Luminescence Properties of Rigid Rod-like Binuclear Ruthenium(II)–Osmium(II) Terpyridine Complexes; Electronic Interaction Through Phenyl Bridges

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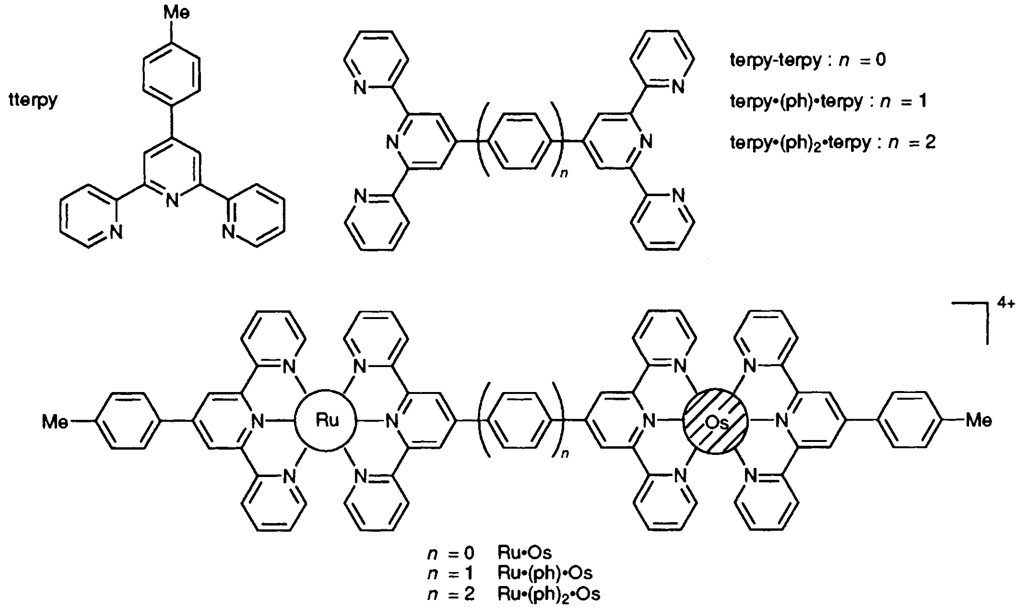
We have synthesized three novel binuclear heterometallic compounds where two $M(tterpy)_2^{2+}$ [tterpy = 4′-(*p*-tolyl)-2,2′ : 6′,2″-terpyridine] building blocks are either directly linked or connected by phenyl spacers in a rigid rod-like structure and we have investigated their luminescence properties and the electronic energy transfer process through the phenyl spacers.

Photoinduced energy- and electron-transfer processes in supramolecular species are currently the object of extensive studies because of their theoretical and practical interest.[1] Ruthenium(II) and osmium(II) oligopyridine complexes[2] are ideal building blocks for the construction of compounds suitable for such investigations. In supramolecular species, a crucial role is played by the spacers that connect the active components. An ideal spacer should allow good electronic communication between the active components and, at the same time, it should impose an extended and rigid structure to



Scheme 1

the supramolecular species in order to make possible long-range vectorial energy or electron migration.

In the field of transition metal complexes, most of the supramolecular species investigated so far for photoinduced energy and electron transfer purposes are based on M(N–N)$_3^{2+}$ components (N–N = bipyridine-type ligand).[3–12] In several cases,[3,4,7,8] such components are bridged by flexible spacers which do not guarantee a unique and well defined geometrical structure. We have synthesized† the binuclear heterometallic compounds shown in Scheme 1 where two M(terpy)$_2^{2+}$ building blocks are either directly linked or connected by phenyl spacers in a rigid rod-like structure. The luminescence properties of these novel compounds are of interest in their own right and allow us to obtain information on electronic energy transfer through phenyl spacers.‡

The absorption spectra of the three novel compounds are shown in Fig. 1, where the spectra of the two mononuclear model compounds Ru(tterpy)$_2^{2+}$ and Os(tterpy)$_2^{2+}$ [tterpy = 4′-(*p*-tolyl)-2,2′ : 6′,2″-terpyridine][11] are also displayed for comparison purposes. It is noteworthy that the spin-allowed metal-to-ligand charge-transfer bands (^{1}MLCT, λ_{max} = 490 nm) are almost identical for the two model compounds, whereas only the Os compound exhibits a relatively intense ^{3}MLCT absorption at $\lambda > 600$ nm. The ^{1}MLCT and ^{3}MLCT absorption bands of the binuclear compounds move to lower energies along the series **Ru·(ph)$_2$·Os** > **Ru·(ph)·Os** > **Ru·Os**. The displacement from the spectrum of **Ru·(ph)$_2$·Os** is small for **Ru·(ph)·Os**, but considerable for **Ru·Os**.

The luminescence data are collected in Table 1. The isolated Ru(tterpy)$_2^{2+}$ component shows a weak and short-lived emission centred at 640 nm, whereas Os(tterpy)$_2^{2+}$ exhibits a much stronger and longer-lived emission centred at 734 nm.[11b] As far as the binuclear compounds are concerned, let us first consider the results obtained on excitation with 650 nm light, which is only absorbed by the Os-based component. Under such conditions, the luminescence behaviour of **Ru·(ph)$_2$·Os** and **Ru·(ph)·Os** is very similar (Fig. 1 and Table 1). For **Ru·Os**, however, noticeable decreases in the energy and lifetime of the luminescent level as well as in the luminescence intensity are observed, again indicating a rather strong intercomponent interaction. When excitation was performed at 500 nm, where the Ru-based and Os-based components of the binuclear compounds are excited in a *ca.* 1 : 1 ratio (Fig. 1), the luminescence behaviour was practically identical to that observed upon 650 nm excitation (Table 1). In particular, for each compound the shape of the luminescence band was exactly the same as that of the band obtained upon 650 nm excitation, where only the Os-based component can be excited. This finding suggests that the luminescent excited state of the Ru-based component is completely

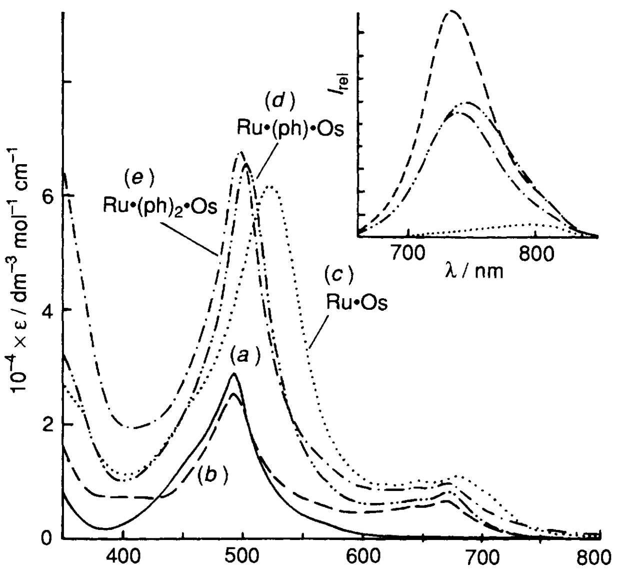


Fig. 1 Absorption spectra of (*a*) Ru(tterpy)$_2^{2+}$, (*b*) Os(tterpy)$_2^{2+}$, and of the binuclear compounds (*c*) **Ru·Os**, (*d*) **Ru·(ph)·Os** and (*e*) **Ru·(ph)$_2$·Os**. The inset shows the luminescence spectra of the Os-containing species excited at 650 nm.

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† The ligands tterpy,[11a] terpy–terpy,[13] terpy·(ph)·terpy,[14] and terpy·(ph)$_2$·terpy[15] have been synthesized following literature methods. The complexes **Ru·Os**, **Ru·(ph)·Os**, and **Ru·(ph)$_2$·Os** have been prepared by reaction of Os(tterpy)Cl$_3$ with the corresponding Ru complex (tterpy)Ru{(terpy)·(ph)$_n$·(terpy)}$^{2+}$ in refluxing Bu^{n}OH for 7 hours. All the new compounds display ^{1}H NMR and FAB mass spectra in agreement with their postulated structures.

‡ The luminescent properties were characterized by using a Spex Fluorolog II spectrophotometer, an IBH single-photon counting equipment, and a picosecond fluorescence spectrometer based on a Nd : YAG PY62-10 Continuum laser and a Hamamatsu C1587 streak camera. For more details, see ref. 11*b*.

Table 1 Luminescence data

	Os-based				Ru-based		
	λ_{max}/nm	τ/ns	I_{rel}[b] (λ_{ex} 650 nm)	I_{rel}[c] (λ_{ex} 500 nm)	λ_{max}/nm	τ/ns	I_{rel}[c] (λ_{ex} 500 nm)
$Os(tterpy)_2^{2+}$[d]	734	230	100[e]	100[e]	—	—	—
$Ru(tterpy)_2^{2+}$	—	—	—	—	640	0.95	100[f]
Ru·Os	800	110	7	6	—	≤0.020[g]	<5[h]
Ru·(ph)·Os	746	190	70	71	—	≤0.020[g]	<5[h]
Ru·(ph)$_2$·Os	738	200	61	72	—	≤0.020[g]	<5[h]

[a] Deaerated butyronitrile solution, room temperature. [b] Only the Os-based chromophoric unit is excited. [c] The Ru-based and Os-based units are excited in a *ca.* 1:1 ratio. [d] Ref. 11*b*. [e] $\Phi_{em} = 2.1 \times 10^{-2}$. [f] $\Phi_{em} = 3.2 \times 10^{-5}$. [g] The signal decay at 650 nm coincides with the excitation pulse. [h] The onset of the Os-based emission precludes a more precise evaluation.

quenched in the binuclear species. Picosecond experiments confirmed this finding and allowed us to evaluate an upper limit of 20 ps for the lifetime of the Ru-based excited state in the binuclear species.

In conclusion, the strong electronic interaction observed between the two components in **Ru·Os** is substantially reduced upon interposition of a phenyl spacer. A second phenyl spacer causes a further, but small, reduction of the interaction. In fact, the absorption and Os-based luminescence properties of **Ru·(ph)$_2$·Os** are only slightly different from those of a 1:1 mixture of $Ru(tterpy)_2^{2+}$ and $Os(tterpy)_2^{2+}$, which may be considered as an approximate model of a supramolecular system where the Ru-based and Os-based components do not interact. The electronic energy transfer process from the Ru-based to the Os-based component, however, is 100% efficient and takes place with a rate constant higher than 5×10^{10} s^{-1} even when the two components are separated by two phenyl rings (metal-to-metal distance, 21 Å). This interesting result prompts us to extend these investigations to analogous rod-like systems that contain a higher number of phenyl spacers and/or more than two metal-based building blocks.

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