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A ruthenium(II) *tris*(2,2′-bipyridine) derivative possessing a triplet lifetime of 42 μs

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Grafting an ethynylated-pyrene moiety to a Ru(II) or Os(II) polypyridine complex perturbs the photophysical properties of the metal fragment and, when the relevant energy levels are properly balanced, provides a 115-fold prolongation of the triplet lifetime.

Ford and Rodgers[1] have described reversible triplet energy transfer between pyrene and a ruthenium(II) polypyridine complex attached *via* a flexible hydrocarbon chain. This strategy prolonged the triplet lifetime of the metal complex by a factor of *ca*. 11-fold; a feat confirmed by Sasse and coworkers[2,3] who achieved a 5-fold extension in triplet lifetime with a similar dyad. In seeking to design improved luminophores for specific analytical applications we note the following points: (i) conformational heterogeneity introduced by the flexible connector, or by direct attachment of the reactants,[4] would be avoided with a rigid spacer. (ii) The rates of forward and reverse triplet energy transfer would be increased with an acetylene group as connector.[5] Consequently, photoactive dyads have been synthesized (Scheme 1) wherein an ethynylated pyrene moiety is grafted onto an Ru(II) or Os(II) polypyridine complex† and the photophysical properties recorded.

The emission spectrum recorded for pyr-bpy-Os (Fig. 1) is characteristic[5] of an 'Os(bpy)' molecular fragment (bpy = 2,2′-bipyridine), allowing[6] the triplet energy (E_T) to be derived (Table 1). The emission quantum yield (Φ_L), peak maximum (λ_L) and lifetime (τ_L) remain as expected for an 'Os(bpy)' fragment while the transient absorption spectrum recorded after laser excitation (FWHM = 20 ps, λ = 532 nm) is entirely consistent[7] with the excited triplet state being localized on the metal complex (Fig. 2). Decay of the triplet absorption signal follows first-order kinetics, giving a lifetime (τ_T) similar to that measured by emission spectroscopy (Table 1). Laser spectroscopy shows that the pyrene triplet is not populated but, since the corrected emission excitation spectrum closely matches the absorption spectrum, photons absorbed by pyrene must be channelled quantitatively to the 'Os(bpy)' fragment. It appears, therefore, that the triplet state of the 'Os(bpy)' fragment lies at lower energy than the pyrene-like triplet state.[8]

Under identical conditions, the emission spectrum of pyr-bpy-Ru is characteristic of the 'Ru(bpy)' fragment (Fig. 1) but emission is exceptionally long-lived for such a species (Table 1). Both λ_L and Φ_L remain typical of a 'Ru(bpy)' fragment bearing an ethynylene group while the corrected excitation spectrum agrees well with the absorption spectrum. Control studies show the free ligand (*i.e.*, pyr-bpy) to be non-phosphorescent at rt. Analysis of the emission spectral profile[6] shows that the triplet energy of the 'Ru(bpy)' fragment greatly exceeds that of the corresponding 'Os(bpy)' fragment (Table 1). However, the transient absorption spectral profile (Fig. 2) is remarkably similar to that recorded for the pyrene unit in pyr-bpy and is unlike that of any 'Ru(bpy)'-based triplet. This pyrene-like triplet decays with the same lifetime as found for the 'Ru(bpy)'-like luminescence. These observations can be satis-

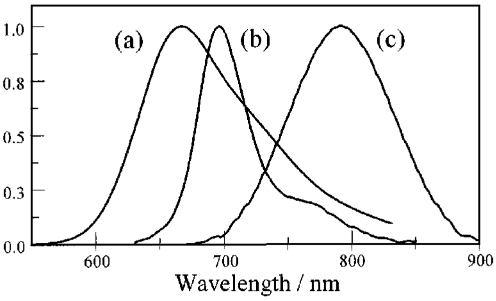
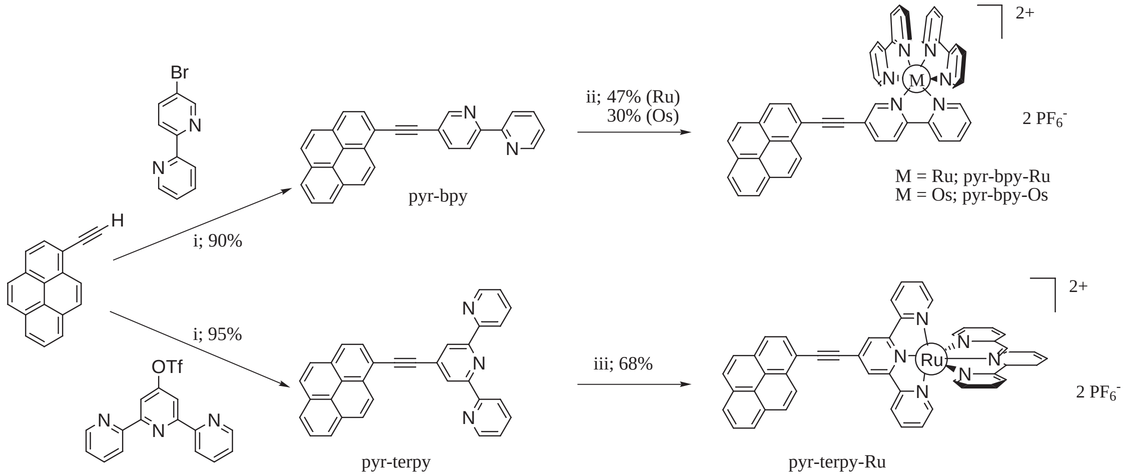


Fig. 1 Corrected luminescence spectra recorded for (a) pyr-bpy-Ru, (b) pyr-terpy-Ru and (c) pyr-bpy-Os in deoxygenated acetonitrile at 20 °C.



Scheme 1 *Reagents and conditions*: i, benzene, diisopropylamine, [Pd^0(PPh$_3$)$_4$] (6 mol %), 80 °C, 1 day; ii, *cis*-[Ru(bpy)$_2$Cl$_2$]·2H$_2$O or *cis*-[Os(bpy)$_2$Cl$_2$], ethanol, 80 °C, 1 day, followed by anion metathesis; iii, [Ru(terpy)(Me$_2$SO)Cl$_2$], AgBF$_4$, methanol, 80 °C, 16 h.

Table 1 Photophysical properties measured for the various pyrene-containing molecular dyads in deoxygenated acetonitrile at 20 °C

Compound	λ_L/nm	Φ_L	τ_L/ns	τ_T/ns	E_T/kJ mol^{-1}	ΔE_{TT}/cm^{-1}	α	K	S
pyr-bpy-Ru	670	0.026	42 000	43 000	195	930	0.98	49	35
pyr-terpy-Ru	698	0.005	580	560	179	−390	0.13	0.15	1.2
pyr-bpy-Os	790	0.001	12	14	162	−1865	0	0	1.0

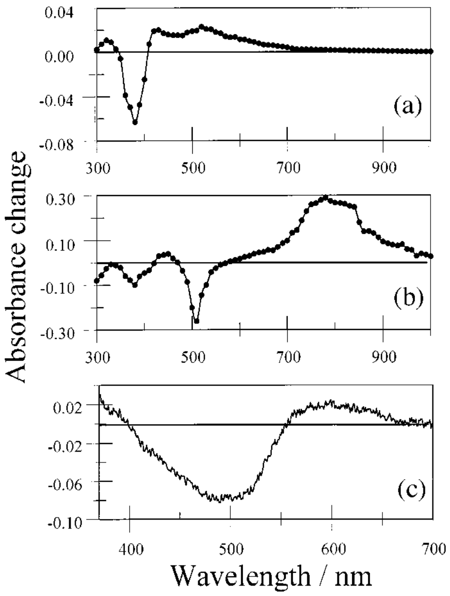


Fig. 2 Transient differential absorption spectra recorded for (a) pyr-bpy-Ru after 500 ns, (b) pyr-terpy-Ru after 100 ns, and (c) pyr-bpy-Os after 1 ns in deoxygenated acetonitrile at 20 °C following excitation with a 20-ps laser pulse at 532 nm.

factorily explained[1] in terms of the two triplet states being in thermal equilibrium at rt, with the balance favouring the pyrene-like triplet. In fact, comparing Φ_L measured for pyr-bpy-Ru with appropriate 'Ru(bpy)'-based reference compounds[5] lacking the pyrene substituent but possessing a similar radiative rate constant, allows the fraction (α) of pyrene-like triplets in the equilibrium distribution to be established at 0.98. On this basis, the energy of the pyrene-like triplet state must be *ca.* 184 kJ mol^{-1} since the equilibrium constant [$K = \alpha/(1-\alpha)$] is calculated to be *ca.* 49.

Confirmation of these energy gaps was sought by measuring the photophysical properties of pyr-terpy-Ru for which r.t. emission (Fig. 1) is characteristic[9] of the 'Ru(terpy)' fragment (terpy = 2,2′:6′,2″-terpyridine). The emission lifetime recorded for pyr-terpy-Ru is long for an ethynylated mononuclear 'Ru(terpy)' fragment (Table 1) whilst the transient absorption spectrum clearly contains important contributions associated with triplet-triplet transitions localized on the metal complex (Fig. 2). Spectral analysis indicates that the triplet energy of the 'Ru(terpy)' fragment in pyr-terpy-Ru is slightly lower than that derived for the pyrene-like triplet with the result that the triplet equilibrium distribution ($K = 0.15$; $\alpha = 0.13$) lies in favour of the metal complex. Reversible energy transfer, therefore, provides only a minor stabilization for the triplet localized on the 'Ru(terpy)' fragment. It should be noted, however, that relative to the parent $[\mathrm{Ru(terpy)_2}]^{2+}$ complex ($\Phi_L < 0.0002$; $\tau_L = 0.56$ ns), pyr-terpy-Ru is strongly luminescent at r.t.

Reversible triplet energy transfer[1–3] between the terminals in pyr-bpy-Ru serves to extend the triplet lifetime of the 'Ru(bpy)' fragment to 42 μs, which is well beyond the range of any related system. The equilibrium distribution is established within the 20 ps excitation pulse, indicating that both forward and reverse energy-transfer steps are rapid. The observed triplet lifetime is set by the inherent decay rate constants for individual triplets localized on pyrene (k_P) and 'Ru(bpy)' (k_R) and by the fractional contribution of each component [eqn. (1)]:

$$k_D = 1/\tau_T = \alpha k_P + (1-\alpha)k_R \qquad (1)$$

Here, α is determined by the energy gap (ΔE_{TT}) between the two triplets (Table 1) while k_P (= 7770 s^{-1}) is obtained by monitoring the triplet state of pyr-bpy under appropriate conditions. This allows k_R to be estimated from the experimental data and the derived value ($k_R = 8.4 \times 10^5$ s^{-1}) is seen to be comparable to decay rates measured for other ethynylated 'Ru(bpy)' fragments, where inherent triplet lifetimes tend to be slightly > 1 μs.[5] Furthermore, it now becomes possible to quantify the effect of the pyrene unit in terms of a stabilization factor ($S = k_R\tau_T$), which for pyr-bpy-Ru has a value of *ca.* 35 and is marginally greater than unity for pyr-terpy-Ru. For both compounds, however, S increases markedly when due allowance is made for the additional stabilization imposed by the ethynylene group. Thus, using k_R values appropriate[10] for simple 'Ru(bpy)' or 'Ru(terpy)' units having the same triplet energy as the metallo-fragments in pyr-bpy-Ru and pyr-terpy-Ru, respectively, gives revised S values of 115 and 10.‡ It is anticipated that this prolongation of the triplet lifetime will advance opportunities for employing the unique luminescence properties of 'Ru(bpy)'-based systems in sophisticated analytical or electro-chemiluminescent applications.

Notes and references

† Full synthetic details will be given elsewhere. All new compounds were authenticated by NMR, FTIR, MS and elemental analyses. *Selected data*: pyr-bpy-Ru, IR (KBr disc): 2195 cm^{-1} [ν(C≡C)];^{13}C{^{1}H} NMR (CDCl$_3$): δ 96.4 (C≡C), 90.7 (C≡C), MS (FAB$^+$, *m*-NBA): 939.0 (M−PF$_6$)$^+$; UV-VIS (MeCN) λ_{max}/nm) (ε/dm^3 mol^{-1} cm^{-1}): 416 (45 200), 280 (118 300). pyr-bpy-Os, IR(KBr disc): 2195 cm^{-1} [ν (C≡C)] MS (FAB$^+$, *m*-NBA): 1029.0 (M − PF$_6$ + H)$^+$; UV-VIS (MeCN) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 408 (23 900), 284 (72 600). pyr-terpy-Ru, IR(KBr disc): 2192 cm^{-1} [ν(C≡C)]; ^{13}C{^{1}H} NMR (CD$_3$CN): δ 97.2 (C≡C), 93.1 (C≡C), MS (FAB$^+$, *m*-NBA): 937.2 (M − PF$_6$)$^+$; UV-VIS (MeCN) λ_{max}/nm, ε/dm^3 mol^{-1} cm^{-1}): 511 (44 800), 281 (53 200).

‡ For example, Cook *et al.*[10] list four $[\mathrm{Ru(bpy)_3}]^{2+}$ analogues with emission maxima at 670 nm and for which the triplet lifetime is (0.36 ± 0.04) μs. Similarly, examination of the photophysical properties of $[\mathrm{Ru(terpy)_2}]^{2+}$ complexes indicates that the triplet lifetime of a compound having an emission maximum at 698 nm should be (60 ± 15) ns.

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