

Photoinduced energy transfer within hydrogen-bonded multi-component assemblies based on a ruthenium–polypyridyl donor and an osmium–polypyridyl or ferrocenyl acceptor

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Formation of multipartite associates driven by the complementary H-bonding abilities of cytosine and guanine appended to $[\text{Ru}(\text{bipy})_3]^{2+}$, $[\text{Os}(\text{bipy})_3]^{2+}$, and ferrocenyl chromophores is probed by exploiting the luminescence properties of the various building blocks and the energy transfer processes occurring between them.

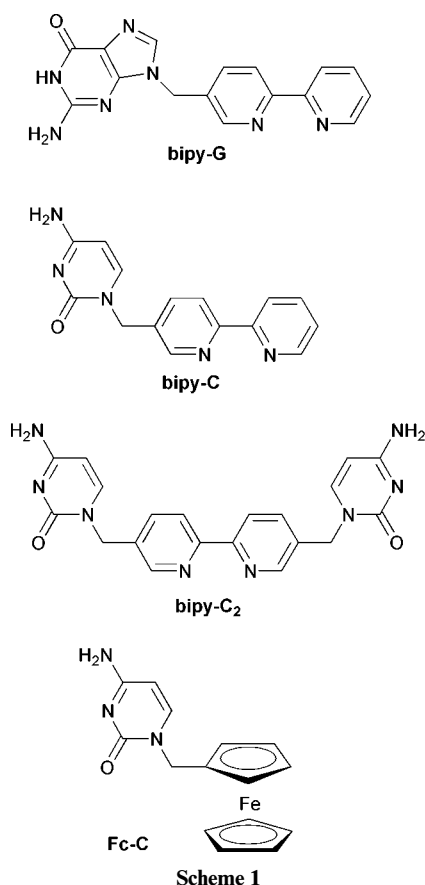
Within the field of polypyridine transition metal complexes, we have been interested in the study of photoinduced energy transfer occurring in multichromophoric systems based on luminescent Ru(II)-, Os(II)- and Re(I) complexes.^{1–5} The design and building up of such systems is aimed at realising precise structural and energy patterns. For instance, compounds incorporating both Ru- and Os-based components may allow the achievement of long-distance excitation energy transport.^{6,7} This process is driven by the different energy content of the Ru- and Os-based ³MLCT luminescent levels (for Ru → Os transfer, $-\Delta G$ is in the range 0.2 to 0.4 eV) and is mediated by the electronic and structural properties of the interposed spacer.⁷

There are numerous examples of multicomponent systems incorporating polypyridine transition metal complexes whose components are assembled *via* covalent linkages. Cases include complexes featuring interesting geometries, like wires (mostly dinuclear cases, which are particularly apt for probing switching conditions),^{6,7} dendrimers (for artificial mimicking of light energy harvesting processes),⁸ and so forth. The use of covalent linkages between components generally guarantees a high degree of control of the topological properties, but may prove difficult because of the multistep synthetic procedures frequently needed.

We have been interested in an alternative approach for the construction of multi-component systems, based on $[\text{Ru}(\text{bipy})_3]^{2+}$ and $[\text{Os}(\text{bipy})_3]^{2+}$ building blocks which bear pendant nucleobase groups appended to one of the coordinated bpy ligands (see Scheme 1).^{3,9} Other groups have also used this approach to link together porphyrin-based chromophore/quencher assemblies by hydrogen-bonding between peripheral substituents.¹⁰ In an earlier report, we described the syntheses of the ligands bipy-C and bipy-G, and showed how a mixture of $[\text{Ru}(\text{Bu}_2\text{bipy})_2(\text{bipy-C})][\text{PF}_6]_2$ and $[\text{Os}(\text{Bu}_2\text{bipy})_2(\text{bipy-G})][\text{PF}_6]_2$ associated strongly in CH_2Cl_2 solution such that Ru → Os photoinduced energy transfer occurred across the hydrogen-bonded bridge linking the components, with a rate constant $k_{\text{en}} = 9.3 \times 10^7 \text{ s}^{-1}$.³ We now describe our investigations into the formation of higher nuclearity hydrogen-bonded assemblies, and also the use of an alternative energy acceptor (the ferrocenyl unit).

Results and discussion

Of the compounds used in this study, $[\text{Ru}(\text{Bu}_2\text{bipy})_2(\text{bipy-G})][\text{PF}_6]_2$ (hereafter **Ru-G**) was prepared from $[\text{Ru}(\text{Bu}_2\text{bipy})_2\text{Cl}_2]$ and bipy-G in the usual way.^{3,9} The new ligand bipy-C was prepared by alkylation of 5,5'-bis(bromomethyl)-2,2'-bipyridine with two equivalents of cytosine, using the same general procedure as for bipy-C.³ Reaction of this with $[\text{Os}(\text{bipy})_2\text{Cl}_2]$ [bipy' = 4,4'-bis(5-nonyl)-2,2'-bipyridine]



afforded $[\text{Os}(\text{bipy}')_2(\text{bipy}-\text{C}_2)][\text{PF}_6]_2$ (hereafter **C-Os-C**), which contains two pendant cytosine units; the nonyl substituents on the ancillary bipy' ligands are necessary to maintain solubility in CH_2Cl_2 . 1-Ferrocenylmethylcytosine (**Fc-C**) was available from earlier work.¹¹

The complexes **Ru-G** and **C-Os-C** are expected to self-assemble because of complementary three-point H-bonding interactions yielding 1 : 1 and 2 : 1 associates (see eqn. 1 and 2 and Scheme 2).

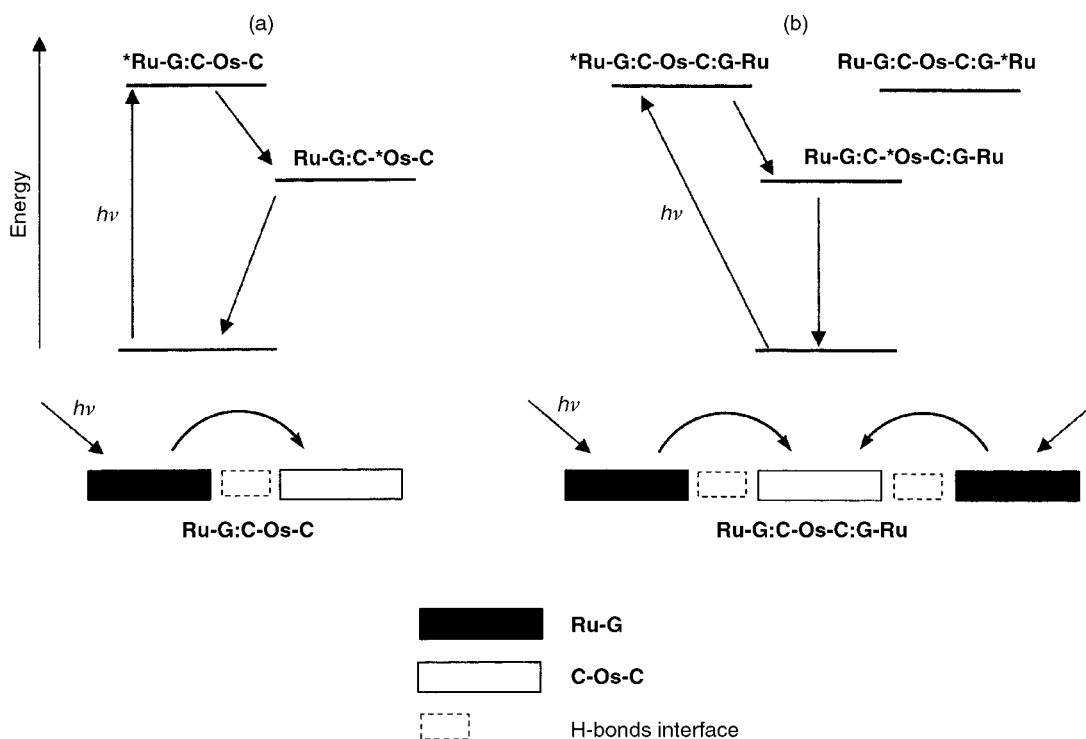


In the case of the 1 : 1 associate, **Ru-G : C-Os-C**, the two photoactive termini can interact thanks to the structural role played by the **G : C** triple bond, [see Scheme 2(a)]. This interaction can provide a sizeable association constant; a value of $K_{\text{ass}} \geq 5 \times 10^3 \text{ M}^{-1}$ was found in CH_2Cl_2 for the similar **Ru-C : G-Os** associate.³ Though 1 : 1 association is an interesting step in itself, the new complex **C-Os-C** was designed to provide more complex assemblies, being potentially capable of simultaneous association with two **Ru-G** units (eqn. 2). Within the desired three-component **Ru-G : C-Os-C : G-Ru** associate, provided the $\text{Ru} \rightarrow \text{Os}$ energy transfer step is effective,^{12–15} light absorption by both of the peripheral Ru-based components would contribute to the emission from the central Os-based component [Scheme 2(b)]; i.e. an antenna effect by which the excitation energy from the two peripheral Ru units is conveyed to a single central point.

Table 1 collects spectroscopic and photophysical properties for **C-Os-C** and **Ru-G**; the absorption spectral properties of **Fc-C** are also reported. **Fc-C** is non-luminescent at wavelengths shorter than 900 nm, and the ferrocene unit is reported to act both as an energy acceptor (its lowest-lying ^3MC excited level is estimated at *ca.* 1.7 eV) and an electron donor (the reduction potential for Fc^+/Fc is +0.39 V *vs.* SCE in MeCN).¹⁶ Thus, we use the couple **Ru-G/Fc-C** for comparison purposes with respect to the behaviour exhibited by the couple **Ru-G/C-Os-C**.

Fig. 1 and 2 summarise the approach we have employed, which is based on the use of luminescence data obtained from CH_2Cl_2 solutions containing mixtures of **Ru-G** and **C-Os-C**, and of **Ru-G** and **Fc-C**, respectively. For all the cases in Fig. 1 and 2 the total concentration of the complexes was $4 \times 10^{-5} \text{ M}$, with variable **Ru-G** to **C-Os-C** and **Ru-G** to **Fc-C** ratios; λ_{exc} was 450 nm, corresponding either to an isoabsorptive point for all the solutions (Fig. 1), or to predominant absorption by **Ru-G** (Fig. 2).

For the mixture of **Ru-G** and **C-Os-C**, the Ru-based luminescence intensity of **Ru-G** ($\lambda_{\text{max}} = 626 \text{ nm}$) is stronger by one order of magnitude than that of **C-Os-C** ($\lambda_{\text{max}} = 750 \text{ nm}$, Table 1), with the latter being hidden by the tail of the former. This is typical behaviour for $[\text{Ru}(\text{bipy})_3]^{2+}$ and $[\text{Os}(\text{bipy})_3]^{2+}$ chromophores and, given the predominance of unassociated over associated species, prevents observation of any sensitisation of the Os-based luminescence; our approach was therefore based on the observation of the quenching of the Ru-based luminescence. At the concentrations used, any quenching of the emission of **Ru-G** can only occur within the



Scheme 2 Possible energy transfer steps in the investigated **Ru-G/C-Os-C** couple.

Table 1 Spectroscopic and photophysical data^a

	Absorption			Emission			
	$\lambda_{\text{max}}/\text{nm}$	$(10^{-3} \text{ } \epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1})$		$\lambda_{\text{max}}/\text{nm}$	$10^2 \Phi$	τ/ns	energy ^b /eV
C-Os-C	291(85.6)	446(13.7)	590(4.2)	750	0.3	33	1.75
Ru-G	288(76.1)	459(12.3)		626	4	450	2.1
Fc-C	261(12.6)	440(0.1)					

^a Room temperature, air-equilibrated CH_2Cl_2 solvent. ^b Estimated from the onset of the emission spectra.

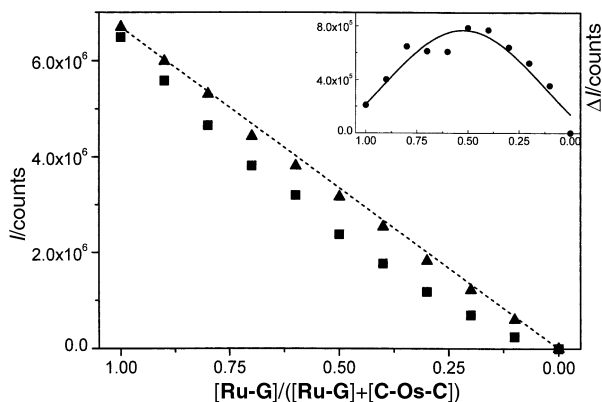


Fig. 1 Luminescence intensities, as observed at 626 nm, for the various **Ru-G/C-Os-C** mixtures (total concentration was 4×10^{-5} M) in neat CH_2Cl_2 (I_{Ru} , ■), and after EtOH addition ($I_{\text{Ru}}^{\text{EtOH}}$, ▲); the dashed line indicates the luminescence intensities expected based solely on the **Ru-G** molar fractions. The inset shows ΔI_{Ru} (●), see text; the full line is the best fit according to a Gaussian distribution.

hydrogen-bonded associates, with diffusional quenching being negligible.^{3,9} For the various proportions of the **Ru-G/C-Os-C** mixture (Fig. 1), the Ru-based luminescence intensity, I_{Ru} , does not lie on the straight line corresponding to the molar fraction of **Ru-G**; instead a bowed, downward trend is registered. A parallel observation is that the time-resolved luminescence, as detected at 626 nm, exhibits a dual behaviour [Fig. 3(a)]; for example, with a **Ru-G** molar fraction of 0.7, τ_1 and τ_2 were 12.5 and 422 ns, respectively, with relative amplitudes of 1.3 and 98.7%. Addition of a few drops of EtOH to the solution in each case caused an increase of the Ru-based luminescence (Fig. 1), and the luminescence intensity ($I_{\text{Ru}}^{\text{EtOH}}$) became close to what was expected based on the molar ratios for **Ru-G**. In agreement with this, after EtOH addition, a single exponential decay is detected [Fig. 3(b)] with $\tau = 390$ ns ($\lambda_{\text{em}} = 626$ nm).

The rationale for these observations is based on formation, in neat CH_2Cl_2 , of an associate between **Ru-G** and **C-Os-C** (eqn. 1 and 2). Within the associate, the Ru-based luminescence is nearly completely quenched, as indicated by the fact that the lifetime τ_1 is only 12.5 ns, as opposed to 450 ns for free **Ru-G**. On this basis the measured Ru → Os inter-component energy transfer rate constant is $k_{\text{en}} = 8.0 \times 10^7 \text{ s}^{-1}$. Addition of EtOH breaks the associate, causing virtually complete restoration of the Ru-based luminescence properties (intensity and lifetime) of free **Ru-G**.

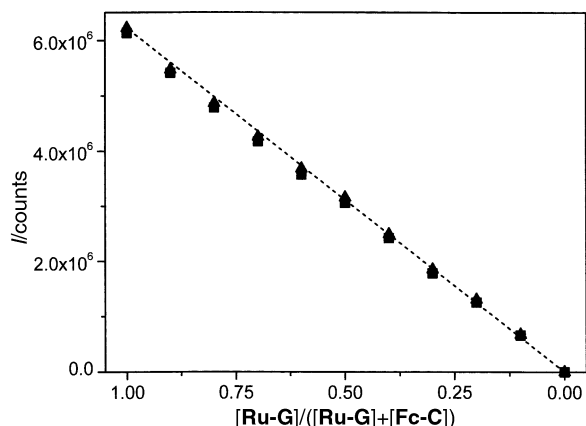


Fig. 2 Luminescence intensities, observed at 626 nm, for the various **Ru-G/Fc-C** mixtures (total concentration was 4×10^{-5} M) in neat CH_2Cl_2 (I_{Ru} , ■), and after EtOH addition ($I_{\text{Ru}}^{\text{EtOH}}$, ▲); the dashed line indicates the luminescence intensities expected based solely on the **Ru-G** molar fractions.

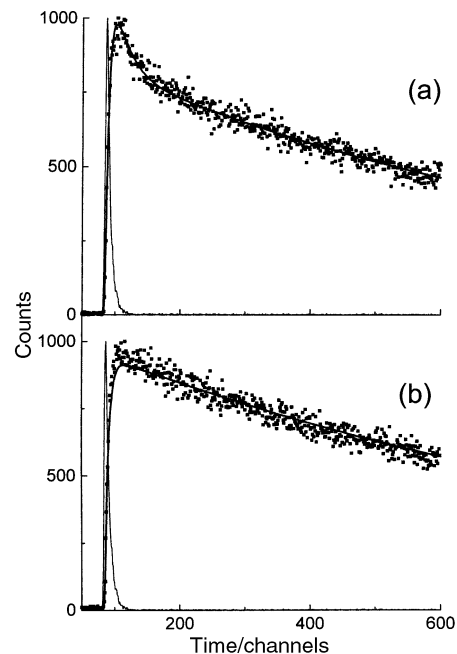


Fig. 3 Luminescence decays, observed at 626 nm, for a CH_2Cl_2 solution of **Ru-G** (9.2×10^{-5} M) and **C-Os-C** (4×10^{-5} M), before (a) and after (b) EtOH addition. Excitation was at 337 nm, and the time axis was $0.511 \text{ ns channel}^{-1}$; the full line is the result of the fit.

In the inset of Fig. 1, $\Delta I_{\text{Ru}} (= I_{\text{Ru}}^{\text{EtOH}} - I_{\text{Ru}})$ is plotted against the **Ru-G/(Ru-G + C-Os-C)** molar ratio; as mentioned above, I_{Ru} and $I_{\text{Ru}}^{\text{EtOH}}$ are luminescence intensities registered in the absence and the presence of EtOH, respectively. Thus, the inset of Fig. 1 corresponds to a Job plot and it can be seen that ΔI_{Ru} peaks at a mol fraction of **Ru-G** of ca. 0.5. This indicates that **Ru-G** and **C-Os-C** associate to form a 1 : 1 complex (eqn. 1), while no clear-cut evidence for a 2 : 1 associate is available from the luminescence behaviour. From the luminescence data of Fig. 1, an association constant of $K_{\text{ass}} = 1.1 \times 10^4 \text{ M}^{-1}$ is obtained by following the method previously described.³

Regarding Fig. 2, it can be seen that the luminescence of **Ru-G** is not much affected by the presence of **Fc-C**; it turns out that addition of EtOH has, likewise, little effect. For the **Ru-G/Fc-C** mixtures, the time-dependent properties of the Ru-based luminescence are always describable in terms of a single exponential decay. Possible explanations for this outcome may be traced back either to (i) a low association constant for this couple or (ii) a low efficiency for the quenching of the Ru-based luminescence by the **Fc** unit within the associate. We note that interaction between **C** and **G** proved to result in K_{ass} values of $\geq 5 \times 10^3 \text{ M}^{-1}$ for both **Ru-C/Os-G** (studied earlier)³ and for the **Ru-G/C-Os-C** pair (this work, see above). It is therefore more likely that **Fc** is poor at both energy-transfer and electron-transfer quenching across the hydrogen-bonded interface of the **Ru-G : C-Fc** associate, compared to the situation where much stronger electronic coupling is provided by covalent linkages between the two centres.⁷

In order to better understand the nature of the photoinduced processes we have performed some calculations regarding the energy transfer steps occurring within the mixtures **Ru-G/C-Os-C** and **Ru-G/Fc-C**, where **Ru-G** always acts as an energy donor (D) towards the accepting partners (A), either **C-Os-C** or **Fc-C**. In general, two mechanisms are available for discussing this process. One may be viewed as a dipole-dipole effect, according to a treatment due to Förster,¹⁷ and the other is based on a description in terms of double electron exchange, dealt with by Dexter.¹⁸ The relevant energy transfer

rate constants k_{en}^{F} and k_{en}^{D} can be evaluated provided some parameters are known (eqn. 3 and 4).

$$k_{\text{en}}^{\text{F}} = \frac{8.8 \times 10^{-25} K^2 \Phi}{n^4 \tau d_{\text{MM}}^6} \cdot J_{\text{F}} \quad (3)$$

$$k_{\text{en}}^{\text{D}} = \frac{4\pi^2 H^2}{h} \cdot J_{\text{D}} \quad (4)$$

Within the Förster approach (eqn. 3), K^2 is a geometric factor (taken to be 2/3 for statistical reasons), Φ and τ are the luminescence quantum yield and lifetime of **Ru-G** (Table 1), respectively, n is the refractive index of the solvent, and d_{MM} is the distance between the interacting centres; the critical transfer radius R_0 (the intercomponent distance for which the intrinsic deactivation of the donor is equal to k_{en}^{F}) can also be evaluated (Table 2). For evaluation of the Dexter rate constant (eqn. 4), an electronic interaction (represented by H , not available here) between D and A is provided by interposed molecular fragments.⁷ J_{F} and J_{D} are overlap integrals (Table 2) between the luminescence spectrum of the donor, $F(\bar{\nu})$, and the absorption spectrum of the acceptor, $\epsilon(\bar{\nu})$, on an energy scale (cm^{-1}). Fig. 4 shows luminescence and absorption spectra for the couples **Ru-G/C-Os-C** and **Ru-G/Fc-C**.

Use of the evaluated parameters in Table 2 provides interesting hints as to the type of energy transfer mechanism, Förster or Dexter, involved. For the couple **Ru-G/Fc-C**, the Förster treatment yields such a low value for J_{F} (Table 2 and Fig. 4) that the critical transfer radius is very small, $R_0 = 6.6$ Å, compared to an Ru-Fc intercentre distance of at least 13 Å (estimated from molecular modelling).¹⁹ Thus, either a Dexter mechanism provides for any $\text{Ru} \rightarrow \text{Fc}$ energy transfer, or $\text{Ru} \leftarrow \text{Fc}$ electron transfer occurs,¹⁶ both of which imply

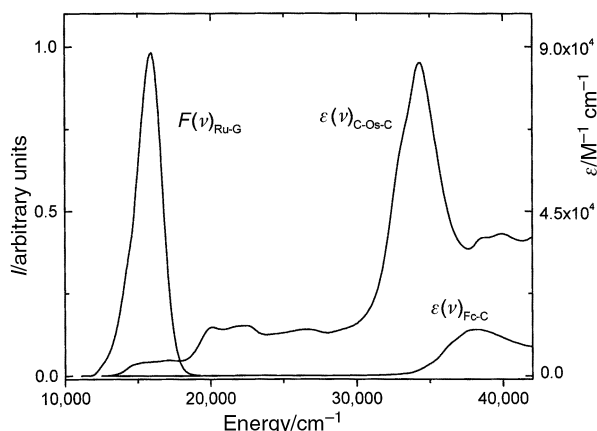


Fig. 4 Luminescence spectrum of **Ru-G** and absorption spectra of **C-Os-C** and **Fc-C** on an energy scale.

Table 2 Energy transfer parameters^a

	Förster			Dexter
	$J_{\text{F}}^b / \text{cm}^6 \text{ mol}^{-1}$	$R_0^c / \text{Å}$	$d^d / \text{Å}$	$J_{\text{D}}^e / \text{cm}$
D/A Couple				
Ru-G/C-Os-C	2.7×10^{-14}	23.2	12.7	1.8×10^{-4}
Ru-G/Fc-C	1.5×10^{-17}	6.6	<4	1.1×10^{-4}

^a Room temperature, CH_2Cl_2 solvent, measured rate constant $k_{\text{en}} = 8.0 \times 10^7 \text{ s}^{-1}$. ^b Förster integral, $J_{\text{F}} = \frac{\int F(\bar{\nu})\epsilon(\bar{\nu})/\bar{\nu}^4 d\bar{\nu}}{\int F(\bar{\nu}) d\bar{\nu}} \text{ cm}^6 \text{ mol}^{-1}$. ^c Critical transfer radius, $R_0 = 9.79 \times 10^{-3} (K^2 n^{-4} \Phi_{\text{Ru-G}} J_{\text{F}})^{1/6} \text{ Å}$. ^d Intercomponent distance (metal to metal) for which the calculated rate constant, $k_{\text{en}}^{\text{F}} = k_{\text{en}}$. ^e Dexter integral, $J_{\text{D}} = \frac{\int F(\bar{\nu})\epsilon(\bar{\nu}) d\bar{\nu}}{\int F(\bar{\nu}) d\bar{\nu} \int \epsilon(\bar{\nu}) d\bar{\nu}} \text{ cm}$.

electronic mediation by the H-bonds (which is weak, as suggested by the results of Fig. 2).^{20,21} In contrast, for the **Ru-G/C-Os-C** couple, the calculated value of J_{F} is large (Table 2) which happens because of the sizeable overlap between donor luminescence and acceptor absorption (Fig. 4) and the evaluated $R_0 = 23.2$ Å is much larger than the estimated Ru-Os intercenter distance of ca. 13–14 Å. Thus, for the couple **Ru-G/C-Os-C**, energy transfer is likely to take place *via* the Förster mechanism, *i.e.* without electronic mediation by H-bonds, which would therefore fulfil the purely structural role of holding the Ru and Os centres close together.

In conclusion, with the help of luminescence techniques we have investigated formation of associates driven by H-bonds involving complementary **C** and **G** units appended to some chromophore and quencher complexes. For the **Ru-G/C-Os-C** case, our approach provided no evidence for a trinuclear assembly, which had been expected to form based on the H-bonding capability of the **C-Os-C** complex (Scheme 2). We note that the derived $K_{\text{ass}} = 1.1 \times 10^4 \text{ M}^{-1}$ for the 1 : 1 association is about double the value previously found for the related **Ru-C/Os-G** couple, $K_{\text{ass}} = 5 \times 10^3 \text{ M}^{-1}$.³ A simple explanation for this outcome may be based on the fact the 'concentration' of cytosine units for **C-Os-C** is effectively double that provided by an equimolar solution of **O-s-C**.

Experimental

Syntheses

Bipy-C₂. To a solution of cytosine (111 mg, 1 mmol) in dry dmf (10 cm^3) at 0 °C under N_2 was added NaH (1 mmol) and the mixture was stirred for 10 min. Then KI (30 mg) was added followed by addition of a suspension of 5,5'-bis(bromomethyl)-2,2'-bipyridine (170 mg, 0.5 mmol) in dry dmf (10 cm^3). The mixture was stirred for 5 h at 50 °C under N_2 . After cooling to room temperature and slow addition of water (50 cm^3), bipy-C₂ precipitated as a pale brown solid which was filtered off, washed with MeOH, and dried. Yield: 28%. EI-MS: m/z 402 [M^+]. The ligand is not sufficiently soluble for NMR spectroscopy, even in dmsO.

Bipy'. 4,4'-Bis(5-nonyl)-2,2'-bipyridine was prepared (60% yield) by reaction of 4-[(1-butyl)pentyl]pyridine with Raney nickel at 150 °C for 2 days, followed by chromatographic purification (Al_2O_3 , CH_2Cl_2), according to the method described for conversion of 4-*tert*-butylpyridine to 4,4'-bis(*tert*-butyl)-2,2'-bipyridine.²²

[Os(bipy')₂Cl₂]. [Os(bipy')₂Cl₂] was prepared (58% yield) by reaction of bipy' with K_2OsCl_6 (1 : 1 molar ratio) in dmf under N_2 at reflux for 24 h, according to the method of ref. 23.

Os-C₂. [Os(bipy')₂(bipy-C₂)](PF₆)₂ was prepared by reaction of [Os(bipy')₂Cl₂] with bipy-C₂ (1 : 1 molar ratio) in ethylene glycol at reflux using the same general method as described previously.⁹ Yield: 20%. ES-MS: *m/z* 1701 [*M* + H]⁺, 1554 [*M* – PF₆]⁺, 705 [*M* – 2PF₆]²⁺, 470 [*M* – 2PF₆ + H]³⁺. ¹H NMR (300 MHz, CD₃CN): δ 0.80 (24 H, m, CH₃ of alkyl substituents on bipy'), 1.25 (32 H, m, CH₂CH₂ of alkyl substituents), 1.68 (16 H, m, CH₂ of alkyl substituents), 2.78 (4 H, m, CH of alkyl substituents), 4.65 (4 H, s, CH₂ of bipy-C₂), 5.72 (2 H, d, *J* 7.5, cytosine CH=CH), 6.11 (4 H, br s, cytosine NH₂), 7.08 (2 H, dd, *J* 1.6, 6.1, bipy), 7.15 (2 H, dd, *J* 1.6, 6.1, bipy), 7.37 (2 H, d, *J* 7.5, cytosine CH=CH), 7.43 (4 H, m, bipy), 7.57 (2 H, br s, bipy), 7.64 (2 H, d, *J* 8.4 Hz, bipy), 8.31 (6 H, m, bipy). Found: C, 50.1; H, 5.8; N, 8.7%. Required for [Os(bipy')₂(bipy-C₂)](PF₆)₂ · HPF₆: C, 49.5; H, 5.8; N 9.1%.

Ru-G. [Ru('Bu₂bipy)₂(bipy-G)](PF₆)₂ was prepared by reaction of [Ru('Bu₂bipy)₂Cl₂] and bipy-G (1 : 1 molar ratio) in ethylene glycol at reflux using the same general method as described previously.⁹ Yield: 30%. ES-MS: *m/z* 1102 [*M* – PF₆]⁺, 478 [*M* – 2PF₆]²⁺. ¹H NMR [300 MHz, (CD₃)₂CO]: δ 1.39 (36 H, m, 'Bu), 5.33 (2 H, s, CH₂ of bipy-G), 6.16 (2 H, br s, guanine NH₂), 7.36 (1 H, s, guanine CH), 7.44 (1 H, m, bipy), 7.55 (4 H, m, bipy), 7.66 (2 H, m, bipy), 7.79 (3 H, m, bipy), 7.95 (1 H, m, bipy), 8.21 (2 H, m, bipy), 8.83 (6 H, m, bipy), 10.32 (1 H, br s, guanine NH). Found: C, 48.2; H, 4.6; N, 11.6%. Required for [Ru('Bu₂bipy)₂(bipy-G)](PF₆)₂ · 2H₂O: C, 48.6; H, 5.1; N, 12.0%.

NMR and mass spectra, ground state absorption spectra, steady state luminescence data and time resolved and photo-physical results were obtained as described in ref. 5. Calculations for the energy transfer steps were performed with the help of Matlab 5.2 (MatWorks).²⁴ Molecular modelling calculations were performed with the program CS Chem-3D (version 5.0).²⁵

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