Electronic energy transfer between ruthenium(II) and osmium(II) polypyridyl luminophores in a hydrogen-bonded supramolecular assembly

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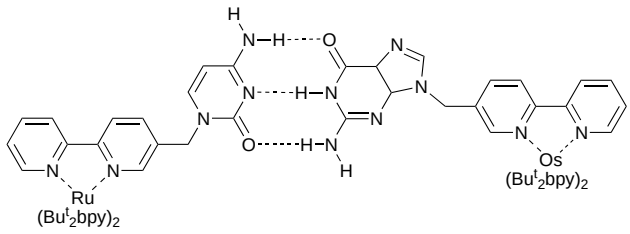
Complexes Ru–C and Os–G are derivatives of $[Ru(bipy)_3]^{2+}$ and $[Os(bipy)_3]^{2+}$ bearing peripheral cytosine (C) or guanine (G) nucleobases respectively; in CH_2Cl_2 these undergo association (K_A > 5000 dm^{-3} mol^{-1}) by hydrogen bonding between the complementary C/G groups, and Ru → Os photoinduced energy-transfer occurs within Ru–C···G–Os associated pair.

Many complexes are now known which display inter-component photoinduced energy transfer.[1–3] The study of such compounds is of fundamental interest both in relation to the mechanism of photosynthesis in nature,[2] and to recent efforts to prepare artificial molecular-scale electronic devices.[3] In virtually all cases the interacting components are covalently linked by a suitable bridging group, as this allows control of the inter-component separation, orientation, and the nature of the pathway between them through which the interaction can occur.

More recently supramolecular complexes have been prepared in which interacting components are associated by non-covalent interactions, in particular hydrogen bonding,[4] and photoinduced energy-transfer has been observed between metalloporphyrins and hydrogen-bonded organic fragments.[5] Although hydrogen bonding is widely used to promote self-assembly processes and to assist molecular recognition with organic compounds,[6] the association of metal complexes in the same way has received much less attention.[7,8]

Here we report on the association of ruthenium(II)– and osmium(II)–polypyridine units[3] driven by a triple hydrogen bond, and which results in photoinduced $Ru^{II} \rightarrow Os^{II}$ energy transfer across the hydrogen-bonded bridge. This was accomplished using metal complex components functionalised with the nucleotide bases cytosine (C) and guanine (G); the C/G pair gives Watson–Crick three-point hydrogen-bonding association with high constants (*ca.* 10^4 dm^3 mol^{-1}) in low polarity solvents.[9]

The ligands bpy-C and bpy-G (Scheme 1) were prepared by alkylation of 5-bromomethyl-2,2′-bipyridine directly with cytosine at position N^1 to give bpy–C, or with 2-amino-6-chloropurine at position N^9 followed by acid hydrolysis to give bpy-G.[10]† Reaction of these with $[M(Bu^t_2bpy)_2Cl_2]$ [M = Ru, Os; Bu^t_2bpy = 4,4′-di(*tert*-butyl)-2,2′-bipyridine][8] afforded $[Ru(Bu^t_2bpy)_2(bpy\text{-}C)][PF_6]_2$ (**Ru–C**) and $[Os(Bu^t_2bpy)_2(bpy\text{-}G)][PF_6]_2$ (**Os–G**).‡ The use of Bu^t_2bpy ancillary ligands ensures good solubility in low-polarity solvents, to maximise association by hydrogen bonding. $[Os(Bu^t_2bpy)_2(bpy)][PF_6]$ (denoted **Os**) was also prepared.



Scheme 1 Structure of the **Ru–C··Os–G** associate

The absorption properties in the visible region of **Ru–C** and **Os–G** dissolved in CH_2Cl_2 are as expected for ruthenium(II)– and osmium(II)–polypyridyl chromophores,[3] with band maxima occurring at 459 nm (ε = 14 200 dm^3 mol^{-1} cm^{-1}) and 484 (11 600), respectively, for population of the lowest-lying ^{1}MLCT excited state. The luminescence band maxima of **Ru–C** and **Os–G** obtained in CH_2Cl_2 solvent are well separated with λ_{max} = 626 and 744 nm, respectively. **Ru–C** is a much stronger emitter than **Os–G**, with $\Phi = 3.6 \times 10^{-2}$ (τ = 350 ns) and 2.9×10^{-3} (τ = 44 ns), respectively.

We have demonstrated formation of a **Ru–C··G–Os** associate (where ··· signifies the triple cytosine/guanine hydrogen-bond; Scheme 1) by luminescence spectroscopy, comparing results obtained on 1 : 1 mixtures of **Ru–C** and **Os–G** in CH_2Cl_2 solution, before (*a*) and after (*b*) addition of drops of EtOH to break the hydrogen bonding between the components. The experiment was performed at three different concentrations: $[\mathbf{Ru–C}]_0 = [\mathbf{Os–G}]_0 = 1.0 \times 10^{-4}$ M, case (*i*); 2.2×10^{-4} M, case (*ii*); and 4.5×10^{-4} M, case (*iii*). Fig. 1 compares luminescence spectra recorded for case (*i*) (before and after additional of EtOH to break the hydrogen bonds), and those observed for a mixture of the reference couple **Ru–C** and **Os**. From Fig. 1 we see that EtOH addition causes an increase of the Ru-based luminescence intensity (I_b/I_a = 1.4) for the **Ru–C**/**Os–G** pair, but has no effect on the Ru-based luminescence intensity for the **Ru–C**/**Os** pair. The absorption spectra of the mixtures are unaffected by the addition of EtOH. It follows that in the **Ru–C··G–Os** associate the Ru-based emission is

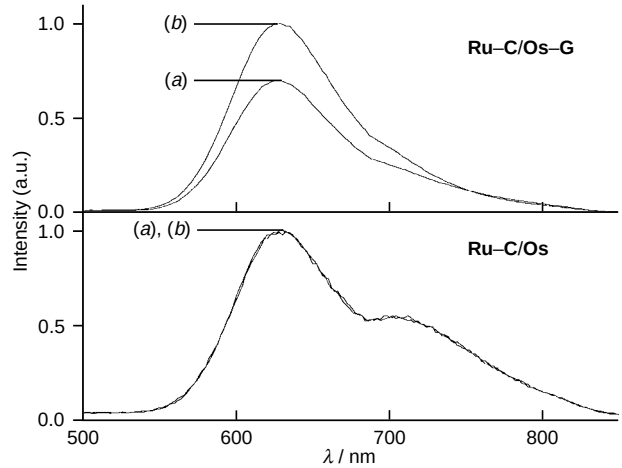


Fig. 1 Upper: luminescence spectra of a CH_2Cl_2 solution of **Ru–C** and **Os–G** (both 1.0×10^{-4} M), before (*a*) and after (*b*) EtOH addition. Lower: luminescence spectra of a CH_2Cl_2 solution of **Ru–C** (3×10^{-4} M) and **Os** (7×10^{-4} M), before (*a*) and after (*b*) EtOH addition. Excitation was at 458 nm.

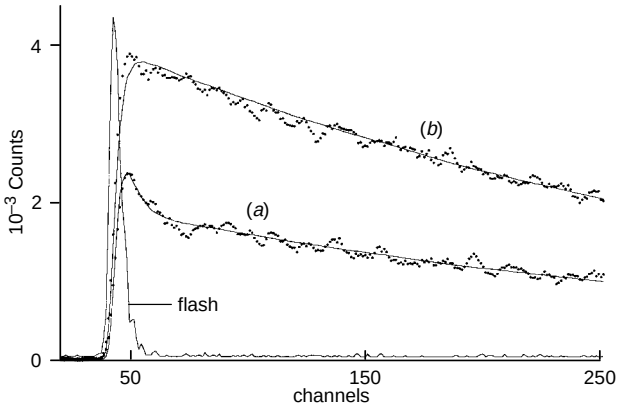


Fig. 2 Decay of the luminescence intensity for a CH_2Cl_2 solution of **Ru**–**C** and **Os**–**G** (both 1.0×10^{-4} M), before (*a*) and after (*b*) EtOH addition. Time axis was 1.03 ns/channel. Excitation was at 337 nm.

quenched, and this quenching is removed when the hydrogen bond is broken. In the latter case (**Ru**–**C**/**Os** pair) no hydrogen-bonding associate can be formed, so addition of EtOH had no effect on the emission properties of the mixture. For cases (*ii*) and (*iii*), the relative increases in luminescence intensity after addition of EtOH (I_b/I_a) were 1.6 and 4.0, respectively.

Fig. 2 shows the Ru-based time-resolved luminescence decay observed for case (*i*), as monitored at λ_{em} = 626 nm. In neat CH_2Cl_2, case (*i*) (*a*), the decay follows a dual exponential law, $I(t) = B_1[\exp(-t/\tau_1)] + B_2[\exp(-t/\tau_2)]$, with τ_1 = 10.5 ns, τ_2 = 290 ns and B_1/B_2 = 0.7. EtOH addition, case (*i*) (*b*), results in a single exponential decay, $I(t) = B[\exp(-t/\tau)]$, with τ = 270 ns. Similar behaviour was shown for cases (*ii*) and (*iii*). From comparison of the luminescence intensity observed in CH_2Cl_2 before [cases (*a*)] and after [cases (*b*)] EtOH addition, and by entirely ascribing the residual Ru-based luminescence intensity of cases (*a*) to the unassociated **Ru**–**C** complex,§ it is possible to estimate an association constant $K_A > 5 \times 10^3$ dm^3 mol^{-1} for formation of **Ru**–**C**··**G**–**Os**.¶

Use of time-resolved luminescence results allows estimates of the rate constants for both intermolecular and intra-associate quenching of the Ru-based luminescence of **Ru**–**C** by **Os**–**G**. Thus, for case (*i*), (*a*) intermolecular quenching controlled by diffusional processes results in τ_2 = 290 ns as compared to τ = 400 ns for **Ru**–**C** alone in dilute solution.‖ The much more efficient quenching, resulting in τ_1 = 10.5 ns, we ascribe to the process taking place within the **Ru**–**C**··**G**–**Os** associate because addition of EtOH [case (*i*), (*b*)], which is expected to cause disruption of the hydrogen bonds, results both in recovery of the Ru-based luminescence intensity at 626 nm (Fig. 1) and loss of the shorter-lived component of the luminescence decay (Fig. 2). Based on $k_{en} = 1/\tau_1 - 1/\tau$, the rate constant for this step is $k_{en} = 9.3 \times 10^7$ s^{-1}. For cases (*ii*) and (*iii*), k_{en} was likewise found to be 9.5×10^7 s^{-1} ± 10%. Attempts to obtain evidence for sensitization of the Os-based luminescence were unsuccessful because the Os-based luminescence (λ_{max} = 744 nm) is hidden by the tail of the much stronger Ru-based luminescence (Fig. 1).

Energy transfer within the **Ru**–**C**··**G**–**Os** associate could in principle occur by the Förster (dipole–dipole)[11] or Dexter (exchange or through-bond)[12] mechanisms. Although the Förster mechanism is feasible at the shortest possible metal-to-metal separation,** estimated at *ca.* 13 Å from CPK models, the Dexter mechanism must be invoked for the greater metal–metal separations which are energetically favoured because of electrostatic repulsion. This implies a double electron exchange[13] *via* the hydrogen-bond interface, consistent with the recent finding that single electron transfer can be effectively mediated by H bonds.[14]

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Footnotes and References

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† bpy-C: NaH (1 mmol) was added to a suspension of cytosine (111 mg, 1 mmol) and KI (30 mg, a catalytic amount) in dry, degassed *N*,*N*-dimethylformamide (dmf) and stirred for 0.5 h. A solution of 5-bromomethyl-2,2′-bipyridine (250 mg, 1 mmol) in dry dmf (2 cm^3) was added slowly to this mixture and the reaction was then stirred under N_2 at 50 °C overnight. Addition of water (100 cm^3) resulted in precipitation of clean bpy–C (175 mg, 62%).

bpy–G: a mixture of 1-amino-6-chloropurine (170 mg, 1 mmol), K_2CO_3 (276 mg, 2 mmol) and KI (30 mg, a catalytic amount) in dry Me_2SO (10 cm^3) was stirred under N_2 for 10 min. A solution of 5-bromomethyl-2,2′-bipyridine (620 mg, 2.5 mmol) in dry Me_2SO was then added slowly and the reaction was stirred under N_2 at room temp. for 3 h. Addition of water (50 cm^3) precipitated the intermediate 2-amino-6-chloro-9-{5-(2,2′-bipyridyl)methyl}purine (bpy–ACP) as an off-white solid (218 mg, 64%). bpy–ACP (215 mg, 0.6 mmol) was then heated to reflux in 0.1 M HCl (20 cm^3) for 4 h. After cooling and neutralisation (KOH), bpy-G precipitated as a white solid (156 mg, 77%). Satisfactory mass and ^{1}H NMR spectroscopic data, and C, H, N, analyses, were obtained for both ligands and the intermediate bipy–ACP.

‡ The complexes were prepared in *ca.* 50% yield by reaction of $[M(Bu^t_2bpy)_2Cl_2]$ (M = Ru, Os, 1 mmol) with bpy-C or bpy-G as required (1 mmol) in ethylene glycol (10 cm^3) at 160 °C for 2 h followed by precipitation with aqueous KPF_6, followed by chromatography on alumina (Brockmann activity III) with CH_2Cl_2 containing 2–5% MeOH. ESMS of **Ru**–**C**: *m*/*z* 1062 $\{Ru(Bu^t_2bpy)_2(bpy–C)(PF_6)\}^+$, 459 $\{Ru(Bu^t_2bpy)_2(bpy–C)\}^{2+}$. ESMS of **Os**–**G**: *m*/*z* 1192 $\{Os(Bu^t_2bpy)_2(bpy–G)(PF_6)\}^+$, 523 $\{Os(Bu^t_2bpy)_2(bpy–G)\}^{2+}$. Satisfactory elemental analyses were also obtained.

§ For instance in case (*i*), $(B_1\tau_1)/(B_2\tau_2)$ = 0.014 (see text), so the contribution of the short-lived component to the steady state luminescence spectrum of Fig. 1 is < 2%.

¶ For instance, for case (*i*) and by using $[\mathbf{Ru}–\mathbf{C}]_0 = [\mathbf{Os}–\mathbf{G}]_0 = 1.0 \times 10^{-4}$ M and $[\mathbf{Ru}–\mathbf{C}]_0/[\mathbf{Ru}–\mathbf{C}]$ = 1.4 from Fig. 1, one may calculate [**Ru**–**C**··**G**–**Os**]; then K_A = [**Ru**–**C**··**G**–**Os**]/([**Ru**–**C**][**Os**–**G**]) is evaluated.

‖ According to $\tau/\tau_2 = 1 + k_q\tau[\mathbf{Os}–\mathbf{G}]$, this is consistent with a second-order quenching constant $k_q = 9.5 \times 10^9$ dm^3 mol^{-1} s^{-1}.

** According to the Förster treatment[11] the dipole–dipole rate constant for an intermetal separation of 13 Å is $k_F = 1.2 \times 10^8$ s^{-1}, to be compared with the experimental value $k_{en} = 9.3 \times 10^7$ s^{-1}, see text.

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