Fine tuning of the photoinduced energy transfer rate in trinuclear Ru/Os 2,2':6',2''-terpyridine complexes through structural modification of the periphery †

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Trinuclear OsRu₂ complexes have been prepared and the role of peripheral thienyl units investigated; the presence of the substituent controls energy transfer from ruthenium to osmium.

Dendrimers based on photoactive and electroactive units are a class of branched macromolecules which are presently undergoing extensive investigation.[1,2] An important type of dendrimer which has received much recent attention is based on metal-oligopyridine complexes, particularly those containing ruthenium(II) and osmium(II) centres.[3] Synthetic strategies for these compounds are well-established and it is possible to selectively incorporate desired metal centres at the core, intermediate points or the periphery of the dendrimer. Although electron-transfer to internal metal sites may be slow, light-driven energy transfer processes can penetrate to the core of a dendritic assembly as commonly observed for ruthenium(II)- and osmium(II)-oligopyridine based systems and is favoured by the 0.2 eV energy gradient between higher-ruthenium based and lower-lying osmium-centred triplet MLCT levels.[1,3–5] It is thus possible to control the vectorial energy flux subsequent to light absorption, for example by positioning ruthenium centres at the periphery and osmium at the core, periphery-to-core excitation energy collection can be observed.[1] Despite numerous studies on the photodriven flux of excitation energy within ruthenium/osmium metallodendrimers, important details such as the energy-transfer rate constant and the nature of the transfer mechanism remain to be clarified.

We have long been interested in "metallostars",[2b,6] which are molecular assemblies related to dendrimers but which possess (in the simplest case) a single branching site at the core of the molecule. Metallostars may be equated to first generation dendrimers but possess functionality allowing linear development along each of the arms. In order to determine the precise nature of Ru ⟶ Os energy transfer within such assemblies we have prepared the trinuclear compounds **1** and **2** and a series of mononuclear reference complexes, **3**, **4**, and **5**, Scheme 1. The new ligand 4'-(3,5-dimethoxyphenyl)-2,2':6',2''-terpyridine was prepared in 55% yield from a one-pot reaction[7] of 2-acetyl-pyridine with 3,5-dimethoxybenzaldehyde and subsequent deprotection by heating with pyridinium chloride[8] gave 4'-(3,5-dihydroxyphenyl)-2,2':6',2''-terpyridine (dhptpy) in quantitative yield.‡ The thienyl ligand was prepared as described previously[7b,9] and mononuclear complexes were prepared by standard methods. The heterotrinuclear compounds **1** and **2** were prepared in 30–50% yield by the reaction of the activated complexes[10] [(tpy)Ru(Brtpy)][PF₆]₂ or [(thtpy)Ru(Brtpy)][PF₆]₂ (tpy = 2,2':6',2''-terpyridine; thtpy = 4'-(2-thienyl)-2,2':6',2''-

terpyridine; Brtpy = 4'-bromo-2,2':6',2''-terpyridine) with [(thtpy)Os(dhptpy)][PF₆]₂ in the presence of K₂CO₃.§ The thtpy ligand was used because we have previously shown that the presence of the thienyl group significantly enhances the lifetime of the ruthenium triplet MLCT state in its complexes.[7b,9]

Mononuclear complex **3** was chosen as a spectroscopic model for the energy donor unit of metallostar **1**; similarly, mononuclear complex **4** was used as the model for the donor unit of metallostar **2**; finally, mononuclear complex **5** is the model for the energy accepting subunit of both complexes **1** and **2**. We note that **3** and **4** are imperfect models for **1** and **2** as the electronic effects within the phenyl rings will differ somewhat. The room temperature absorption spectra¶ of the Ru complexes **3** and **4** and the Os complex **5** are shown in Fig. 1. The absorption profiles in the visible region exhibit a ¹MLCT band maximum peaking at 480–500 nm; for **5** the absorption tail extending at λ > 600 nm is assigned to the spin-forbidden ³MLCT transition. Comparison of the spectra for **3** and **4** indicates that the thienyl group causes a red-shift of the absorption maximum of the ¹MLCT band (with a concomitant enhancement of the absorption intensity). The absorption spectra of the trinuclear species overlap with the sum of the component spectra, and are not shown. This is consistent with a substantial ground state electronic decoupling of the components, as a consequence of the insulating character of the ether connections.[5]
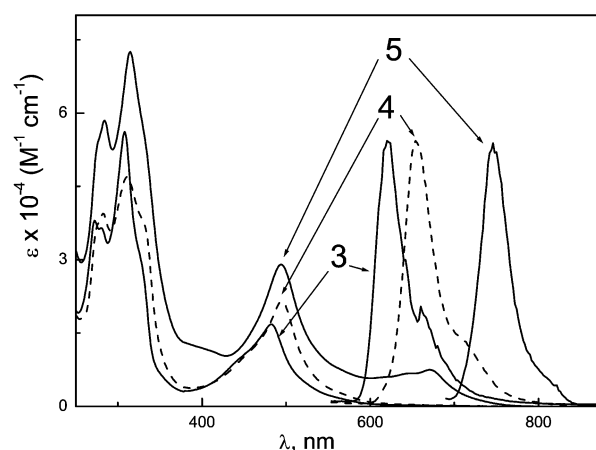

Fig. 1 Absorption and luminescence (at 77 K, normalized) spectra of the indicated components of the mononuclear complexes.

The room temperature luminescence properties of **3** and **4** are as expected for {Ru(tpy)₂}²⁺ chromophores;[11] in particular, the luminescence quantum yield is very low, φ < 10⁻⁴ with lifetimes τ = 0.56 and 6.4 ns for **3** (λ_max = 630 nm) and **4** (λ_max = 670 nm), respectively. Complex **5** has an emission maximum at 744 nm with φ and τ 1.2 × 10⁻² and 150 ns, respectively. In accord
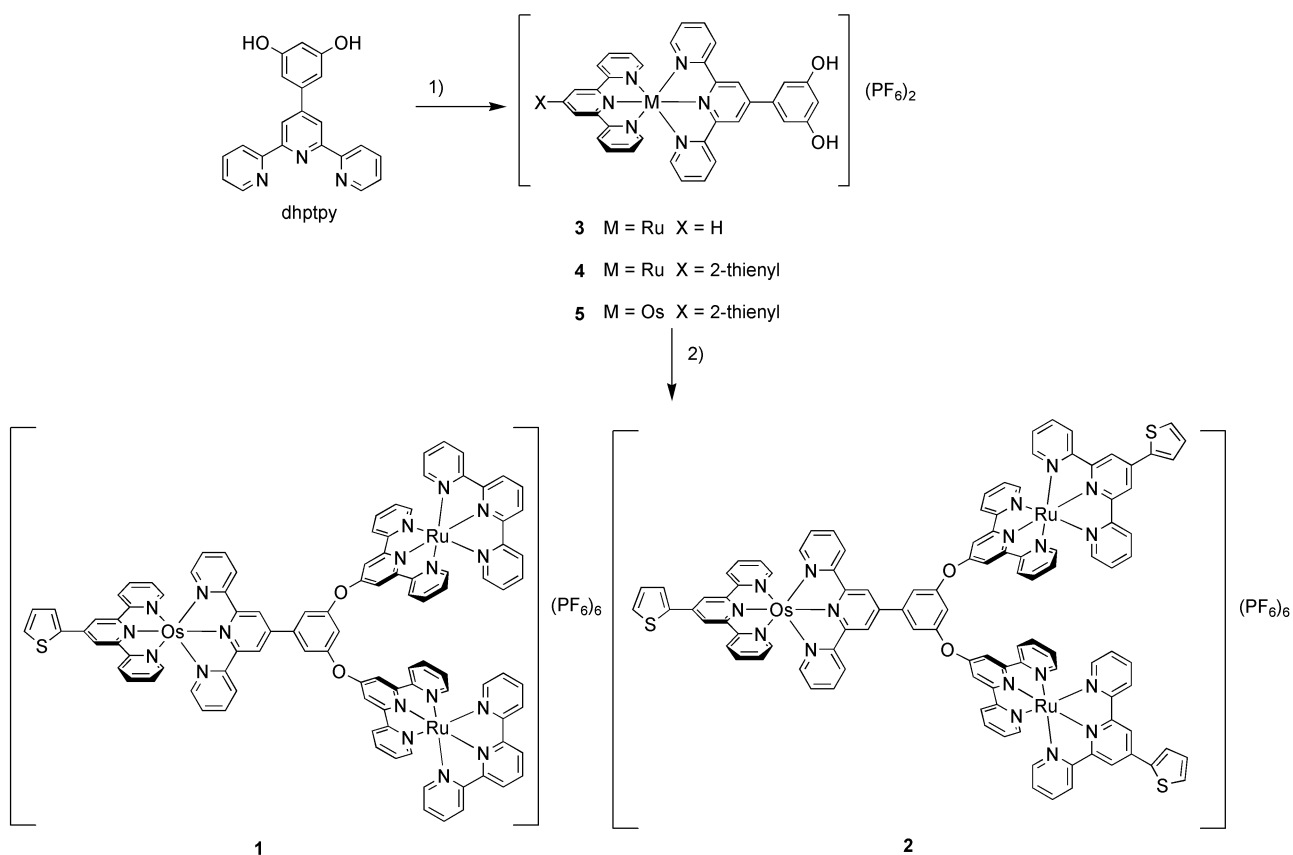
Scheme 1 General scheme for the synthesis of the complexes investigated. 1) [(Xtpy)MCl$_3$] (Xtpy = tpy or thtpy; M = Os or Ru), N-ethylmorpholine, EtOH; 2) [(Xtpy)Ru(Brtpy)][PF$_6$]$_2$, MeCN, K$_2$CO$_3$.

with the absorption features of Fig. 1, excitation of complexes **1** and **2** (which contain two Ru-based and one Os-based units) at 480 nm, produces an excess of Ru-based excited component over the Os-based one. On this basis, one can see that for both trinuclear complexes, no Ru ⟶ Os energy transfer takes place at room temperature. In fact, comparison of the luminescent properties of isoabsorbing solutions (λ_{exc} = 480 nm) of **5**, **1**, and **2**, shows that in the latter two complexes the observed Os-based luminescence intensity is *ca.* half that of **5** instead of being the same, as would be expected for fully efficient energy transfer. In particular, our findings indicate that for both **1** and **2** at room temperature, Os-based luminescence only originates from direct excitation of the Os-based chromophore.

At 77 K, complexes **3** and **4** exhibit a strong luminescent signal typical of {Ru(tpy)$_2$}$^{2+}$ complexes in frozen solvent;[11] the spectra shown in Fig. 1 are characterized by maxima peaking at 615 and 650 nm, respectively, with lifetimes $\tau^{77 K}$ = 11 and 11.5 μs, respectively. The luminescence spectrum for **5** (also in Fig. 1) exhibits λ_{max} = 745 nm, τ = 1.96 μs. For both **1** and **2** at 77 K, the Os-based luminescence intensity was strong and easily detectable while the Ru-based luminescence intensity was reduced to less than 1% with respect to **3** or **4**, respectively. Use of the streak camera apparatus¶ allowed time-resolved detection of the weak Ru-centered luminescence band (monitored at 630 nm) and provided a lifetime decay of 1.8 ns for the trinuclear compound **1**; the Ru-based lifetime in the trinuclear species **2** was too long (*i.e.* > 5 ns) to be determined with this equipment. For both **1** and **2**, Os-based time-resolved properties (as monitored at λ > 700 nm, 77 K), were observed (Fig. 2). These could be described by a dual exponential behaviour,

$$I(t) = b_1\exp(-t/\tau_1) + b_2\exp(-t/\tau_2)$$

where b_1 and b_2 are preexponential parameters. Fig. 2 top panel shows the decay profiles obtained for **1** (initial portion of the decay, observation wavelengths 630 and 750 nm) and **2** (bottom panel, longer time scale, observation wavelength >700 nm). For

both trinuclear complexes, b_1 was a negative value, indicating that τ_1 (1.6 and 36 ns for complexes **1** and **2**, respectively), is a risetime, corresponding to the Ru ⟶ Os sensitisation. This is also confirmed by the good agreement between the decay lifetime of the Ru-based luminescence (1.8 ns) and the Os-based rise (1.6 ns), for **1**, Fig. 2 top panel. On the other hand, the determined τ_2 = 1.96 μs for both **1** and **2** corresponds to the intrinsic decay properties of the Os-based component. From these results, intramolecular Ru ⟶ Os energy transfer rate constants k_{en} = 5.8 × 10^8 and 2.8 × 10^7 s^{-1} could be evaluated for **1** and **2**, respectively. Given that Ru ⟶ Os energy transfer is practically independent of temperature or (fluid or frozen) state of the solvent,[12] our results explain why no energy transfer is observed at room temperature. Here, the intrinsic excited state decay of the Ru-based donor of **1** and **2** (as inferred from the behaviour of the model complexes **3** and **4**) is substantially faster than the competing Ru ⟶ Os energy transfer step.

Given the insulating character of the ether linkage,[5] one can adopt the dipole–dipole Förster approach for describing the Ru ⟶ Os energy transfer step within **1** and **2**.[13] By using the spectroscopic properties of the model complexes (Ru-based luminescence of **3** and **4** at 77 K, with ϕ = 0.3 in both cases) and the absorption spectrum of **5** (room temperature, Fig. 1), we have obtained estimates of the Förster overlap integral for the trinuclear complexes **1** and **2**; this was in both cases, J_F ~ 1 × 10^{-13} cm^3 M^{-1} with a critical transfer radius of 42 Å.[13,14] The experimental k_{en} values (5.8 × 10^8 and 2.8 × 10^7 s^{-1}, for **1** and **2** respectively) give an interchromophore distance of *ca.* 10 for **1** and 16.5 Å for **2** respectively.[14] These results are consistent with a different spatial localisation of the Ru-based ^{3}MLCT luminescent levels in **1** and **2**. In the former case, the Ru-based ^{3}MLCT state appears to reside *between* the metal centres; for **2**, the presence of the thiophene groups causes a displacement of the Ru-based excitation, which appears localised at the thtpy fragment, able to provide a stabilized ^{3}MLCT luminescent level ($\lambda_{max}^{77 K}$ = 650 nm). This is consistent with our earlier observ-
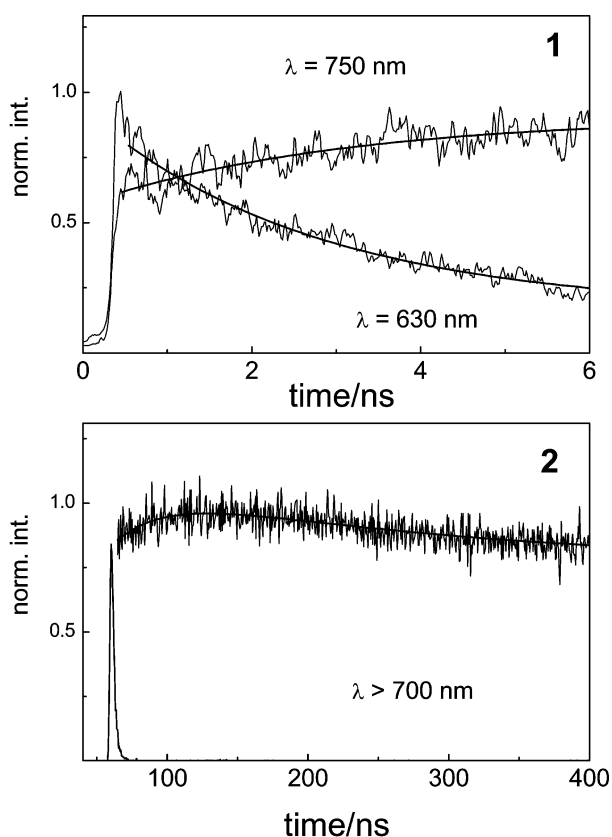
Fig. 2 Time resolved properties observed for the trinuclear complexes in butyronitrile at 77 K. Top: streak camera time profiles for the faster portion of the decays of **1**, τ was 1.8 ns (at 630 nm, decay of the Ru-based luminescence) and 1.6 ns (at 750 nm, rise of the Os-based luminescence). The laser profile (FWHM = 35 ps) is not shown. Bottom: single-photon time profiles on a large time scale for the Os-based spectral region of **2**, rise (τ_1 = 36 ns) and decay (τ_2 = 1.96 µs) components of a dual exponential decay are shown (see text; the same value for τ_2 was observed in the case of **1**). The flash profile of the N$_2$ lamp (FWHM = 3 ns) is also shown.

ations on thtpy and related complexes[7] and correspond unexpectedly well with simple molecular mechanics calculations on the compounds (MM2+, metal coordination geometry constrained to crystallographic values, otherwise let free) which give average Os–Ru distances of 10.5 Å and average metal–centroid of thienyl ring distances of 16.0 Å.

In conclusion, the structurally similar trinuclear complexes **1** and **2** exhibit different Ru $\longrightarrow$ Os intramolecular energy transfer rate constants; this rate is 20-fold lower in **2** than **1**. We have shown that intramolecular energy transfer rates in polynuclear metallostars may be fine-tuned by the interplay of structural and electronic effects of substituents at the periphery.

Notes and references

‡ ES MS m/z (calc.): 364 (364, [M + Na$^+$]$^+$), 342 (342, [M + H$^+$]$^+$); HR MS: (calc.) C$_{21}$H$_{16}$N$_3$O$_2$ [M + H$^+$] 342.124, found: 342.123; ^{1}H-NMR

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