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Folding of a poly(oxyethylene) chain as probed by photoinduced energy transfer between Ru– and Os–polypyridine termini

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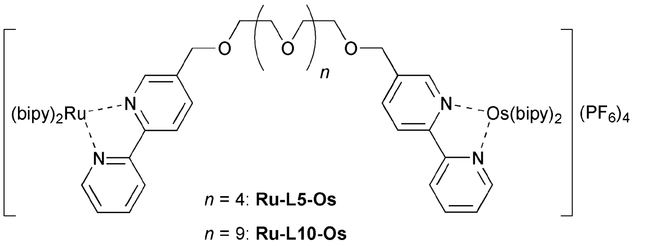
The extent of photoinduced energy-transfer between $[Ru(bipy)_3]^{2+}$ and $[Os(bipy)_3]^{2+}$ units attached to either end of a deca(oxoethylene) 33-atom chain can be used to show how the distribution of end-to-end distances in the ensemble of conformations changes in different solvents.

Photoinduced energy transfer involving polypyridyl complexes of Ru(II), Os(II) and Re(I) has been extensively studied in relation to development of artificial systems for solar energy harvesting,[1] the construction of 'molecular wires' allowing long-range information transfer,[2] and anion/cation sensing[3] and switching devices.[4] Accordingly, very many dinuclear heterometallic complexes have been designed and investigated for the assessment of the role played by structural and electronic factors of the bridging ligand (**BL**) – which provides the covalent link between the photoactive termini – in controlling the energy-transfer process.[5–8] In general **BL**s containing unsaturated components are likely to mediate the transfer of excitation energy *via* a Dexter-type electron-exchange process,[9] whereas the use of saturated components within the **BL** only allows for the dipole-type, Förster mechanism,[10] which is typical of organic chromophores but may also occur for polypyridine complexes of Ru(II) and Os(II) and other metal centers.

In most dinuclear complexes where photoinduced energy-transfer is studied, the **BL**s are rigid such that energy-transfer is occurring over a well-defined distance, and the efficiency of energy-transfer can then be related to the particular properties of the bridging ligand.[1,2] In contrast, the study of photoinduced energy-transfer between chromophore and quencher units attached to either end of highly *flexible* molecules (such as polyalkanes[11] or polypeptides[12]) has been used to provide information on their conformational behaviour under different conditions, which is of value for comparison with results of conformational models and molecular dynamics simulations. In this vein we recently described the complex **Ru-L5-Os** (Scheme 1) in which $[Ru(bipy)_3]^{2+}$ and $[Os(bipy)_3]^{2+}$ termini are linked by a flexible 18-atom bridge derived from attachment of bipyridine units to either end of a penta(ethyleneglycol) chain.[13] The conformations of oligomeric chains containing $-(CH_2CH_2O)-$ units are sensitive to the polarity of the solvent,[14,15] and we found that for **Ru-L5-Os** the efficiency of photoinduced Ru→Os energy transfer decreased smoothly as the solvent polarity increased, due to a solvent-induced conformational change which increases the $Ru\cdots Os$ separation in more polar solvents. We could accordingly use the Ru→Os energy transfer rate as a 'ruler' to determine the variation in $Ru\cdots Os$ separation as a consequence of the conformational changes in the chain.

Since the study of the conformational properties of poly(oxoethylene) chains is a topic of considerable importance,[14,15] we have extended this work by preparing and studying the complex **Ru-L10-Os** (Scheme 1), in which a flexible 33-atom chain separates the $[Ru(bipy)_3]^{2+}$ energy-donor and $[Os(bipy)_3]^{2+}$ energy-acceptor termini. We have found that Ru→Os energy transfer is again a useful probe of the conformational behaviour of this system in solution, and that the conformational behaviour of **Ru-L10-Os** in different solvents is significantly different from that of **Ru-L5-Os**.



Scheme 1

Whereas the bridging ligand in **Ru-L5-Os** was prepared in a single step from 5-(bromomethyl)-2,2′-bipyridine and commercially available penta(ethyleneglycol), for **Ru-L10-Os** we had to devise a more elaborate stepwise synthesis as deca(ethyleneglycol) is not readily available. The synthesis is summarised in Scheme 2,† which shows how the 10-mer chain is constructed in two steps from shorter commerically available starting materials. Addition of the metal termini by stepwise reaction with $[Ru(bipy)_2Cl_2]$ and then $[Os(bipy)_2Cl_2]$, followed by isolation of the complex as its hexafluorophosphate salt, follows the previously-published method.[13,†]

Our study of the solvent effect on the conformation of **Ru-L10-Os** follows a spectroscopic approach that has been described before.[16,‡] We have employed CH_2Cl_2 as a low polarity, low viscosity solvent [relative permittivity $\varepsilon = 9.08$, viscosity $\eta = 0.449$ cp where 1 centipoise (cp) $= 10^{-3}$ Pa s]; as a highly polar and viscous solvent, we used an ethylene glycol/MeOH mixture (0.8 : 0.2 v/v, with resulting bulk $\varepsilon = 36.7$ and $\eta = 16.04$ cp; solubility factors prevented the use of higher viscosity solvents), which we abbreviate hereafter as EG.[17] Table 1 collects absorption and luminescence properties for **Ru-L10-Os** in both solvent systems. Fig. 1 compares absorption and luminescence spectra for **Ru-L5** (a mononuclear model complex available from previous work)[13] and **Ru-L10-Os** as obtained in CH_2Cl_2; similar results were obtained in EG. The luminescence spectra were obtained by excitation at 415 nm; from the absorption spectral properties (see Fig. 1), excitation at this wavelength results in equal excitation of both the Ru-based and Os-based ^{1}MLCT transitions. The Os-based luminescence occurs at $\lambda > 700$ nm and is obscured by the tail of the much more intense emission from the Ru-based luminophore. For reference purposes, data for the mononuclear complex **Ru-L5** in the same solvents are also reported.[13]

The bridging ligand **L10** does not include low-energy conducting units; actually the energy level of the HOMOs of the **L10** chain is lower by *ca.* 3 eV than that of the bpy ligand to which it is attached, and for the corresponding LUMOs the

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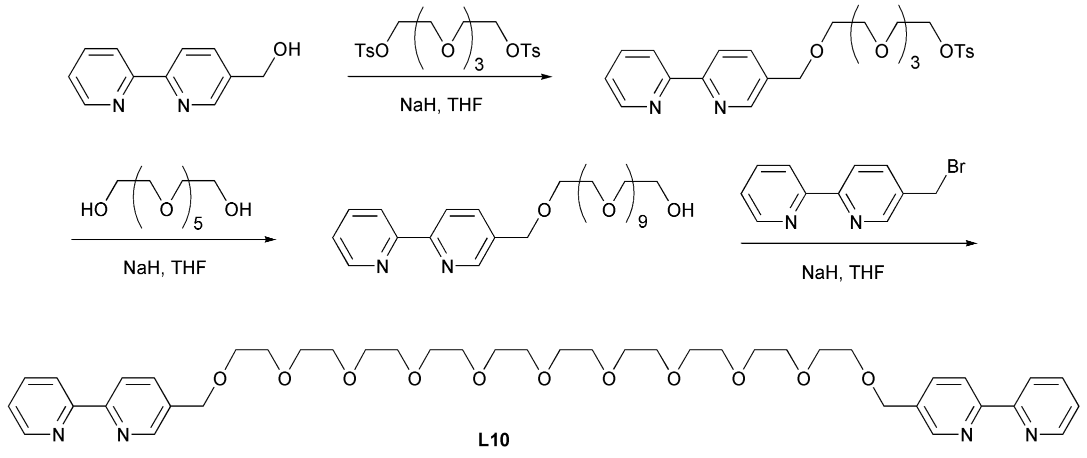
Table 1 Spectroscopic and photophysical data[a]

	Absorption		Emission[b]			$f(r)$[c]	
	λ_{max}/nm ($10^{-3}\varepsilon$/dm^3 mol^{-1} cm^{-1})		λ_{max}/nm	$10^2\,\Phi$	τ_d/ns	μ/Å	a/Å
CH_2Cl_2							
Ru-L5	287 (91.0)	453 (14.4)	608	1.6	310		
Ru-L10-Os	289 (149.7)	452 (26.6)	602	*ca.* 0.5	256[d]	14.1	4.2
EG							
Ru-L5	287 (90.0)	450 (16.1)	608	2.4	540		
Ru-L10-Os	291 (155.0)	450 (25.5)	610	*ca.* 0.8	430[d]	14.7	2.7

[a] Room temperature, in air-equilibrated solvents; sample concentrations were 2×10^{-5} M. [b] Ru-based luminescence properties: excitation was at 415 nm. [c] μ and a are parameters for the intermetal distance distribution, as obtained from the least squares analysis according to eqns. (3) and (4); see text. [d] This is what the emission lifetime of the Ru chromophore of **Ru-L10-Os** would be in the absence of any quenching by the Os component; calculated from eqn. (3), see text.



Scheme 2

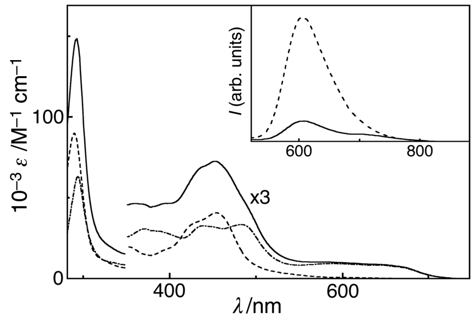


Fig. 1 Absorption spectra for **Ru-L10-Os** (solid line), **Ru-L5** (----), and $[Os(bpy)_3]^{2+}$ (-·-·-·-·-) in CH_2Cl_2. The inset shows the luminescence spectra for **Ru-L10-Os** (solid line) and **Ru-L5** (----) as observed for excitation of isoabsorbing solutions at 415 nm.

energy gap is >20 eV, as evaluated from EHMO calculations.[18] On this basis, we expect no significant orbital interactions between the donor and acceptor metal complex units and the bridging poly(oxyethylene) chain,[19] such that Ru→Os photoinduced energy transfer step over the intermetal distance d_{MM} can only take place *via* the dipole–dipole (Förster) mechanism,[10] eqns. (1) and (2).

$$k_{en} = \frac{1}{\tau_d}\left(\frac{R_o}{d_{MM}}\right)^6 \tag{1}$$

$$\text{with}\quad R_o^6 = \frac{9000(\ln 10)\kappa^2\phi_d}{128\pi^5 N n^4}\,\frac{\int F_d(\bar{\nu})\varepsilon_a(\bar{\nu})/\bar{\nu}^4\,d\bar{\nu}}{\int F_d(\bar{\nu})d\bar{\nu}} \tag{2}$$

In eqns. (1) and (2), R_o is the critical transfer distance, *i.e.* the distance at which the deactivation rate of the $[Ru(bipy)_3]^{2+}$ donor is equal to k_{en}, the energy-transfer rate, such that the luminescence and energy-transfer deactivation pathways are equally balanced. The parameters ϕ_d and τ_d are the intrinsic luminescence quantum yield and lifetime of the $[Ru(bipy)_3]^{2+}$ donor, respectively; κ^2 is a geometric factor taken as 2/3 for statistical reasons; the integral in eqn. (2) is the overlap between the emission spectrum of the donor and the absorption spectrum of the acceptor and is evaluated on an energy scale (cm^{-1}). By using eqns. (1) and (2) and the available spectroscopic parameters (Table 1) we find that $R_o = 24$ Å for both CH_2Cl_2 and EG solvents.

The long and flexible poly(oxyethylene) chain in **L10** is expected to undergo conformational rearrangements, arising from the change in the preferential conformation about each C–C bond from *anti* in low-polarity solvents to *gauche* in high-polarity solvents.[14,15] We have probed these changes as illustrated below. From Fig. 1, we see that the Ru-based luminescence intensity for **Ru-L10-Os**, as detected at 610 nm, is *ca.* 1/3 that of the reference mononuclear complex **Ru-L5**. This is due to Ru→Os energy transfer, which is thermodynamically allowed by *ca.* −0.3 eV.[5–8,13] For the extensively studied cases of rigid dinuclear Ru/Os complexes, where the photoactive units are separated by a fixed distance, the Ru-based luminescence decay is describable by a single exponential law, $I(t)^{Ru} = A\exp(-t/\tau)$, and $k_{en} = 1/\tau - 1/\tau_d$, with τ_d being the lifetime of a suitable reference Ru-based complex (A is a preexponential factor). We also found this behaviour in **Ru-L5-Os**, with a single Ru···Os separation being measured at each solvent composition.[13] For **Ru-L10-Os** however, the Ru-based decay shows a more complicated behaviour, arising from the fact that the greater conformational flexibility of the chain allows a *range* of Ru···Os separations even at a fixed solvent composition. We have found that the following expression, in accord with the spectroscopic approach described by Lakowicz,[16] fits our results well.

$$I(t) = A\int_0^{\infty} f(r)\exp\left[-\frac{t}{\tau_d}\left(\frac{R_o}{r}\right)^6\right]dr \tag{3}$$

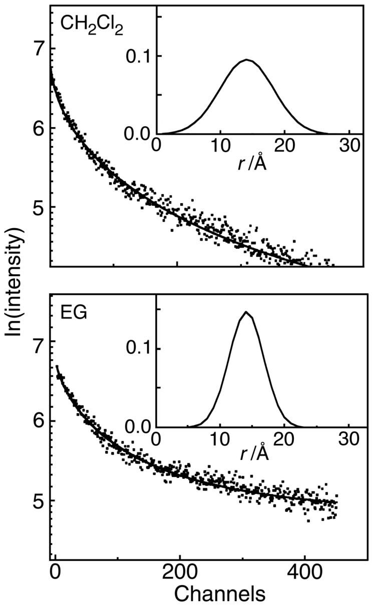


Fig. 2 Luminescence decays of **Ru-L10-Os** as observed at 610 nm. The full curves are the fit to the experimental points according to eqns. (3) and (4) of the text. The insets show the $f(r)$ gaussian distribution of the intermetal distances. Channel of time axis was 1.02 ns.

$$\text{with}\quad f(r) = \frac{1}{a\sqrt{2\pi}}\exp\left[-0.5\left(\frac{r-\mu}{a}\right)^2\right] \qquad (4)$$

Here, τ_d is the *unquenched* luminescence lifetime of the Ru-based donor unit of **Ru-L10-Os** (to be compared with that for the reference complex **Ru-L5**); R_o is the critical transfer radius [from eqns. (1) and (2)]; and $f(r)$ describes a gaussian distribution centred around μ, the average Ru $\cdots$ Os separation in **Ru-L10-Os**, with a representing the width of the distribution. Analyses of the Ru-based luminescence decays of **Ru-L10-Os**, as monitored at 610 nm in the employed solvents, were therefore performed according to eqn. (3) by using an iterative least-squares non-linear approach;[20] results are collected in Table 1. Fig. 2 displays representative decays observed in the two solvents; the derived $f(r)$ distributions are illustrated in the insets.

From the detailed analysis of the time resolved luminescence we can draw the following conclusions. The average intermetal distance in **Ru-L10-Os** is evaluated as 14–15 Å in both solvents employed, which does not correspond to a full extension of the connecting chain (estimated as 38 Å).[18] According to the obtained $f(r)$ distributions (insets of Fig. 2) this indicates that in most cases the Ru→Os energy transfer takes place within the "critical sphere", with $R_o = 24$ Å. The conformational picture emerging from this result is consistent with the chain of **L10** undergoing a high degree of folding whose *average* extent (based on the Ru $\cdots$ Os average separation) is not solvent dependent. The *distribution* of Ru $\cdots$ Os separations [parameter a in eqns. (3) and (4)] is however significantly solvent dependent, with the $f(r)$ distribution (Fig. 2) being remarkably narrower in EG than in CH_2Cl_2, suggesting that in the EG solvent **Ru-L10-Os** behaves like a more rigidified dinuclear system compared to the behaviour in CH_2Cl_2. This behaviour contrasts with that shown by the shorter complex **Ru-L5-Os**, where a single exponential decay for the Ru-based emission was observed at each solvent composition, corresponding to a Ru $\cdots$ Os separation of 12 Å in CH_2Cl_2 and 15 Å in MeOH.

The majority of recent studies on the conformation of poly(oxoethylenes)[14] (and simple model complexes such as dimethoxyethane[15]) have concentrated on how the proportion of *anti* and *gauche* conformers varies in the ensemble under different conditions, using a wide variety of techniques such as ^{13}C NMR, infrared, Raman, and neutron- and electron-diffraction methods. It is clear from our new work that use of luminescence methods can play an important rôle in helping to determine the overall distribution of different chain conformations in these flexible oligomers.

Acknowledgements

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Notes and references

‡ 2,2′-Bipy-5-(CH_2OCH_2)$_4$$CH_2$OTs. To a solution of 5-hydroxymethyl-2,2′-bipyridine[21] (0.10 g, 0.54 mmol) in dry THF (20 cm^3) was added NaH (0.021 g of 60% dispersion in oil, 0.54 mmol) and the mixture was stirred under N_2 for 15 min. To this was added a solution of tetra(ethylene gylcol) ditosylate (0.50 g, 1.0 mmol) in THF (10 cm^3). The reaction was then monitored by TLC (Silica; MeOH/CH_2Cl_2, 1 : 9 v/v) until most of the 5-hydroxymethyl-2,2′-bipyridine had disappeared. The solvent was then removed and the resulting oil dissolved in CH_2Cl_2 (50 cm^3) and washed with water (2 × 20 cm^3). The crude material was purified by repeated column chromatography (silica; MeOH/CH_2Cl_2, 1 : 9 v/v). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.68 (1 H, d; bipy H$^{6'}$), 8.64 (1 H, br s; bipy H^6), 8.38 (2 H, m; bipy), 7.78–7.82, [4 H, m; bipy (×2) and phenyl H^2/H^6]; 7.30–7.35 [3 H, m; bipy (×1) and phenyl H^3/H^5], 4.64 (2 H, s; bipy-C*H*$_2$O), 4.15 (2 H, m; CH_2), 3.60–3.70 (14 H, m; CH_2), 2.35 (3 H, s; CH_3). EIMS: *m*/*z* 516 (5%, M$^+$).

2,2′-Bipy-5-(CH_2OCH_2)$_{10}$$CH_2$OH. To a solution of NaH (0.013 g of 60% dispersion in oil, 0.32 mmol) in THF (20 cm^3) was added hexa(ethylene gylcol) (0.09 g, 0.32 mmol) and the reaction stirred under N_2 for 1 h. After this time 2,2′-bipy-5-(CH_2OCH_2)$_4$$CH_2$OTs (0.082 g, 0.16 mmol) was added and the reaction was refluxed overnight. The reaction was then quenched with water, and extracted with CH_2Cl_2; the extract was evaporated to dryness to give a crude oil which was purified by column chromatography (silica; MeOH/CH_2Cl_2, 1 : 9 v/v) to give the product as a pale yellow oil (yield: 46%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.66 (2 H, m; bipy); 8.38 (2 H, m; bipy); 7.82, (2 H, m; bipy); 7.31 (1 H, m; bipy); 4.65 (2 H, s; bipy-C*H*$_2$O); 3.65 (40 H, m; CH_2). EIMS: *m*/*z* 626 (50%, M$^+$).

L10. To a solution of 2,2′-bipy-5-(CH_2OCH_2)$_{10}$$CH_2$OH in dry, degassed THF (30 cm^3) was added NaH (0.026 g of 60% dispersion in oil, 0.64 mmol) and the mixture was stirred for 1 h. To this was added a solution of 5-bromomethyl-2,2′-bipyridine[22] (0.060 g, 0.24 mmol) in dry THF (5 cm^3) and the mixture was stirred at reflux for 24 h. Removal of the solvent afforded a brown oil which was purified by column chromatography (silica; MeOH/CH_2Cl_2, 1 : 9 v/v) to give **L10** as a viscous oil (yield: 32%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.68 (4 H, m; bipy); 8.45 (4 H, m; bipy); 7.85, (4 H, m; bipy); 7.35 (2 H, m; bipy); 4.65 (4 H, s; bipy-C*H*$_2$O); 3.66 (40 H, m; CH_2). EIMS: *m*/*z* 794 (3%, M$^+$).

[Ru(bipy)$_2$(**L10**)][PF$_6$]$_2$ (**Ru-L10**). Reaction of **L10** (0.035 g, 0.044 mmol) and [Ru(bipy)$_2$Cl$_2$]·2H$_2$O (ref. 23) (0.023 g, 0.044 mmol) in EtOH (30 cm^3) at reflux for 6 h afforded a red solution. The solvent was removed *in vacuo* and the product chromatographed on Sephadex-SP25, eluting with 0.3 M aqueous NaCl. The major red band yielded **Ru-L10** after precipitation with aqueous NH_4PF_6, extraction with CH_2Cl_2, and evaporation to dryness. Yield: 42%. FAB-MS: *m*/*z* 1208 ({M + H − 2PF$_6$}$^+$). Found: C, 46.0; H, 4.1; N, 6.4%. Required for [Ru(bipy)$_2$(**L10**)][PF$_6$]$_2$·2CH$_2$Cl$_2$: C, 46.1; H, 4.7; N, 6.7%. In addition a small amount of the dinuclear complex [{Ru(bipy)$_2$}$_2$(**L10**)][PF$_6$]$_4$ was isolated (11% yield) after further elution with 0.5 M NaCl.

[(bipy)$_2$Ru(**L10**)Os(bipy)$_2$][PF$_6$]$_4$ (**Ru-L10-Os**). **Ru-L10** (0.040 g, 0.027 mmol) was added to a slight excess of [Os(bipy)$_2$Cl$_2$] (ref. 24) (0.017 g, 0.030 mmol) in ethylene glycol (15 cm^3) and heated at 120 °C for 24 h. The dark green reaction mixture was allowed to cool, added to distilled water (100 cm^3) and introduced onto Sephadex-SP25. Firstly, the mixture was eluted with a further 100 cm^3 of water, and then with 0.5 M aqueous NaCl which afforded a primary green band which was collected. Addition of aqueous NH_4PF_6, extraction with CH_2Cl_2, and evaporation to dryness afforded **Ru-L10-Os** in 63% yield. FAB-MS: *m*/*z* 2148 ({M + H − PF$_6$}$^+$), 1999 ({M + H − 2PF$_6$}$^+$), 1707 ({M + H − 4PF$_6$}$^+$). Found: C, 41.6; H, 3.7; N, 6.6%. Required for [(bipy)$_2$Ru(**L10**)Os(bipy)$_2$][PF$_6$]$_4$·CH$_2$Cl$_2$: C, 42.0; H, 3.9; N, 7.1%.

§ Absorption spectra of dilute solutions (2×10^{-5} M) of the complexes were measured in the indicated solvents at room temperature with Perkin-Elmer Lambda 5, Lambda 9 or Lambda 19 UV/Vis spectrophotometers. For the luminescence experiments, air-equilibrated solutions of the samples were used. Luminescence spectra were obtained from solutions whose absorbance values were ≤0.2 at the employed excitation wavelength (415 nm) 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 and used as a reference $[Ru(bpy)_3]^{2+}$ ($\Phi = 0.028$ in air-equilibrated water) as a reference standard.[25] Band maxima and relative luminescence intensities are subject to uncertainties of *ca.* 2 nm and 20%, respectively. Luminescence lifetimes were obtained using an IBH single-photon counting equipment equipped with a nitrogen-filled thyratron gated lamp. The uncertainty in the lifetime values is within 8%.

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