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FULL PAPER

Switching of the inter-component photoinduced electron- and energy-transfer properties of a Ru(II)–aza-crown–Re(I) complex; effects of changing temperature, and of incorporation of Ba^{2+} ion into the macrocyclic spacer between the chromophores

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The binuclear complex $[\{Ru(bipy)_2\}(\mu\text{-}L^1)\{Re(CO)_3(H_2O)\}][PF_6]_3$ (**Ru-crw-Re**), and its mononuclear counterpart $[Ru(bipy)_2(L^1)][PF_6]_2$, were synthesised. The bridging ligand L^1 contains two bipyridyl binding sites which are attached *via* methylene spacers to each of the N atoms of a diaza-18-crown-6 macrocycle spacer (**crw**), such that addition of a metal ion to the macrocycle affects the pathway linking the two chromophores. The absorption spectra, luminescence spectra and excited-state lifetimes, and electrochemical properties of acetonitrile solutions of these complexes were investigated. Luminescence studies on **Ru-crw-Re** showed the presence of two competing types of photoinduced intramolecular process involving the Re-based excited state as a donor, *viz.*: (i) electron transfer from an amine group(s) of the aza-crown ether; and (ii) Re→Ru energy transfer. These processes were monitored by time-resolved luminescence spectroscopy both at room temperature and at 77 K, and in the presence and absence of a cation (Ba^{2+}) hosted within the aza-crown macrocyclic unit. In fluid solution at room temperature, there is no photoinduced Re→Ru energy transfer; instead photoinduced electron transfer occurs in the absence of Ba^{2+} ($k_{el} = 1.2 \times 10^{10}\ s^{-1}$), which is inhibited by the presence of Ba^{2+}. In frozen solvent (77 K), *only* Re→Ru photoinduced energy transfer occurs, with $k_{en} = 2 \times 10^8\ s^{-1}$ in the absence of Ba^{2+} and $k_{en}^{Ba} = 7 \times 10^6\ s^{-1}$ in the presence of Ba^{2+}. Thus, Re→Ru energy transfer is strongly affected by Ba^{2+} being hosted within the aza-crown cavity, *i.e.* a switching effect. The role of the diverse factors affecting the two processes is discussed in detail.

Introduction

Studies of photoinduced energy- and electron-transfer between the components of multi-chromophoric supramolecular species are of interest for their relevance to naturally occurring processes in photosynthesis, to the development of artificial light-driven photochemical molecular devices, and for possible applications such as sensors.[1,2] In many cases, rigid covalent linkages between donor and quencher units are used, which allows precise control of the separation of components and of the pathway through which the interactions are transmitted. Within the field of polypyridine transition metal complexes, we have been interested in the study of photoinduced energy transfer in dyads based on $[Ru(bipy)_3]^{2+}$ and $[Os(bipy)_3]^{2+}$ units in which the energy-transfer process is switchable (bipy is 2,2′-bipyridine). This can be achieved, for instance, either because of a conformational change in a flexible linker,[3,4] or because the two components are associated by a non-covalent hydrogen-bonding interaction whose formation relies on the solvent properties.[5,6]

In this paper we describe how the photophysical properties of a dyad containing $\{Ru(bipy)_3\}^{2+}$ and $\{Re(bipy)(CO)_3(H_2O)\}^+$ chromophores are affected by binding of an additional metal ion (Ba^{2+}) to an aza-crown macrocyclic unit which separates the metal fragments.[7] The molecule is $[\{Ru(bipy)_2\}(\mu\text{-}L^1)\{Re(CO)_3(H_2O)\}][PF_6]_3$ (**Ru-crw-Re**; see Scheme 1) and is based on the bridging ligand L^1 in which two bipyridyl binding sites are attached *via* methylene spacers to the N atoms of a diaza-18-crown-6 macrocycle. This ligand has been used by others in metal-ion extraction studies.[8] We have recently described related complexes based on bis(terpyridyl)-substituted derivatives of diaza-18-crown-6,[9] and indeed the principle of using metal-ion binding at a peripheral macrocyclic site to modulate the luminescence properties of a metal chromophore is now well established.[7,10] In this work we show how the binding of Ba^{2+} to the macrocyclic site of **Ru-crw-Re** allows control over intercomponent photoinduced electron- and energy-transfer processes.

Results and discussion

Synthesis and characterisation of mononuclear ruthenium complexes $[Ru(bipy)_2(L^2)][PF_6]_2$ and $[Ru(bipy)_2(L^1)][PF_6]_2$

We investigated two synthetic routes to complex **Ru-crw-Re** (Scheme 1). The first involved initial synthesis of L^1, by alkylation of 1,10-diaza-18-crown-6 with two equivalents of 5-bromomethyl-2,2′-bipyridine.[8] Reaction of this with one equivalent of $[Ru(bipy)_2Cl_2]$ was then carried out in order to prepare the mononuclear 'complex ligand' $[Ru(bipy)_2(L^1)][PF_6]_2$, in which one bipyridyl site is still vacant. This method does work but the reaction is complicated by the obvious problem of competing formation of the undesired dinuclear complex $[\{Ru(bipy)_2\}_2(\mu\text{-}L^1)][PF_6]_4$. Although mononuclear $[Ru(bipy)_2(L^1)][PF_6]_2$ could be separated from this chromatographically, its yield was only 24% by this method.

We therefore investigated a longer but potentially more efficient stepwise synthesis in which the two bipyridyl units are attached to the 1,10-diaza-18-crown-6 core in separate steps.[9] Reaction of 1,10-diaza-18-crown-6 with only one equivalent of

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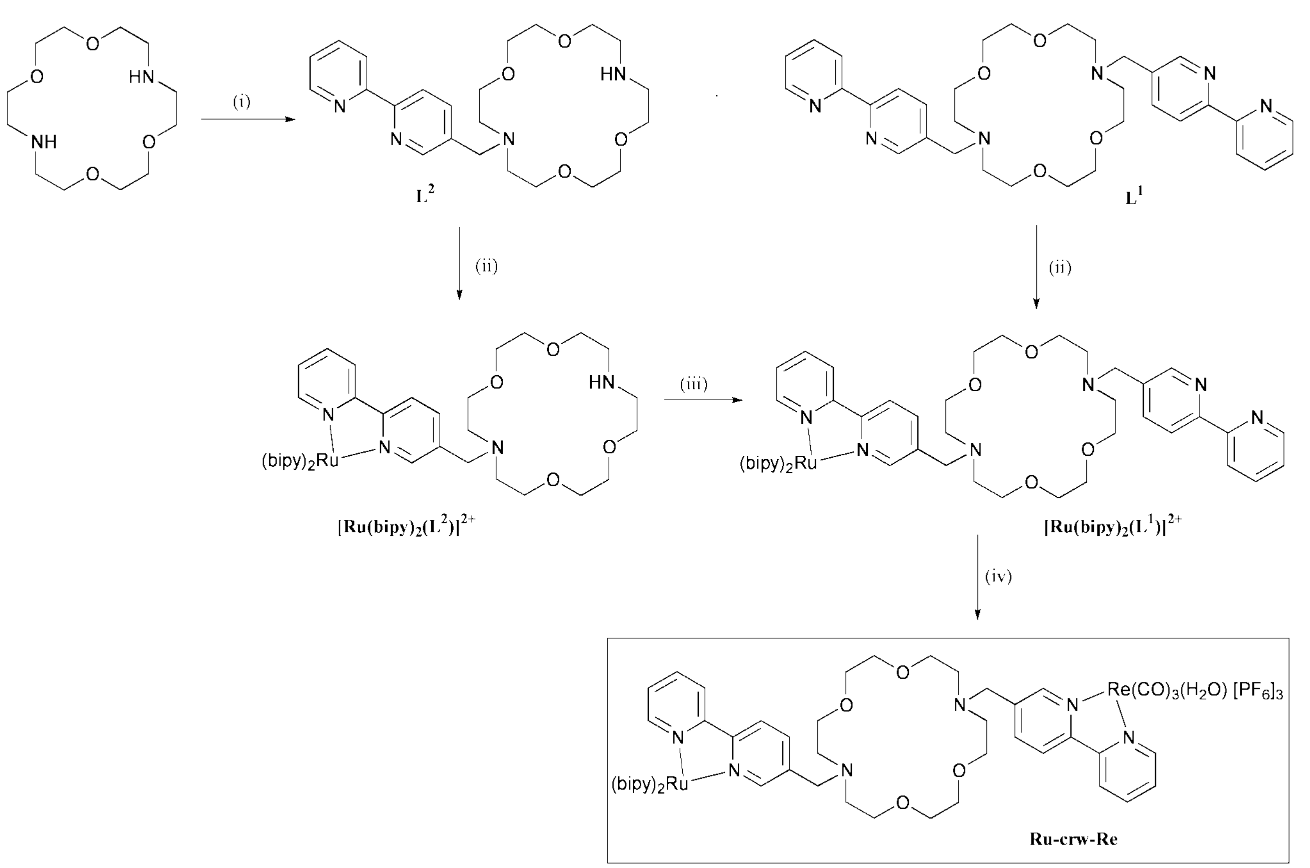


Scheme 1 (i) 5-Bromomethyl-2,2′-bipyridine, ^{i}Pr$_2$EtN, EtOH; (ii) [Ru(bipy)$_2$Cl$_2$]·2H$_2$O, EtOH; (iii) 5-bromomethyl-2,2′-bipyridine, ^{i}Pr$_2$EtN, CH$_2$Cl$_2$: MeCN (1 : 1); (iv) [Re(CO)$_5$Cl] followed by chromatography on silica using MeCN : H$_2$O : saturated aqueous KNO$_3$ (14 : 2 : 1). All complexes were isolated as their hexafluorophosphate salts.

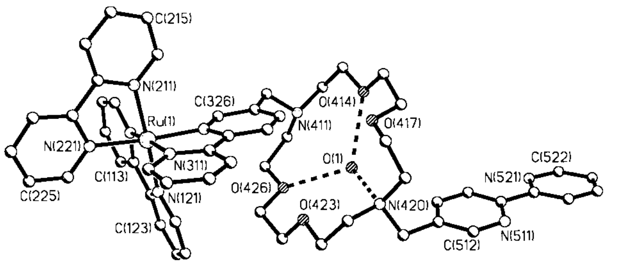


Fig. 1 Crystal structure of the complex cation of [Ru(bipy)$_2$(L^1)][PF$_6$]$_2$·HPF$_6$·H$_2$O·1.5Me$_2$CO.

5-bromomethyl-2,2′-bipyridine in basic conditions afforded a good yield of the intermediate ligand L^2, which readily afforded the mononuclear complex [Ru(bipy)$_2$(L^2)][PF$_6$]$_2$. Alkylation of the second N site of the macrocycle of [Ru(bipy)$_2$(L^2)][PF$_6$]$_2$ with another equivalent of 5-bromomethyl-2,2′-bipyridine then afforded the mononuclear complex [Ru(bipy)$_2$(L^1)][PF$_6$]$_2$ in good yield and with no possibility of forming the undesired by-product.

X-Ray quality crystals of [Ru(bipy)$_2$(L^1)][PF$_6$]$_2$·HPF$_6$·H$_2$O·1.5Me$_2$CO could be obtained from acetone : diethyl ether and the crystal structure is shown in Fig. 1. The three components, *viz.* the [Ru(bipy)$_3$]$^{2+}$ core, the macrocycle, and the vacant bipyridyl unit, are individually unremarkable, with the Ru–N distances all lying in the range 2.054(3) [for Ru(1)–N(321)] to 2.067(3) Å [for Ru(1)–N(211)] and the bite angles of the chelating bipyridyl fragments all being *ca.* 79°. The molecule adopts a folded conformation in which the two bipyridyl units attached to the macrocycle lie partially blocking each face. This is a consequence of the arrangement of substituents around the pyramidal N atoms in the macrocycle, and also occurs in related complexes containing terpyridyl binding sites attached to the 1,10-diaza-18-crown-6 core.[9] In addition there is a water molecule held in the centre of the macrocyclic cavity by three hydrogen-bonding interactions; the relevant distances are O(1)···O(414), 2.87 Å; O(1)···O(426), 2.91 Å; O(1)···N(420), 2.79 Å. The first two of these are consistent with short, strong O–H···O bonds which can be accounted for by the two hydrogen atoms of the water molecule interacting with the ether oxygen atoms of the macrocycle. The N···O separation of 2.79 Å is also indicative of a strong hydrogen bond, which must be of the form N–H···O with the water molecule acting as the acceptor and a protonated nitrogen acting as the donor. This is consistent with the observation of three hexafluorophosphate anions for the Ru^{2+} complex, and protonation of the pendant aza-crown unit was observed in our earlier terpyridyl-based complexes.[9] The pendant bipyridyl unit has the expected transoid conformation.[11]

Synthesis and characterisation of the heterodinuclear complex [{Ru(bipy)$_2$}(μ-L^1){Re(CO)$_3$(H$_2$O)}][PF$_6$]$_3$ (Ru-crw-Re)

Reaction of the mononuclear complex [Ru(bipy)$_2$(L^1)][PF$_6$]$_2$ with [Re(CO)$_5$Cl] in toluene : MeCN under N$_2$, followed by removal of solvents, afforded a red material which we expected to be [{Ru(bipy)$_2$}(μ-L^1){Re(CO)$_3$Cl}][PF$_6$]$_2$, following the well-known preparation of [Re(bipy)(CO)$_3$Cl] by the simple reaction of [Re(CO)$_5$Cl] with bipy.[12] Thin-layer chromatography showed this to be a mixture of two species, a major and a minor one which eluted close together and which were the same orange-red colour. The occurrence of a mixture of two similar components was also obvious from the ^{1}H NMR spectrum. An electrospray mass spectrum of the mixture showed peaks corresponding to the expected product [{Ru(bipy)$_2$}(μ-L^1){Re(CO)$_3$Cl}][PF$_6$]$_2$ and another set corresponding to a compound in which the cation is lighter than this by *ca.* 18 mass units. One obvious possibility for this is [{Ru(bipy)$_2$}(μ-L^1){Re(CO)$_3$(H$_2$O)}][PF$_6$]$_3$, in which the monodentate chloride ligand attached to the Re(I) centre has been replaced by H$_2$O.

Attempts to isolate the (initially) major product $[\{Ru(bipy)_2\}(\mu\text{-}L^1)\{Re(CO)_3Cl\}][PF_6]_2$ chromatographically were frustrated because it appeared to convert to the minor one during the chromatography. Consequently, after repeated chromatography the initially-generated Re(I)–chloride complex was all converted to the Re(I)–aqua complex **Ru-crw-Re** which could be isolated pure. Its formulation as the aqua complex, apart from being consistent with the mass spectrometric data, is also consistent with its IR spectrum. The mononuclear complex $[Re(bipy)(CO)_3Cl]$ has its CO stretching bands at 2020, 1920 and 1900 cm^{-1} in CH_2Cl_2; the initially-generated complex $[\{Ru(bipy)_2\}(\mu\text{-}L^1)\{Re(CO)_3Cl\}][PF_6]_2$ (slightly contaminated with the aqua complex **Ru-crw-Re**) gave a very similar IR spectrum in this region, with ν_{CO} at 2020, 1913 and 1891 cm^{-1}. In contrast, in the IR spectrum of the known complex $[Re(bipy)(CO)_3(H_2O)]^+$,[13] these carbonyl bands are shifted to higher energy at 2035 and 1930 cm^{-1} (the latter peak consisting of two overlapping components) because H_2O is a poorer electron-donor than chloride. For **Ru-crw-Re**, the carbonyl bands in the IR spectrum occur at 2039, 1941 and 1927 cm^{-1}, in good agreement with the behaviour of $[Re(bipy)(CO)_3(H_2O)]^+$.[13]

The facile hydrolysis of $[\{Ru(bipy)_2\}(\mu\text{-}L^1)\{Re(CO)_3Cl\}][PF_6]_2$ to **Ru-crw-Re** on the silica column is surprising considering that conversion of mononuclear $[Re(bipy)(CO)_3Cl]$ to $[Re(bipy)(CO)_3(H_2O)]^+$ is difficult, requiring treatment with an Ag^+ salt to remove the chloride ligand before addition of water.[13] We have not seen such a hydrolysis reaction during our previous work with complexes containing the $\{Re(bipy)(CO)_3Cl\}$ fragment, despite our routine use of aqueous solvents for chromatographic purification.[14,15] It is tempting to suggest that the unexpected reactivity of $[\{Ru(bipy)_2\}(\mu\text{-}L^1)\{Re(CO)_3Cl\}][PF_6]_2$ is related to the fact that the central macrocyclic unit can hold a hydrogen-bonded water molecule in close proximity to the Re centre {*cf.* the crystal structure of $[Ru(bipy)_2(L^1)][PF_6]_2\cdot HPF_6\cdot H_2O\cdot 1.5Me_2CO$, above}. The substitution would therefore be an intramolecular process rather than an intermolecular one, with the aza-crown macrocycle acting as a catalyst for the reaction at the adjacent Re centre. Identical behaviour has been seen in hydrolysis of imine-containing molecules which contain a boronic acid group close to the imine site; prior coordination of water to the boronic acid group resulted in intramolecular rather than intermolecular hydrolysis of the imine and a consequent increase in reaction rate.[16] Whatever the exact reason, the mass spectrometric and IR data, and the elemental analysis, confirm the formulation of **Ru-crw-Re** as $[\{Ru(bipy)_2\}(\mu\text{-}L^1)\{Re(CO)_3(H_2O)\}][PF_6]_3$.

Electrochemistry

The mononuclear complexes $[Ru(bipy)_2(L^1)][PF_6]_2$ and $[Ru(bipy)_2(L^2)][PF_6]_2$ show reversible Ru(II)/Ru(III) couples at +0.93 V and +0.96 V *vs.* Fc/Fc^+ respectively. Complex $[Ru(bipy)_2(L^1)][PF_6]_2$ also shows the expected bipyridyl-centred reductions at −1.74, −1.95 and −2.21 V *vs.* Fc/Fc^+; for $[Ru(bipy)_2(L^2)][PF_6]_2$ only the first two were detected, at −1.73 and −1.94 V. The potentials of these metal-centred and ligand-centred redox processes are in excellent agreement with those expected for an almost unperturbed $[Ru(bipy)_3]^{2+}$ unit.[17] In addition a broad, low-intensity irreversible feature at *ca.* −1.2 V *vs.* Fc/Fc^+ could be ascribed to reduction of macrocycle-bound water (the thermodynamic reduction potential for H_2O is −0.83 V *vs.* NHE).

Electrochemical studies on dinuclear **Ru-crw-Re** revealed (Fig. 2) a wave at *ca.* +0.93 V *vs.* Fc/Fc^+ which is a superposition of the expected chemically reversible Ru(II)/Ru(III) couple[17] and the irreversible Re(I)/Re(II) couple.[12] A shoulder corresponding to the irreversible Re(I)/Re(II) couple is just visible, in both the cyclic and square-wave voltammograms, on the low-potential side of the reversible Ru(II)/Ru(III) wave. We have observed before similar behaviour in other complexes containing both Ru(II)- and Re(I)–bipyridyl chromophores.[14,15] Reversible bipyridyl-centred reductions occur at −1.73 V and −1.93 V *vs.* Fc/Fc^+, and again an irreversible feature at *ca.* −1.2 V *vs.* Fc/Fc^+ we ascribe to reduction of water, either bound in the macrocycle, coordinated to the Re(I) centre, or both.

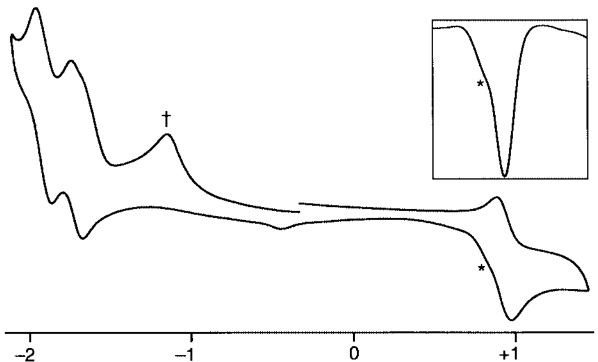


Fig. 2 Cyclic voltammogram of **Ru-crw-Re** in MeCN (scan rate, 0.2 V s^{-1}). The label * denotes the irreversible Re(I)/Re(II) process, which is overlapping with the Ru(II)/Ru(III) process (see the square-wave voltammogram, inset). The label † denotes an irreversible process possibly associated with macrocycle-bound water.

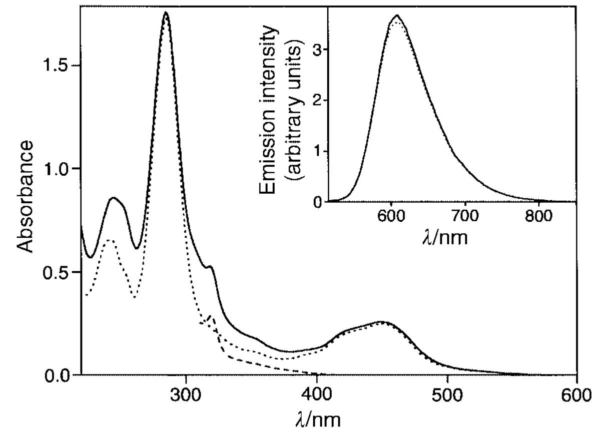


Fig. 3 Room temperature absorption spectra of 2×10^{-5} M acetonitrile solutions of **Ru-crw-Re** (——) and $[Ru(bipy)_2(L^1)][PF_6]_2$ (····). The difference spectrum (— —), ascribed to the Re-based absorption of **Ru-crw-Re** is also shown. The inset shows luminescence spectra obtained with λ_{exc} = 380 nm.

Spectroscopy and photophysics

Ground state absorption spectra of acetonitrile 2×10^{-5} M solutions of **Ru-crw-Re** and $[Ru(bipy)_2(L^1)][PF_6]_2$ are shown in Fig. 3. In the figure is also shown the difference spectrum (for $\lambda > 300$ nm), which is ascribed to the absorption spectrum of the $\{Re(bipy)(CO)_3(H_2O)\}^+$ moiety of **Ru-crw-Re**. Comparison with data from the extensive literature concerned with Ru(II)–polypyridine[17] and Re(I)–bipy–tricarbonyl[12,14,15,18,19] complexes allows the following assignments. (i) For both **Ru-crw-Re** and $[Ru(bipy)_2(L^1)][PF_6]_2$, the wavelength maximum at 450 nm ($\varepsilon = 1.3 \times 10^4$ M^{-1} cm^{-1}) is to be ascribed to the lowest-lying ^{1}Ru→bipy CT transitions. (ii) For the Re-based chromophore of **Ru-crw-Re** the lowest-energy transition occurring in the range 300–400 nm ($\varepsilon_{320} = 1.5 \times 10^4$ M^{-1} cm^{-1}) is of ^{1}Re→bipy CT character. For **Ru-crw-Re**, selective excitation of the Ru-based chromophore could be achieved by using λ_{exc} in the range 400–500 nm (see Fig. 3). Conversely, use of shorter wavelengths gave excitation of both Ru- and Re-based chromophores; for instance excitation at 380 nm gave a Ru : Re excited state ratio of ≈3 : 1.

In Table 1 are collected some luminescence results, obtained in acetonitrile solvent, both at room temperature and at 77 K.

Table 1 Luminescence properties of the complexes[a]

	295 K			77 K	
	λ_{max}[b]/nm	$10^2\,\Phi$[b]	τ/ns	λ_{max}[b]/nm	τ/μs
$[Ru(bipy)_2(L^1)][PF_6]_2$	608	3.0	170	588	5.0
$[Ru(bipy)_2(L^1)][PF_6]_2 + Ba^{2+}$	612	3.6	200	588	6.0
Ru-crw-Re	608	2.8	0.08,[c] 170[d]	586	0.005,[c] 5.0[d]
Ru-crw(Ba)-Re	530,[e] 612[d]	1.2,[e] 3.6[d]	62,[e] 195[d]	500,[e] 588[d]	0.14,[e] 6.0[d]
$[Re(QP)(CO)_3Cl]$[f]	616	1.5	22	535	3.2

[a] Air-equilibrated acetonitrile solvent. [b] λ_{exc} = 380 nm (for **Ru-crw-Re** and its Ba^{2+} associate, Ru- and Re-based absorption occurs in a ≈3:1 ratio). [c] Very weak Re-based emission observed at 520 nm, see text. [d] Ru-based emission, see text. [e] Re-based emission, see text. [f] From ref. 14; solvent was DMF : CH_2Cl_2 (9 : 1); QP is 2,2′ : 3′,2″ : 6″,2‴-quaterpyridine.

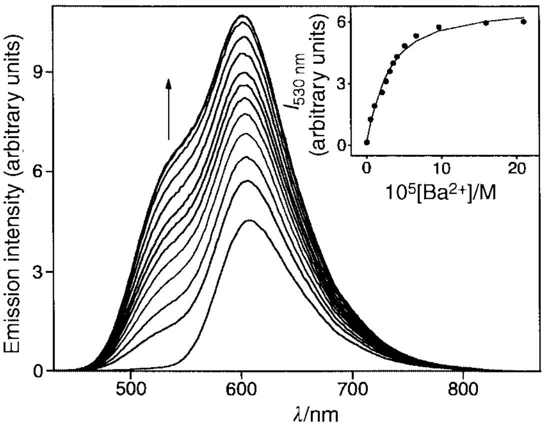


Fig. 4 Changes of the luminescence spectrum of a 2×10^{-5} M acetonitrile solution of **Ru-crw-Re** after Ba^{2+} addition; λ_{exc} was 323 nm. Inset: fitting of the luminescence data points registered at 530 nm to determine the association constant; see text for details.

For the sake of comparison, data for the Re(I)–tricarbonyl complex of 2,2′ : 3′,2″ : 6″,2‴-quaterpyridine are also included.[14] The room temperature luminescence spectra of 2×10^{-5} M acetonitrile solutions of **Ru-crw-Re** and $[Ru(bipy)_2(L^1)][PF_6]_2$, obtained using λ_{exc} = 380 nm, exhibit overlapping profiles with λ_{max} = 608 nm (Fig. 3, inset); the 77 K case will be examined below. According to a wealth of experimental evidence, for the Ru-based luminophore of **Ru-crw-Re** and for $[Ru(bipy)_2(L^1)][PF_6]_2$ (Table 1), the luminescent state is of ^{3}MLCT nature in each case.[17] From literature sources,[12,14,15,18,19] a Re-based emission would be expected at 500–650 nm (*i.e.* in about the same region) and the absence of a sizeable such emission from **Ru-crw-Re** must be due to quenching of the Re-based excited state by intramolecular processes. In fact, upon laser excitation at 355 nm, by monitoring the wavelength region around 520 nm, a weak emission with lifetime of τ = 80 ps was detected (Table 1), which we ascribe to such a residual Re-based emission.

The luminescence of these complexes proved to be affected by the presence of the Ba^{2+} cation, which can be hosted within the aza-crown unit.[7,20] Fig. 4 illustrates the changes in emission spectra for **Ru-crw-Re** observed after titration with $Ba(ClO_4)_2$, using an excitation wavelength of 323 nm (the ground state absorption spectra were practically unaffected during the titration experiments). Addition of Ba^{2+} resulted in the appearance of a broad luminescence band centred at ≈530 nm, characterised by a lifetime τ = 62 ns, which is Re-based in origin.[12,14,15,18] As to the nature of the Re-based luminescent state, the majority of cases reported in the literature for $\{Re(L)(CO)_3\}^+$ complexes are for ^{3}MLCT states,[12,18] but ^{3}LC states have also been identified for some complexes.[19] Based on a comparison of the observed luminescence features we assign the Re-based contribution as ^{3}MLCT in nature.

The changes in luminescence intensity at 530 nm as a function of the Ba^{2+} concentration, due to formation of the complex **Ru-crw(Ba)-Re** in which Ba^{2+} occupies the aza-crown macrocyclic cavity, are plotted in the inset of Fig. 4. From the data points, and according to approaches based on iterative least-squares fits (see Experimental section),[21] an association constant $K_{ass} = 5 \times 10^4$ M^{-1} is evaluated for the Ba^{2+} binding, according to eqn. (1) below.

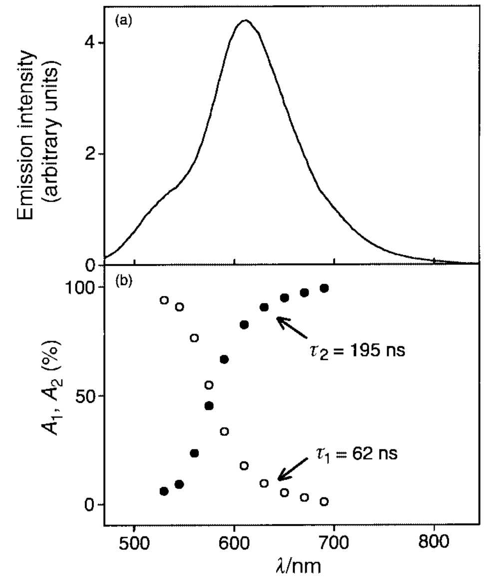


Fig. 5 (a) Luminescence spectrum (in acetonitrile and at room temperature) of **Ru-crw-Re** after addition of more than 2 equivalents of Ba^{2+}; λ_{exc} was 380 nm. (b) Wavelength dependence of the preexponential factors, A_1 and A_2, for Re-based (τ_1, ○) and Ru-based (τ_2, ●) emissions; see text for details.

$$\textbf{Ru-crw-Re} + Ba^{2+} \rightleftharpoons \textbf{Ru-crw(Ba)-Re} \qquad (1)$$

This may be compared with $K_{ass} > 10^6$ M^{-1}, as found for the analogous 1 : 1 equilibrium between dialkyl-1,10-diaza-18-crown-6 compounds and Ba^{2+} in acetonitrile.[20] The relatively low binding constant of eqn. (1) may be ascribed to both an electronic effect (the electrostatic problem of binding a dication to something that is already carrying a 3+ charge) and a steric effect (the crystal structure shows how the faces of the macrocycle are blocked by the bulky substituents, and this conformation may persist in solution). It is to be noticed that the uptake of Ba^{2+} by **Ru-crw-Re** at room temperature results in some enhancement (by ≈20%) of the Ru-based luminescence intensity, which is paralleled by an increase of the Ru-based lifetime from τ = 170 to *ca.* 200 ns both for **Ru-crw-Re** and $[Ru(bipy)_2(L^1)][PF_6]_2$ (Table 1).

The presence of independent Ru-based and Re-based luminophores within the **Ru-crw(Ba)-Re** associate is confirmed by the results of a global analysis of the time-dependent luminescence properties over the range 500–700 nm (Fig. 5, (b)). Two components are present in the emission of **Ru-crw(Ba)-Re**, with lifetimes of τ_1 = 62 and τ_2 = 195 ns, ascribable

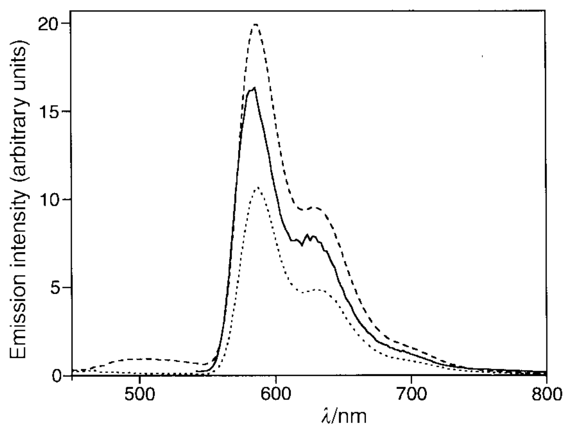


Fig. 6 Luminescence spectra of **Ru-crw-Re** (——), [Ru(bipy)$_2$(L^1)][PF$_6$]$_2$ (····) and the **Ru-crw(Ba)-Re** associate (— —) in acetonitrile glass at 77 K; λ_{exc} was 320 nm. Spectral intensities are arbitrarily scaled.

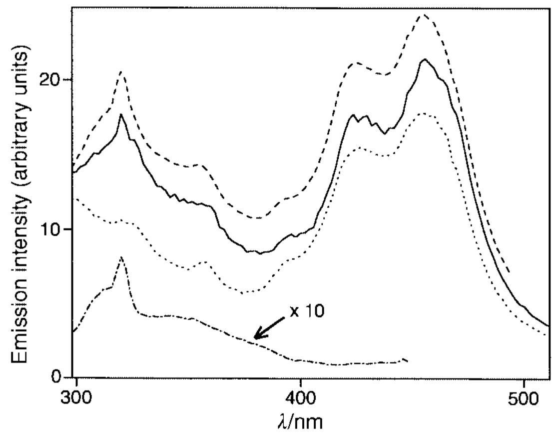


Fig. 7 Uncorrected excitation spectra (acetonitrile, 77 K) obtained under fixed emission at 600 nm of **Ru-crw-Re** (——), [Ru(bipy)$_2$(L^1)][PF$_6$]$_2$ (····) and **Ru-crw(Ba)-Re** (— —). The excitation spectrum at 500 nm emission for **Ru-crw(Ba)-Re** is also shown (— • —).

to the Re-based and Ru-based components respectively. The analysis was performed using eqn. (2), and the evaluated

$$I(t) = A_1\exp(-t/\tau_1) + A_2\exp(-t/\tau_2) \qquad (2)$$

pre-exponential factors, A_1 and A_2, are consistent with the ratio of the emission intensities of the two independent luminophores (Fig. 5).

In summary, *at room temperature* (fluid solution) and in the presence of Ba^{2+}, the Re-based luminescence of **Ru-crw(Ba)-Re** is not quenched, in contrast with what happens in **Ru-crw-Re** where only very weak Re-based emission was observed.

The luminescence properties of the complexes were affected also by the temperature, *i.e.* by the solvent being fluid or glassy.[17,22] For **Ru-crw-Re** *at 77 K*, *i.e.* in a frozen glass,[17,22] using $\lambda_{exc} = 320$ nm, an intense vibronically-resolved luminescence spectrum is observed which arises from the Ru-based luminophore ($\lambda_{max} = 586$ nm, $\tau = 5$ μs, Table 1); the relevant luminescence spectra are in Fig. 6. For **Ru-crw-Re**, the excitation spectrum obtained at $\lambda_{em} = 600$ nm showed features typical both of the Ru- and Re-based absorption (Fig. 7). On this basis, one concludes that sensitisation of the Ru-based luminescence occurs, which corresponds to *nearly complete* quenching of the Re-based luminescence; consistent with this, a very short lifetime $\tau_q = 5$ ns was detected at 500 nm (Table 1) upon excitation at 355 nm, consistent with residual Re-based luminescence. Thus, for **Ru-crw-Re** in frozen solvent at 77 K, a Re→Ru photoinduced energy transfer process is operative.

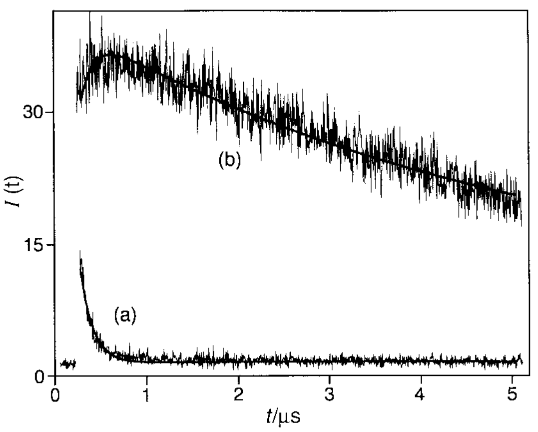


Fig. 8 Time-resolved luminescence profiles for the **Ru-crw(Ba)-Re** associate (acetonitrile, 77 K) as monitored at 500 nm (a) and 620 nm (b).

For **Ru-crw(Ba)-Re** *at 77 K*, two well-separated luminescence band maxima are obtained, with λ_{max} 500 nm and 588 nm, Fig. 6.[23] The time-resolved luminescence profiles, as monitored at these two wavelengths, conform to a dual-luminescent behaviour (Fig. 8 and Table 1). For the emission at 500 nm, a decay time of $\tau_1 = 140$ ns was measured, according to $I(t) = A\exp(-t/\tau_1)$; conversely, for emission at 620 nm (the low-energy side of the 588 nm emission peak) the observed decay law was $I(t) = A_1\exp(-t/\tau_1) + A_2\exp(-t/\tau_2)$, with $\tau_2 = 6$ μs, and a rise time $\tau_1 = 140$ ns (*i.e.* A_1 has a negative value, see Fig. 8). These findings indicate the occurrence of *partial* quenching of the Re-based luminescence and concomitant sensitisation of the Ru-based luminescence in **Ru-crw(Ba)-Re** (*cf.* the nearly complete quenching of the Re component in the absence of Ba^{2+}, above). Consistent with this, excitation spectra taken at 600 nm show a peak maximum at 320 nm, typical of the absorbing Re-based chromophore, Fig. 7.

Competing electron and energy transfer processes

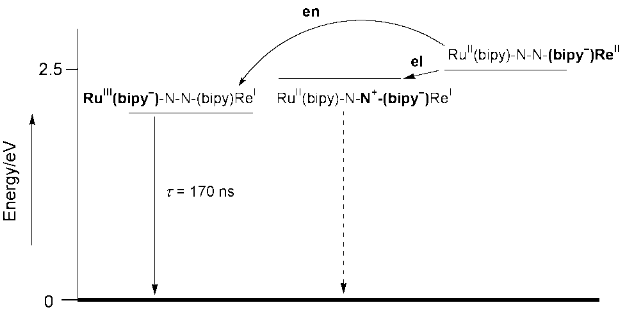
For the ease of discussion, we indicate henceforth the Re-based MLCT excited state of **Ru-crw-Re** as {Ru^{II}(bipy)–N–N–(bipy$^-$)Re^{II}}, where (bipy)–N–N–(bipy) denotes the bridging ligand L^1 and the other terminal ligands (bipy attached to the Ru terminus, carbonyl and H$_2$O at the Re terminus) are omitted for the sake of clarity. In this MLCT excited state the Re is oxidised and the associated bipy unit of the bridging ligand is reduced. A similar description holds for the Ru-based MLCT excited state, which we write as {Ru^{III}(bipy$^-$)–N–N–(bipy)Re^{I}}.

Two types of intramolecular quenching of the Re-based excited state in **Ru-crw-Re** can be examined: (i) an electron transfer involving the closer N position of the aza-crown unit, *i.e.* Re^{II}←N$_{crw}$ [eqn. (3)], or (ii) a Re→Ru energy transfer [eqn. (4)].

$$\{\mathrm{Ru^{II}(bipy)\text{–}N\text{–}N\text{–}(bipy^-)Re^{II}}\} \longrightarrow \{\mathrm{Ru^{II}(bipy)\text{–}N\text{–}N^+\text{–}(bipy^-)Re^{I}}\} \qquad (3)$$

$$\{\mathrm{Ru^{II}(bipy)\text{–}N\text{–}N\text{–}(bipy^-)Re^{II}}\} \longrightarrow \{\mathrm{Ru^{III}(bipy^-)\text{–}N\text{–}N\text{–}(bipy)Re^{I}}\} \qquad (4)$$

The energy level diagram of Scheme 2 shows the two intramolecular steps that are concerned with effective deactivation of the excited levels of **Ru-crw-Re** (as obtained by using excitation at a wavelength <380 nm). The energies of the luminescent Ru- and Re-based states, 2.1 and 2.5 eV respectively, have been estimated from the emission band maxima observed at 77 K (Table 1). The level for the charge-separated state following the Re^{II}←N$_{crw}$ step, eqn. (3), is 2.4 eV as evaluated by using the redox potentials available from this study and from literature sources[24] (a practically identical figure is obtained for the analogous Ru^{III}←N$_{crw}$ electron-transfer step).



Scheme 2 Intramolecular electron (el) and energy (en) transfer processes in **Ru-crw-Re**. For the abbreviations used to denote the excited states, see main text; the localisation of the excited states is emphasised by use of bold type.

According to the energy levels of Scheme 2 and to the above results, control over the competing electron and energy processes in **Ru-crw-Re** can be gained (i) by changing the state of the solvent (fluid at room temperature and frozen at 77 K) or (ii) by incorporation of the Ba^{2+} cation within the aza-crown unit. Below are examined different combinations of these factors and their precise influence over the intramolecular processes occurring in excited **Ru-crw-Re** and **Ru-crw(Ba)-Re**; Scheme 3 illustrates the various cases reported.

Case (a): room temperature, Ba^{2+} absent. In fluid solvent, only the Ru-based luminescence is detected (Fig. 3, inset). Quenching of the Re-based excitation is energetically allowed either by electron [eqn. (3)], or energy [eqn. (4)] transfer, with $\Delta G_{el} = -0.1$ and $\Delta G_{en} = -0.4$ eV, respectively (Scheme 2). By comparing the luminescence intensity of 2×10^{-5} M solutions of $[Ru(bipy)_2(L^1)]^{2+}$ and **Ru-crw-Re**, obtained using $\lambda_{exc} = 380$ nm (Fig. 3, inset), we see no sensitisation of the Ru-based luminescence for **Ru-crw-Re** under these conditions. Excitation spectra taken at $\lambda_{em} = 620$ nm do not show absorbing features from the Re-based chromophore. Thus, at room temperature and in the absence of Ba^{2+}, the Re-based excited state is deactivated by electron transfer from an N atom of the aza-crown unit according to eqn. (3).[25] Based on the lifetime of $\tau_q = 80$ ps for the weak residual Re-based emission, we calculate a rate constant of $k_{el} = 1.2 \times 10^{10}$ s^{-1} for this process. We note that an analogous electron-transfer quenching of the Ru-based excited state, *i.e.* $Ru^{III} \leftarrow N_{crw}$, is never observed (Scheme 2), probably because it is endoergonic, with $\Delta G = +0.3$ eV.

Case (b): room temperature, Ba^{2+} hosted within crw. Formation of the **Ru-crw(Ba)-Re** associate at room temperature is expected to result in an increase of the oxidation potential of the N position(s),[7] possibly inhibiting $Re^{II} \leftarrow N_{crw}$ electron transfer, eqn. (3). Our finding that no quenching of the Re-based luminescence is observed (Fig. 5) indicates that neither electron transfer nor energy transfer [eqn. (4)] is taking place, in agreement with this expectation. In kinetic terms, the rate constants for both of these intramolecular processes, k_{el} and k_{en} respectively, must be $<1.6 \times 10^7$ s^{-1} [the competing intrinsic deactivation of the Re-based luminophore is $k_d^{Re} = 1/(62 \times 10^{-9})$ s^{-1}].

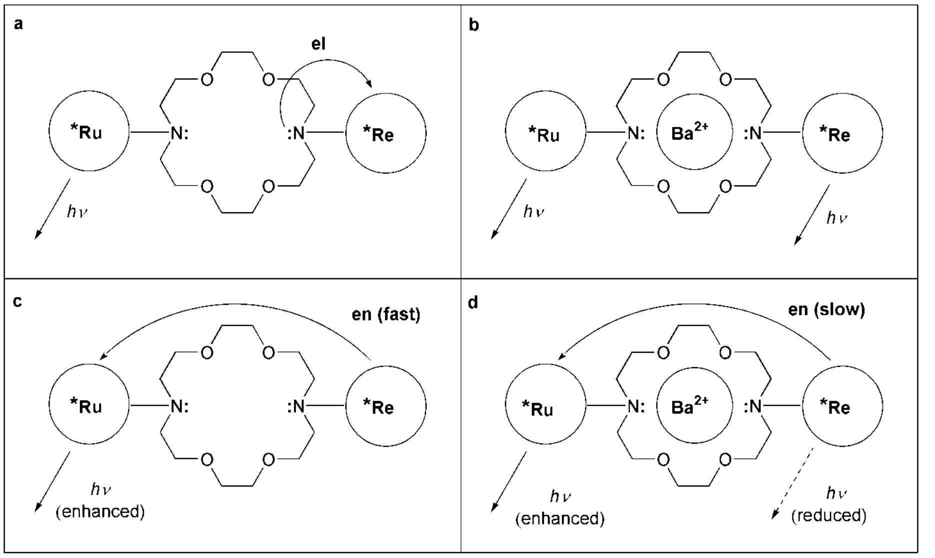
Case (c): 77 K, Ba^{2+} absent. In frozen solvent, the charge-separated excited state {Ru^{II}(bipy)–N–N$^+$–(bipy$^-$)Re^I} which follows the $Re^{II} \leftarrow N_{crw}$ electron transfer [eqn. (3)] is expected to be destabilized by at least 0.5 eV with respect to what happens in fluid solvent.[26] In contrast, the luminescent energy levels undergo only minor changes on passing from fluid to frozen medium.[14,17,18] Thus, electron transfer involving the Re-based excited level and the N position(s) of **crw** becomes energetically disallowed at 77 K (Scheme 2). In fact, by using excitation with $\lambda_{exc} < 380$ nm, nearly complete quenching of the Re-based luminescence and sensitisation of the Ru-based luminescence is observed, consistent with a Re→Ru energy transfer step [eqn. (4)]. The residual, weak luminescence exhibited a lifetime of $\tau_q^{Re,77K} = 5$ ns, as opposed to typical values of several μs for Re–polypyridine–tricarbonyl luminophores at 77 K.[12,14,18] On this basis, we conclude that $k_{en}^{77K} \approx 1/\tau_q^{Re,77K} = 2.0 \times 10^8$ s^{-1}.

Case (d): 77 K, Ba^{2+} hosted within crw. Again, electron transfer quenching of the Re-based excited state is prevented by the frozen state of the solvent, whereas Re→Ru energy transfer remains energetically allowed (Scheme 2). Consequently, the energy transfer takes place (Fig. 7 and 8 show excitation spectra and time resolved results, respectively). However compared to case (c) above (in the absence of Ba^{2+}), a substantial increase in the Re-based lifetime is observed, from 5 ns in the absence of Ba^{2+} to 140 ns in the presence of Ba^{2+}. Since the near-complete quenching of Re-based emission in the absence of Ba^{2+} could be ascribed to Re→Ru energy transfer, the partial restoration of the Re-based emission in the presence of Ba^{2+} is indicative of a slower Re→Ru energy transfer step (evidence for the occurrence of this process is provided by the results of Fig. 7 and 8). Also, however, changes in the intrinsic Re-based emission on Ba^{2+} binding might in principle be implied. We note that for the mononuclear complex $[Ru(bipy)_2(L^1)][PF_6]_2$, the lifetime of the Ru-based emission at 77 K increased from 5.0 to 6.0 μs in the presence of Ba^{2+} (Table 1, *i.e.* non-radiative deactivation of the luminescent excited state became a slower process). This could arise, for example, because binding of Ba^{2+} made the molecule more rigid so that vibrational modes responsible for non-radiative deactivation are damped. Similarly, a slight increase in the Re-based intrinsic emission lifetime at 77 K (on the μs time scale, Table 1), arising from these effects is to be expected. Thus, the Re-based excited state of **Ru-crw(Ba)-Re** should deactivate according to a scheme involving slowed down competing processes: (i) the intrinsic deactivation, and (ii) the Re→Ru energy transfer. The fact that the *observed* lifetime for the Re-based emission is $\tau_q^{Re,77K,Ba} = 140$ ns is consistent with energy transfer being much faster than the intrinsic Re-based deactivation. On this basis, we conclude that the change in emission lifetime of the Re centre in the presence of Ba^{2+} is ascribable to a change in the Re→Ru energy transfer rate, *i.e.* $k_{en}^{77K,Ba} \approx 1/\tau_q^{Re,77K,Ba} = 1/(140\ \text{ns}) = 7 \times 10^6$ s^{-1}. Comparison with the value of $k_{en}^{77K} = 2.0 \times 10^8$ s^{-1} in the absence of Ba^{2+} (case (c)) shows that incorporation of Ba^{2+} into the macrocycle of **Ru-crw-Re** at 77 K slows down the Re→Ru energy transfer process by about a factor of 30.

The reason for the effect of Ba^{2+} on the Re→Ru energy transfer rate is not known, although the most likely explanation is that binding of Ba^{2+} in the aza-crown moiety results in a conformational rearrangement such that the Ru and Re centres move further apart. The Ru centre has a 2+ charge and the Re centre is 1+; it is reasonable that a dication in the macrocycle should repel them both, giving a greater Ru···Re separation, on electrostatic grounds. Unfortunately we were unable to obtain crystals of the Ba^{2+} adduct of **Ru-crw-Re** to prove this.

Conclusions

There is a large interest in photoinduced processes involving the *termini* of model binuclear species,[27] especially when switching procedures can be used to control these intramolecular processes. With reference to Scheme 3, we have shown that by acting on temperature [cases (a) and (b) are for room temperature, cases (c) and (d) are for 77 K] and by using Ba^{2+} ions in the **crw** units (cases (b) and (d)) it is possible to switch between four different types of behaviour in **Ru-crw-Re**. The arrangement of energy levels of the photoactive units of **Ru-crw-Re** allow the occurrence of Re→Ru energy transfer, provided the electron transfer step involving the N position of **crw** is blocked by freezing the solvent. For this reason, energy transfer never occurs at room temperature (cases (a) and (b)), probably



Scheme 3 Predominant photophysical processes in **Ru-crw-Re** under four different sets of conditions: (a) room temperature, no Ba^{2+}; (b) room temperature, with Ba^{2+}; (c) 77 K, no Ba^{2+}; (d) 77 K, with Ba^{2+}.

because the two photoactive units are too far apart, and are separated by a saturated **crw** fragment which is not a very good mediator of electronic interactions. In contrast, Re→Ru energy transfer takes place at 77 K (with $k_{en} = 2 \times 10^8$ s^{-1}) because the competition against the much slower intrinsic deactivation of the Re-based unit, $k_d^{Re,77K} = 3.3 \times 10^5$ s^{-1}, is now favourable (case (c)). When the **crw** cavity contains Ba^{2+}, the energy transfer step is slowed down to $k_{en} = 7 \times 10^6$ s^{-1} but still it is fast enough to favourably compete against $k_d^{Re,77K}$ (case (d)). So we can use the change in temperature to switch between Re←N$_{crw}$ electron-transfer and Re→Ru energy transfer processes, and the presence or absence of Ba^{2+} to modulate further the efficiency of both of these processes.

Experimental

General details

Instrumentation used for routine NMR and mass spectroscopic analyses, and electrochemical studies, has been described in previous papers.[14] The compounds [Ru(bipy)$_2$Cl$_2$]·2H$_2$O,[28] and 5-bromomethyl-2,2′-bipyridine[29] were prepared according to published procedures.

Syntheses

Combined synthesis of L^1 and L^2. This is a modification of the published procedure for preparing L^1.[7] A mixture of 5-bromomethyl-2,2′-bipyridine (475 mg, 1.91 mmol), 1,10-diaza-18-crown-6 (500 mg, 1.91 mmol) and ^{i}Pr$_2$EtN (1.65 cm^3, 9.5 mmol, excess) in ethanol (50 cm^3) was heated to reflux for 3 h. The mixture was then evaporated to dryness and the crude mixture was purified by column chromatography on alumina (Brockmann activity III), initially using 1% MeOH in CH$_2$Cl$_2$ as eluent, rising to 2% MeOH after the first band had been eluted. L^1 was obtained as the second band off the column as a pale brown solid in 21% yield; L^2 was obtained as the third band as a pale brown solid in 46% yield. Characterisation data for L^1 were in agreement with those reported previously.[7]

Data for L^2: *m*/*z* 430 (32%, *M*$^+$), 170 (100%, bipy − CH$_2^+$). ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.68 (1 H, ddd, J = 4.8, 1.9, 1.0; H$^{6'}$), 8.62 (1 H, d, J = 1.7; H^6), 8.36 (2 H, m; H^3 and H$^{3'}$), 7.84 (2 H, m; H^4 and H$^{4'}$), 7.31 (1H, ddd, J = 7.5, 4.7, 1.3; H$^{5'}$), 3.77 (2 H, br s; bipy-C*H*$_2$N), 3.59 (16 H, m; crown C*H*$_2$O), 2.90 (4 H, t, J = 4.7; crown C*H*$_2$N), 2.82 (4 H, t, J = 5.3 Hz; crown C*H*$_2$N). Found: C, 57.4; H, 8.5; N, 11.3%. Required for C$_{23}$H$_{34}$N$_4$O$_4$·3H$_2$O: C, 57.0; H, 8.3; N, 11.6%.

[Ru(bipy)$_2$(L^2)][PF$_6$]$_2$. A mixture of L^2 (300 mg, 0.70 mmol) and [Ru(bipy)$_2$Cl$_2$]·2H$_2$O (400 mg, 0.77 mmol) in ethanol (50 cm^3) was heated to reflux for 4 h. After cooling, an aqueous solution of NH$_4$PF$_6$ was added and the mixture concentrated *in vacuo* to remove the ethanol and precipitate the crude product, which was filtered off, washed with water, and dried. The product was purified by column chromatography on flash silica eluting initially with 18 : 2 : 1 acetonitrile : water : saturated aqueous KNO$_3$ solution, increasing the polarity to 16 : 2 : 1 once the first impurities had come off the column. The major orange band was collected. Aqueous NH$_4$PF$_6$ was added and the mixture concentrated *in vacuo* to precipitate the pure orange solid, which was filtered off, washed with water, and dried. Yield: 50%. ^{1}H NMR (300 MHz, CD$_3$CN): δ 8.61 (1 H, d, J = 8.3; LH$^{3'}$), 8.55 (1 H, d, J = 8.6; LH^3), 8.51 (4 H, dd, J = 8.3, 0.6; bipy H^3/H$^{3'}$), 8.13 (1 H, d, J = 7.7; LH^4), 8.02–8.10 (5 H, m; bipy H^4/H$^{4'}$ and LH$^{4'}$), 7.68–7.80 (5 H, m; bipy H^6/H$^{6'}$ and LH$^{6'}$), 7.58 (1 H, br s; LH^6), 7.36–7.44 (5 H, m; bipy H^5/H$^{5'}$ and LH$^{5'}$), 3.72 (4H, t, J = 4.7; crown C*H*$_2$), 3.24–3.60 (14 H, m; bipy-C*H*$_2$N and crown C*H*$_2$), 3.22 (4 H, t, J = 4.9 Hz; crown C*H*$_2$), 2.61 (4 H, br s; crown C*H*$_2$). The assignments prefixed with ‘L’ (*e.g.* LH$^{3'}$) refer to the bipyridyl fragment of ligand L^2, in contrast to the ancillary 2,2′-bipyridyl ligands.

ES-MS: *m*/*z* 1134.8 (10%, {M + H}$^+$), 421.7 (100%, {M − 2PF$_6$}$^{2+}$). FAB-MS: *m*/*z* 1157 (10%, {M + Na}$^+$), 1136 (15%, {M + H}$^+$), 990 (100%, {M + H − PF$_6$}$^+$), 844 (80%, {M − 2PF$_6$}$^+$). Found: C, 39.2; H, 4.0; N, 8.5%. Required for [Ru(bipy)$_2$(L^2)][PF$_6$]$_2$·HPF$_6$· 2H$_2$O: C, 39.2; H, 4.2; N, 8.5%.

[Ru(bipy)$_2$(L^1)][PF$_6$]$_2$. *Method 1.* A mixture of [Ru(bipy)$_2$(L^2)][PF$_6$]$_2$ (270 mg, 0.21 mmol), 5-bromomethyl-2,2′-bipyridine (105 mg, 0.42 mmol, 2 equivalents) and ^{i}Pr$_2$EtN (0.2 cm^3, excess) in acetonitrile : dichloromethane solution (1 : 1, 25 cm^3) was stirred and heated to reflux for 4 h. After cooling, excess aqueous NH$_4$PF$_6$ was added, and the mixture was shaken vigorously. The colourless aqueous phase was removed and the organic phase, containing the product, was evaporated to dryness. The crude product was dissolved in acetonitrile (5 cm^3), and diethyl ether added dropwise until a precipitate began to appear. The mixture was then cooled to −20 °C overnight and then the supernatant solution was decanted off the resulting precipitate. The product was then recrystallized by vapour diffusion of diethyl ether into a concentrated acetone solution. Yield: 88%.

Method 2. A mixture of L^1 (154 mg, 0.257 mmol) and [Ru(bipy)$_2$Cl$_2$]·2H$_2$O (134 mg, 0.257 mmol) in ethanol (50 cm^3) was heated to reflux for 4 h. After cooling, an aqueous solution of

NH_4PF_6 was added and the mixture concentrated *in vacuo* to remove the ethanol and precipitate the crude product, which was filtered off, washed with water and dried. The product was purified by column chromatography on flash silica eluting with 10 : 2 : 1 acetonitrile:water:saturated aqueous KNO_3 solution. Of the two major orange bands, the former was collected. Aqueous NH_4PF_6 was added and the mixture concentrated *in vacuo* to precipitate the pure product as an orange solid, which was filtered off, washed with water, and dried. The product was recrystallized by vapour diffusion of diethyl ether into a concentrated solution in acetone. Yield: 24%. The second band was the undesired dinuclear complex $[\{Ru(bipy)_2\}_2(\mu\text{-}L^1)][PF_6]_4$. ^1H NMR (300 MHz, CD_3CN): δ 8.74 (1 H, s; $LH^{6''}$), 8.65 (1 H, ddd, $J = 4.9$, 1.7, 0.9; $LH^{6'''}$), 8.43–8.54 (7 H, m; bipy $H^3/H^{3'}$, LH^3, $LH^{3'}$ and $LH^{3''}$), 8.40 (1 H, dt, $J = 8.1$, 1.0; $LH^{3'''}$), 7.96–8.14 (7 H, m; bipy $H^4/H^{4'}$, LH^4, $LH^{4'}$ and $LH^{4''}$), 7.90 (1 H, td, $J = 7.8$, 1.8; $LH^{4'''}$), 7.70–7.80 (5 H, m; bipy $H^6/H^{6'}$and $LH^{6'}$), 7.61 (1 H, s; LH^6), 7.36–7.46 (6 H, m; bipy $H^5/H^{5'}$, $LH^{5'}$ and $LH^{5'''}$), 4.34 (2 H, s; bipy-CH_2N), 3.10–3.90 (22 H, m; crown CH_2 and bipy-CH_2N), 2.70 (4 H, br s; crown CH_2). The assignments prefixed with 'L' (*e.g.* $LH^{6'}$) refer to the bipyridyl fragments of ligand L^1, in contrast to the ancillary 2,2′-bipyridyl ligands. ES-MS: *m*/*z* 1303.2 (2%, $\{M + H\}^+$), 1157.1 (2%, $\{M - PF_6\}^+$), 578.8 (5%, $\{M + H - PF_6\}^{2+}$), 505.7 (100%, $\{M - 2PF_6\}^{2+}$). FAB-MS: *m*/*z* 1450 (10%, $\{M + 2H + PF_6\}^+$), 1324 (15%, $\{M + Na\}^+$), 1302 (40%, M^+), 1157 (100%, $\{M - PF_6\}^+$), 1013 (20%, $\{M + H - 2PF_6\}^+$). Found: C, 45.6; H, 4.8; N, 8.9%. Required for $[Ru(bipy)_2(L^1)][PF_6]_2\cdot HPF_6\cdot H_2O\cdot 1.5CH_3COCH_3$: C, 45.2; H, 4.5; N, 9.0%.

$[Ru(bipy)_2(L^1)Re(CO)_3(H_2O)][PF_6]_3$ (Ru-crw-Re, 1). A mixture of $[Ru(bipy)_2(L^1)][PF_6]_2$ (120 mg, 83 μmol) and $Re(CO)_5Cl$ (60 mg, 166 μmol, 2 equivalents) in degassed toluene : MeCN (1 : 1; 30 cm^3) was stirred and heated to reflux under nitrogen for 1.5 h. After cooling to room temperature, the mixture was concentrated *in vacuo* to remove the acetonitrile and precipitate the product. The mixture was then cooled to −20 °C and the solution decanted off the crude solid. The crude product obtained in this way was a mixture of two species, $[\{Ru(bipy)_2\}(L^1)\{Re(CO)_3Cl\}][PF_6]_2$ (**1′**) as the major product and $[\{Ru(bipy)_2\}(L^1)\{Re(CO)_3(H_2O)\}][PF_6]_3$ (**1**) as the minor product, as shown by the electrospray mass spectrum: *m*/*z* 1609.4 (4%, $\{$**1′** $+ H\}^+$), 658.6 (100%, $\{$**1′** $- 2PF_6\}^{2+}$), 650.2 (82%, $\{$**1** $- 3PF_6\}^{2+}$), 427.3 (56%, $\{Ru(bipy)_2(L^1)Re(CO)_3\}^{3+}$).

The products were separated by column chromatography on flash silica eluting with 14 : 2 : 1 acetonitrile:water:saturated aqueous KNO_3 solution. Both the major band (**1′**, first) and the minor band (**1**, second) were collected. To each solution, aqueous NH_4PF_6 was added and the mixture concentrated *in vacuo* to precipitate the product, which was filtered off, washed with water and dried. The minor product **1** was then found to be pure, but the major one had partially decomposed to become a mixture of **1′** and **1** once again. Attempts to isolate the major product **1′** by recrystallisation or by extraction techniques were similarly unsuccessful. Repeated chromatography allowed isolation of moderate quantities (*ca.* 20 mg) of pure **1** (= **Ru-crw-Re**).

Data for **Ru-crw-Re**. ES-MS: *m*/*z* 1760.1 (2%, $\{M + Na\}^+$), 1614.1 (2%, $\{M + Na - PF_6\}^+$), 650.5 (100%, $\{M - 3PF_6\}^{2+}$), 427.3 (85%, $\{M - H_2O - 3PF_6\}^{3+}$). FAB-MS: *m*/*z* 1759 (20%, $\{M + Na\}^+$), 1614 (15%, $\{M + Na - PF_6\}^+$), 1447 (100%, $\{M - [Re(CO)_3(H_2O)]\}^+$), 1301 (22%, $\{M - [Re(CO)_3(H_2O)] - PF_6\}^+$), 1157 (14%, $\{M - [Re(CO)_3(H_2O)] - 2PF_6\}^+$). Found: C, 38.3; H, 3.6; N, 7.3%. Required for $[\{Ru(bipy)_2\}(L^1)\{Re(CO)_3(H_2O)\}][PF_6]_3\cdot 3H_2O$: C, 38.3; H, 3.7; N, 7.8%.

X-Ray crystallography

Crystal data for complex $[Ru(bipy)_2(L^1)][PF_6]_2\cdot HPF_6\cdot H_2O\cdot 1.5Me_2CO$. $C_{58.5}H_{70}F_{18}N_{10}O_{6.5}P_3Ru$, $M = 1553.2$, triclinic, space group $P\bar{1}$, $a = 12.719(1)$, $b = 13.568(1)$, $c = 22.289(3)$ Å, $\alpha = 77.37(1)$, $\beta = 85.72(1)$, $\gamma = 62.30(1)°$, $V = 3321.4(7)$ Å^3, $T = 173$ K, $Z = 2$, $\mu(\text{Mo-K}\alpha) = 0.417$ mm^{-1}. 33735 reflections were measured with $2\theta_{max} = 55°$, which after merging afforded 12970 unique data ($R_{int} = 0.033$). All data were used in subsequent calculations. Final $wR2$ (all data) = 0.1724; $R1$ [selected data with $F > 4\sigma(F)$] = 0.0561. The instrument used was a Siemens SMART-CCD diffractometer. Software used: SHELXS-97 for structure solution;[30] SHELXL-97 for structure refinement;[30] SADABS for the absorption correction.[31] A total of 31 restraints was used to keep the geometry and thermal parameters of the solvent molecules reasonable.

CCDC reference number 186/1933.

See http://www.rsc.org/suppdata/dt/b0/b001594f/ for crystallographic files in .cif format.

Equipment and methods for photophysical studies

Air-equilibrated dilute solutions (spectroscopic grade acetonitrile) of the complexes **Ru-crw-Re** and $[Ru(bipy)_2(L^1)][PF_6]_2$ were used for the spectroscopic studies, with diazabicyclo-[2.2.2]octane, DABCO, employed as a proton scavenger to ensure that the aza-crown units were fully deprotonated. Based on the oxidation potential of DABCO ($E_{ox} = +\ 0.68$ V)[32] and on the reduction potential of coordinated bipy units in the complexes ($E_{red} = -1.2$ to -1.3 V *vs.* SCE), DABCO can efficiently quench MLCT excited states with an energy content ≥2.0 eV by an intermolecular diffusion-controlled process, eqn. (5),

$$\frac{I_0}{I} = 1 + k_q\tau_0[\text{DABCO}] \qquad (5)$$

where I_0 and τ_0 are the luminescence intensity and lifetime values in the absence of the quencher, and I is the reduced intensity because of quenching. For instance, a 10% quenching of the Ru-based emission of **Ru-crw-Re** occurred for $[\text{DABCO}] = 4 \times 10^{-3}$ M, consistent with $k_q = 1.4 \times 10^8$ M^{-1} s^{-1} as derived from Stern–Volmer plots and according to eqn. (5).[33] In our cases, the concentration of DABCO employed as a proton scavenger was much lower, *viz.* 2×10^{-5} M, and the observed quenching of the Re-based luminescence of **Ru-crw-Re** is therefore ascribed to intramolecular quenching.

Absorption spectra of 2×10^{-5} M solutions were measured in acetonitrile at room temperature with a Perkin-Elmer Lambda 5 UV/Vis spectrophotometer. For the luminescence experiments, acetonitrile solutions of the samples were used, both at room temperature and at 77 K. Uncorrected luminescence spectra were obtained from solutions whose absorbance values were ≤0.2 at the employed excitation wavelength by using a conventional Spex Fluorolog II spectrofluorimeter equipped with a Hamamatsu R928 phototube. Uncorrected luminescence maxima are used throughout the text, unless otherwise specified. Relative luminescence intensities were evaluated from the area (on an energy scale) of the corrected luminescence spectra, according to standard procedures.[14,34] Luminescence quantum yields Φ for the samples were obtained with reference to a standard $\{[Ru(bipy)_3]Cl_2$, $\Phi = 0.028$ in air-equilibrated water$\}$.[35] The experimental uncertainty on the absorption and luminescence maxima is 2 nm, the Φ values are affected by 20% uncertainty.

Luminescence lifetimes were obtained using $\lambda_{exc} = 337$ nm from an IBH single-photon counting equipment or $\lambda_{exc} = 355$ nm from a picosecond fluorescence spectrometer (time resolution 30 ps) based on a Nd:YAG laser (Continuum PY62-10) and a Hamamatsu C1587 streak camera. Both apparatuses have been described previously.[34] The uncertainty in the lifetime values is 10%.

According to eqn. (1) of the Results and discussion section, addition of $Ba(ClO_4)_2$ resulted in formation of the 1 : 1 associate **Ru-crw(Ba)-Re**. Titration experiments provided an estimate for K_{ass} by exploiting the Re-based luminescence intensity of **Ru-crw(Ba)-Re** and by performing an iterative analysis in accord with eqn. (6),[21]

$$I = I_0 + \frac{\Delta I}{2S_0}\left[K_{diss} + X + S_0 - \sqrt{(K_{diss} + X + S_0)^2 - 4XS_0}\right] \quad (6)$$

where I, I_0 and ΔI are luminescence intensities observed at 530 nm (see Fig. 4), $K_{diss} = 1/K_{ass}$, and X and S_0 are the titrant and substrate concentrations, respectively.

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