CHAPTER 3

Study of Photoinduced Electron Transfer Properties of Mononuclear and Dinuclear Os (II) - aza crown Re(I) Complex; Effects of Changing Temperature, and of Introduction of Ba$^{12}$ into the Macrocyclic Spacer Between the Chromophore.
1. Introduction

Studies of photoinduced energy - and electron transfer between the components of multichromophoric 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. 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 polyridine transition metal complexes, we have been interested in the study of photoinduced energy transfer in dyads based on [Ru(bipy)] and [Os(bipy)] units in which the energy transfer processes are switchable. This can be achieved, for instance either because of a conformational change in a flexible linker, or because the two components are associated by a non-covalent hydrogen bonding interaction whose formation relies on the solvent properties.

We are interested here to describe how the photo-physical properties of a dyad containing [Os(bipy)] and (Re(bipy) (CO)₃ (H₂O)] chromophores are affected by binding of an additional metal ion (Ba²⁺) to an aza - crown macrocyclic unit which separates the metal fragments. The ligand has been used by others in metal - ion extraction studies. we also show how the binding of Ba²⁺ to the macrocyclic site of Os - Crw - Re allows control over inter component photoinduced electron - and energy transfer processes.

2. Experimental Section

(a) General Details

Instrumentation used for routine NMR and mass spectroscopic
analyses, and electrochemical studies, have been carried out as given in literature.  

(b) X-Ray Crystallography

Crystal data for complex [Os(bipy)$_2$(L$^\dagger$)][PF$_6$]$_2$ · HPF$_6$·H$_2$O·1.5
Me$_2$CO·C$_{58.5}$H$_{70}^+$F$_{18}^-$N$_{10}^-$O$_{6.5}^-$P$_3$Os, M = 1553.2, triclinic, space group P$ar{1}$, a = 12.719(1), b = 13.568(1), c = 22.289 (3) Å, $\alpha = 77.37(1)$, $\beta = 85.72(1)$, $\gamma = 62.30(1)^\circ$, $\nu = 3321.4(7)$ Å$^3$, $T = 173K$, $Z = 2$, $\mu (M_o - K_o) = 0.417$ mm$^{-1}$, 33735 reflection were measured with $2\theta_{\text{max}} = 55^\circ$, which after merging afforded 12970 unique data ($R_{\text{int}} = 0.033$). All data were used in subsequent calculations. Final wR2 (all data) = 0.1724; RI [selected data with F > 4$\sigma$ (F)] = 0.0561. The instrument used was a Siemens SMART-CCD diffractometer. Software used: SHELXS$^9$-97 for structure solution, SHELXL$^9$-97 for structure refinement, SADABS$^{10}$ for the absorption correction.$^{10}$ A total of 31 restraints was used to keep the geometry and thermal parameters of the solvent molecules reasonable.

(c) Apparatus & Procedure

Air-equilibrated dilute solutions (spectroscopic grade acetonitrile) of the complexes Os-crw-Re and [Os(bipy)$_2$(L$^\dagger$)][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 ($E_{\text{ox}} = + 0.68$ V)$^{11}$ and on the reduction potential of coordinated bipy units in the complexes ($E_{\text{red}} = -1.2$ to -1.3 V vs. SCE), DABCO can efficiently quench MLCT excited states with an energy content $\geq 2.0$ eV by an intermolecular diffusion-controlled process, eqn. (1). diffusion-controlled process, eqn. (1).
\[ \frac{I}{I_0} = 1 + k_q \pi_o [\text{DABCO}] \]  

where \( I_0 \) and \( \pi_0 \) 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 Os-based emission of Os-crw-Re occurred for [DABCO] = 4 x 10^{-3} M, consistent with \( k_q = 1.4 \times 10^8 \text{ M}^{-1} \text{s}^{-1} \) as derived from Stern-Volmer plots and according to eqn. (1).\(^{12}\) In our cases, the concentration of DABCO employed as a proton scavenger was much lower, viz. 2 x 10^{-3} M, and the observed quenching of the Re-based luminescence of Os-crw-Re is therefore ascribed to intramolecular quenching.

Absorption spectra of 2 x 10^{-3} 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 \( \leq 0.2 \) at the employed excitation wavelength by using a conventional Spex Fluorolog 11 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.\(^{8,13}\)

Luminescence quantum yields \( \phi \) for the samples were obtained with reference to a standard \{[Os(bipy)_3]Cl_2, \( \phi = 0.028 \) in air-equilibrated water\}.\(^{14}\) The experimental and luminescence maxima is 2 nm, the \( \phi \) values are affected by 20% uncertainty.

According to eqn. (3) of the Results and discussion section, addition of Ba(ClO\(_4\))\(_2\) resulted in formation of the 1:1 associate Os-crw(Ba)-Re. Titration experiments provided an estimate for \( K_{\text{ass}} \) by exploiting the Re-based luminescence intensity of Os-crw(Ba)-Re and by performing an iterative analysis in accord with
equation (2)²¹.

\[ I + \frac{AI}{2S_0} K_{diss} + X + S_0 - (K_{diss} + X + S_0)^2 - 4X S_0 \]  \( (2) \)

where \( I \), \( I_0 \) and \( AI \) are luminescence intensities observed at 530 nm \( K_{diss} = 11K_{ass} \) and \( X \) and \( S_0 \) are the titrant and substrate concentrations, respectively.

(d) Synthesis

The compounds [Os(bipy)₂Cl₂].2H₂O,¹³ and 5-bromomethyl-2, 2-bipyridine¹⁶ were prepared according to published procedures.

(I) 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 \(^1\)Pr₂EtN (1.65 cm³, 9.5 mmol, excess) in ethanol (50 cm³) 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 CH₂Cl₂ 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

(II) [Os(bipy)₂(L²)][PF₆]₂. A mixture of \( L^2 \) (300 mg, 0.70 mmol) and [Os(bipy)₂H₂O (400 mg, 0.77 mmol) in ethanol (50 cm³) was heated to reflux for 4 h. After cooling, an aqueous solution of NH₄PF₆ 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 KNO₃ solution, increasing the polarity to 16:2:1 once the first impurities had come off the column. The major orange band was collected. Aqueous NH₄PF₆ 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%. The assignments prefixed with ‘L’ (e.g. LH²) refer to the bipyridyl fragment of ligand L², in contrast to the ancillary 2,2'-bipyridyl ligands.

(III) [Os(bipy)₂(L¹)][PF₆]₂. Method(A). A mixture of [Os(bipy)₂ - (L²)] [PF₆]₂ (270 mg, 0.21 mmol), 5-bromomethyl-2,2'-bipyridine (105 mg, 0.42 mmol, 2 equivalents) and ¹Pr₂EtN (0.2 cm³), idine (105 mg, 0.42 mmol, 2 equivalents) and ¹Pr₂EtN (0.2 cm³, excess) in acetonitrile : dichloromethane solution (1:1, 25 cm³) was stirred and heated to reflux for 4 h. After cooling, excess aqueous NH₄PF₆ 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 cm³), 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(B). A mixture of L¹ (154 mg, 0.257 mmol) and (Ru(bipy)₂Cl₂).2H₂O (134 mg, 0.257 mmol) in ethanol (50 cm³) was heated to reflux for 4h. After cooling, an aqueous solution of NH₄PF₆ was added and the mixture concentrated in vacuo to remove the ethanol and precipitate the crude products, 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 KNO₃ solution. Of the two major orange bands, the former was collected.
Aqueous NH₄PF₆ 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 [{Os(bipy)₂}₂(μ - L¹)][PF₆]₄. The assignments prefixed with L² (e.g. LH⁶) refer to the bipyridyl fragments of Ligand L¹, in contrast to the ancillary 2,2'-bipyridyl ligands.

(IV) [Os(bipy)₄(L¹)Re(CO)₅(H₂O)][PF₆]₃ (Os-crw-Re, 1). A mixture of [Os(bipy)₄(L¹)][PF₆]₂ (120 mg, 83 μmol) and Re(CO)₅Cl (60 mg, 166 μmol, 2 equivalents) in degassed toluene; MeCN (1:1:30 cm³) was stirred and heated to reflux under nitrogen for 1.5h. After cooling to room temperature, the mixture was concentrated in vacuo to remove the acetonitrile and precipitate the poroduct. 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, [{Os(bipy)₂}(L¹)-{Re(CO)₅Cl}][PF₆]₂ (1') as the major product and [{Os(bipy)₄}(L¹){Re(CO)₅(H₂O)}][PF₆]₃ (1) as the minor product.

The products were separated by column chromatography on flash silica eluting with 14:21:1 acetonitrile : water : saturated aqueous KNO₃ solution. Both the major band (1', first) and the minor band (1, second) were collected. To each solution, major band (1', first) and the minor band (1, second) were collected. To each solution, aqueous NH₄PF₆ 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 (ed. 20 mg) of pure 1 (=Os-crw-Re).

**Mononuclear Osmium complexes**

(V) \[\text{Os (bipy)}_2 (L^2)\] \[\text{PF}_6\]_2 and \[\text{Os (bipy)}_2 (L^3)\] \[\text{PF}_6\]_2. We were able to investigate 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\textsuperscript{17}. Reaction of 1, 10 - diaza - 18 - crown - 6 with only one equivalent of 5 - bromomethyl - 2, 2' - bipyridine in basic conditions afforded a good yield of the intermediate ligand L, which redialy afforded the mononuclear complex \[\text{Os (bipy)}_2 (L^2)\] \[\text{PF}_6\]_2. Alkylation of the second N - site of the macrocycle of \[\text{Os (bipy)}_2 (L^3)\] \[\text{PF}_6\]_2 with another equivalent 5 - bromomethyl - 2, 2' - bipyridine then afforded the mononuclear complex \[\text{Os (bipy)}_2 (L^3)\] \[\text{PF}_6\]_2 in good yield and with no possibility of forming the undesired by product.

**Hetero-dinuclear complex**

(VI) \[\{\text{Os (bipy)}_2\} (\mu - L^1) \{\text{Re (CO)}_3 (H_2O)\}\] \[\text{PF}_6\]_3 (Os - Crw - Re)

Reaction of the mononuclear complex \[\{\text{Os (bipy)}_2\} (L^1)\] \[\text{PF}_6\]_2 with \[\text{Re(CO)}_3 \text{Cl}\] in toluene, afforded a red material which we expected to be \[\{\text{Os (bipy)}_2 (\mu-L^1) \{\text{Re (CO)}_3 \text{Cl}\}\} \[\text{PF}_6\]_2 following the well known preparation of \[\text{Re (bipy) (CO)}_3 \text{Cl}\] by the simple reaction of \[\text{Re (CO)}_3 \text{Cl}\] with bipy\textsuperscript{18}. 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 color. The occurrence of a mixture of two similar components was also obvious from the \textsuperscript{1}HNMR spectrum.
3. Results and Discussions

(a) Crystallographic Studies

X-ray quality crystals of [Os (bipy)$_2$ (L')]$_2$ [PF$_6$], HPF$_6$. H$_2$O. 1.5 Me$_2$CO could be obtained from acetone : diethylether and the crystal structure is shown in Fig.1. The three components viz., The [Os (bipy)$_3$]$^{12}$ core, the macrocycle, and the vacant bipyridyl unit, are individually unremarkable, with the Os - N distances all lying in the range 2.064 (3) [for Os(1) - N (321)] to 2.078 (3) Å [for Os (1) - N(211)] and the bite angles of the chelating bipyridyl fragments all being ca 80°.

The molecule adopts a folded conformation in which the two bipyridyl units attached to the macrocycle be partially blocking each face. This is a consequence of the arrangement of the substituents around the pyramidal N-atoms in the macrocycle, and also occurs in the related complexes containing terpyridyl binding sites attached to the 1, 10 - diaza - 18 - crown - 6 core$^{17}$. 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 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.

Attempts to isolate the major product [{Os (bipy)$_2$} (μ-L')]$_2$ (Re (CO)$_3$ Cl)] [PF$_6$]$_2$ chromatographically were frustrating because it appeared to convert to the minor one during the chromatography. Consequently, after repeated chromatography the initially generated Re$_2$(I) - Chloride complex
Fig. 1 Crystal structure of the complex cation of \([\text{Os(bpy)}_2(L')][\text{PF}_6]_2\).

Fig. 2 Cyclic voltammogram of Os-crw-Re in MeCN (scan rate 0.2 V s\(^{-1}\)). The label * denotes the irreversible Re(I)/Re(II) processes, which is overlapping with the Os(II)/Os(III) process. The symbol + denotes an irreversible process possibly associated with macrocycle-bound water.
was all converted to the Re(1) aqua complex Os - 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)$_3$ Cl] has CO stretching bonds at 2030, 1930 and 1910 cm$^{-1}$ in CH$_2$Cl$_2$; the initially - generated complex [{Os (bipy)$_2$ (μ - L$^1$)} {Re (CO)$_3$ Cl}] [PF$_6$]$_2$ (slightly contaminated with the aqua complex (Os - crw - Re) gave a very similar IR spectrum in this region, with at Vco at 1900, 1813 and 1791 cm$^{-1}$. In contrast, in the IR spectrum of the known complex [Re (bipy) (CO)$_3$ (H$_2$O)]$^+$ $^{19}$, these carbonyl bonds are shifted to higher energy at 2010 and 1830 cm$^{-1}$ (the latter peak consisting of two overlapping components) because H$_2$O is poorer electron donor than chloride. For Os - Crw - Re, the carbonyl bonds in the IR spectrum occur at 2020, 1891 and 1880 cm$^{-1}$, in good agreement with the behaviour of [{Re (bipy) (CO)$_3$ (H$_2$O)}$^+$.

The facile hydrolysis of [{Os (bipy)$_2$} (μ - L$^1$) {Re (CO)$_3$ Cl}] [PF$_6$]$_2$ to Os - Crw - Re on the silica column is surprising considering that conversion of mononuclear (Re (bipy) (CO)$_3$ Cl) to [Re (bipy) (CO)$_3$ — (H$_2$O)]$^+$ is difficult requiring treatment with an Ag$^+$ salt to remove the chloride ligand before addition of water. It is tempting to suggest that the unexpected reactivity of [{Os (bipy)$_2$} (μ - L$^1$) {Re(CO)$_3$ Cl}] [PF$_6$]$_2$ is related to the fact the central macrocyclic unit can hold a hydrogen bonded water molecule in close proximity to the Re centre. 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 behavior has been seen in hydrolysis of imine containing molecules which contain a bosonic acid group close to the imine site; prior coordination of water to the boronic acid group resulted in
intramolecular rather than inter molecular hydrolysis of the imine and a consequent increase in reaction rate. Whatever the exact reason, the mass spectrometric and IR data, and the elemental analysis, confirm the formulation of Os - Crw - Re as [{Os(bipy)}₂(μ - L₁) {Re(CO)}₃(H₂O)}] [PF₆]₃.

(b). Electrochemistry

The mononuclear complexes [Os(bipy)₂(L₁)] [PF₆]₂ and [Os(bipy)₂(L₂)][PF₆]₂ show reversible Os(II)/Os(III) couples at +0.993 V and +0.96 V vs. Fe/Fe¹ respectively. Complex [Os(bipy)₂(L₁)] [PF₆]₂ also shows the expected bipyridyl-centred reductions at -1.74 - 1.95 and -2.21 V vs. Fe/Fe¹: for [Os(bipy)₂(L₂)][PF₆]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 [Os(bipy)]²⁺ unit. In addition, a broad, low-intensity irreversible feature at ea. -1.2 V vs. Fe/Fe¹ could addition a broad, low-intensity irreversible feature at ea. -1.2 V vs. Fe/Fe¹ could be ascribed to reduction of macrocycle-bound water (the thermodynamic reduction potential for H₂O is -0.83 V vs. NHE).

Electrochemical studies on dinuclear Os-crw-Re revealed (Fig.-2) a wave at ca. +0.93 V vs. Fe/Fe¹ which is a superposition of the expected chemically reversible Os(n)/Os(m) couple and 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 Os(I)/Os(III) wave. It has been observed before similar behaviour in other complexes containing both Os(II) - and Re(I)-bipyridyl chromophores. Reversible bipyridyl-centred reductions occur at -1.73 V and -1.93 V vs. Fe/Fe¹ and again an irreversible feature at ca. -1.2 V vs. Fe/Fe¹ we ascribe to reduction of water, either bound in the macrocycle, coordinated to the
Re(I) centre, or both.

(c) Spectroscopic and Photophysical Properties

Ground state absorption spectra of acetonitrile 2x10⁻³ M solutions of Os-erw-Re and [Ru(bipy)₂(L¹)][PF₆]₂ are shown in fig.-3. The difference spectrum (for λ > 300 nm), which is ascribed to the absorption spectrum of the [Re(bipy)(CO)₅((H₂O))]⁺ moiety of Os-erw-Re. Comparison with data from the extensive literature concerned with Ru(II)-polypyridine²¹ and Re(I)-bipy-tricarbonyl¹⁸,²²,²³,²⁴ complexes allows the following assignments. (i) For both Os-erw-Re and [Ru(bipy)₂(L¹)][PF₆]₂ the wavelength maximum at 450 nm (g=1.3 x 10⁻⁴ M⁻¹cm⁻¹) is of ¹Re-bipy CT character. For Os-erw-Re, selective excitation of the Os-based chromophore could be achieved by using λₖₑₓ in the range 400-500 nm (fig.-3). Conversely, use of shorter wavelengths gave excitation of both Os- and Re-based chromophores; for instance excitation at 380 nm gave a Os : 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. For the sake of comparison, data for the Re(I)-tricarbonyl complex of 2,2':3',2":6",2"-quaterpyridine are also included.⁸ The room temperature luminescence spectra of 2x10⁻³M acetonitrile solutions of Os-erw-Re and Ru(bipy)₂(L¹)][PF₆]₂ obtained using λₖₑₓ = 380 nm, exhibit overlapping profiles with λₘₐₓ = 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 Os-erw-Re and for Os(bipy)₂(L¹)][PF₆]₂ (Table-1) the luminescent state is of ³MLCT nature in each case.²¹ From literature sources,¹⁸,⁸,²²,²³,²⁴ a Re-based emission would be expected at 500-650 nm (i.e. in
Fig. 3 Room temperature absorption spectra of $2 \times 10^{-5} \text{ M}$ acetonitrile solution of Os-crw-Re ( ) and [Os(bipy),L][PF$_6$]$_2$ (.........), the difference spectrum ( ) ascribed to the Re based absorption of Os-crw-Re is also shown. The inset shows luminescence spectra obtained with $\lambda_{exc} = 380 \text{ nm}$.

Fig. 4 Changes of the luminescence spectra of a $2 \times 10^{-5} \text{ M}$ acetonitrile solution of the Os-crw-Re after Ba$^{2+}$ addition; $\lambda_{exc}$ was 323 nm. Inset: fitting of the luminescence data points registered at 530 nm to determine the association constant; see text for details.
about the same region) and the absence of a sizeable such emission from Os-erw-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 $\tau = 80$ 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.\textsuperscript{7,25} Fig.-4 illustrates the changes in emission spectra for Os-erw-Re observed after titration 4 illustrates the changes in emission spectra for Os-erw-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 $\lambda = 530$ nm, characterised by a lifetime $\tau = 62$ ns, which is Re-based in origin.\textsuperscript{18,8,22,23} As to the nature of the Re-based luminescent state, the majority of cases reported in the literature for $\{\text{Re(L)(CO)}\}_2^+$ complexes are for $^3\text{MLCT}$ states,\textsuperscript{18,23} but $^3\text{LC}$ states have also been identified for some complexes.\textsuperscript{24} Based on a comparison of the observed luminescence features we assign the Re-based contribution as $^3\text{MLCT}$ in nature.

The changes in luminescence intensity at 530 nm as a function of the Ba$^{2+}$ concentration, due to formation of the complex Os-erw(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, an association constant $K_{ass} = 5 \times 10^4$ M$^{-1}$ is evaluated for the Ba$^{2+}$ binding, according to eqn.(3) below.

$$\text{Os-erw-Re} + \text{Ba}^{2+} = \text{Os-erw(Ba)-Re}$$  \hspace{1cm} (3)
Table 1 Luminescence properties of complexes

<table>
<thead>
<tr>
<th></th>
<th>$\lambda_{\text{em}}$/nm</th>
<th>$10^2 \phi$</th>
<th>$\tau$/ns</th>
<th>$\lambda_{\text{em}}$/nm</th>
<th>$\tau$/µs</th>
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<tr>
<td>[Os(bpy)$_2$(L)][PF$_6$]</td>
<td>608</td>
<td>3.0</td>
<td>170</td>
<td>588</td>
<td>5.0</td>
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<tr>
<td>[Os(bpy)$_2$(L)][PF$_6$] + Ba$^{2+}$</td>
<td>612</td>
<td>3.6</td>
<td>200</td>
<td>588</td>
<td>6.0</td>
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<td>Os-crv-Re</td>
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<td>2.8</td>
<td>0.08, 170d</td>
<td>586</td>
<td>0.005, 5.0$^d$</td>
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<td>Os-crw(Ba)-Re</td>
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<td>1.2$^a$, 3.6$^d$</td>
<td>62$^a$, 195$^a$</td>
<td>500a, 588d</td>
<td>0.14, 6.0$^d$</td>
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<td>1.5</td>
<td>22</td>
<td>535</td>
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$^a$Air equilibrated acetonitrile solvent. $^b \lambda_{\text{exe}} = 380$ nm for Os-crv-Re and its Ba$^{2+}$ associate. Os and Re based absorption occurs in a $\approx$3:1 ratio. $^c$ Very weak Re based emission observed at 520 nm; see text. $^d$ Os-based emission, see text. $^f$ Re based emission, see text. From ref 14; solvent was DMF-CH$_2$Cl$_2$ (9:1); QP is 2,2':3',2''-quaterpyridine.
This may be compared with \( K_{\text{ass}} > 10^6 \text{ M}^{-1} \), as found for the analogous 1:1 equilibrium between dialkyl-1, 10-diaza-18-crown-6 compounds and \( \text{Ba}^{2+} \) in acetonitrile\(^{23}\). 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 macro-cycle are blocked by the bulky substituents, and this conformation may persist in solution). It is to be noticed that the uptake of \( \text{Ba}^{2+} \) by Os-crw-Re at room temperature results in some enhancement (by \( \approx 20\% \)) of the Ru-based luminescence intensity from \( \tau = 170 \) to ca. 200 ns both for Os-crw-Re and Os(bipy)_2(L^1)[PF_6]_2 (Table-1).

The presence of independent Os-based and Re-based luminophores within the Os-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). Two components are present in the emission of Os-crw(Ba)-Re, with lifetime of \( \tau_1 = 62 \) and \( \tau_2 = 195 \) ns, ascribable to the Re-based and Os-based components respectively. The analysis was performed using eqn. (4), and the evaluated

\[
I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)
\]

(4)

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 \( \text{Ba}^{2+} \), the Re-based luminescence of Os-crw(Ba)-Re is not quenched, in contrast with what happens in Os-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.\(^{21,27}\) For Os-crw-Re at 77 K, i.e.
Fig. 5 Luminescence spectrum (in acetonitrile and at room temperature) of Os-crw-Re after addition of more than 2 equivalents of Ba\(^{2+}\); \(\lambda_{\text{exe}}\) was 380 nm. (b) Wavelength dependence of the preexponential factors, A1 and A2, for Re-based (\(\tau_1\), O) and Os-based (\(\tau_2\), O) emissions; see texts for details.

Fig. 6 Luminescence spectrum of Os-crw-Re(____[Os(bipy)\(_2\)](L')\)[PF\(_6\)](____) and the Os-crw-(Ba)-Re associate (---) in acetonitrile glass at 77 K; \(\lambda_{\text{exe}}\) was 320 nm. Spectral intensities are arbitrarily scaled.
in a frozen glass, using $\lambda_{ex} = 320$ nm, an intense vibronically-resolved luminescence spectrum is observed which arises from the Os-based luminophore ($\lambda_{max} = 586$ nm, $\tau = 5$ \mu s Table-1); the relevant luminescence spectra are in Fig.-6. For Os-crw-Re, the excitation spectrum obtained at $\lambda_{es} = 600$ nm showed features typical both of the Os- and Re-based absorption (Fig.-7). On this basis, one concludes that sensitisation of the Os-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 Os-crw-Re in frozen solvent at 77 K, a Re $\rightarrow$ Os photoinduced energy transfer process is operative.

For Os-crw(Ba)-Re at 77 K, two well-separated luminescence band maxima are obtained, with $\lambda_{max}$ 500 nm and 588 nm (Fig.-6)\textsuperscript{28}. The time-resolved luminescence profiles, as monitored at these two wavelengths, conform to a dual-luminescent behaviour (Fig.-8 & 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 $\tau_2 = 6$ \mu s, and a rise time $\tau_1 = 140$ ns (i.e. $A_1$ has a negative value Fig.-8). These findings indicate the occurrence of partial quenching of the Re-based luminescence and concomitant sensitisation of the Os-based luminescence in Os-crw(Ba)-Re (cf. the nearly complete quenching of the Re component in the absence of Ba\textsuperscript{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).

(d). Photoinduced electron transfer Studies.

For the case of discussion, we indicate henceforth the Re-based MLCT excited state of Os-crw-Re as $\{\text{Os(bipy)N-N-(bipy)Re}\}^{29}$, where (bipy)-N-N-(bipy)
Fig. 7 Uncorrected excitation spectra (acetonitrile, 77K) obtained under fixed emission at 600 nm of Os-crw-Re (— [Os(bipy)$_2$(L)][PF$_6$]$_2$. (...) and the Os -crw-(Ba)-Re associate (— —). The excitation spectrum at 500 nm emission for Os -crw-(Ba)-Re is also shown (— —).

Fig. 8 Time resolved luminescence profiles for the Os -crw-(Ba)-Reassociate (acetonitrile, 77K) as monitored at 500nm (a) and 620nm (b).
denotes the bridging ligand $L^1$ and the other terminal ligands (bipy attached to the Os terminus, carbonyl and $H_2O$ 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 Os-based MLCT excited state, which we write as \{Os$^{III}$((bipy)-N-N-(bipy))Re$^I$\}.

Two types of intramolecular quenching of the Re-based excited state in Os-crw-Re can be examined: (i) an electron transfer involving the closer N position of the aza-crown unit, i.e. Re$^{II}$ $\longrightarrow$ N$_{crw}$ [eqn. (5)], or (ii) a Re $\longrightarrow$ Os energy transfer [eqn. (6)].

\[
\begin{align*}
\text{Os}^{II}(\text{bipy}) \text{ N N (bipy)Re}^{II} & \rightarrow \text{Os}^{III}(\text{bipy}) \text{ N N (bipy)Re}^{I} \\
\text{Os}^{II}(\text{bipy})\text{-N-N-(bipy)Re}^{II} & \rightarrow \text{Os}^{III}(\text{bipy}) \text{ N N (bipy)Re}^{I}
\end{align*}
\]

The energy level diagram of Scheme 2 shows the two intramolecular steps that are concerned with effective deactivation of the excited levels of Os-crw-Re (as obtained by using excitation at a wavelength <380 nm). The energies of the luminescent Os and Re-based states, 2.1 and 2.5 eV respectively, have been estimated from the emission band maxima observed at 77 K. The level for the charge-separated state following the Re$^{II}$ $\leftarrow$ N$_{crw}$ step, eqn. (5), is 2.4 eV as evaluated by using the redox potentials available from this study and from literature sources\(^{30}\) (a practically identical figure is obtained for the analogous Os$^{III}$ $\leftarrow$ N$_{crw}$ electron-transfer step). According to the energy levels of Scheme 2 and to the above results, control over the competing electron and energy processes in Os-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 Os-crw-Re and Os-crw(Ba)-Re; Scheme 3 illustrates the various cases reported.

**Case (a): room temperature, Ba\textsuperscript{2+} absent.** In fluid solvent, only the Os-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 \( G_{el} = 0.1 \) and \( G_{en} = -0.4 \text{eV} \), respectively (Scheme 2). By comparing the luminescence intensity of 2x10\textsuperscript{-3} M solutions of [Os(bipy)_2 - (L\textsuperscript{i})]\textsuperscript{2+} and Os-crw-Re, obtained using \( \lambda_{exc} = 380\text{nm} \) (Fig.-3), we see no sensitisation of the Os-based luminescence for Os-crw-Re under these conditions. Excitation spectra taken at \( \lambda_{em} = 620 \text{nm} \) do not show absorbing features from the Re-based chromophore. Thus, at room temperature and in the absence of Ba\textsuperscript{2+}, the Re-based excited state is deactivated by electron transfer from an N atom of the aza-crown unit according to eqn. (5).\textsuperscript{31} Based on the lifetime of \( \pi_{a} = 80 \text{ps} \) for the weak residual Re-based emission, we calculate a rate constant of \( \kappa_{el} = 1.2 \times 10^{10} \text{s}^{-1} \) for this process. We note that an analogous electron-transfer quenching of the Os-based excited state, i.e. Os\textsuperscript{III} \( \leftarrow \) N\textsubscript{crw} is never observed (Scheme 2), probably because it is endoergic, with \( \Delta G = +0.3 \text{eV} \).

**Case (b): room temperature, Ba\textsuperscript{2+} hosted within crw.** Formation of the Os-crw (Ba)-Re associate at room temperature is expected to result in an increase of the oxidation potential of the N position(s)\textsuperscript{7}, possibly inhibiting Re\textsuperscript{III} \( \leftarrow \) N\textsubscript{crw} electron transfer, eqn. (5). 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, \( \kappa_{el} \) and \( \kappa_{en} \) respectively, must be \(<1.6 \times 10^{7} \text{s}^{-1} \) [the competing intrinsic deactivation of the Re-
based luminophore is \( \kappa_{d}^{Re} = 1 / (62 \times 10^{-9}) \) s\(^{-1}\).

**Case (c) : 77 K, Ba\(^{2+}\) absent.** In frozen solvent, the charge-separated excited state \([\text{Os}^{II} (\text{bipy}) - \text{N} - \text{N}^{+} (\text{bipy}) \text{Re}^{1}\]) which follows the \( \text{Re}^{II} \leftarrow \text{N}_{\text{crw}} \) electron transfer (eqn. (5)) is expected to be destabilized by at least 0.5 eV with respect to what happens in fluid solvent.\(^{32}\) In contrast, the luminescent energy levels undergo only minor changes on passing from fluid to frozen medium.\(^{8,21,23}\) Thus, electron transfer involving the Re-based excited level and the N position(s) of \text{crw} becomes energetically disallowed at 77 K (Scheme 2). In fact, by using excitation with \( \lambda_{\text{exe}} < 380 \) nm; nearly complete quenching of the Re-based luminescence and sensitisation of the Os-based luminescence is observed, consistent with a Re → Os energy transfer step [eqn.(6)]. The residual, weak luminescence exhibited a lifetime of \( \pi_{q}^{\text{Re,77K}} = 5 \) ns, as opposed to typical values of several \( \mu \)s for Re-polypyridine-tricarbonyl luminophores at 77 K.\(^{18,8,23}\) On this basis, we conclude that \( k_{en}^{77K} \approx 1 / \tau_{q}^{\text{Re,77K}} = 2.0 \times 10^{8} \) s\(^{-1}\).

**Case (d) : 77 K, Ba\(^{2+}\) hosted within \text{crw}.** Again, electron transfer quenching of the Re-based excited state is prevented by the frozen state of the solvent, whereas Re → Os energy transfer remains energetically allowed (Scheme 2). Consequently, the energy transfer takes place (Fig.-7 & 8 shows 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 → Os energy transfer, the partial restoration of the Re-based emission in the presence of Ba\(^{2+}\) is indicative of a slower Re → Os energy transfer step (evidence for the occurrence of this process is provided by the results of Fig.-7 & 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 \([\text{Os(bipy)}_2(L^1)][\text{PF}_6]\)\(_2\), the lifetime of the
Os-based emission at 77 K increased from 5.0 to 6.0 \(\mu\)s 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 \(\mu\)s time scale Table-1), arising from these effects is to be expected. Thus, the Re-based excited state of Os-crw (Ba)-Re should deactivate according to a scheme involving slowed down competing processes: (i) the intrinsic deactivation, and (ii) the Re \(\rightarrow\) Os energy transfer. The fact that the observed lifetime for the Re-based emission is \(\tau^{\text{Re,77K,Ba}}_q = 140\) 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 change in the Re \(\rightarrow\) Os energy transfer rate, i.e. \(k^{77K,\text{Ba}}_{\text{em}} \approx 1/\tau^{\text{Re,77K,Ba}}_q = 1/140\) ns = 7 \times 10\(^6\) \(s^{-1}\). Comparison with the value of \(k^{77K}_{\text{em}} = 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 Os-crw-Re at 77 K slows down the Re \(\rightarrow\) Os energy transfer process by about a factor of 30.

The reason for the effect of Ba\(^{2+}\) on the Re \(\rightarrow\) Os 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 Os and Re centres move further apart. The Os 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 Os ... Re separation on electrostatic grounds. Unfortunately we were unable to obtain crystals of the Ba\(^{2+}\) adduct of Os-crw-Re to prove this.
Conclusions

There is a large interest in photoinduced processes involving the termini of model binuclear species, 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\textsuperscript{2+} ions in the crw units (cases (b) and (d) it is possible to switch between four different types of behaviour in Os-crw-Re. The arrangement of energy levels of the photoactive units of Os-crw-Re allow the occurrence of Re → Os 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 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 → Os energy transfer takes place at 77 K (with $\kappa_{\text{en}} = 2 \times 10^8$ s\(^{-1}\)) because the competition against the much slower intrinsic deactivation of the Re-based unit, $k_{d, \text{Re,77K}} = 3.3 \times 10^3$ s\(^{-1}\), is now favourable.

When the crw cavity contains Ba\textsuperscript{2+}, the energy transfer step is slowed down to $\kappa_{\text{en}} = 7 \times 10^6$ s\(^{-1}\) but still it is fast enough to favourably compete against $k_{d, \text{Re,77K}}$. So we can use the change in temperature to switch between Re ← N\text{crw} electron-transfer and Re → Os energy transfer processes, and the presence or absence of Ba\textsuperscript{2+} to modulate further the efficiency of both of these processes.
References


10. G.M. Sheldrick, SADABS, A program for absorption correction with the
Siemens SMART area-detector system, University of Gottingen, 1996.


12. In acetonitrile solvent, the diffusion occurs at a high rate \( k_{dir} = 1.9 \times 10^{10} \) M\(^{-1}\) s\(^{-1}\) (see ref. 32, p. 291) suggesting that the rate determining step is electron transfer within the encounter \( k_q \), according to \( k_q^{-1} = k_{dir}^{-1} + k_w^{-1} \).


28. We assume that for the *Os-crw(Ba)-Re* associate the association constant at 77K is \( K_{ass} \geq 5 \times 10^4 \) M\(^{-1}\) the value found at room temperature.


30. The oxidation potential for triethylamine in acetonitrile is in the range 0.96
L 15 V SCE, sec S.L. Murov, I. Carmlehnel and G.L. Hag, in *Hanbook of Photochemistry*, Marcel Dekker, New York, 1993, p. 269 and ref. 32, p. 44; the conversion factor between SCE and Fe/Fe¹ reference electrodes is 0.38 V.


Scheme-1 (I) [Os(bpy)$_2$Cl$_2$].2H$_2$O.EtOH ; (II) [Re(CO)$_3$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.
Scheme-2 Intramolecular electron (el) and energy (en) transfer processes in Os-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.

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