Use of photoinduced energy-transfer to probe solvent-dependent conformational changes in a flexible Ru/Os dinuclear complex

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Solvent-dependent conformational changes of a poly(oxoethylene) bridge linking $[Ru(bipy)_3]^{2+}$ and $[Os(bipy)_3]^{2+}$ units can be probed by measuring the extent of Ru→Os photoinduced energy transfer.

Photoinduced energy-transfer between Ru(II) and Os(II) polypyridine units across nanometric bridging ligands has been extensively studied recently,[1–5] largely because of the relevance of such complexes to potential applications such as light energy collection and conversion[5] and luminescence-based sensors and switches.[6–8] In such complexes the bridging ligand is of fundamental importance. It can be either geometrically rigid or flexible, so that the distance between the photoactive partners may be fixed or may vary; and it may contain electronically conducting or insulating units. In some cases, some units of the bridge can also interact with the environment, so that modulation or switching of the Ru→EOs energy transfer process can be observed.[2]

We describe here a Ru(II)/Os(II) dyad in which the two metal components are separated by a flexible poly(oxoethylene) chain derived from penta(ethylene glycol).† In these complexes the conformation of the poly(oxoethylene) chain is expected to be solvent dependent, based on the known properties of poly(ethylene glycol)[9] and various simple model compounds,[10] and this in turn is expected to lead to controllable variation of the metal–metal separation, d_{MM}. In this study, by using steady-state and time-resolved luminescence measurements, we show that for **Ru-L⁵-Os** the Ru→Os energy transfer can indeed be influenced by the solvent and we ascribe this effect to differences in the conformation of the poly(oxoethylene) chain.[11]‡

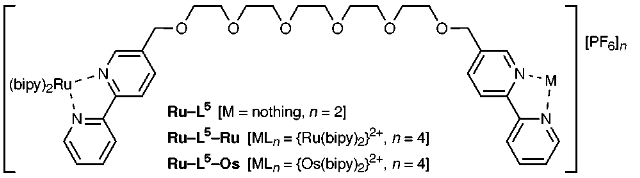

Table 1 lists some spectroscopic and photophysical properties for the mononuclear model complex **Ru-L⁵**, and the heterodinuclear complex **Ru-L⁵-Os**, as obtained in neat MeOH (protic) and CH_2Cl_2 (aprotic) solvents. Fig. 1 compares the luminescence spectra obtained by exciting samples of **Ru-L⁵-Os** in mixed MeOH–CH_2Cl_2 solvent of varying proportions. The excitation wavelength was 450 nm so that both the Ru and Os-based chromophores were excited, approximately in a 1:0.8 ratio, (Table 1). The luminescence spectra of **Ru-L⁵-Os** (Fig. 1) feature two band maxima, occurring in the ranges 600–606 and 710–715 nm. The relative intensities of these are consistent with the occurrence of partial quenching (*ca.* 90%) of the Ru unit, owing to Ru→Os energy transfer (ΔG *ca.* −0.3 eV). Thus, the band at *ca.* 600 nm is due to a residual Ru-based emission, and the band at *ca.* 710 nm is Os-based, with a luminescence intensity which includes contributions from both direct excitation and Ru→Os sensitisation. It will be seen that as the solvent polarity decreases (from MeOH to CH_2Cl_2), the Ru-based emission relatively decreases in intensity with respect to the Os-based emission, consistent with improved Ru→Os energy transfer arising from a shorter metal–metal separation.

This was confirmed by analysis of the time-resolved luminescence decay of **Ru-L⁵-Os**, which was measured in the same mixed-solvent system at the wavelengths of the two emission band maxima. At 600 nm a single (Ru-based) exponential decay was found; at 710 nm the Os-based decay took place according to a dual exponential law, with a rise time and a decay time. We found that in each case the Ru-based decay time (obtained at 600 nm) corresponds to the Os-based rise time (observed at 710 nm), consistent with the occurrence of Ru→Os energy transfer. Also, on the basis of $k_{en} = 1/\tau_q - 1/\tau$ we can obtain the Ru→Os energy transfer rate constant as a function of solvent composition (τ is the lifetime of the reference complex, **Ru-L⁵**). The results are shown graphically

Table 1 Spectroscopic and photophysical data[a]

	Absorption		Emission[b]		
	λ_{max}/nm (10^{-3} ε/dm^3 mol^{-1} cm^{-1})		λ_{max}/nm	10^2 Φ	τ/ns
MeOH					
Ru-L⁵	287 (90.0)	450 (13.4)	604	1.6	240
Ru-L⁵-Ru	287 (147)	450 (27.6)	606	1.5	210
Ru-L⁵-Os	289 (145)	450 (24.6)	606,[c] 715[d]		18.8,[c] 32[d]
CH_2Cl_2					
Ru-L⁵	287 (97.0)	453 (14.4)	598	3.3	410
Ru-L⁵-Ru	288 (145)	452 (27.6)	600	3.5	405
Ru-L⁵-Os	289 (150)	452 (26.6)	600,[c] 710[d]		5.8,[c] 65[d]

[a] Room temperature, in the indicated air-equilibrated solvents. Sample concentrations were 2 × 10^{-5} M. [b] Excitation wavelength 450 nm. The emission maxima (±2 nm) are from uncorrected spectra. Quantum yield values (±20%) are from corrected spectra. Lifetimes are accurate to ±8%. [c] Ru-based luminescence. [d] Os-based luminescence.

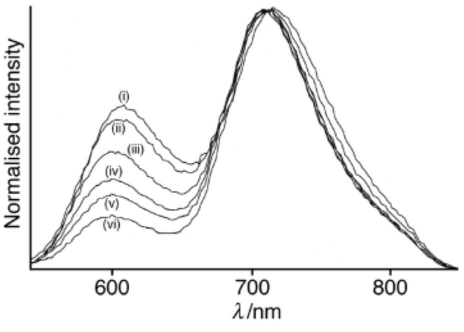

Fig. 1 Normalised luminescence spectra of **Ru-L⁵-Os** in mixed MeOH–CH_2Cl_2 solvents (spectroscopic grade) of proportions (MeOH–CH_2Cl_2): (i) 100:0; (ii) 80:20; (iii) 60:40, (iv) 40:60; (v) 20:80; (vi) 0:100. The solutions were isoabsorptive at the excitation wavelength (450 nm) and the spectra are normalised to the Os-based emission.

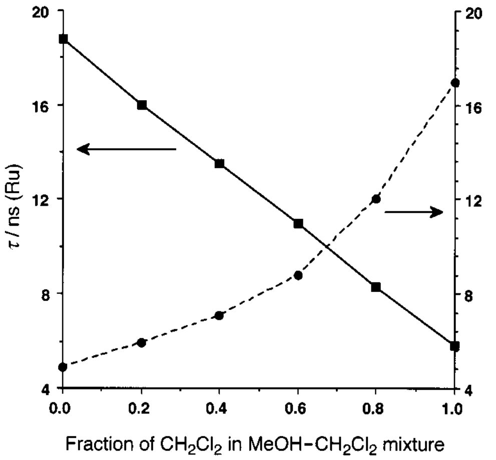

Fig. 2 Photophysical behaviour of **Ru-L^5-Os** in mixed MeOH–CH_2Cl_2 solvents, showing the steady decrease of Ru-based emission lifetime (squares, solid line) and the concomitant increase in Ru→EOs energy-transfer rate constant (circles, dashed line) as solvent polarity decreases.

in Fig. 2. It is clear that improved quenching of the Ru emission as the solvent polarity decreases is accompanied by improved Ru→Os energy transfer. The extent of quenching for the Ru-based emission in **Ru-L^5-Os** is therefore solvent dependent, being maximised in neat CH_2Cl_2. As a control experiment, a 1:1 mixture of **Ru-L^5** and $[Os(bipy)_3]^{2+}$ (each 2×10^{-5} M) resulted in no detectable quenching of the Ru-based luminescence, confirming that intermolecular effects are not significant, as would be expected at these low concentrations.

Two possible mechanisms, exchange and dipole–dipole, can be invoked to account for Ru→EOs energy transfer.[12] It is well documented that through-bond, two-electron exchange is likely to be involved for cases where the bridging ligand is highly unsaturated,[1,2,4] because the energetically accessible HOMO and LUMO orbitals of the bridge provide a pathway linking the appropriate metal orbitals.[13] In contrast, saturated units behave like insulators towards electronic communication because the HOMO–LUMO energy separation is large. EHMO calculations on the poly(oxoethylene) chain [taken as $Me(OCH_2CH_2)_5OMe$] indicate that its HOMO–LUMO energy gap (32 eV) is comparable to that of the corresponding hydrocarbon chain [taken as $Me(CH_2)_{16}Me$] (41 eV),[14] so the amount of the intermetal electronic communication mediated by the bridging ligand L^5 is expected to be negligible. On this basis, we ascribe the occurrence of energy transfer in **Ru-L^5-Os** to the dipole–dipole (Förster) mechanism, [eqn. (1)].[12]

$$k_{\mathrm{en}}^{\mathrm{F}} = \frac{8.8\times10^{-25} K^2 \Phi}{d_{\mathrm{MM}}{}^6 n^4 \tau} J^{\mathrm{F}} \qquad (1)$$

where Φ and τ are the luminescence quantum yield and lifetime, respectively, of the energy donor (**Ru-L^5**); J^F is the integral overlap between the luminescence spectrum of the donor (Ru chromophore) and the absorption spectrum of the acceptor (Os chromophore), K^2 is a geometric factor (taken as 2/3), and n is the refractive index of the solvent. From eqn. (1) and by using the pertinent spectroscopic (Table 1) and calculated parameters ($J^F = 4.7 \times 10^{-14}$ cm^6 mol^{-1} in both solvents), we conclude that d_{MM} = 15 and 12 Å in neat MeOH and CH_2Cl_2, respectively. These values may be compared with the calculated[14] end-to-end distance of 22 Å for the fully extended ligand L^5.

This solvent-dependence of the bridging ligand conformation is exactly consistent with the known behaviour of both poly(ethylene glycol)[9] and simple model compounds such as dimethoxyethane.[10] In these molecules the conformation about the central C–C bond of the OCH_2CH_2O unit is predominantly *trans* in a low-polarity medium, but predominantly *gauche* in a high-polarity medium. The *gauche* conformation, which results in a higher dipole moment for the poly(oxoethylene)chain, is also associated with a more expanded structure for the chain—in exact agreement with our observations.

In conclusion, with **Ru-L^5-Os** we have used Ru→EOs energy transfer as a diagnostic tool for probing solvent-specific conformational properties of a flexible bridging ligand. This is an appealing way of providing quantitative information on the conformations of soluble polymers, an area of considerable importance.[9] Work is also in progress to probe the use of metal cations to control the conformation of the bridging ligand and hence the metal–metal interaction.[15]

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Notes and references

† *Preparations*: L^5: penta(ethylene glycol) (0.310 g, 1.26 mmol) in dry THF (100 ml) was treated with NaH (60% dispersion in mineral oil; 0.40 g, 10.0 mmol) and stirred at room temp. for 40 min. When effervescence ceased, 5-bromomethyl-2,2′-bipyridine (1.30 g, 5.20 mmol) was added, and the mixture was refluxed for 24 h. After removal of the solvent the brown residue was chromatographed on silica, eluting with 10% methanol in CH_2Cl_2, to give the product (the second major fraction off the column) as a clear oil after removal of the solvent. Yield 0.704 g, 97%.

$[Ru(bipy)_2(L^5)][PF_6]_2$ **Ru-L^5**: reaction of L^5 (327 mg, 57 μmol) and $[Ru(bpy)_2Cl_2]\cdot 2H_2O$ (240 mg, 0.46 mmol) in EtOH at reflux for 3 h afforded an orange–red solution. Chromatography on Sephadex-SP25, eluting with 0.3 M aqueous NaCl, afforded a red band from which **Ru-L^5** precipitated on addition of NH_4PF_6: yield, 0.262 g (35%). Also isolated was the dinuclear complex $[\{Ru(bipy)_2\}_2(L^5)][PF_6]_4$ **Ru-L^5-Ru** (eluted with 0.5 M aqueous NaCl); yield, 0.088 g (9%).

$[(bipy)_2Ru(L^5)Os(bipy)_2][PF_6]_4$ **Ru-L^5-Os**: A mixture of **Ru-L^5** (74.6 mg, 0.58 mmol) and $[Os(bpy)_2Cl_2]$ (60 mg, 98 μmol) were heated together at 120 °C for 24 h in ethylene glycol (10 ml). The reaction mixture was cooled, added to water (100 ml) and introduced onto Sephadex SP25, and the primary green band eluted with 0.55 M aqueous sodium chloride solution. The product was precipitated with NH_4PF_6 and collected on Celite. The nearly pure compound was further purified by chromatography on Sephadex-LH20 eluting with acetone–methanol (1:1) to give pure **Ru-L^5-Os**: yield; 84.3 mg (70%). Satisfactory ^{1}H NMR and mass spectroscopic data, and elemental analyses, have been obtained for all new compounds.

‡ The solvent-dependent conformation of a polypeptide chain has been exploited to modulate photoinduced electron-transfer between covalently linked $[Ru(bipy)_3]^{2+}$ (donor) and fullerene (acceptor) units: see ref. 11.

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