C151)$_2$-Os** (—), (b) **Ru-ph-Os** (—), **Os-ph-Os** (···) and (c) **(C151)$_2$-Ru-ph-Os** (—) and **(C151)$_2$-Ru-azo-Os** (···) in CH_3CN except for **(C151)$_2$-tpy** (in DMF) at 25 °C.

the ligand-centered π–π* transition. A broad band between 420 and 550 nm consists of the spin-allowed MLCT (^{1}MLCT) band. For the Os(II) containing complexes, the spin-forbidden MLCT (^{3}MLCT) band appeared between 550 and 750 nm. In the case of **(C151)$_2$-Ru-azo-Os**, Ru and Os ⟶ ttpy ^{1}MLCT (469 nm) band, a mixture of Ru ⟶ azotpy ^{1}MLCT and Os ⟶ ttpy ^{3}MLCT (625 nm), and Os ⟶ azotpy ^{3}MLCT (773 nm) bands were observed.[3,9] The spectra of the multichromophore compounds match nearly exactly the summation of those of the component chromophore units. This allows us to estimate accurately the amount of light absorbed by each chromophore at a given wavelength.

The emission spectra of the compounds (1.00×10^{-5} M) were measured at 25 °C by excitation at 390 nm, and the data are collected in Table 1.† Emission from the coumarin center appeared at 460–485 nm, while those from the Os(II) center appeared at 738–752 nm in **(C151)$_2$-Os** and **(C151)$_2$-Ru-ph-Os**. However, no emission from the Ru(II) center was observed for these compounds. To enhance the comparison, intensities of the emission from the coumarin and the Os(II) centers are reported in parentheses as relative values to those of **(C151)$_2$-tpy** and **Os**, respectively, under the same conditions. In **(C151)$_2$-Os** and **(C151)$_2$-Ru-ph-Os**, more than 99% of the emission from the coumarin moiety was quenched, suggesting that intramolecular energy transfer takes place very efficiently from the coumarin units to the Os(II) and Ru(II) centers, respectively. The azotpy-containing complex, **(C151)$_2$-Ru-azo-Os**, exhibited no luminescence, suggesting that the coumarin-to-Ru(II) energy transfer efficiency is very high in this compound as well.

Electrochemistry

Cyclic voltammetry of the compounds in *N,N*-dimethylformamide (DMF) was carried out in the range between +1.4 V and −2.1 V *vs.* Fc/Fc$^+$, and the redox potentials are summarized in Table 2. In the positive region, the complexes exhibited reversible one-electron redox peaks due to the Ru^{2+}/Ru^{3+} couple in the range +0.77 to +0.80 V *vs.* Fc/Fc$^+$ and/or reversible one-electron redox peaks due to the Os^{2+}/Os^{3+} couple in the range +0.44 to +0.49 V *vs.* Fc/Fc$^+$.

In the negative region, **(C151)$_2$-Ru-azo-Os** exhibited reversible one-electron reduction couples successively at −0.82 V and −1.19 V *vs.* Fc/Fc$^+$ due to the reduction of the azo group,[3] which were less negative than those of the two-electron reduction due to the ttpy ligands. This provides evidence that the π* level of azotpy is lower in energy than that of ttpy. Thus, it is possible to carry out redox reaction of the azotpy ligand without affecting the ttpy ligands and metal centers.

Spectroelectrochemistry

We carried out spectroelectrochemical measurements in order to study the switching behavior of **(C151)$_2$-Ru-azo-Os**. A solution of the complex (1.00×10^{-5} M) in DMF containing 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) was electrolyzed at a constant potential (−0.95 V *vs*, Fc/Fc$^+$) in a modified 1 × 1 cm^2 quartz cell until the completion of changes in the electronic spectra was attained. The absorption and emission spectra before and after this one-electron reduction of **(C151)$_2$-Ru-azo-Os** are shown in Fig. 3.

Discussion

Energy transfer in the dyad system, (C151)$_2$-Os

In **(C151)$_2$-tpy**, the absorption band due to the coumarin moiety appears at 390 nm (ε = 30400 M^{-1} cm^{-1}), where Ru(II)/Os(II) complexes have only a small absorption. Therefore, good coumarin-selective excitation in this wavelength region can be achieved. The molar extinction coefficients at 390 nm increase from 7800 M^{-1} cm^{-1}, 15400 M^{-1} cm^{-1} and 12600 M^{-1} cm^{-1} for the complexes having no coumarin moieties, **Os**, **Ru-ph-Os** and **Ru-azo-Os**,[3] respectively, to 34100 M^{-1} cm^{-1}, 45600 M^{-1} cm^{-1} and 41800 M^{-1} cm^{-1} for the complexes containing coumarin

Table 2 Redox potentials (V *vs.* Fc/Fc^+)

Compound	Other reductions		azotpy$^{1-/2-}$	azotpy$^{0/1-}$	$Os^{3+/2+}$	$Ru^{3+/2+}$
$(C151)_2$-tpy	−2.00[a]					
$(C151)_2$-Os	−1.89	−1.61			0.45	
$(C151)_2$-Ru-ph-Os	−1.88[b]	−1.60[b]			0.44	0.77
$(C151)_2$-Ru-azo-Os	−1.91[b]		−1.19	−0.82	0.49	0.80

[a] Peak potential of the reduction wave. [b] Two electron reduction.

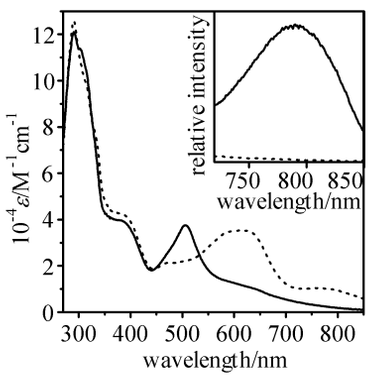

Fig. 3 Absorption spectral change of **$(C151)_2$-Ru-azo-Os** in DMF containing 0.1 M Bu_4NPF_6 before (···) and after (—) reduction at 25 °C. The inset shows the corresponding emission spectral change. λ_{ex} = 390 nm.

units, **$(C151)_2$-Os**, **$(C151)_2$-Ru-ph-Os** and **$(C151)_2$-Ru-azo-Os**, respectively. Thus, the coumarin chromophores are estimated to account for 77, 66 and 70% of the light absorbed at 390 nm in **$(C151)_2$-Os**, **$(C151)_2$-Ru-ph-Os** and **$(C151)_2$-Ru-azo-Os**, respectively, confirming that the coumarin-based absorptions are largely responsible at 390 nm in all the complexes having the coumarin moieties. Another advantage of using **C151** as the light input site is manifested in the fact that **$(C151)_2$-tpy** shows a strong coumarin-based emission band peaked at 485 nm, † which overlaps effectively with the absorption band of the Ru(II)/Os(II) polypyridine complexes, enabling efficient energy transfer to these metal complexes.

The emission intensity from the coumarin moiety in **$(C151)_2$-Os** upon excitation at 390 nm is greatly decreased by the presence of the Os(II) unit, which is only 0.5% of **$(C151)_2$-tpy**. Assuming that the fluorescence quenching is due to the intramolecular energy transfer from the coumarin units to the Os(II) center (the distance between two units was estimated to be 2.15 nm by molecular mechanics calculation[10]), the energy transfer efficiency is estimated to be 99.5%. Though the lifetimes of related coumarin-based emissions are known to be of the order of ns,[11] those in this coumarin-containing complexes were too fast[11b,c] to be measured with our instruments.[2l,12] Therefore, photophysical processes within these complexes have been analyzed by comparison with the reference complexes. To estimate the contribution of light absorption at the coumarin units to the Os(II)-centered emission, excitation spectra of **$(C151)_2$-Os** and **Os** were compared (Fig. 4a). The emission was monitored at 740 nm, which is the maximum wavelength of the Os(II)-based emission, and the spectra are normalized at the 660 nm peak, at which only the Os(II)-based component is excited. Except for the range between 350 and 450 nm where the absorption band of **C151** lies, the excitation spectra of the two compounds agreed well with each other. The intensity of **$(C151)_2$-Os** was 3.45 times higher than that of **Os** at 390 nm, indicating that the light absorbed by the coumarin units is 2.45 times higher than that of the Os(II) unit, and accounts for 71% of the Os(II)-centered emission in **$(C151)_2$-Os**. As the absorbance at 390 nm of the coumarin units is 3.37 times larger than that of the Os(II) unit in **$(C151)_2$-Os**, the efficiency of excitation transfer from the coumarin center to the Os(II) center is determined as 73%. The

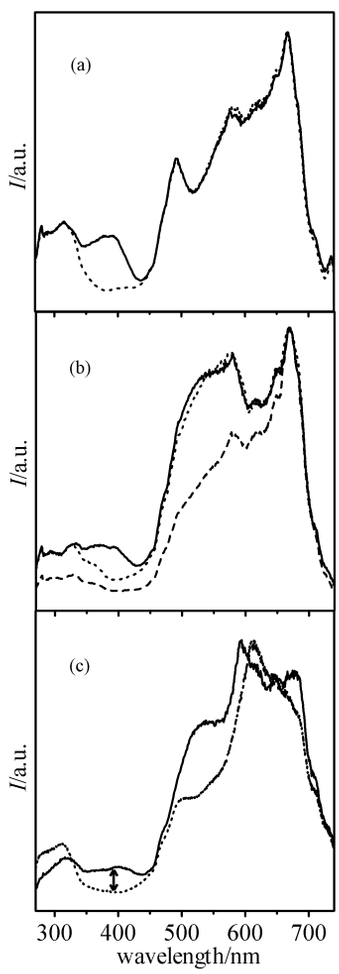

Fig. 4 Excitation spectra for (a) **$(C151)_2$-Os** (—) and **Os** (···), monitored at 740 nm in CH_3CN at 25 °C, the intensity is normalized at 660 nm where only the Os(II)-based unit is excited, (b) **$(C151)_2$-Ru-ph-Os** monitored at 750 nm (—), **Ru-ph-Os** monitored at 756 nm (···) and **Os-ph-Os** monitored at 756 nm (---) in CH_3CN at 25 °C, the intensity is normalized at 660 nm where only the Os(II)-based unit is excited and (c) the reduced **$(C151)_2$-Ru-azo-Os** (—) and **Ru-azo-Os** (···) containing 0.1 M Bu_4NPF_6 (**($(C151)_2$-Ru-azo-Os)** or Bu_4NClO_4 (**Ru-azo-Os**), monitored at 790 (**($(C151)_2$-Ru-azo-Os)** or 775 (**Ru-azo-Os**) nm in DMF at 25 °C, the intensity is normalized at the respective peaks around 600 nm where only the Os(II)-based unit is excited.

efficiency obtained by this method is smaller than that suggested from the quenching of the donor emission (>99%, *vide supra*). This apparent discrepancy can be explained by considering that the factors causing the quenching of the donor emission should include non-radiative excited-energy dissipation through the Os(II) complex moiety, in addition to the excitation transfer to the Os(II) center.[13]

Energy transfer in the triad system, $(C151)_2$-Ru-ph-Os

Photophysical properties of **$(C151)_2$-Ru-ph-Os** were analyzed similarly by comparing with those of **$(C151)_2$-tpy**, **Ru-ph-Os** and **Os-ph-Os**. In **$(C151)_2$-Ru-ph-Os**, more than 99% of the emission from the coumarin moiety was quenched, suggesting

that the energy transfer efficiency from the coumarin center is very high. The excitation spectra of **$(C151)_2$-Ru-ph-Os**, **Ru-ph-Os** and **Os-ph-Os** normalized at the 660 nm peak are shown in Fig. 4b. From the height of these spectra at 390 nm, the relative contributions of the coumarin units, the Ru(II) center and the Os(II) center to the Os(II)-centered emission are similarly estimated to be 51 (1.62), 18 (0.56) and 31% (≡1), respectively (relative values are shown in parentheses). Therefore, approximately 70% of the Os(II)-centered emission originates from the excitation of the coumarin and/or the Ru(II) center and subsequent energy transfer. From the absorbance at 390 nm of **Ru-ph-Os** (ε = 15400 M^{-1} cm^{-1}) and **Os-ph-Os** (ε = 19700 M^{-1} cm^{-1}, or 9850 M^{-1} cm^{-1} per Os(II) unit), the absorbance of **$(C151)_2$-Ru-ph-Os** is the sum of the contributions of the coumarin units, the Ru(II) center and the Os(II) center in proportions of 66 (3.03), 12 (0.56) and 22% (≡1), respectively. Thus, the energy transfer efficiencies from the coumarin moiety and the Ru(II) center to the Os(II) center in **$(C151)_2$-Ru-ph-Os** are estimated to be 54 and 100%, respectively. The distance from the coumarin moiety to the Os(II) center in this triad system was estimated to be 3.7 nm by molecular mechanics calculation.[10] The estimated energy transfer efficiency from the coumarin units to the Os(II) center is comparable to that of the Ru(II)/Os(II) dyad system having the same distance connected by the all-conjugated oligophenylene spacer.[14]

Switching of energy transfer in triad system, $(C151)_2$-Ru-azo-Os

The one-electron reduction of the azotpy bridging ligand in **$(C151)_2$-Ru-azo-Os** caused a decrease in absorption of the longer wavelength band and an increase in the shorter wavelength one as shown in Fig. 3. The change in the absorption spectrum can be explained by assuming that the reduction of azotpy in **$(C151)_2$-Ru-azo-Os** makes the π* level of azotpy higher in energy, at least up to that of ttpy.[3] It is noted that the absorbance of 390 nm in the reduced form (ε = 38700 M^{-1} cm^{-1}) is almost the same as that in the neutral form, and the coumarin chromophores account for 79% of the light absorbed at this wavelength, taking into consideration that the molar extinction coefficient of **$(C151)_2$-tpy** at 390 nm is 30400 M^{-1} cm^{-1}. Thus, this system is an improvement from the previously reported **Ru-azo-Os**[3] in terms of input selectivity for the attainment of directional photophysical processes in molecular systems. The reduced form exhibited the Os(II)-based emission at 790 nm by the excitation at 390 nm, whereas the neutral form showed no emission (Fig. 3, inset). Upon reoxidation, the absorption and emission spectra of the reduced form of this complex nearly returned to the original shapes, although the repetition of this redox cycle resulted in some deterioration of response (the absorbance at 600 nm recovered to 64% of the original value after three cycles).

In order to evaluate the contribution of the energy transfer from the coumarin moieties and the Ru(II) center to the Os(II)-centered emission in the reduced form, we compared the excitation spectra for the reduced forms of **Ru-azo-Os** and **$(C151)_2$-Ru-azo-Os** (Fig. 4c). The emission was monitored at the maximum wavelength of the Os(II)-based emission, 775 nm for **Ru-azo-Os** and 790 nm for **$(C151)_2$-Ru-azo-Os**. The spectra are also normalized at their respective peaks around 600 nm. It is noted that these spectra differ at wavelengths longer than 450 nm. This is due to the fact that **Ru-azo-Os** has tpy ligands while **$(C151)_2$-Ru-azo-Os** has a ttpy ligand with an additional phenyl substituent at the 4′-position of tpy. Another difference observed in the excitation spectra of the reduced forms of **$(C151)_2$-Ru-azo-Os** and **Ru-azo-Os** in the range 350 nm to 450 nm is, on the other hand, due to the presence of the coumarin units in the former complex. As indicated by the arrow in the figure, the increased intensity of the Os(II)-based emission in the reduced form of **$(C151)_2$-Ru-azo-Os**, when excited at 390 nm comes from the excitation of the coumarin moiety through intramolecular energy transfer, which comprises 56% of the Os(II)-centered emission. In **Ru-azo-Os**, 40% of the Os(II)-centered emission was shown to originate from the excitation of the Ru(II) center and subsequent energy transfer.[3] Therefore, absorption at the Ru(II) center is responsible for approximately 18% of the Os(II)-centered emission in **$(C151)_2$-Ru-azo-Os**. Thus, it is estimated that the energy transfer from the coumarin units and the Ru(II) center through the reduced azo group accounts for 74%, or roughly 70% of the Os(II)-centered emission. This contribution of energy transfer is nearly matched in the case of phenylene-bridged triad system, **$(C151)_2$-Ru-ph-Os**. This *directional* energy transfer process is switched on and off by the redox reaction of the azo group, as schematically shown in Fig. 5.

Conclusion

In conclusion, we have examined energy transfer processes in the new dyad, **$(C151)_2$-Os**, and the triads, **$(C151)_2$-Ru-ph-Os** and **$(C151)_2$-Ru-azo-Os**, focusing mainly on the contribution of the input chromophores to achieve truly directional processes. The latter triad compound, **$(C151)_2$-Ru-azo-Os**, is an improvement from the previously reported molecular energy transfer switch, **Ru-azo-Os**, in terms of this directionality. The contribution of the coumarin moieties and the Ru(II) center to the Os(II)-centered emission is increased, by introducing the chromophores, which absorb light in a wavelength range in which Ru(II)/Os(II) complexes show only a small absorption, into the **Ru-azo-Os** dyad, and extending to the triad chromophore system, **$(C151)_2$-Ru-azo-Os**. In this study, the energy transfer among three chromophores separated by a distance of 3.5 nm has been switched, demonstrating a way toward the realization of more elaborate multichromophore systems in which various functional groups, which are responsive to external stimuli, are introduced between chromophores.

Experimental

General methods

DMF used on photopysical and electorochemical studies was distilled over P_2O_5. CH_3CN used for spectral measurements was of spectrophotometric grade from DOJIN Chem. Co. and used as received. The ^1H NMR spectra were recorded on a JEOL JNM-LA400 spectrometer in $CDCl_3$, CD_3COCD_3 or CD_3CN. Mass spectra were recorded on a JEOL JMS-600H spectrometer equipped with MS-ESIP09 for ES-MS. Elemental analyses were carried out on FISONS Instruments EA1108 Elemental Analyzer. Absorption and emission spectra were measured with a Shimadzu UV-2500PC spectrophotometer and Shimadzu RF-5300PC spectrofluorophotometer, respectively. Emission spectra were measured in N_2-purged solutions. Cyclic voltammetry was conducted in N_2-purged DMF containing 0.1 M Bu_4NPF_6 as supporting electrolyte with a BAS Electrochemical Analyser Model 720 A. A platinum disk was used as the working electrode, a Ag/Ag^+ electrode as the reference and a Pt wire as the counter electrode. All redox waves were referenced to internal ferrocene added at the end of each experiment. Redox potentials are quoted *vs.* the ferrocene/ferrocenium couple (Fc/Fc^+ = 0.0 V). Spectroelectrochemical experiments were performed on 1.00×10^{-5} M samples in N_2-purged DMF containing 0.1 M Bu_4NPF_6 in a spectrofluorimetric cell (optical path 1 cm), with a Pt mesh, a Ag/Ag^+ and a Pt wire separated with absorbent cotton, as the working, reference and counter electrodes, respectively.

Synthesis

All reactions were performed under an N_2 atmosphere. Solvents and reagents were of reagent grade quality and used as received

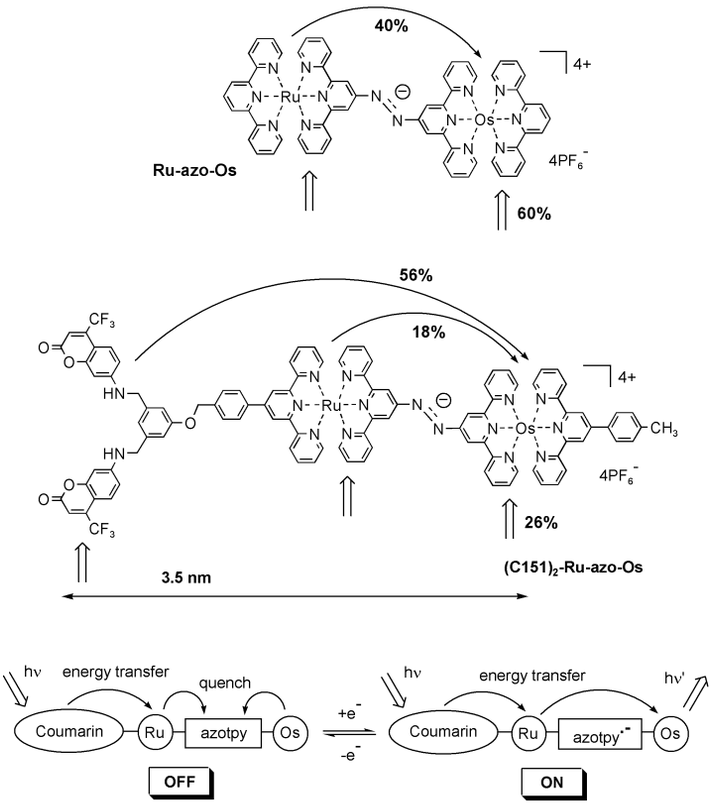

Fig. 5 Schematic illustration of the energy transfer switching in **$(C151)_2$-Ru-azo-Os**. The percentage numbers indicate the proportion of light absorbed by each chromophore that contributes to the emission from the Os(II) unit in the reduced species.

unless otherwise specified. CH_2Cl_2 and CH_3CN were distilled over P_2O_5, and tetrahydrofuran (THF) over Na wire, immediately before use. Potassium carbonate was ground and dried *in vacuo* at 70 °C overnight before use. 3,5-Bis(bromomethyl)-anisole,[5] 4′-(*para*-bromomethylphenyl)-2,2′:6′,2″-terpyridine,[15] $[Os(ttpy)_2][PF_6]_2$ (**Os**),[15] $Ru(ttpy)Cl_3$,[15] $Os(ttpy)Cl_3$[16] and **azotpy**[3] were prepared according to the literature procedures.

3,5-Bis(*N*-(3-trifluoromethyl-7-aminocoumarin)methyl)-anisole. A solution of 3,5-bis(bromomethyl)anisole (270 mg, 0.92 mmol) in dry CH_3CN (7 mL) was added to a mixture of 7-amino-3-trifluoromethylcoumarin (coumarin 151) (630 mg, 2.75 mmol, 3 equiv.) and potassium carbonate (760 mg, 5.5 mmol, 6 equiv.) in dry CH_3CN (50 mL) dropwise over 2 h at 50 °C, and this mixture was refluxed for 4 days. The reaction mixture was cooled to room temperature and filtered. The filtrate was evaporated and the residue was dried *in vacuo* to give a yellowish-brown powder (752 mg). The crude product was purified by column chromatography on silica with CH_2Cl_2–$CHCl_3$ (1 : 1) as eluent. The first major fraction was unreacted coumarin 151 (335 mg), and the second major fraction was collected to give the desired compound as a pale yellow powder (123 mg, 23%). Mp 249.0–249.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 7.47 (dd, J = 9.0, 2.0 Hz, 2H, H-5′), 6.89 (s, 1H, H-4), 6.81 (s, 2H, H-2), 6.59 (dd, J = 9.0, 2.4 Hz, 2H, H-6′), 6.46 (d, J = 2.4 Hz, 2H, H-8′), 6.44 (s, 2H, H-3′), 4.86 (t, J = 5.4 Hz, 2H, NH), 4.40 (d, J = 5.4 Hz, 4H, CH_2), 3.80 (s, 3H, OCH_3); FAB-MS m/z = 591 $[M + H]^+$; Elemental analysis calcd. (%) for $C_{29}H_{20}F_6N_2O_5$: C, 58.99; H, 3.41; N, 4.74; found: C, 58.66; H, 3.47; N, 4.46.

3,5-Bis(*N*-(3-trifluoromethyl-7-aminocoumarin)methyl)-phenol. To a solution of 3,5-bis(*N*-(3-trifluoromethyl-7-aminocoumarin)methyl)anisole (110 mg, 0.19 mmol) in dry CH_2Cl_2 (300 mL) was added a solution of BBr_3 in CH_2Cl_2 (1.0 M, 2 mL, 2 mmol, 11 equiv.) dropwise for 10 min at room temperature. The solution initially turned to pale orange, and then a dense orange precipitate appeared as the color of the solution turned dense. After stirring for 3 h at room temperature, H_2O (100 mL) was added to this solution. The pale yellow organic phase was extracted, and washed with saturated $NaHCO_3$ aq. (100 mL) and H_2O (100 mL), and evaporated to dryness to yield a yellow viscous solid (134 mg) which was recrystallized from ethyl acetate (*ca*. 2 mL) to give a yellowish-orange microcrystalline solid (82 mg, 76%). Mp 259.6–260.7 °C; ^{1}H NMR (400 MHz, CD_3COCD_3, 20 °C): δ = 8.51 (s, 1H, OH), 7.42 (dd, J = 9.0, 2.0 Hz, 2H, H-5′), 6.97 (s, 1H, H-4), 6.88 (t, J = 5.4 Hz, 2H, NH), 6.78–6.81 (overlapping dd, 2H, H-6′ + s, 2H, H-2, J = 9.0, 2.4 Hz), 6.51 (d, J = 2.4 Hz, 2H, H-8′), 6.38 (s, 2H, H-3′), 4.44 (d, J = 5.4 Hz, 4H, CH_2); FAB-MS m/z = 577 $[M + H]^+$; Elemental analysis calcd. (%) for $C_{28}H_{18}F_6N_2O_5$: C, 58.34; H, 3.15; N, 4.86; found: C, 58.09; H, 3.34; N, 4.97.

4′-(4-(3,5-Bis(*N*-(3-trifluoromethyl-7-aminocoumarin)-methyl)phenoxymethyl)phenyl)-2,2′:6′,2″-terpyridine ($(C151)_2$-tpy). A mixture of 4′-(*para*-bromomethylphenyl)-2,2′:6′,2″-terpyridine (33 mg, 0.082 mmol), 3,5-bis(*N*-(3-trifluoromethyl-7-aminocoumarin)methyl)phenol (56 mg, 0.097 mmol, 1.2 equiv.), potassium carbonate (70 mg, 0.51 mmol, 6 equiv.) and 18-crown-6 (9 mg, 0.034 mmol, 0.4 equiv.) in dry THF (10 mL) was refluxed for 2 days. The reaction mixture was cooled to room temperature and filtered. The filtrate was evaporated and dried *in vacuo* to give a yellowish-brown viscous solid (124 mg). This solid was dissolved in $CHCl_3$ (30 mL) and the solution was washed with brine (3 × 20 mL) and dried over Na_2SO_4. The solvent was evaporated to give a yellowish-orange viscous solid, which solidified after standing for several hours and dried *in vacuo* overnight at 70 °C (70 mg, 95%). Mp 262.1–263.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 8.74 (d, J = 7.6 Hz, 2H, H-t6), 8.72 (s, 2H, H-t3′), 8.68 (d, J = 7.6 Hz, 2H, H-t3), 7.88–7.92 (overlapping d, 2H, H-*o* + t, 2H, H-t4, J = 8.0, 7.6 Hz), 7.52 (d, J = 8.0 Hz, 2H, H-*m*), 7.46 (dd, J = 9.0, 2.0 Hz, 2H, H-c5′), 7.37 (t, J = 7.6 Hz, 2H, H-t5), 6.90–6.92 (overlapping s, 1H, H-4 + s, 2H, H-2), 6.60 (dd, J = 9.0, 2.4 Hz, 2H, H-c6′), 6.47 (d, J = 2.4 Hz, 2H, H-8′), 6.42 (s, 2H, H-3′), 5.13 (s, 2H, O–CH_2), 4.91 (t, J = 5.4 Hz, 2H, NH), 4.40 (d, J = 5.4 Hz, 4H,

N–CH_2); FAB-MS *m*/*z* = 898 $[M + H]^+$; Elemental analysis calcd. (%) for $C_{50}H_{33}F_6N_5O_5$: C, 66.89; H, 3.70; N, 7.80; found: C, 66.63; H, 3.92; N, 7.60.

(Ru((C151)$_2$-tpy))Cl$_3$. A mixture of **(C151)$_2$-tpy** (40 mg, 0.045 mmol) and ruthenium trichloride hydrate (12 mg, 0.046 mmol) in EtOH (10 mL) was refluxed for 3 h. The reaction mixture was cooled to room temperature to give a brown precipitate which was filtered from the yellowish-brown solution. The residue was washed with EtOH and diethyl ether, and dried *in vacuo* to give a brown powder (42 mg, 85%). FAB-MS *m*/*z* = 1070 $[M - Cl]^+$, 1034 $[M - 2Cl]^+$, 899 $[M - (RuCl_3) + H]^+$.

[((C151)$_2$-tpy)Os(ttpy)][PF$_6$]$_2$ ((C151)$_2$-Os). A solution of **(C151)$_2$-tpy** (30 mg, 0.033 mmol) and Os(ttpy)Cl_3 (21 mg, 0.034 mmol) in ethylene glycol (10 mL) was stirred at reflux for 1 h. The reaction mixture was cooled to room temperature, to which excess aqueous NH_4PF_6 (150 mg) was added. The precipitate was collected by filtration on Celite, washed with water and diethyl ether, and re-dissolved in CH_3CN. The filtrate was evaporated and the residue was dried *in vacuo* to give a dark brown powder (51 mg). The crude product was purified by column chromatography on silica with CH_3CN–0.4 M aqueous KNO_3 (100 : 1) to give a dark brown powder (11 mg, 19%). R_f (Silica) = 0.31: CH_3CN–0.4 M aqueous KNO_3 (19:1); 0.92: NH_4PF_6 (4 mg)–CH_3CN (1 mL); Mp > 375 °C; ^{1}H NMR (400 MHz, CD_3CN, 20 °C): δ = 9.03 (s, 2H), 9.00 (s, 2H), 8.63 (d, *J* = 8.3 Hz, 4H), 8.10 (d, *J* = 8.1 Hz, 2H), 8.08 (d, *J* = 8.1 Hz, 2H), 7.80 (dt, *J* = 8.1, 1.5 Hz, 4H), 7.72 (d, *J* = 8.1 Hz, 2H), 7.59 (d, *J* = 8.1 Hz, 2H), 7.43 (dd, *J* = 9.0, 2.0 Hz, 2H), 7.33 (d, *J* = 4.9 Hz, 2H), 7.32 (d, *J* = 4.9 Hz, 2H), 7.12 (d, *J* = 6.1 Hz, 2H), 7.09 (d, *J* = 5.9 Hz, 2H), 7.01 (s, 1H), 6.98 (s, 2H), 6.70 (dd, *J* = 9.0, 2.4 Hz, 2H), 6.41 (d, *J* = 2.4 Hz, 2H), 6.33 (s, 2H), 6.13 (t, *J* = 6.1 Hz, 2H), 5.31 (s, 2H), 4.42 (d, *J* = 6.1 Hz, 4H), 2.57 (s, 3H); ES-MS *m*/*z* = 1556 $[M - PF_6]^+$, 706 $[M - 2PF_6]^{2+}$.

[(tpy-ph-tpy)Os(ttpy)][PF$_6$]$_2$. A solution of tpy-ph-tpy (436 mg, 0.81 mmol, 2 equiv.) and Os(ttpy)Cl_3 (250 mg, 0.403 mmol) in ethylene glycol (40 mL) was stirred at reflux for 1 h. The reaction mixture was cooled to room temperature, to which excess aqueous NH_4PF_6 (1000 mg) was added. The precipitate was collected by filtration on Celite, washed with water and diethyl ether, and re-dissolved with CH_3CN. The filtrate was evaporated and the residue was dried *in vacuo* to give a dense purple powder (469 mg). A portion of this crude product (200 mg) was purified by column chromatography on silica with CH_3CN–0.4 M aqueous KNO_3 (initially 10 : 1) to give a brown-purple powder (70 mg, 30%), which was characterized as [(tpy-ph-tpy)Os(ttpy)][PF$_6$]$_2$. Mp > 375 °C; ^{1}H NMR (400 MHz, CD_3CN, 20 °C): δ = 9.11 (s, 2H), 9.03 (s, 2H), 8.93 (s, 2H), 8.79 (dd, *J* = 4.7, 1.9 Hz, 2H), 8.76 (d, *J* = 8.1 Hz, 2H), 8.67 (d, *J* = 8.1 Hz, 2H), 8.63 (d, *J* = 8.3 Hz, 2H), 8.39 (d, *J* = 8.3 Hz, 2H), 8.30 (d, *J* = 8.3 Hz, 2H), 8.08 (d, *J* = 8.1 Hz, 2H), 8.03 (dt, *J* = 7.8, 2.0, 1.7 Hz, 2H), 7.83 (dt, *J* = 7.6, 1.2 Hz, 2H), 7.81 (dt, *J* = 7.8, 1.5 Hz, 2H), 7.59 (d, *J* = 7.8 Hz, 2H), 7.52 (dt, *J* = 5.9, 1.2 Hz, 2H), 7.33 (d, *J* = 5,6 Hz, 4H), 7.14 (dt, *J* = 5.9, 1.5, 1.2 Hz, 2H), 7.12 (dt, *J* = 5.9, 1.5, 1.2 Hz, 2H), 2.58 (s, 3H); ES-MS *m*/*z* = 1200 $[M - PF_6]^+$.

Then eluent was changed to CH_3CN–0.4 M aqueous KNO_3 (8 : 1 to 5 : 1) to give a dense purple powder (51 mg, 22%), which was characterized as [(ttpy)Os(tpy-ph-tpy)Os(ttpy)]-[PF$_6$]$_4$ (**Os-ph-Os**). R_f (Silica) = 0.45: CH_3CN–0.4 M aqueous KNO_3 (5 : 1); Mp > 375 °C; ^{1}H NMR (400 MHz, CD_3CN, 20 °C): δ = 9.19 (s, 4H), 9.06 (s, 4H), 8.74 (d, *J* = 8.3 Hz, 4H), 8.66 (d, *J* = 8.3 Hz, 4H), 8.57 (d, *J* = 8.1 Hz, 4H), 8.10 (d, *J* = 8.1 Hz, 4H), 7.87 (dt, *J* = 8.1, 7.8, 1.5 Hz, 4H), 7.84 (dt, *J* = 8.1, 7.8, 1.2 Hz, 4H), 7.60 (d, *J* = 8.1 Hz, 4H), 7.37 (d, *J* = 5.9 Hz, 4H), 7.35 (d, *J* = 5.9 Hz, 4H), 7.17 (dt, *J* = 6.5, 1.2 Hz, 4H), 7.15 (dt, *J* = 7.3, 1.2 Hz, 4H), 2.59 (s, 6H); ES-MS *m*/*z* = 2001 $[M - PF_6]^+$, 929 $[M - 2PF_6]^{2+}$.

[(ttpy)Ru(tpy-ph-tpy)Os(ttpy)][PF$_6$]$_4$ (Ru-ph-Os). A solution of [(tpy-ph-tpy)Os(ttpy)][PF$_6$]$_2$ (50 mg, 0.037 mmol) and Ru(ttpy)Cl_3 (20 mg, 0.038 mmol) in MeOH (20 mL) with 6 drops of *N*-ethylmorpholine was stirred at reflux for 2 h. The reaction mixture was cooled to room temperature, and filtered through Celite to remove unreacted Ru(ttpy)Cl_3. To the filtrate, excess aqueous NH_4PF_6 (200 mg) was added. The precipitate was collected by filtration on Celite, washed with water and diethyl ether, and re-dissolved in CH_3CN. The filtrate was evaporated and the residue was dried *in vacuo* to give a reddish-purple powder (66 mg). The crude product was purified by preparative TLC on silica with CH_3CN–0.4 M aqueous KNO_3 (5 : 1) to give a reddish-purple powder (6.5 mg, 8.5%). R_f (Silica) = 0.50: CH_3CN–0.4 M aqueous KNO_3 (5 : 1); Mp > 375 °C; ^{1}H NMR (400 MHz, CD_3CN, 20 °C): δ = 9.19 (s, 2H), 9.17 (s, 2H), 9.06 (s, 2H), 9.03 (s, 2H), 8.75 (d, *J* = 8.1 Hz, 2H), 8.73 (d, *J* = 8.1 Hz, 2H), 8.68 (d, *J* = 8.8 Hz, 2H), 8.65 (d, *J* = 8.8 Hz, 2H), 8.59 (d, *J* = 3.4 Hz, 2H), 8.57 (d, *J* = 3.7 Hz, 2H), 8.14(d, *J* = 8.1 Hz, 2H), 8.10 (d, *J* = 8.1 Hz, 2H), 8.01 (dt, *J* = 8.1, 7.8, 1.5, 1.2 Hz, 2H), 7.98 (dt, *J* = 8.1, 7.8, 1.5, 1.2 Hz, 2H), 7.87 (dt, *J* = 8.1, 7.8, 1.5, 1.2 Hz, 2H), 7.84 (dt, *J* = 8.1, 7.8, 1.5, 1.2 Hz, 2H), 7.60 (d, *J* = 8.1 Hz, 4H), 7.49 (d, *J* = 4.6 Hz, 2H), 7.48 (d, *J* = 4.2 Hz, 2H), 7.37 (d, *J* = 5.9 Hz, 2H), 7.35 (d, *J* = 6.6 Hz, 2H), 7.24 (dt, *J* = 5.9, 5.6, 1.2 Hz, 2H), 7.22 (dt, *J* = 5.9, 1.2 Hz, 2H), 7.17 (dt, *J* = 7.6, 1.2 Hz, 2H), 7.15 (dt, *J* = 7.6, 1.2 Hz, 2H), 2.59 (s, 3H), 2.56 (s, 3H); ES-MS *m*/*z* = 1913 $[M - PF_6]^+$, 884 $[M - 2PF_6]^{2+}$.

[((C151)$_2$-tpy)Ru(tpy-ph-tpy)Os(ttpy)][PF$_6$]$_4$ ((C151)$_2$-Ru-ph-Os). A solution of (Ru((C151)$_2$-tpy))Cl_3 (22 mg, 0.020 mmol) and $AgBF_4$ (12 mg, 0.062 mmol, 3 equiv.) in acetone (5 mL) was heated at reflux in air for 2 h. The reddish-brown reaction mixture was cooled to room temperature and filtered to remove AgCl. The filtrate was evaporated and *N,N*-dimethylacetamide (3 mL) was added to the resulting residue. This solution was added to a solution of [(tpy-ph-tpy)Os(ttpy)][PF$_6$]$_2$ (27 mg, 0.020 mmol) in *N,N*-dimethylacetamide (3 mL) and this mixed solution was heated at 120 °C under N_2 for 3 h. The reaction mixture was cooled to room temperature and filtered through Celite, and the filtrate was evaporated and the residue dried. The resulting solid was dissolved in a minimum amount of CH_3CN and excess aqueous NH_4PF_6 (150 mg) was added. The precipitate was collected by filtration, washed with water and diethyl ether, and the reddish-brown powder (50 mg) was purified by chromatography on silica with CH_3CN–0.4 M aqueous KNO_3 (initially 20 : 1) as eluent to give a reddish-brown powder (10 mg, 19%), which was characterized as **(C151)$_2$-Ru-ph-Os**. R_f (Silica) = 0.63: CH_3CN–0.4 M aqueous KNO_3 (5 : 1); 0.35: NH_4PF_6 (4 mg)–CH_3CN (1 mL); Mp > 375 °C; ^{1}H NMR (400 MHz, CD_3CN, 20 °C): δ = 9.21 (s, 2H), 9.19 (s, 2H), 9.06 (s, 2H), 9.02 (s, 2H), 8.77 (d, *J* = 8.5 Hz, 2H), 8.75 (d, *J* = 8.5 Hz, 2H), 8.68 (d, *J* = 8.1 Hz, 2H), 8.66 (d, *J* = 8.8 Hz, 2H), 8.61 (d, *J* = 8.4 Hz, 2H), 8.57 (d, *J* = 8.4 Hz, 2H), 8.16 (d, *J* = 8.1 Hz, 2H), 8.10 (d, *J* = 8.1 Hz, 2H), 8.02 (t, *J* = 7.8 Hz, 2H), 7.98 (t, *J* = 8.1 Hz, 2H), 7.88 (t, *J* = 8.4 Hz, 2H), 7.84 (t, *J* = 7.8 Hz, 2H), 7.74 (d, *J* = 8.1 Hz, 2H), 7.60 (d, *J* = 8.1 Hz, 2H), 7.52 (d, *J* = 5.4 Hz, 2H), 7.51 (d, *J* = 5.6 Hz, 2H), 7.44 (dd, *J* = 9.0, 2.0 Hz, 2H), 7.37 (d, *J* = 5.9 Hz, 2H), 7.36 (d, *J* = 5.6 Hz, 2H), 7.24 (t, *J* = 6.1, 5.9 Hz, 4H), 7.17 (t, *J* = 6.5 Hz, 2H), 7.15 (t, *J* = 6.1 Hz, 2H), 7.02 (s, 1H), 6.99 (s, 2H), 6.71 (dd, *J* = 9.0, 2.4 Hz, 2H), 6.42 (d, *J* = 2.4 Hz, 2H), 6.35 (s, 2H), 6.15 (t, *J* = 6.1 Hz, 2H), 5.31 (s, 2H), 4.43 (d, *J* = 6.1 Hz, 4H), 2.59 (s, 3H); ES-MS *m*/*z* = 2487 $[M - PF_6]^+$, 1172 $[M - 2PF_6]^{2+}$, 732 $[M - 3PF_6]^{3+}$.

Then eluent was changed to CH_3CN–0.4 M aqueous KNO_3 (10 : 1) to give a brown-purple powder (1.3 mg, 2.5%), which was characterized as [(ttpy)Os(tpy-ph-tpy)Ru(tpy-ph-tpy)-Os(ttpy)]$^{6+}$. R_f (Silica) = 0.51: CH_3CN–0.4 M aqueous KNO_3 (5 : 1); Mp > 375 °C; ^{1}H NMR (400 MHz, CD_3CN, 20 °C): δ = 9.22 (s, 4H), 9.21 (s, 4H), 9.06 (s, 4H), 8.80 (d, *J* = 8.1 Hz, 4H),

8.75 (d, J = 8.1 Hz, 4H), 8.66 (d, J = 8.1 Hz, 4H), 8.63 (d, J = 8.8 Hz, 4H), 8.61 (d, J = 8.5 Hz, 4H), 8.10 (d, J = 8.1 Hz, 4H), 8.05 (dt, J = 8.1, 7.8, 1.5, 1.2 Hz, 4H), 7.88 (dt, J = 8.3, 7.8, 1.5, 1.2 Hz, 4H), 7.84 (dt, J = 8.3, 8.1, 1.5, 1.2 Hz, 4H), 7.61 (d, J = 7.8 Hz, 4H), 7.55 (d, J = 8.1 Hz, 4H), 7.37 (d, J = 6.4 Hz, 4H), 7.36 (d, J = 6.6 Hz, 4H), 7.28 (dt, J = 7.6, 1.2 Hz, 4H), 7.17 (dt, J = 7.6, 1.2 Hz, 4H), 7.16 (dt, J = 7.6, 1.2 Hz, 4H), 2.59 (s, 6H); ES–MS m/z = 2932 $[M(PF_6)_5]^+$, 1394 $[M(PF_6)_4]^{2+}$, 881 $[M(PF_6)_3]^{3+}$, 1354 $[M(PF_6)_3(NO_3)]^{2+}$, 854 $[M(PF_6)_2(NO_3)]^{3+}$.

[(azotpy)Os(ttpy)][PF$_6$]$_4$. A solution of azptpy (79 mg, 0.16 mmol, 1.2 equiv.) and Os(ttpy)Cl$_3$ (83 mg, 0.13 mmol) in ethylene glycol (80 mL) was stirred at 160 °C for 30 min. The reaction mixture was cooled to room temperature, to which excess aqueous NH_4PF_6 (500 mg) was added. The precipitate was collected by filtration on Celite, washed with water and diethyl ether, and re-dissolved in CH_3CN. The filtrate was evaporated and the residue was dried *in vacuo* to give a dense purple powder (166 mg). The crude product was purified by column chromatography on silica with CH_3CN–0.4 M aqueous KNO_3 (20 : 1) to give, after $[Os(ttpy)_2]^{2+}$ (19 mg, 13%) as a brown powder, a reddish-purple powder which was characterized as [(azotpy)Os(ttpy)][PF$_6$]$_2$ (16 mg, 9%). Mp > 375 °C; ^{1}H NMR (400 MHz, CD_3CN, 20 °C): δ = 9.34 (s, 2H), 9.13 (s, 2H), 9.07 (s, 2H), 8.82 (d, J = 5.9 Hz, 2H), 8.80 (d, J = 9.5 Hz, 2H), 8.73 (d, J = 8.1 Hz, 2H), 8.64 (d, J = 8.1 Hz, 2H), 8.09 (d, J = 8.1 Hz, 2H), 8.08 (dt, J = 6.1, 1.5 Hz, 2H), 7.87 (dt, J = 8.1, 7.8, 1.5, 1.2 Hz, 2H), 7.83 (dt, J = 8.1, 7.8, 1.5, 1.2 Hz, 2H), 7.60 (d, J = 8.3 Hz, 2H), 7.57 (dd, J = 7.6, 1.0 Hz, 2H), 7.40 (d, J = 5.6 Hz, 2H), 7.30 (d, J = 5,6 Hz, 2H), 7.22 (dt, J = 6.7, 6.5, 1.5, 1.2 Hz, 2H), 7.11 (t, J = 7.1, 6.1 Hz, 2H), 2.59 (s, 3H); FAB-MS m/z = 1008 $[M - 2PF_6]^+$.

[((C151)$_2$-tpy)Ru(azotpy)Os(ttpy)][PF$_6$]$_4$ ((C151)$_2$-Ru-azo-Os). A solution of (Ru((C151)$_2$-tpy))Cl$_3$ (16 mg, 0.015 mmol) and $AgBF_4$ (9 mg, 0.046 mmol, 3 equiv.) in acetone (4 mL) was heated at reflux in air for 2 h. The reddish-brown reaction mixture was cooled to room temperature and filtered to remove AgCl. The filtrate was evaporated and *N,N*-dimethylacetamide (3 mL) was added to the resulting residue. This solution was added to a solution of [(azotpy)Os(ttpy)][PF$_6$]$_2$ (18 mg, 0.014 mmol) in *N,N*-dimethylacetamide (2 mL) and this mixed solution was heated at 120 °C under N_2 for 2 h. The reaction mixture was cooled to room temperature and filtered through Celite. The filtrate was evaporated and the residue dried. The resulting solid was dissolved in a minimum amount of CH_3CN and excess aqueous NH_4PF_6 (150 mg) was added. The resulting precipitate was collected by filtration, washed with water and diethyl ether. The thus obtained purple powder (39 mg) was purified by chromatography on silica with CH_3CN–0.4 M aqueous KNO_3 (20 : 1) as eluent to give, after the unreacted [(azotpy)Os(ttpy)][PF$_6$]$_2$ as a reddish-purple powder (7 mg, 19%), a blue-purple powder which was characterized as **(C151)$_2$-Ru-azo-Os** (4 mg, 11%). R_f (Silica) = 0.55: CH_3CN–0.4 M aqueous KNO_3 (5 : 1); 0.32: NH_4PF_6 (4 mg)–CH_3CN (1 mL); Mp > 375 °C; ^{1}H NMR (400 MHz, CD_3CN, 20 °C): δ = 9.50 (s, 2H), 9.45 (s, 2H), 9.11 (s, 2H), 9.05 (s, 2H), 8.84 (dd, J = 8.1, 1.2 Hz, 4H), 8.70 (d, J = 7.6 Hz, 2H), 8.68 (d, J = 8.1 Hz, 2H), 8.18 (d, J = 8.3 Hz, 2H), 8.11 (d, J = 8.3 Hz, 2H), 8.06 (dt, J = 8.1, 1.2 Hz, 2H), 8.00 (dt, J = 8.1, 1.2 Hz, 2H), 7.92 (dt, J = 8.1, 1.2 Hz, 2H), 7.85 (dt, J = 8.1, 1.2 Hz, 2H), 7.75 (d, J = 8.3 Hz, 2H), 7.62 (d, J = 7.8 Hz, 2H), 7.57 (dd, J = 4.9, 1.2 Hz, 2H), 7.52 (dd, J = 5.6, 1.2 Hz, 2H), 7.44 (dd, J = 5.6, 0.7 Hz, 4H), 7.36 (d, J = 5.1 Hz, 2H), 7.30 (dt, J = 6.5, 6.1, 1.5, 1.2 Hz, 2H), 7.27 (dt, J = 6.5, 6.1, 1.5, 1.2 Hz, 2H), 7.23 (dt, J = 7.3, 6.1, 5.9, 1.5, 1.2 Hz, 2H), 7.15 (dt, J = 7.3, 6.1, 5.9, 1.5 Hz, 2H), 7.02 (s, 1H), 6.99 (s, 2H), 6.71 (dd, J = 9.0, 2.4 Hz, 2H), 6.42 (d, J = 2.4 Hz, 2H), 6.35 (s, 2H), 6.14 (t, J = 6.1 Hz, 2H), 5.32 (s, 2H), 4.43 (d, J = 6.1 Hz, 4H), 2.60 (s, 3H); ES-MS m/z = 2439 $[M - PF_6]^+$, 1147 $[M - 2PF_6]^{2+}$, 716 $[M - 3PF_6]^{3+}$.

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