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Solvatochromism as a mechanism for controlling intercomponent photoinduced processes in a bichromophoric complex containing $[Ru(bpy)_3]^{2+}$ and $[Ru(bpy)(CN)_4]^{2-}$ units

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The dinuclear complex $[(bpy)_2Ru(\mu\text{-}L^1)Ru(CN)_4]$ (**1**) contains $\{Ru(bpy)_3\}^{2+}$-type (**Ru-bpy**) and $\{Ru(bpy)(CN)_4\}^{2-}$-type (**Ru-CN**) chromophores covalently linked by a short, saturated $–CH_2OCH_2CH_2OCH_2–$ chain. Since the photophysical properties of the **Ru-CN** chromophore are strongly solvent-dependent, whereas those of the **Ru-bpy** chromophore are not, it follows that altering the solvent provides a means of altering the driving force for inter-component photoinduced energy- or electron transfer processes. At room temperature, in a mixed solvent system varying from pure water to pure dmso, the characteristic luminescence of the excited **Ru-bpy** unit is progressively quenched as the proportion of dmso in the mixture increases. This behaviour is consistent with both ***Ru-bpy** ⟶ **Ru-CN** energy transfer quenching and with **Ru-CN** ⟶ ***Ru-bpy** electron transfer quenching, because as the proportion of dmso in the solvent increases, the ^{3}MLCT excited state of the **Ru-CN** unit drops in energy (which facilitates the energy transfer process) and its Ru(III)/Ru(II) reduction potential also becomes less positive (which facilitates the electron transfer process). Consideration of the solvent composition at which luminescence quenching of **Ru-bpy** by **Ru-CN** occurs, the saturated nature of the spacer, and the metal–metal separation, collectively point towards Förster energy transfer being the quenching process which is switched on by the change in solvent composition. In contrast, at 77 K (frozen solvent) the ^{3}MLCT state of the **Ru-CN** unit is raised in energy above that of the **Ru-bpy** unit, such that the energy transfer gradient is reversed and ***Ru-CN** ⟶ **Ru-bpy** energy-transfer occurs with strong emission from the **Ru-bpy** terminus.

Introduction

The study of inter-component photoinduced electron transfer (PET) and photoinduced energy transfer (PEnT) in multi-component complexes is of interest for a wide variety of applications, varying from mimicking the fundamental steps of photosynthesis[1] to the development of new materials and devices such as solar cells,[2] luminescent sensors[3] and 'molecular wires'.[4] In the particular context of switches and sensors, compounds displaying the ability to modulate the photoinduced inter-component process by some external perturbation are of particular interest. For example, PET involving amine quencher units can be suppressed by protonation or coordination of a metal ion to the amine group which prevents it from acting as an electron-donor;[5,6] likewise, redox interconversions of a quencher fragment adjacent to a luminophore can switch on/off its ability to participate in PET processes.[7] As regards PEnT, known switching mechanisms include reversible conformational changes which affect the chromophore/quencher separation in flexible complexes,[6,8] and altering the relative ordering of the excited states associated with the different chromophores by protonation of one component[9] or by a large change in temperature.[10]

We describe in this paper a dyad **1** (Scheme 1) containing a $[Ru(bpy)_3]^{2+}$ unit[11] covalently linked to a $[Ru(bpy)(CN)_4]^{2-}$ unit[12,13] (bpy = 2,2′-bipyridine), in which the strong solvatochromism of the $[Ru(bpy)(CN)_4]^{2-}$ unit can be used to modify its ability to quench the emission of the $[Ru(bpy)_3]^{2+}$ chromophore. This provides a sensitive mechanism for altering the degree of luminescence from the $[Ru(bpy)_3]^{2+}$ chromophore according to the properties of the solvent. The same principle has been used before to alter the gradient for PEnT in a dyad consisting of $[Ru(bpy)_3]^{2+}$-type and $[Ru(bpy)_2(CN)_2]$-type units linked by a methylenephenylene bridge, because the $[Ru(bpy)_2(CN)_2]$ chromophore is also solvatochromic, although to a lesser extent than $[Ru(bpy)(CN)_4]^{2-}$.[14]

Results and discussion

Synthesis of the dinuclear complex 1 and solvatochromism of the $[Ru(bpy)(CN)_4]^{2-}$ unit

The bridging ligand L^1 was simply prepared by reaction of ethylene glycol with two equivalents of 5-bromomethyl-2,2′-bipyridine[15] in thf in the presence of NaH. Reaction of L^1 with $[Ru(bpy)_2Cl_2]$ in the usual way afforded the mononuclear complex $[Ru(bpy)_2(L^1)][PF_6]_2$ in which the second bipyridyl binding site of L^1 is vacant; further reaction of this with $K_4[Ru(CN)_6]$ afforded the dyad complex $[(bpy)_2Ru(\mu\text{-}L^1)Ru(CN)_4]$ (**1**) in moderate yield. For convenience we will refer to the $\{Ru(bpy)_3\}^{2+}$ unit of **1** as the **Ru-bpy** unit, and the $\{Ru(bpy)(CN)_4\}^{2-}$ unit as the **Ru-CN** unit.

Complex **1** was satisfactorily characterised on the basis of its ^{1}H NMR spectrum and electrospray and FAB mass spectra. Both types of mass spectrum show a molecular ion signal for **1** with the correct isotopic pattern; adducts with Na^+ and K^+ are also apparent. In the ^{1}H NMR spectrum most of the signals in the aromatic region (from four non-equivalent bipyridyl units) are overlapping and not individually resolved. However it is clear that (i) the ratios of aliphatic to aromatic signals are as expected; (ii) the bipyridyl H^6 protons of the **Ru-CN** unit have their characteristic highly deshielded signals at around 9.5 ppm;

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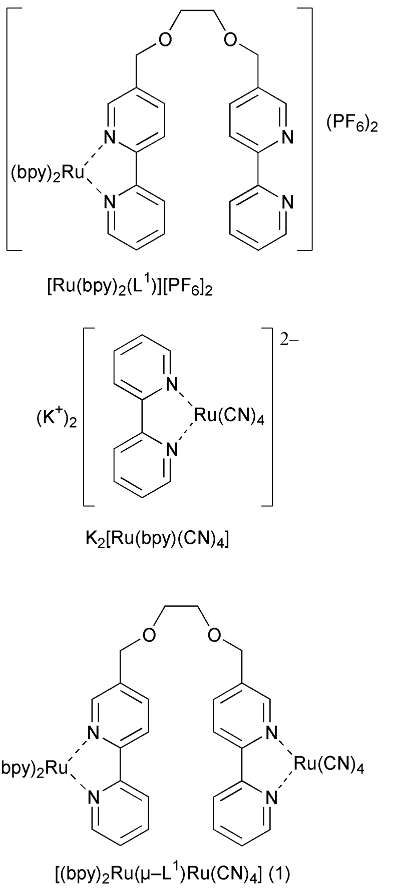

Scheme 1

and (iii) the two sets of CH_2 protons of the methylene units attached to the bipyridyl ligands are inequivalent, with the set closer to the **Ru-bpy** unit split into an AB multiplet because of the chirality of the adjacent **Ru-bpy** core. Reproducible elemental analyses indicate the presence of several molecules of water of crystallisation, which is characteristic of the **Ru-CN** unit; for example the salt $[PPN]_2[Ru(bpy)(CN)_4]$ crystallises with 15 H_2O.[16] As mononuclear units to model the component parts of **1** we used $[Ru(bpy)_2(L^1)][PF_6]_2$ and $K_2[Ru(bpy)(CN)_4]$ (Scheme 1).[12,13]

The basis of the switching mechanism is the well-documented solvatochromism of the $[Ru(bpy)(CN)_4]^{2-}$ chromophore, which arises from the interaction of the externally directed lone pairs of the cyanide ligands with the solvent.[13] In solvents with a high Gutmann acceptor number (AN), the ^{1}MLCT and ^{3}MLCT excited states are considerably higher in energy than they are in solvents with a low AN where the MLCT levels are stabilised. Since the orbital energies of $[Ru(bpy)_3]^{2+}$ are in contrast very little solvent dependent,[11] altering the solvent properties will affect the MLCT excited state energy of one metal unit in **1** but not the other. Thus the gradient for intermolecular PEnT will be solvent dependent,[12–14] and its direction might even be reversed by using suitable solvents. Similarly, the Ru(III)/Ru(II) redox potential of $[Ru(bpy)(CN)_4]^{2-}$ is strongly solvent-dependent, being +0.77 V *vs.* ferrocenium/ferrocene (Fc^+/Fc) in water and −0.28 V in dmf,[13] which means that its ability to act as an electron-donor quencher of the excited state of $[Ru(bpy)_3]^{2+}$ is also increased in solvents with a low AN. Since the Ru(III)/*Ru(II) redox potential of the excited state of $[Ru(bpy)_3]^{2+}$ lies between these values, being 0.44 V *vs.* Fc^+/Fc,[11] we also expect that a **Ru-CN** → (**Ru-bpy**)* PET process within **1** (where * denotes the MLCT excited state) can be thermodynamically favourable in some solvents or solvent mixtures but not in others. The only organic solvent in which **1** is significantly soluble is dmso, which has a low acceptor number, AN = 19.3; it is also sparingly soluble in water which has a high AN (54.8).[13] Accordingly, we used dmso–water mixtures for our studies of the solvent-dependence of its photophysical properties as these two solvents provide almost the extremes of spectroscopic and redox behaviour for the $[Ru(bpy)(CN)_4]^{2-}$ unit.[13]

In order to confirm that linking the two chromophores together has not resulted in a significant perturbation of their individual properties – which is not expected to be a problem, given the saturated nature of the linkage – we examined the redox properties of **1** in water using KCl as base electrolyte. The limited window of this solvent prevented observation of the Ru(III)/Ru(II) couple associated with the **Ru-bpy** unit, but the Ru(III)/Ru(II) couple of the **Ru-CN** terminus of **1** was observed at +0.815 V *vs.* our Ag/AgCl reference electrode. Under identical conditions, the redox potential of the Ru(III)/Ru(II) couple for $[Ru(bpy)(CN)_4]^{2-}$ was found to be +0.819 V. These numbers are identical within the limits of accuracy of the measurement, and there is clearly no significant electronic interaction between the **Ru-bpy** and **Ru-CN** components of **1** in their ground states. An exactly similar picture emerged from comparison of the redox properties of **1** and $[Ru(bpy)(CN)_4]^{2-}$ in dmso, and also from the absorption spectra (next section).

Spectroscopic and photophysical studies

Like the parent complex $[Ru(bpy)_3]^{2+}$,[11] the photophysical properties of mononuclear $[Ru(bpy)_2(L^1)]^{2+}$ are very little affected by solvent (Table 1). The luminescence band maxima λ^{em} are 615 and 621 nm in water and dmso, respectively; and both the luminescence quantum yield and lifetime exhibit similar values in the two pure solvents, $\Phi_w = 0.026$ and $\tau_w = 410$ ns; $\Phi_{dmso} = 0.022$ and $\tau_{dmso} = 450$ ns. In contrast, for mononuclear $[Ru(bpy)(CN)_4]^{2-}$ the lowest-lying ^{1}MLCT absorption maximum (λ^{abs}) shifts from 404 to 550 nm on passing from neat water to neat dmso, which amounts to an energy difference of *ca.* 6600 cm^{-1} (Fig. 1). For the ^{3}MLCT luminescence, the band maximum λ^{em} gradually shifts from 620 to 810 nm on passing from pure water to pure dmso, an energy difference of *ca.* 3800 cm^{-1}, and the emission becomes greatly reduced in intensity ($\Phi_w = 6 \times 10^{-3}$; $\Phi_{dmso} < 1 \times 10^{-4}$; see Table 1 and Fig. 2).[13]

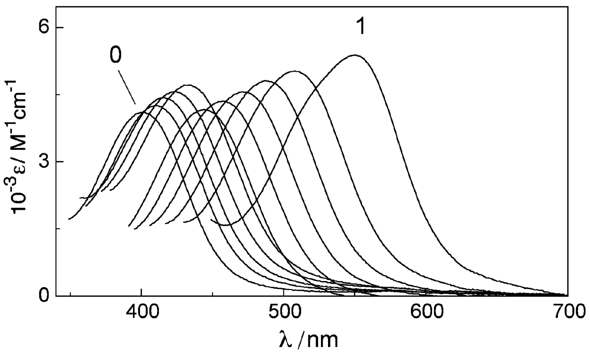

Fig. 1 Solvent sensitivity of the lowest-energy absorption band of $K_2[Ru(bpy)(CN)_4]$ in various dmso–water mixtures; pure water is 0, pure dmso is 1.

In complex **1**, we expect accordingly that the spectroscopic properties of the **Ru-bpy** terminus are scarcely affected by the solvent, whereas the behaviour of the **Ru-CN** terminus should be highly solvent-sensitive. Fig. 3 shows the visible region of the absorption spectrum of **1** recorded in pure water and pure dmso; in the same figure the absorption profile (in the visible region) for $[Ru(bpy)(CN)_4]^{2-}$ in dmso is included. Comparison of the spectral profiles in Fig. 3 and inspection of the absorption data in Table 1, reveals that for **1** in dmso, the absorption band at λ_{max} 550 nm ($\varepsilon = 3900$ M^{-1} cm^{-1}) arises from the **Ru-CN** component: in water this band shifts to higher energy (Table 1) such that it overlaps with the ^{1}MLCT absorption of the **Ru-bpy**

Table 1 Spectroscopic and photophysical parameters[a]

	Absorption		Luminescence		
	λ^{abs}/nm (ε/M^{-1} cm^{-1})	λ^{em}/nm[b]	Φ[c]	τ/ns	
water					
$[Ru(bpy)_2(L^1)][PF_6]_2$	286 (80700)	452 (12300)	615	0.026	410
$K_2[Ru(bpy)(CN)_4]$	284 (27300)	404 (4100)	624	0.006	100
1	287 (76300)	452 (11400)	618	0.026	360
dmso					
$[Ru(bpy)_2(L^1)][PF_6]_2$	286 (81000)	452 (14000)	621	0.022	450
$K_2[Ru(bpy)(CN)_4]$	299 (34600)	550 (5400)	806[d]	$<1 \times 10^{-4}$	[e]
1	292 (70500)	457 (13100) 550 (3900)	620[f]	$<5 \times 10^{-4,f}$	4.0[f]

[a] Room temperature, in the indicated solvents, air-equilibrated conditions. [b] Band maxima for uncorrected spectra. [c] Luminescence quantum yield obtained from corrected spectra. [d] Ref. 13. [e] Too weak to measure. [f] Ascribed to residual emission from the **Ru-bpy** luminophore of **1**, see text.

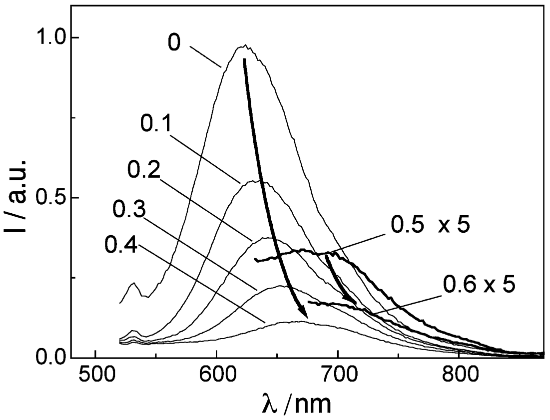

Fig. 2 Luminescence spectrum of $K_2[Ru(bpy)(CN)_4]$ in the indicated dmso : water volume fractions; isoabsorbing solutions were excited at 450 nm.

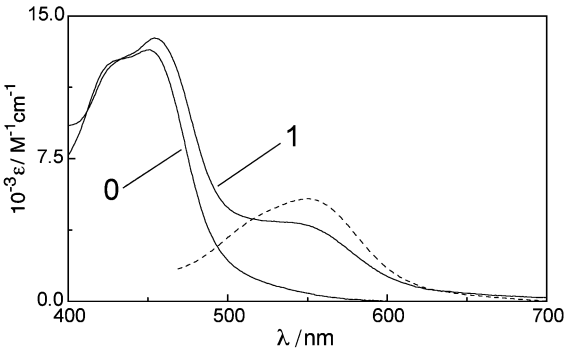

Fig. 3 Absorption spectrum for dyad **1** (full line) in pure water (0) and dmso (1) and as compared with that of $K_2[Ru(bpy)(CN)_4]$ (lowest-energy band, dashed line) in pure dmso.

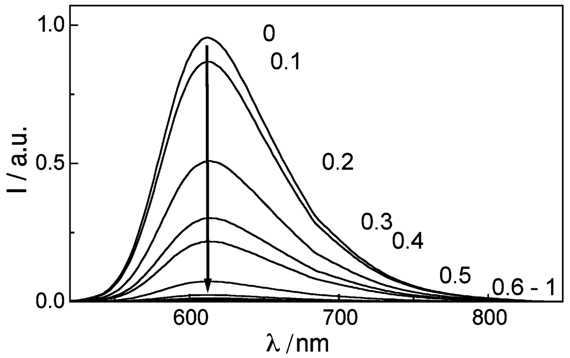

Fig. 4 Luminescence spectra of dyad **1** (2×10^{-5} M) in the indicated dmso : water volume fractions; excitation was at 450 nm.

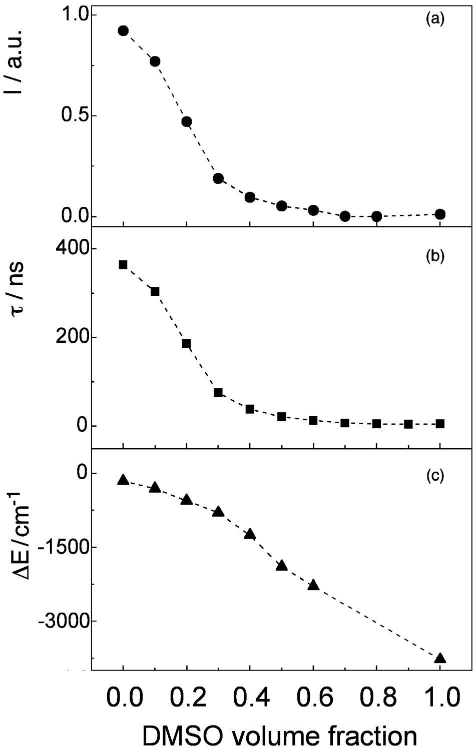

Fig. 5 Effect of changing dmso : water volume fractions on (a) the luminescence intensity of **1** (2×10^{-5} M, λ_{exc} 450 nm), as recorded at 620 nm; (b) the luminescence lifetime of **1**, as observed at 620 nm; and (c) the calculated energy gap between the triplet levels centred on the **Ru-bpy** and **Ru-CN** moieties of dyad **1**.

unit which is observed at 457 nm (ε = 13100 M^{-1} cm^{-1}) in dmso, and 452 nm (ε = 11400 M^{-1} cm^{-1}) in water.

The luminescence spectra of **1** in various dmso : water mixtures are shown in Fig. 4; excitation was performed at 450 nm and the small changes of absorbance values with solvent composition were taken into account. The spectra exhibit a nearly constant emission maximum (λ^{em} lies between 615 and 620 nm in all cases) with intensities that progressively diminish on passing from pure water to pure dmso [see also Fig. 5(a)]. In parallel with this, we observe a progressive shortening of the luminescence lifetime [Fig. 5(b)]. Thus, as the proportion of dmso in the solvent mixture increases, the luminescence of the **Ru-bpy** component is progressively quenched by the **Ru-CN** component which becomes both a better energy acceptor (lower-energy ^{3}MLCT level) and a better electron donor [less positive Ru(III)/Ru(II) reduction potential] due to its solvatochromism.[13] That this quenching is genuinely intramolecular was confirmed by a control experiment in which the luminescence intensity of a 10^{-5} M solution of $[Ru(bpy)_3]Cl_2$ in dmso was measured after addition of one equivalent of $K_2[Ru(bpy)(CN)_4]$; the characteristic emission of the $[Ru(bpy)_3]^{2+}$ was reduced in intensity only by about 3% in dmso and 2% in water, presumably due to a small degree of ion-pairing of the oppositely-charged species.

Any quenching of luminescence from the **Ru-bpy** terminus of **1** must therefore be intramolecular.

Energy transfer. Considering first the possibility of ***Ru-bpy** ⟶ **Ru-CN** energy transfer being responsible for the quenching, by using the available λ^{em} values for $[Ru(bpy)(CN)_4]^{2-}$ in the various dmso : water solvent mixtures we can construct a diagram for the energy gap ΔE between the two ^{3}MLCT levels concerned [Fig. 5(c)]. In water we expect the two components to have very similar ^{3}MLCT energies (Table 1). The emission that was detected from **1** in water ($\Phi = 0.026$, $\tau = 360$ ns) has very similar characteristics to that which occurs from the isolated $[Ru(bpy)_2(L^1)]^{2+}$ model complex ($\Phi = 0.026$, $\tau = 410$ ns), indicating that the luminescence of **1** originates mainly from the **Ru-bpy** moiety. The presence of a single exponential decay [separate emission from the **Ru-CN** unit at about the same wavelength but with a shorter lifetime (Table 1) would give dual-exponential behaviour] indicates that the two chromophores in water are in thermal equilibrium. This equilibrium can be modelled according to Fig. 6(a), where the two possible excited states are *$[(bpy)_2Ru^{III}(bpy^{\bullet-}\text{-S-bpy})Ru^{II}(CN)_4]$ (**Ru-bpy** component excited) and *$[(bpy)_2Ru^{II}(\text{bpy-S-bpy}^{\bullet-})Ru^{III}(CN)_4]$ (**Ru-CN** component excited), with $\tau_{\text{Ru-bpy}} = 410$ ns and $\tau_{\text{Ru-CN}} = 100$ ns (Table 1), where bpy-S-bpy is the bridging ligand L^1. To reproduce the experimental finding ($\tau^{obs} = 360$ ns) requires that the excited **Ru-CN** level should actually be slightly higher in energy than the excited **Ru-bpy** level by 200 cm^{-1}. This is not apparent from the properties of the mononuclear model complexes in Table 1 (which suggests that the **Ru-bpy** component should have the slightly higher ^{3}MLCT level by *ca.* 200 cm^{-1}), but it only requires a small perturbation of the properties of the mononuclear component parts when linked into a dinuclear complex to account for this. In fact the alkyl substituent provided by the spacer group will cause a small perturbation of the **Ru-CN** chromophore in the required direction compared to the unsubstituted model complex $[Ru(bpy)(CN)_4]^{2-}$, by slightly raising its ^{3}MLCT level. It is in any event quite clear from the photophysical measurements that a single-exponential emission occurs from **1** in water, and that this is largely **Ru-bpy** centred.

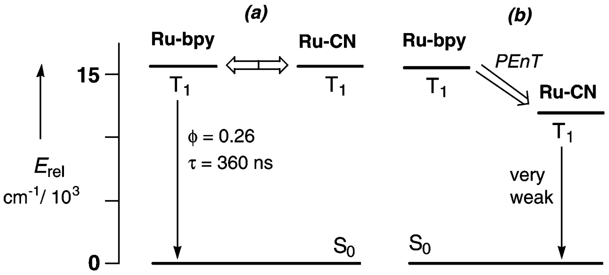

Fig. 6 Limiting behaviour of the excited states of **1** in (a) water, (b) dmso, assuming that PEnT is the dominant quenching mechanism (see text).

As the proportion of dmso in the solvent is increased, the gradient for PEnT increases [Fig. 5(c)] and the **Ru-bpy** emission becomes progressively quenched [Figs. 4, 5(a)]. Such an intramolecular energy transfer process may be described as *$[(bpy)_2Ru^{III}(bpy^{\bullet-}\text{-S-bpy})Ru^{II}(CN)_4] \longrightarrow$ *$[(bpy)_2Ru^{II}(\text{bpy-S-bpy}^{\bullet-})Ru^{III}(CN)_4]$. In pure dmso, the energy gradient for PEnT in this direction is over 3500 cm^{-1}. Nearly complete quenching of the **Ru-bpy** luminescence is observed, with a quenched lifetime $\tau_q = 4$ ns (Table 1). From $k_{en} = 1/\tau_q - 1/\tau$, the evaluated experimental rate constant is $k_{en} = 2.5 \times 10^8$ s^{-1} if PEnT is occurring. Since the saturated linkage between the chromophores is expected to interrupt electronic communication between them, the exchange (Dexter) mechanism for energy transfer should be negligible and PEnT will be by the Förster mechanism.[17] Based on the observed energy transfer rate constant, the Förster equation yields an interchromophoric distance of $d_{cc} = 8$ Å.[18] Given that the critical transfer radius (the distance below which energy transfer to the quencher is faster than the intrinsic deactivation of the chromophore) is evaluated to be $R_c = 16.5$ Å, energy transfer according to the Förster mechanism is quite reasonable. In fact this calculated separation of 8 Å represents a considerable degree of folding of the flexible chain linking the components, since the metal–metal separation with the ligand fully opened out is estimated from molecular modelling as *ca.* 14 Å.

Following energy transfer in this way we might expect to observe sensitised luminescence from the **Ru-CN** component; however, no such emission could be detected, by performing both steady-state and time resolved experiments. Possible reasons for this failure are as follows. (i) For low dmso volume fractions, emission from the **Ru-CN** unit is expected to overlap with, but be hidden by, the much stronger luminescence from the incompletely quenched **Ru-bpy** unit (Table 1). (ii) For high dmso fractions, where nearly quantitative quenching of the **Ru-bpy** excited state greatly reduces the luminescence intensity centred at 620 nm, the luminescence band of the **Ru-CN** component is expected to be red-shifted with respect to case (i), however intrinsically extremely weak (Table 1, Fig. 1) and the sensitised emission may likewise have escaped detection. Alternatively, if the quenching mechanism is *electron* transfer (PET) then such emission is not expected.[19]

Electron transfer. Given the value of +0.84 V *vs.* NHE (*ca.* 0.44 V *vs.* Fc$^+$/Fc depending on solvent)[20] for the redox potential of $[Ru(bpy)_3]^{2+}$ in its excited state, Ru(III)/*Ru(II), we expect that **Ru-CN** ⟶ ***Ru-bpy** PET can become thermodynamically favourable when the Ru(III)/Ru(II) redox potential of the **Ru-CN** component is below this value. Thus, from the photophysical studies in fluid solution at room temperature, the increased quenching of the **Ru-bpy** luminescence by the **Ru-CN** component of **1** as the proportion of dmso increases in the solvent may be ascribed to either PET or PEnT quenching (and the experimental difficulties for detection of any weak sensitised emission from the **Ru-CN** component may hamper evidence for PEnT). From the known Ru(III)/Ru(II) potentials of **Ru-CN** [+0.77 V in water and −0.18 V in dmso, both *vs.* Fc$^+$/Fc],[13] and assuming that the **Ru-CN** redox potential in a mixed-solvent system varies approximately linearly with solvent composition,[21] we expect PET quenching to become thermodynamically favourable when the proportion of dmso in the dmso–water mixture is 35% or more. In fact, Fig. 5(a) shows that substantial quenching of the **Ru-bpy** unit of **1** occurs when the solvent composition is *ca.* 20% dmso, at which point PET would be endergonic because the Ru(III)/Ru(II) potential of the **Ru-CN** unit is too positive, which suggests that PET is not the quenching mechanism.[21]

Low temperature experiments. The nature of the quenching mechanism can sometimes be clarified by examining the photophysical properties of the complexes at 77 K in a frozen matrix, because under these conditions PET is made difficult (due to lack of solvent repolarisation)[22] but PEnT is not.[23] We accordingly compared the luminescent behaviour of complexes $[Ru(bpy)(CN)_4]^{2-}$ and **1** in dmso at 77 K. Results are illustrated in Fig. 7. For $[Ru(bpy)(CN)_4]^{2-}$, the broad emission band maximum peaks at *ca.* 590 nm ($\tau = 2$ μs), *i.e.* it is strongly hypsochromically shifted with respect to what happens at room temperature (Table 1). Thus, in frozen solvent inhibition of solvent repolarisation is responsible for a large destabilisation of the ^{3}MLCT level of $[Ru(bpy)(CN)_4]^{2-}$.[24] The extent of this effect is so large that the triplet level for this complex becomes slightly higher in energy than that for $[Ru(bpy)_2(L^1)]^{2+}$ (τ = 2.5 μs), whose emission band maximum is found at 602 nm (Fig. 7). Interestingly, $[Ru(bpy)_2(L^1)]^{2+}$ and **1** ($\tau = 2.5$ μs) exhibit matching luminescence profiles featuring the characteristic vibrational progression (with spacing *ca.* 1300–1400 cm^{-1}) ascribable to a $[Ru(bpy)_3]^{2+}$-type emitter.[11] This may be taken as

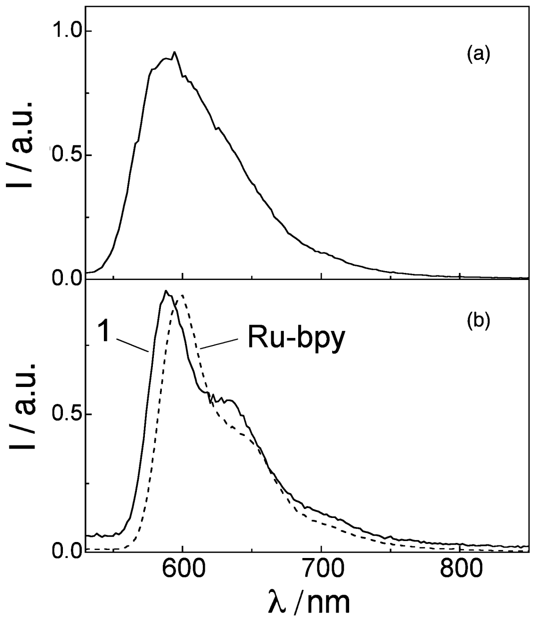

Fig. 7 Luminescence spectra obtained at 77 K for (a) $K_2[Ru(bpy)(CN)_4]$, (b) $[Ru(bpy)_2(L^1)][PF_6]_2$ and dyad **1**; dmso solvent, λ_{exc} 450 nm.

an indication of a ***Ru-CN** ⟶ **Ru-bpy** PEnT process in **1**, *i.e.* the ordering of the **Ru-bpy** and **Ru-CN** excited states is exactly reversed compared to the situation at room temperature. This reversal of the ordering of excited states is rare but has been demonstrated in other systems which contain two different types of chromophore with one being more affected by freezing the solvent than the other.[10]

Of course, this result in itself does not provide clear cut evidence regarding which mechanism – energy or electron transfer – predominates in dmso at room temperature. What can be said, however, is that also at room temperature electron transfer seems disfavoured. The quenching process at room temperature starts at a solvent composition at which PET is expected to be unfavourable; and even when the energetic requirements for PET are met [in neat dmso, the exothermicity for **Ru-CN** ⟶ (**Ru-bpy**)* PET is larger than 0.6 eV], a good electronic contact between the partners is required in order to have efficient electron transfer.[1,25] For complex **1**, this is not the case because the polyethylene glycol chain is saturated, and this is known to lead to a poor electronic factor for the occurrence of PET.[1] On the contrary, the description employed above for the energy transfer step is that of Förster, which takes place *via* dipole–dipole interaction,[17,18] and does not require electronic mediation by an intervening unit.

Conclusions

In conclusion, it is clear that the solvent-dependence of the excited-state properties of the $[Ru(bpy)(CN)_4]^{2-}$ chromophore can be exploited to provide an effective mechanism for controlling with some precision the extent of inter-component quenching in a multi-chromophore system in which the other components are not solvatochromic. Extension of this principle to higher-nuclearity systems such as dendrimers, where controlling gradients for energy or electron transfer could be used to fine-tune the antenna effect,[26] is a particularly interesting prospect.

Experimental

General details

$K_4[Ru(CN)_6]\cdot 3H_2O$ and $RuCl_3\cdot xH_2O$ were purchased from Johnson Matthey and used as received. Organic starting materials were purchased from Aldrich or Fluka and used as received. Electrospray mass spectra of the complexes were recorded on aqueous solutions using a VG Quattro instrument; FAB mass spectra were recorded on a VG-Autospec instrument; ^1H NMR spectra were recorded on Jeol GX-270 or λ-300 spectrometers.

Syntheses

Synthesis of L^1. A mixture of dry ethylene glycol (0.059 g, 0.95 mmol) and NaH (0.2 g, excess) in dry thf (30 cm^3) under $N_2(g)$ was stirred for 40 minutes. 5-Bromomethyl-2,2′-bipyridine (0.53 g, 2.1 mmol)[15] was added and the reaction mixture was heated to reflux for 18 h. After cooling, MeOH was added to destroy residual NaH and the solvent was removed *in vacuo*. The crude mixture was loaded onto a silica column and eluted with 20% MeOH in CH_2Cl_2 to yield L^1 as a pale yellow oil (0.27 g, 72%) which is hygroscopic. EIMS: *m*/*z* 398 [M^+], 229 [M^+ − bpy-CH_2]. ^1H NMR [270 MHz, $CDCl_3$, 25 °C]: δ 3.74 (4 H, s, –OCH_2CH_2O–), 4.66 (4 H, s, bpy-CH_2–), 7.30 (2 H, ddd, bpy $H^{5'}$), 7.87–7.76 (4 H, m, bpy $H^{4,4'}$), 8.42–8.35 (4 H, m, bpy $H^{3,3'}$), 8.72–8.65 (4 H, m, bpy $H^{6,6'}$).

Synthesis of $[Ru(bpy)_2(L^1)][PF_6]_2$. A mixture of $[Ru(bpy)_2Cl_2]\cdot 2H_2O$ (0.206 g, 0.4 mmol)[27] and L^1 (0.200 g, 0.5 mmol) was heated to reflux in EtOH for 3 h to give an orange solution. After evaporation of the solvent the crude mixture was loaded onto a silica column and eluted using MeCN–water–$KNO_{3(aq,sat)}$ (14 : 2 : 1, v/v). The second (major) band was collected; concentration *in vacuo* and addition of NH_4PF_6 precipitated the mononuclear complex $[Ru(bpy)_2(L^1)][PF_6]_2$ which was extracted from the suspension with several portions of CH_2Cl_2. Drying the combined extracts afforded pure $[Ru(bpy)_2(L^1)][PF_6]_2$ (0.136 g, 31%). ESMS: *m*/*z* 405.8 $\{M - 2PF_6\}^{2+}$, 478.81 $\{M + H - PF_6\}^{2+}$. FAB-MS: *m*/*z* 1142 $\{M + H + K\}^+$, 1126 $\{M + H + Na\}^+$, 1104 $\{M + 2H\}^+$, 958 $\{M + H - PF_6\}^+$, 813 $\{M + H - 2PF_6\}^+$. ^1H NMR [270 MHz, CD_3CN]: δ = 3.66–3.52 (4 H, m, –OCH_2CH_2O–), 4.47 (2 H, s, bpy-CH_2), 4.59 (2 H, s, Ru(bpy-CH_2–)), 7.27 (5 H, m, bpy), 7.79–7.54 (7 H, m, bpy), 8.21–7.91 (8 H, m, bpy), 8.55–8.32 (8 H, m, bpy), and 8.77–8.59 (2 H, m, bpy). Found: C, 41.9; H, 3.0; N, 9.1; calc. for $C_{44}H_{38}N_8O_2P_2F_{12}Ru\cdot HPF_6$: C, 42.4; H, 3.2; N, 9.0%.

Synthesis of $[(bpy)_2Ru(L^1)Ru(CN)_4]$ (1). A sample of $[Ru(bpy)_2(L^1)][PF_6]_2$ (0.121 g, 0.11 mmol) was converted to the chloride salt by dissolving it in the minimum amount of acetone and precipitating it by addition of an acetone solution of LiCl. This was filtered off, washed with acetone, and dried; it was then added to a stirred solution of $K_4Ru(CN)_6\cdot 3H_2O$ (56 mg, 0.12 mmol) in 1 : 1 MeOH–H_2O (15 cm^3) containing one drop of H_2SO_4 to give a pH of between 3 and 4 (see ref. 12). The mixture was heated to reflux under N_2 for 16 h. After cooling the brown precipitate (**1**) was filtered off, washed with cold water, MeOH and acetone, and dried. A further crop of **1** was obtained by reduction in volume of the filtrate. Yield of **1**: 47 mg (42%). ESMS: *m*/*z* 531.7 $\{M + 2Na\}^{2+}$. FAB-MS: *m*/*z* 1058 $\{M + H + K\}^+$, 1042 $\{M + H + Na\}^+$, 1019 $\{M + H\}^+$. ^1H NMR [300 MHz, $(CD_3)_2SO$]: δ = 3.55 (4 H, m, –OCH_2CH_2O–), 4.45 [2 H, m, $(CN)_4$Ru-bpyCH_2], 4.61 [2 H, m, $(bpy)_2$Ru-bpyCH_2–], 7.42 (1 H, m, bpy), 7.77–7.45 (1 H, m, bpy), 7.86–7.79 (2 H, m, bpy), 8.22–8.10 (4 H, m, bpy), 8.29–8.21 (2 H, m, bpy), 8.39–8.30 (2 H, m, bpy), 8.83 (2 H, m, bpy), 8.90 (1 H, d, bpy), 8.98 (1 H, d, bpy), 9.09 (2H, m, bpy), 9.45 [1 H, d, $H^{6'}$ of $(bpy)Ru(CN)_4$] and 9.53 [1H, s, H^6 of $(bpy)Ru(CN)_4$]. Found: C, 50.0; H, 4.2; N, 14.6; calc. for $C_{48}H_{38}N_{12}O_2Ru_2\cdot 7H_2O$: C, 50.4; H, 4.6; N, 14.7%.

Absorption and emission spectroscopy

Absorption spectra of dilute solutions (2 × 10^{-5} M) of the investigated complexes were measured in the indicated solvents and solvent mixtures at room temperature with Perkin-Elmer Lambda 5, Lambda 9 or Lambda 19 UV/Vis spectrophotometers. Where necessary, dmso was dried by storing over activated molecular sieves for several days before use. Luminescence spectra were obtained from air-equilibrated solutions whose absorbance values were <0.2 at the employed excitation wavelength using a Spex Fluorolog II spectrofluorimeter, equipped with a Hamamatsu R928 phototube. While uncorrected band maxima are used throughout the text, for the determination of the luminescence quantum yields, corrected spectra were employed. The correction procedure accounts for the wavelength dependent phototube response either by using a software provided by the firm or by employing a calibrated 45 W quartz-halogen tungsten filament lamp (Optronic Laboratories) as a standard. From the area of the corrected luminescence spectra on an energy scale (cm^{-1}), we obtained luminescence quantum yields Φ for the samples with reference to $[Ru(bpy)_3]_{2+}$ ($\Phi = 0.028$ in air-equilibrated water) as a reference standard.[11] Low temperature measurements were performed in capillary tubes immersed in liquid nitrogen within home-made quartz dewars. Band maxima and relative luminescence intensities were affected by an uncertainty of 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%. Modelling of excited state equilibria and energy transfer was performed with the help of Matlab 5.0.[28]

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18 In the Förster mechanism for energy transfer, the energy transfer rate constant $k_{en}{}^F$ is governed by the spectral overlap integral, J_F, between the luminescence spectrum of the donor moiety **Ru-bpy**, $F(\bar{\nu})$, and the absorption spectrum of the acceptor moiety **Ru-CN**, $\varepsilon(\bar{\nu})$, on an energy scale (cm^{-1}), eqn. 1:

$$J_F = \frac{\int F(\bar{\nu})\varepsilon(\bar{\nu})/(\bar{\nu})^4 \, d\bar{\nu}}{\int F(\bar{\nu}) \, d\bar{\nu}} \qquad (1)$$

From the emission spectrum of $[Ru(bpy)_2(L^1)][PF_6]_2$ (which is nearly invariant in the various solvent mixtures employed) and the absorption spectrum of **1**, whose lowest-energy absorption portion pertains to the strongly solvent-sensitive **Ru-CN** moiety, J_F is calculated to be 1.85×10^{-14} cm^3 M^{-1} in neat dmso. By using the spectroscopic data in Table 1, and according to eqn. 2:

$$k_{en}{}^F = \frac{8.8 \times 10^{-25} K^2 \Phi}{n^4 \tau d_{cc}{}^6} J_F \qquad (2)$$

[where K^2 is a geometric factor (taken as 2/3); Φ and τ are the luminescence quantum yield and lifetime of the reference donor, respectively, n is the refractive index of the solvent], the observed value of $k_{en}{}^F = 2.5 \times 10^8$ s^{-1} yields an interchromophoric distance $d_{cc} = 8$ Å. This is much less than the critical transfer radius, *i.e.* the intercomponent distance for which the energy transfer efficiency is 50 %, which is evaluated to be $R_c = 16.5$ Å.

19 Transient absorption experiments are unlikely to be helpful because of the nature of the excited and transient species of complex **1** that might be involved. Actually, the excited states can be described in terms of electron promotion from the metal centre towards the ligand(s), and the presence of Ru(III)-(bpy$^{\bullet-}$) species from both chromophores of **1** can be foreseen. On these bases, very similar spectral properties for excited donor and acceptor partners (for PEnT) or for reduced partners (for PET) are expected for **1**.

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21 In principle, preferential solvation of species could result in a non-linear behaviour of bulk properties like absorption spectra, redox potentials, and so on, against solvent composition. In our case, the spectral results of Fig. 1 seem to indicate that preferential solvation does not play an important role.

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