

Photophysical properties of an assembly containing a $[\text{Ru}(\text{bpy})_3]^{2+}$ chromophore and a $[\text{Ru}(\text{bpy})(\text{CN})_4]^{2-}$ quencher unit linked by a hydrogen-bonded interface based on the $[\text{Ru}(\text{bpy})(\text{CN})_4]^{2-}$ /aza-crown association

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Received 27th February 2002, Accepted 16th April 2002

First published as an Advance Article on the web 7th May 2002

The two complexes $[(\text{bpy})_2\text{Ru}(\text{bpy-cyclamH}_2)]^{4+}$ (**Ru-cy**; bpy = 2,2'-bipyridine; bpy-cyclam = 1-(2,2'-bipyridin-5-yl-methyl)-1,4,8,11-tetraazacyclotetradecane) and $[\text{Ru}(\text{bpy})(\text{CN})_4]^{2-}$ (**Ru-CN**) associate in MeCN solution *via* a hydrogen-bonding interaction between the externally-directed lone pairs of the cyanide ligands on the **Ru-CN** unit, and the protonated amine sites of the cyclam macrocycle which is pendant from the $[\text{Ru}(\text{bpy})_3]^{2+}$ core of the **Ru-cy** unit. Due to the sensitivity of the **Ru-CN** chromophore to interactions of the cyanide lone pairs, this association results in characteristic changes in its absorption and emission properties; *viz.* the ¹MLCT absorption is blue-shifted, from 535 to 480 nm, and the ³MLCT emission is also blue-shifted, from 790 nm to 680 nm. In addition, the association between the components results in quenching of the characteristic ³MLCT luminescence of the **Ru-cy** unit. Analysis of the absorption and emission properties of mixtures of the two components in varying proportions indicates that a 2 : 1 associate **Ru-cy**:**Ru-CN**:**Ru-cy** forms, in which two of the cyanide ligands of **Ru-CN** interact with each of the **Ru-cy** units. The overall association constant for formation of this is $K_{\text{ass}} = 2.6 \times 10^{11} \text{ M}^{-2}$; under the dilute conditions necessary for luminescence experiments the association is not complete however and some free **Ru-CN** and **Ru-cy** are also present in the equilibrium mixture. Within the hydrogen-bonded associate, quenching of the ³MLCT luminescence of the **Ru-cy** unit occurs, most likely by a Förster energy transfer mechanism, with *ca.* 88% efficiency and a rate constant of $k_q = 3.8 \times 10^7 \text{ s}^{-1}$, corresponding to an inter-chromophore separation of *ca.* 11.5 Å.

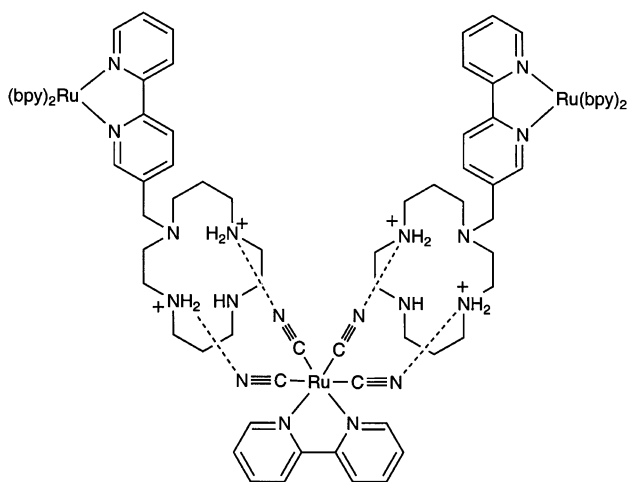
Introduction

The study of photoinduced processes (energy or electron transfer) in multi-chromophoric complexes based on metal-polypyridyl or metalloporphyrin luminophores remains one of the most popular areas of inorganic chemistry.¹ Precise control of the movement of excitation energy or of excited electrons in complicated multi-component systems is of particular interest both for understanding and mimicking natural photosynthetic processes,² and for making artificial molecules which exploit light in a similar manner.^{1,2}

The majority of such assemblies contain components which are covalently linked.¹ Covalent linkages allow preparation of chemically robust species in which the separation between components, and the pathways (bridging ligands) through which interactions are transmitted tend to be well-defined and subject to precise synthetic control. Of considerable recent interest however is the study of the photophysical properties of assemblies in which the component parts are linked by relatively weak, non-covalent interactions.³⁻⁶ The advantage of these is that the synthesis of elaborate, one-off bridging ligands is avoided: appropriately-functionalised mononuclear components can be 'assembled' simply by mixing them together and allowing the supramolecular interactions between them to take their course. Hydrogen bonding has been by far the most popular interaction to use to assemble component parts in this way, because of the strength, rigidity, directionality and chemical controllability of hydrogen bonds compared to other non-covalent interactions.⁷ We⁴ and others⁵ have exploited the triple hydrogen bond between complementary cytosine and guanine

units pendant from mononuclear complexes as a basis for assembling components in solution, and other more elaborate hydrogen-bonding interfaces have been developed as a means for assembly of chromophore and quencher components.⁶

In this paper we describe an assembly in which $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Ru}(\text{bpy})(\text{CN})_4]^{2-}$ chromophores are associated by a multiple hydrogen-bonding interaction between the externally-directed lone pairs of the $[\text{Ru}(\text{bpy})(\text{CN})_4]^{2-}$ unit (hereafter abbreviated as **Ru-CN**),⁸⁻¹⁰ which acts as the hydrogen-bond acceptor, and a protonated aza-crown macrocycle – which acts as the hydrogen-bond donor – pendant from the $[\text{Ru}(\text{bpy})_3]^{2+}$ unit. It has been known for a while that anionic cyano-metal complexes form stable 'supercomplexes' with protonated aza-crown macrocycles *via* multiple M–CN...H–N charge-assisted hydrogen bonds.¹¹⁻¹⁴ In these supercomplexes the redox and spectroscopic properties of the cyano-metal complexes can be strongly perturbed, because involvement of the cyano ligands in hydrogen-bonding interactions results in a decrease in the electron density at the metal centre,¹³ this effect is exactly analogous to the well-known solvatochromism of such complexes.¹⁰ In particular, **Ru-CN** forms strong 1 : 1 adducts with $([\text{32}] \text{ane-N}_8\text{H}_8)^{8+}$ and $([\text{24}] \text{ane-N}_6\text{H}_6)^{6+}$,^{11,12} which results in blue-shifts in the MLCT absorption and emission energies of the **Ru-CN** chromophore as well as a substantial increase in its luminescence lifetime and quantum yield. The perturbation is more pronounced with $([\text{32}] \text{ane-N}_8\text{H}_8)^{8+}$ than with $([\text{24}] \text{ane-N}_6\text{H}_6)^{6+}$, which reflects the fact that $([\text{32}] \text{ane-N}_8\text{H}_8)^{8+}$ can interact with all four cyanide ligands of **Ru-CN** simultaneously whereas $([\text{24}] \text{ane-N}_6\text{H}_6)^{6+}$ can only interact with three of them.



Scheme 1 Proposed structure of the trinuclear associate incorporating two **Ru-cy** and one **Ru-CN** units. The positions of the protonated sites on the cyclam unit are chosen arbitrarily.

The complex $[(bpy)_2Ru(bpy\text{-}cyclamH_2)]^{4+}$ [hereafter abbreviated as **Ru-cy**; *bpy-cyclam* is 1-(2,2'-bipyridin-5-yl-methyl)-1,4,8,11-tetraazacyclotetradecane] (Scheme 1)¹⁵ combines the functions of a hydrogen-bond donor to bind the **Ru-CN** unit, with that of a luminophore in its own right. The strong association expected^{11,12} between **Ru-CN** and the protonated aza-crown macrocycle of **Ru-cy** provides a method of allowing the **Ru-CN** and $[Ru(bpy)_3]^{2+}$ chromophores to assemble in solution such that photoinduced inter-component interactions can occur within the assembly. These results may be compared with the inter-component interactions which occur between the same two chromophores in a covalently linked assembly, described in the previous paper.¹⁶

Results and discussion

Syntheses of complexes and possible nature of the hydrogen-bonded associates

The two complexes used in this study, $(Bu_4N)_2[Ru-CN]$ ^{8,10} and $[Ru-cy][PF_6]_4$ ¹⁵ have both been reported before, although we have modified the original published syntheses slightly (see Experimental section). $(Bu_4N)_2[Ru(bpy)(CN)_4]$ was chosen as a highly soluble source of the anionic **Ru-CN** chromophore. In the complex cation $[(bpy)_2Ru(bpy\text{-}cyclamH_2)]^{4+}$ (**Ru-cy**) the pendant cyclam macrocycle unit is doubly protonated, as indicated by reproducible elemental analysis and as also observed by Rawle *et al.*¹⁵

Following the recent results of Rampi *et al.*¹¹ and of Borsarelli *et al.*¹² mentioned above, it is to be expected that these two components should associate strongly in MeCN; for example, the 1 : 1 supercomplex formation between **Ru-CN** and $[(32)\text{-}ane\text{-}N_8H_8]^{8+}$ is complete in 10^{-4} M aqueous solution.¹¹ The hydrogen-bonding interaction between **Ru-CN** and aza-crown macrocycles relies on the amine sites being protonated and therefore cationic. Since only two of the four amine sites of the pendant cyclam in **Ru-cy** are protonated under the conditions of our experiments (*i.e.* approximately neutral pH),¹⁵ it is reasonable to suggest that one **Ru-cy** unit can interact with two of the four cyanide groups of **Ru-CN**. This could in principle afford a 1 : 1 **Ru-CN:Ru-cy** adduct in which two of the cyanide ligands of **Ru-CN** remain free to interact with the solvent, or a 1 : 2 **Ru-cy:Ru-CN:Ru-cy** adduct in which all four cyanide ligands are involved in hydrogen-bonding interactions with two **Ru-cy** units (Scheme 1), eqn. (1)–(3).

$$K_1 = \frac{[Ru-CN : Ru-cy]}{[Ru-CN][Ru-cy]} \quad (1)$$

$$K_2 = \frac{[Ru-cy : Ru-CN : Ru-cy]}{[Ru-CN : Ru-cy][Ru-cy]} \quad (2)$$

$$K_{as} = K_1 K_2 \quad (3)$$

It might be expected that K_2 is less than K_1 for both statistical reasons (the second **Ru-cy** has only one site available on **Ru-CN** rather than two) and electrostatic reasons (the first association is between a cation and an anion, whereas the second is between two cations). It may be however that the distances between the charged units are too large for this electrostatic effect to be of much significance.

We attempted to study the association of **Ru-CN** and **Ru-cy** in CD_3CN solution by a ¹H NMR spectroscopic titration involving addition of small amounts of $(Bu_4N)_2[Ru-CN]$ to a 0.01 M solution of $[Ru-cy][PF_6]_4$. This caused a steady downfield shift of the *bpy-CH₂* methylene protons of the **Ru-cy** fragment from 3.73 to 3.81 ppm, which stopped after addition of 0.5 equivalents of **Ru-CN**, apparently indicating formation of a 1 : 2 **Ru-cy:Ru-CN:Ru-cy** adduct. However after addition of more than one equivalent of **Ru-CN** precipitation of an insoluble material occurred, an effect which persisted even at high dilutions. The NMR titration therefore provides some evidence of formation of a 1 : 2 adduct at relatively high concentrations. More insight into the association behaviour of the components is provided by UV/Vis spectroscopic and photophysical studies (below).

Absorption and luminescence properties of the mononuclear complex units

$[(bpy)_2Ru(bpy\text{-}cyclamH_2)]^{4+}$. The spectroscopic properties of $[Ru-cy][PF_6]_4$ in acetonitrile are collected in Table 1. The absorption spectrum features an ¹MLCT band at 450 nm ($\epsilon = 13000 \text{ M}^{-1} \text{ cm}^{-1}$) and an intense ¹LC band at 288 nm ($\epsilon = 80400 \text{ M}^{-1} \text{ cm}^{-1}$), which are very similar to those of the prototypical $[Ru(bpy)_3]^{2+}$ complex (Table 1);^{17a} the luminescence quantum yield ($\Phi = 0.026$) and lifetime ($\tau = 200 \text{ ns}$) of $[Ru-cy][PF_6]_4$ are likewise similar to those reported for $[Ru(bpy)_3]^{2+}$ (Table 1). It is noteworthy that for a previously investigated $[(bpy)_2Ru(bpy\text{-}cyclamH_2)]^{4+}$ analogue, in which the methylcyclam unit is appended at the 6 position of a *bpy* ligand rather than (as here) the 5 position, both the luminescence intensity and lifetime were reduced by more than 2 orders of magnitude compared to the present **Ru-cy** complex.¹⁸ This can be ascribed to steric crowding caused by the 6-substituted *bpy* ligand, resulting in a significant lengthening of one of the Ru–N bonds. This in turn causes a reduced ligand field at the metal centre, thereby decreasing the energy gap between the luminescent ³MLCT level and higher lying ³MC levels, and allowing efficient radiationless deactivation of the ³MLCT excited state.^{17a} Thus, the fact that the luminescence properties of the 5-substituted **Ru-cy** complex are very close to those of $[Ru(bpy)_3]^{2+}$ suggests that the cyclam unit appended at the 5 position of *bpy* exerts a negligible steric effect on the metal centre, and also has on its own no significant electronic quenching effect.

$[Ru(bpy)(CN)_4]^{2-}$. Some spectroscopic properties of **Ru-CN**, as observed in acetonitrile, are listed in Table 1.^{9–11} The lowest-energy ¹MLCT absorption band maximum is at 535 nm ($\epsilon = 4800 \text{ M}^{-1} \text{ cm}^{-1}$) while a ¹LC band at 295 nm ($\epsilon = 34500 \text{ M}^{-1} \text{ cm}^{-1}$) shows an intensity related to the presence of only one *bpy* ligand. The luminescence properties ($\lambda_{\text{max}} = 790 \text{ nm}$; $\Phi \leq 1 \times 10^{-4}$; $\tau = 6 \text{ ns}$) are as expected for ³MLCT levels of this weak luminophore.^{9–11} Detailed studies of solvent effects on the spectroscopic properties of CN-containing complexes of the Ru-polypyridine type have shown that the absorption and luminescence features are closely correlated to the Gutmann's acceptor number, A.N., of the solvent.¹⁰ In solvents with high A.N., the solvent–cyanide interaction draws electron density

Table 1 Spectroscopic and photophysical parameters^a

	Absorption		Luminescence		
	$\lambda^{\text{abs}}/\text{nm}$ ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$)		$\lambda^{\text{em}}/\text{nm}$	Φ^c	τ/ns
Ru-cy	288 (80400)	450 (13000)	610	0.026	200
Ru-CN	295 (34500)	535 (4800)	790	≤ 0.0001	6
Ru-CN/M^d		480 (7000)	680		65
Ru-CN/M^e		≈ 410	640	0.022	330
[Ru(bpy)₃]²⁺f		452 (13000)	615	0.016	170

^a Room temperature, in air-equilibrated acetonitrile. ^b Band maxima for uncorrected spectra. ^c Luminescence efficiency obtained from corrected spectra. ^d Within the associate with M; M = cyclamH₂²⁺ macrocycle attached to **Ru-cy**, this work. ^e Within the associate with M'; M' = [32]-ane-N₈H₈⁸⁺ macrocycle, ref. 11. ^f Ref. 17.

from the metal centre, which results in destabilization of any MLCT transition. Acetonitrile can be considered an intermediate case regarding the solvent accepting properties, its A.N. being 19.3.¹⁹ We will see below that the sensitivity of **Ru-CN** to its environment (be it interactions with solvent, or hydrogen-bonding with another molecule) can provide a diagnostic basis for the assessment of its association with the cyclam unit of **Ru-cy**.

Absorption and luminescence properties of mixtures of **Ru-cy** and **Ru-CN**

A. Absorption spectra. Fig. 1 (top) shows absorption profiles obtained for mixtures of **Ru-cy** and **Ru-CN**, with molar fractions *mf* of **Ru-cy**, ($mf = [\text{Ru-cy}]/([\text{Ru-cy}] + [\text{Ru-CN}])$), varied

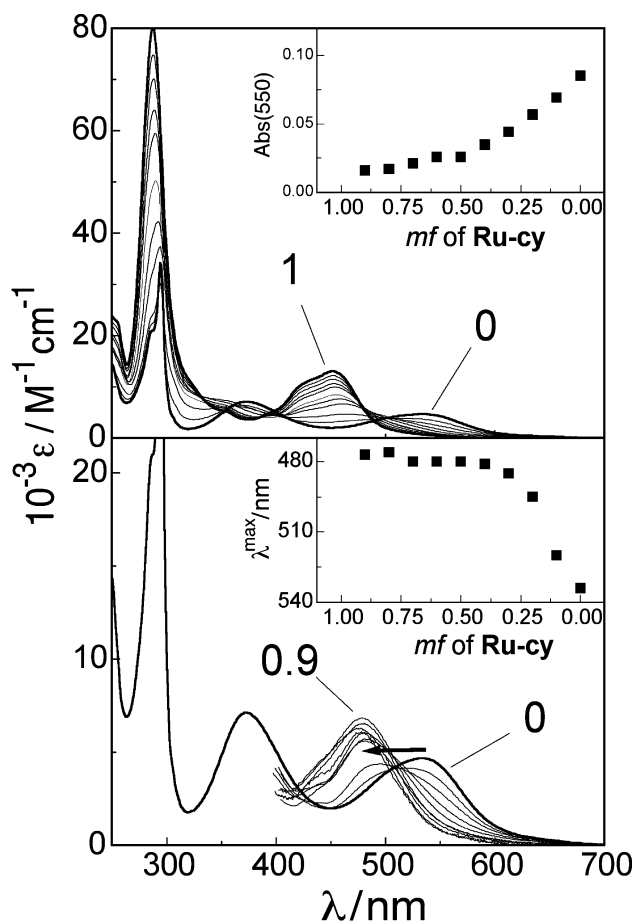


Fig. 1 Top: absorption spectra of 2×10^{-5} M acetonitrile solutions of **Ru-cy/Ru-CN** mixtures for *mf* of **Ru-cy** running from 0 to 1 (see text); the inset shows the absorbance changes at 550 nm. Bottom: changes of the absorption profile for the **Ru-CN** component for *mf* = 0 to 0.9; the inset shows the changes in the position of lowest-energy absorption band maximum.

between 1 and 0 and for a total constant concentration of 2×10^{-5} M for the two complexes. In the absence of any interaction between **Ru-cy** and **Ru-CN** the absorption spectra for these mixtures should be just the sum of the spectra of the mononuclear components, with isoabsorbing points apparent in the spectra. The results shown in Fig. 1 (top) indicate that this is not the case, because of the environmental sensitivity of the **Ru-CN** species; *i.e.* the absorption spectrum of the **Ru-CN** unit will vary depending on whether or not it is involved in hydrogen-bonding interactions with the [cyclamH₂]²⁺ unit of **Ru-cy**.^{11,12} In contrast, the absorption spectrum of the [Ru(bpy)₃]²⁺ chromophore of **Ru-cy** is scarcely affected by environmental changes.^{17a} On this basis, the changes of absorption intensity registered at 550 nm, against *mf*, are expected to be related to the amount of free **Ru-CN** in the various mixtures; the inset of Fig. 1 (top) shows absorbance values, as scaled to a concentration of 2×10^{-5} M of **Ru-CN**. From this inset, one sees that free **Ru-CN** approaches a residual plateau in concentration for $mf \leq 0.5$. In order to further address the point, for the various **Ru-cy-Ru-CN** mixtures, we have subtracted the (invariant) spectral component pertaining to **Ru-cy** from the cumulative absorption profiles. Results are displayed in Fig. 1 (bottom), where the derived spectra, attributable to the **Ru-CN** component, have been further scaled to a concentration of 2×10^{-5} M. We can see how the ¹MLCT absorption maximum of free **Ru-CN** at 535 nm decays and is replaced by a new ¹MLCT maximum at 480 nm corresponding to the 'bound' form of **Ru-CN** (that is, hydrogen-bonded to **Ru-cy**). The inset of Fig. 1 (bottom) shows the changes in the position of the lowest energy ¹MLCT band maximum for **Ru-CN** against *mf*, from which it appears that **Ru-CN** is *predominantly*²⁰ associated with **Ru-cy** for $mf \geq 0.4$.

For comparison, the ¹MLCT absorption maximum of **Ru-CN** undergoes a much more substantial shift, from 535 nm to *ca.* 410 nm, when a 1 : 1 adduct is formed with ([32]-ane-N₈H₈)⁸⁺ in MeCN, with formation of 4 hydrogen bonds.¹¹ The fact that the shift observed for binding of **Ru-CN** to **Ru-cy** is much less (Table 1 and Fig. 1) suggests that there are fewer hydrogen-bonding interactions with the cyanide groups in our system; this could be consistent with formation of a 1 : 1 **Ru-CN:Ru-cy** adduct in which two of the cyanide ligands interact with the two protonated amine sites of a single [cyclamH₂]²⁺ unit and the other two remain free to interact with the solvent (Scheme 1). Of course, it might well be that a 1 : 2 **Ru-cy:Ru-CN:Ru-cy** adduct does form in our case (see luminescence results below), with the absorption properties of the bound **Ru-CN** chromophore exhibiting different characteristics with respect to the case of the adduct with the ([32]-ane-N₈H₈)⁸⁺ because of a different role of electrostatic and geometric factors.

B. Luminescence properties. Fig. 2 shows luminescence spectra recorded for acetonitrile mixtures of **Ru-cy** and **Ru-CN**, for *mf* values ranging from 1 to 0 with a total constant concentration of 2×10^{-5} M; excitation was at 490 nm. From these results, one sees that (i) on passing from *mf* 1 to 0.5, the

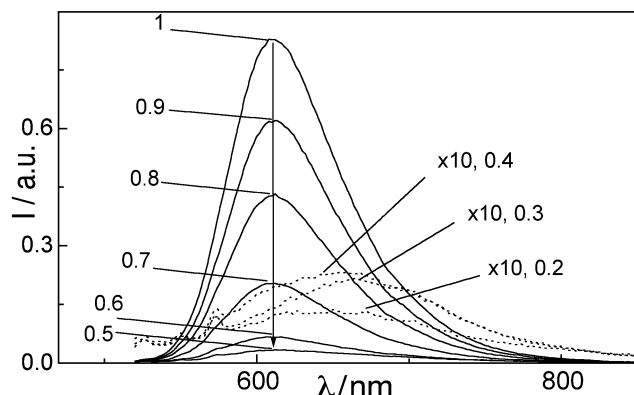


Fig. 2 Luminescence spectra of 2×10^{-5} M **Ru-cy/Ru-CN** acetonitrile mixtures at the indicated *mf* of **Ru-cy**; excitation was at 490 nm.

luminescence spectrum emission maximum at 610 nm exhibits a steep decrease in intensity, and (ii) for $mf \leq ca. 0.4$ the band moves to lower energies, with a maximum at *ca.* 680 nm. We ascribe the strong emission at 610 nm as being of **Ru-cy** origin (see Table 1), and the weaker emission at 680 nm as being of **Ru-CN** origin, but from the *bound* species since free **Ru-CN** emits at 790 nm and only very weakly (Table 1). As with the absorption spectra (above), the blue-shift we observe in the emission spectrum of **Ru-CN** when it is bound (from 790 to 680 nm) is less than that observed when all four cyanide groups interact with $([32]-ane-N_8H_8)^{8+}$ (from 790 to 640 nm, Table 1).¹¹

In order to draw conclusions about the association conditions for mixtures of **Ru-CN** and **Ru-cy** (*i.e.* whether it is 1 : 1 or 1 : 2, see below) we have plotted the changes in luminescence intensity observed at 610 nm for various mixtures, see Fig. 3

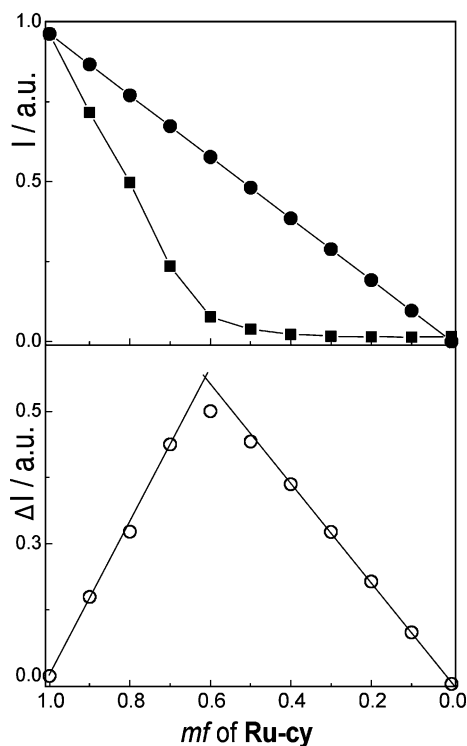


Fig. 3 Top: luminescence intensity of 2×10^{-5} M **Ru-cy/Ru-CN** acetonitrile mixtures, as recorded at 610 nm (solid squares) and as compared to expected values on the basis solely of the *mf* of **Ru-cy** (solid circles); excitation was at 490 nm. Bottom: degree of quenching of **Ru-cy** (*i.e.* ΔI is the difference between the two sets of luminescence intensity data points of the above graph) vs. *mf* of **Ru-cy**.

(top). In the same plot are reported the luminescence intensity points expected solely on the basis of the *mf* of **Ru-cy** (and actually found upon addition of triethylamine to the solution to

disrupt the **Ru-CN:Ru-cy** association). The difference between the corresponding points of the two sets of data (Fig. 3, bottom) represents the extent of reduction in **Ru-cy** luminescence intensity ascribed to a quenching process involving the bound **Ru-CN** component. Because of the dilution conditions employed, diffusional quenching cannot be involved and the quenching process has to take place within a **Ru-cy:Ru-CN** hydrogen-bonded associate.²¹

Time resolved analysis of the luminescence decays provided hints about the kinetics of the quenching step. We separately analysed two wavelength regions, $\lambda = 610$ and >650 nm. In the former case, the luminescence of **Ru-cy** predominates, particularly for $mf > 0.5$, see Fig. 2. Global analysis of the decays recorded at this wavelength nm, for the interval $mf = 1$ to 0.5 and according to a dual exponential law (eqn. 4),

$$I(t) = b_1 \exp(-t/\tau_1) + b_2 \exp(-t/\tau_2) \quad (4)$$

yielded $\tau_1 = 200$ and $\tau_2 = 23$ ns, with the values of the pre-exponential factors b_1 and b_2 varying as shown in Fig. 4. These

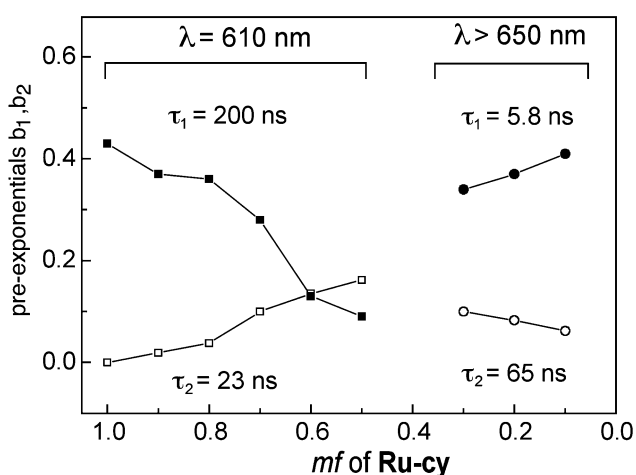


Fig. 4 Analysis of the luminescence decays at the indicated wavelength regions and for varied molar fractions of **Ru-cy**; a dual exponential law was employed in the global analysis, $I(t) = b_1 \exp(-t/\tau_1) + b_2 \exp(-t/\tau_2)$, see text.

results are consistent with the presence of unbound ($\tau_1 = 200$ ns, see Table 1) and associated ($\tau_2 = 23$ ns) **Ru-cy**, respectively, in agreement also with the trends for b_1 and b_2 (Fig. 4; the amount of free **Ru-cy** decreases, and of bound **Ru-cy** increases, as the proportion of **Ru-CN** in the mixture increases). From $k_q = 1/\tau_2 - 1/\tau_1$, the rate of the quenching step taking place within the associate is evaluated to be 3.8×10^7 s⁻¹, amounting to a quenching efficiency of *ca.* 0.88.

Luminescence from **Ru-CN** is most conveniently detected on the red side of the emission spectrum and for $mf < 0.4$ (Fig. 2). Fig. 4 shows results of a global analysis of the emission decays recorded at $\lambda > 650$ nm according to eqn. 4. The obtained lifetimes were $\tau_1 = 5.8$ ns and $\tau_2 = 65$ ns. Comparison with data of Table 1 and from literature,⁹⁻¹¹ and inspection of the trend for b_1 and b_2 (Fig. 4), allows identification of these two luminescence components as corresponding to free and bound **Ru-CN**, respectively, with the amounts of each varying in the expected manner as the proportion of added **Ru-CN** increases.

As mentioned above, for the cases where nearly complete quenching of the **Ru-cy** luminescence takes place, the weak **Ru-CN**-based luminescence can be detected (Fig. 2). From the concerned luminescence band maxima (*i.e.* 610 and 680 nm, for the **Ru-cy** and **Ru-CN** components respectively within the associate) the energy gap between the luminescent levels of the associated partners is calculated as *ca.* 1700 cm⁻¹.

C. Quenching mechanism. Regarding the type of mechanism involved, one should consider (i) $^*\text{Ru-cy} \leftarrow \text{Ru-CN}$ photo-induced electron transfer, (ii) $^*\text{Ru-cy} \rightarrow \text{Ru-CN}$ energy transfer by the dual electron exchange (Dexter),²² and (iii) $^*\text{Ru-cy} \rightarrow \text{Ru-CN}$ energy transfer by the dipole–dipole (Förster) mechanism.²³ From the luminescence properties of **Ru-cy** and bound **Ru-CN** (Table 1), mechanisms (ii) and (iii) are allowed by *ca.* 0.2 eV. Also photoinduced electron transfer is thermodynamically allowed, being exothermic by *ca.* 0.5 eV (the energy stored by $^*\text{Ru-cy}$ is 2.1 eV, oxidation at **Ru-CN** is at +0.27 V^{10,11} and reduction of **Ru-cy** is at −1.33 V,¹⁸ (vs. SCE in acetonitrile solvent). However, for the present case, the electronic interaction between the partners must be extremely weak, at odds with what happens for cases where electron transfer is allowed because of mediation of intervening bridging ligands, mostly of the unsaturated type.¹ The same type of argument holds for dual electron exchange (*i.e.* through-bond) energy transfer. Regarding the dipole–dipole mechanism, evaluation of the spectral overlap J_F between the luminescence profile of **Ru-cy** and the absorption profile of bound **Ru-CN** (see Fig. 1, bottom), allows estimates of the critical transfer radius, R_0 (Å), and the rate constant at a separation d_{cc} (not known in our case), between the partners, eqn. 5–7.

$$J_F = \frac{\int F(\bar{\nu})\varepsilon(\bar{\nu})/(\bar{\nu})^4 d\bar{\nu}}{\int F(\bar{\nu})} \quad (5)$$

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

$$R_0 = 9.79 \times 10^{-3} (K^2 n^{-4} \Phi J_F)^{1/6} \quad (7)$$

In the above equations, $F(\bar{\nu})$ and $\varepsilon(\bar{\nu})$ are the luminescence and absorption profiles on an energy scale (cm^{-1}) of **Ru-cy** and **Ru-CN**, respectively, K^2 is a geometric factor (taken as 2/3),²³ Φ and τ are the luminescence quantum yield and lifetime of **Ru-cy** (the excitation energy donor), respectively, n is the refractive index of the solvent, and R_0 is the critical transfer radius. The results were: $J_F = 2.95 \times 10^{-15} \text{ cm}^3 \text{ M}^{-1}$ and $R_0 = 15.5 \text{ \AA}$. From the measured rate constant, $k_q = 3.8 \times 10^7 \text{ s}^{-1}$, we calculate that $d_{cc} = 11.5 \text{ \AA}$. These results support a view in which dipole–dipole energy transfer is responsible for the observed photo-induced intramolecular quenching, in agreement with our conclusions for quenching of an excited $[\text{Ru}(\text{bpy})_3]^{2+}$ unit by a $[\text{Ru}(\text{bpy})(\text{CN})_4]^{2-}$ unit in a covalently-bonded dyad.¹⁶ In order to gain definite evidence for this step, one should observe the time resolved sensitisation of the acceptor luminescence by the excited state of the donor. This however could not be accomplished in the present case, given that the absorption spectra of the components overlap closely and selective excitation of the donor is not possible.

D. Stoichiometry of the associate. Inspection of the Job plot in Fig. 3 (bottom) reveals that quenching of the **Ru-cy** luminescence in the **Ru-cy–Ru-CN** mixtures is maximised for $mf = \text{ca. } 0.62$. For a 1 : 1 **Ru-CN:Ru-cy** adduct we would expect the maximum to be at $mf = 0.5$; for a 1 : 2 **Ru-cy:Ru-CN:Ru-cy** adduct the maximum would be at 0.66. Given that in the 1 : 1 and 1 : 2 adducts the luminescence of excited **Ru-cy** is quenched to a comparable extent [we can ignore the contribution from the doubly-excited triad (**Ru-cy**)*:**Ru-CN**:(**Ru-cy**)* as statistically insignificant], this Job plot therefore indicates that a 1 : 2 associate is predominant and responsible for the majority of the quenching of the **Ru-cy** luminescence (*cf.* Scheme 1), even if some amount of a 1 : 1 associate is present and contributes to it.

According to an approach developed earlier,⁴ and based on the fact that nearly quantitative quenching (88%) takes place

within the associates, it is possible to use the changes of luminescence intensity of the donor, as observed at 610 nm (Fig. 3), to obtain estimates of the concentration of the involved species. For instance, at $mf = 0.7$, one finds $[\text{Ru-cy}] = 4.91 \times 10^{-6} \text{ M}$ for the unbound luminophore. By considering a 1 : 2 stoichiometry, this results in $[\text{Ru-cy:Ru-CN:Ru-cy}] = 9.09 \times 10^{-6}$ and $[\text{Ru-CN}] = 1.5 \times 10^{-6} \text{ M}$, yielding a cumulative association constant of $K_{\text{ass}} = 2.6 \times 10^{11} \text{ M}^{-2}$. Notice that the unbound **Ru-cy** and **Ru-CN** partners remain 35 and 25% unbound, respectively, at $mf = 0.7$. The fact that also at other mf values the concentration of surviving unbound species is not negligible, might explain why we were unable to unravel the absorption contributions from the species involved, see Fig. 1.

Conclusions

The complex units **Ru-cy** and **Ru-CN** associate in MeCN by a hydrogen-bonding interaction involving the lone pairs of the cyanide ligands of **Ru-CN** and the protonated amine residues of the pendant cyclam macrocycle in **Ru-cy**. There is good evidence for formation of a 2 : 1 associate **Ru-cy:Ru-CN:Ru-cy** with an overall formation constant of $K_{\text{ass}} = 2.6 \times 10^{11} \text{ M}^{-2}$. This is not strong enough, at the high dilutions necessary for UV/Vis and luminescence spectroscopy, to afford complete formation of the adduct and there is accordingly some 1 : 1 **Ru-cy:Ru-CN** adduct as well as free **Ru-cy** and **Ru-CN**. The association results in clear changes in the absorption and emission properties of the **Ru-CN** unit, and also results in quenching of the characteristic ³MLCT luminescence of **Ru-cy**, most likely by Förster energy transfer to the **Ru-CN** unit with a quenching rate constant of $k_q = 3.8 \times 10^7 \text{ s}^{-1}$ (corresponding to 88% quenching of the **Ru-cy** luminescence).

Experimental

General details

The compounds 5-bromomethyl-2,2'-bipyridine,²⁴ $[\text{Ru}(\text{bpy})_2\text{Cl}_2] \cdot 2\text{H}_2\text{O}$ ²⁵ and $\text{K}_2[\text{Ru}(\text{bpy})(\text{CN})_4]$ ⁸ were prepared according to the literature methods. 1,4,8,11-Tetraazacyclotetradecane (cyclam) was purchased from Aldrich and used as received. The following instruments were used for routine characterisation: FAB mass spectra, a VG-Autospec instrument; electrospray mass spectra, a VG-Quattro instrument; NMR spectra, a JEOL-GX270 spectrometer.

Syntheses

$[\text{Bu}_4\text{N}]_2[\text{Ru}(\text{bpy})(\text{CN})_4]$. This is a variant on a published method.¹⁰ To a solution of $\text{K}_2[\text{Ru}(\text{bpy})(\text{CN})_4]$ (0.100 g) in the minimum amount of distilled water was added dropwise 1 M HCl until a fine precipitate of $\text{H}_2[\text{Ru}(\text{bpy})(\text{CN})_4]$ appeared. After cooling to ensure that precipitation was complete the suspension was filtered through a cotton wool plug in a Pasteur pipette. The solid was then dissolved in aqueous Bu_4NOH and the solution was evaporated to dryness. The residue was redissolved in the minimum amount of MeOH and purified by passing down a column of Sephadex-LH20, eluting with MeOH, until a ¹H NMR spectrum showed that there was no excess Bu_4NOH remaining. The red solution was evaporated to dryness yielding $[\text{Bu}_4\text{N}]_2[\text{Ru}(\text{bpy})(\text{CN})_4]$ as a hygroscopic purple solid which was stored under N_2 . ¹H NMR [270 MHz, CD_3CN]: δ 0.98 [24H, t; ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$)₄N], 1.50 [16H, m; ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$)₄N], 1.70 [16H, m; ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$)₄N], 3.45 [16H, m; ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$)₄N], 7.15 (2H, ddd; bpy H^{5,5}), 7.60, (2H, ddd; bpy H^{4,4}), 7.87 (2H, dd; bpy H^{3,3}) and 9.61 (2H, dd; bpy H^{6,6}).

1-(2,2'-Bipyridin-5-yl-methyl)-1,4,8,11-tetraazacyclotetradecane (bpy-cyclam). This was prepared according to the published

method,¹⁵ by reaction of 5-bromomethyl-2,2'-bipyridine²⁴ with excess cyclam, but using ethanol as solvent rather than chlorobenzene. After the reaction the excess free cyclam was recovered from the reaction mixture by partitioning the reaction mixture between water and CH₂Cl₂; removal of the solvent from the organic layer afforded pure bpy-cyclam whose spectroscopic properties were consistent with the original report.¹⁵

[(bpy)₂Ru(bpy-cyclamH₂)]PF₆·4. A mixture of bpy-cyclam (0.395 g, 1.07 mmol) and Ru(bipy)₂Cl₂·2H₂O²³ (0.465 g, 0.89 mmol) in ethanol (20 cm³) was heated to reflux with stirring under N₂ for 4 hours. After cooling the solvent was removed *in vacuo* and the red solid was purified by chromatography on a silica column eluting with 8 : 2 : 1 acetonitrile : water : saturated aqueous KNO₃. The major red band was collected and the solvent removed *in vacuo*. The solid was dissolved in the minimum amount of MeCN and an excess of aqueous NH₄PF₆ was added to precipitate the complex. The resultant orange suspension was extracted with CH₂Cl₂ and the organic layer dried *in vacuo* yielding [(bpy)₂Ru(bpy-cyclamH₂)]PF₆·4 as a red solid (0.752 g, 62%). ES-MS, *m/z* = 1072.66 {M - H - 2PF₆}⁺, 390.24 {M - 2H - 4PF₆}²⁺. FAB-MS, *m/z* = 1219 {M - PF₆}⁺, 1074 {M - 2PF₆}⁺, 928 {M - 3PF₆}⁺, 781 {M - 4PF₆}⁺, 728 {M - 3PF₆ - cyclam}⁺. ¹H NMR [270 MHz, CD₃CN]: δ 1.62 (2H, m; cyclam -CH₂-), 1.84 (2H, m; cyclam), 2.30–2.45 (4H, m; cyclam), 2.76–2.93 (4H, m; cyclam), 3.00 (2H, m; cyclam), 3.06–3.31 (6H, m; cyclam), 3.74, (2H, s; bpy-CH₂-), 7.34 (1H, m; bpy), 7.38–7.50 (5H, m; bpy), 7.67–7.80 (5H, m; bpy), 7.89 (1H, dd; bpy), 7.99–8.15 (5H, m; bpy) and 8.44–8.60 (6H, m; bpy). Found: C, 36.1; H, 3.9; N, 10.1. (Calc. for C₄₁H₅₂N₁₀P₄F₂₄Ru: C, 36.1; H, 3.7; N, 10.3%).

Spectroscopic measurements

Absorption spectra of dilute solutions (2 × 10⁻⁵ M) of the investigated complexes were measured in acetonitrile at room temperature with Perkin-Elmer Lambda 5, Lambda 9 or Lambda 19 UV/Vis spectrophotometers. Acetonitrile was dried by storing over activated molecular sieves for several days before use. Luminescence spectra were obtained from air-equilibrated solutions whose absorbance values were <0.2 at the employed excitation wavelength using a Perkin Elmer LS50-B or Spex Fluorolog II spectrofluorimeter. While uncorrected band maxima are used throughout the text, for the determination of the luminescence quantum yields, corrected spectra were employed. The correction procedure takes care of the wavelength dependent phototube response and from the area of the corrected luminescence spectra on an energy scale (cm⁻¹), we obtained luminescence quantum yields for the samples with reference to [Ru(bpy)₃]²⁺ (Φ = 0.028 in air-equilibrated water) as a reference standard.^{17a} Band maxima and relative luminescence intensities were affected by an uncertainty of 2 nm and 20%, respectively. Luminescence lifetimes were obtained using an IBH single-photon counting equipment equipped with deuterium-filled (with useful λ_{exc} < 350 nm) or nitrogen-filled (λ_{exc} = 358 or 337 nm) thyratron gated lamp, and by monitoring the decay at the wavelengths detailed in the text. The uncertainty in the lifetime values is within 8%.

Acknowledgements

We thank the EPSRC (UK), the TMR contract no. CT98-0226 (A. F. M.), the EU-COST network D11/0004/98, and Agenzia 2000, CNRC00B91D/004 (B. V.), for financial support.

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- 20 The fact that the 480 nm transition appears to be dominant at $mf \geq 0.4$ may in part be a consequence of its larger intensity with respect to the 535 nm transition, Table 1. Thus, some caution must be exerted while drawing definite conclusions from the spectral findings illustrated in Fig. 1. Furthermore, it is worth pointing out that at any wavelength the absorption spectrum is the sum of three components (**Ru-cy**, free **Ru-CN** and bound **Ru-CN**, the latter two in an unknown ratio and with different spectral properties) which made it difficult to perform standard spectrophotometric titrations to determine the stoichiometry and association constants for formation of the adducts.
- 21 The rate constant for diffusional quenching is estimated as $k_q = k^{\text{diff}}[\text{quencher}]$, where the solvent diffusional rate constant k^{diff} in acetonitrile is $1.9 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ (see S. L. Murov, I. Carmichael and G. L. Hug, *Handbook of Photochemistry*, Marcel Dekker, New York, 1993, p. 207). For the employed range of concentration of quencher $[\text{Ru-CN}] \leq 2 \times 10^5 \text{ M}^{-1}$, $k_q \leq 4 \times 10^5 \text{ s}^{-1}$ is practically never competitive against intrinsic deactivation of the donor, $k = 1/\tau = 5 \times 10^6 \text{ s}^{-1}$.
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