Charge-transfer Luminescence from Mixed-ligand, 2,2′,2″-Terpyridine–Phosphine, Complexes of Osmium(II)

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Summary The first example of intense room temperature charge-transfer (CT) emission from a series of metal–terpyridine complexes {[Os^{II}(trpy)(diphosph)L]$^{n+}$ (trpy = 2,2′,2″-terpyridine and diphosph is, *e.g.*, $Ph_2PCH_2PPh_2$)} in fluid solution is reported; the complexes can have relatively long CT excited-state lifetimes while also exhibiting substitutional photochemistry.

The observation of metal–ligand charge-transfer (MLCT)-based luminescence for d^6 low-spin transition-metal complexes of the polypyridine ligands 2,2′-bipyridine (bpy) and 1,10-phenanthroline (phen) is common.[1] However, complexes of the closely related 2,2′,2″-terpyridine (trpy) ligand either exhibit weak or no luminescence in fluid solutions at room temperature.[2]† Where data are available for MLCT-based luminescence, *e.g.* Ru(trpy)$_2^{2+}$ [2] and Os(trpy)$_2^{2+}$,[3] and for d–d luminescence, *e.g.* Cr(trpy)$_2^{2+}$,[4] excited-state lifetimes have been found to be short (typically less than 100 ns).‡ It has been suggested that the lack of luminescence is due to extremely rapid non-radiative processes. The origins of

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† An apparent exception is an Ir^{III}–trpy complex of unknown composition for which the origin of the emission is also unknown (D. W. Fink and W. E. Ohnesorge, *Anal. Chem.*, 1969, **41**, 39).

‡ Recently, the Ru(tsite)$_2^{2+}$ complex (tsite = 4,4′,4″-triphenyl-2,2′,2″-terpyridine) with τ *ca.* 200 ns has been reported (M. L. Stone and G. A. Crosby, *Chem. Phys. Lett.*, 1981, 169).

the non-radiative processes may be due to a spin-paired–spin-free equilibrium within the excited-state complex[5] or, perhaps to a specific role of the solvent in excited-state deactivation, such as direct vibrational coupling between the metal core and bulk solvent in the excited state.[6]

We have prepared a series of mixed-ligand, monoterpyridine complexes of Os^{II} which contain strong-field chelating ligands such as *cis*-$Ph_2PCH{=}CHPPh_2$ (dppe) and $Ph_2PCH_2PPh_2$ (dppm). The complexes appear to be the first well characterized§ examples in which a strong MLCT-based luminescence from a trpy–metal chromophore can be observed in fluid solutions at room temperature. The emission and absorption maxima and excited-state lifetimes, obtained by laser flash-photolysis, for the new complexes are summarized in the Table. The complexes were synthesized [equations (1) and (2)] using the known starting

$$\mathrm{Os^{III}(trpy)Cl_3} + \text{diphosph} \xrightarrow{\text{i}} [\mathrm{Os^{II}(trpy)(diphosph)Cl}]^+ \quad (1)$$

$$[\mathrm{Os^{II}(trpy)(diphosph)Cl}]^+ + \mathrm{L} \xrightarrow{\text{i}} [\mathrm{Os^{II}(trpy)(diphosph)L}]^{2+} + \mathrm{Cl^-} \quad (2)$$

Reagents: i, Heat, H_2O–ethylene glycol.

material Os^{III}(trpy)Cl_3.[7] Purification of the products, which were isolated as PF_6^- salts, was achieved by non-aqueous chromatographic methods which have been previously described.[8]§

That the emission is π^*(trpy) → dπ(Os) in character is suggested by the earlier assignment made for $Os(trpy)_2^{2+}$.[3] The assignment is supported by the fact that the emission energy of the luminescence varies directly as the difference in ground-state redox potentials between the metal-donor and ligand-acceptor sites, [$E_{\frac{1}{2}}(\mathrm{Os^{III/II}}) - E_{\frac{1}{2}}(\mathrm{trpy/tr\bar{p}y})$] (see the Table). It should be noted, however, that the emission for $[\mathrm{Os(trpy)(dppe)CO}]^{2+}$ could be ligand-localized, $\pi^* \rightarrow \pi$, since the luminescence maximum of the complex is nearly co-incidental with that for the $\pi^* \rightarrow \pi$ phosphorescence from [trpy$^+$].[9] The Figure shows typical absorption and emission spectra for two of the new complexes.

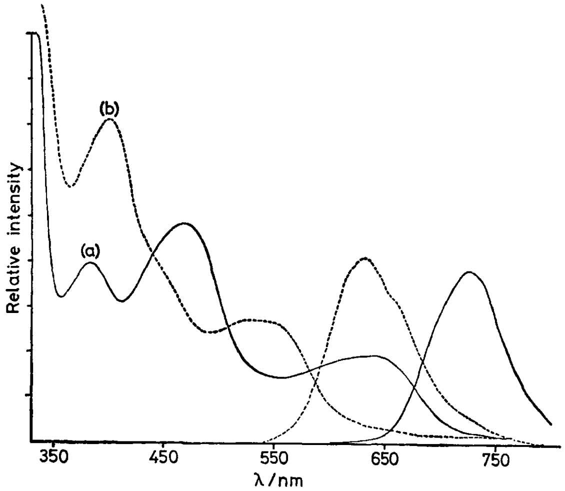

FIGURE. Absorption and emission spectra of (a) [Os(trpy)(dppm)Cl](PF_6) and (b) [Os(trpy)(dppe)MeCN]$(PF_6)_2$, taken in an oxygen-saturated MeCN solution at room temperature.

Estimations of excited-state redox potentials for the complexes have been made from spectral data using the procedure suggested by Balzani *et al.*[1b] (see the Table). A comparison of potentials of the excited states as oxidants, $M^{II*} + e \rightarrow M^{I}$, between $[\mathrm{Os(trpy)(dppm)_2}^{2+}]^*$ (1·10 V), which contains both chelate and monodentate dppm-ligands, and $[\mathrm{Ru(bpy)_3}^{2+}]^*$ (0·80 V)[10] shows that even though the excited-state energies are similar (622 nm *vs.* 608 nm), the trpy-complex is *ca.* 300 mV more oxidizing than the bpy-complex. This observation may have important consequences for the use of Os–trpy MLCT-excited-states as photoredox catalysts.

It is significant that all the trpy–Os^{II} complexes shown in the Table, except the chloro-complexes [Os(trpy)(diphosph)Cl]$^+$, are photolabile, as shown in equation (3).

$$[\mathrm{Os(trpy)(dppe)CO}]^{2+} \xrightarrow{h\nu} [\mathrm{Os(trpy)(dppe)L}]^{2+} + \mathrm{CO} \quad (3)$$

Photochemical substitution is not an important reaction for related complexes of the type $(\mathrm{phen})_2\mathrm{OsL_2}^{2+}$ or $(\mathrm{bpy})_2\mathrm{OsL_2}^{2+}$.[1a,11] This observation suggests a possible origin for the relatively short-lived excited-state lifetimes found for trpy-complexes (at least for Ru^{II} and Os^{II}). For $\mathrm{Ru(bpy)_3}^{2+}$ photosubstitution appears to occur from a d–d state which is thermally accessible after population of the low-energy MLCT excited-states.[12] For the trpy-complexes the symmetry is lower and significant deviations in ligand–metal–ligand angles compared with the angles of an octahedra exist.[6,13] One effect of the ligand-imposed distortion from octahedral symmetry is a mixing of the e_g- and t_{2g}-type d-orbitals. Mixing of e_g–t_{2g} orbitals could lead to the

TABLE. Spectral and electrochemical properties of the (trpy)Os^{III} complexes.

(trpy)OsR, R	$E_{\frac{1}{2}}^{ox}$/V[a,b]	$E_{\frac{1}{2}}^{red}$/V[a,c]	λ_{abs}/nm[d]	λ_{em}/nm[d]	τ_0/ns[e]	E_{ox}^*/V[f]	E_{red}^*/V[g]
$(Ph_2PCH{=}CHPPh_2)Cl^+$	0·96	−1·18	624	712	101	+0·66	−0·88
$(Ph_2PCH_2PPh_2)Cl^+$	0·93	−1·18	632	725	99	+0·65	−0·89
$(Ph_2PCH{=}CHPPh_2)py^{2+}$	+1·41	−0·99	570	653	455	+1·01	−0·56
$(Ph_2PCH{=}CHPPh_2)MeCN^{2+}$	+1·43	−1·01	553	629	43	+1·06	−0·64
$(Ph_2PCH_2PPh_2)_2^{2+}$	+1·70[c], 1·42	−0·99	409	622	768	+1·10	−0·39
$(Ph_2PCH{=}CHPPh_2)CO^{2+}$ [h]	> 1·9	−0·95	[i]	529	26	+1·49	< −0·54

[a] Measured in MeCN solution with 0·1M tetraethylammonium perchlorate as supporting electrolyte. [b] Reversible potential; $E_{\frac{1}{2}} = (E_{p,a} + E_{p,c})/2$. [c] Irreversible peak potential at half current, $E_{p/2}$. [d] Measured in MeCN solution, air saturated; the wavelength is of maximum absorption or emission. [e] Measured in MeCN solution, N_2 saturated. [f] Estimated by the method of Balzani, *et al.* (see ref. 1b) using 0·1 eV as the Stokes shift. The potential is the excited-state reduction potential; $M^{II*} + e \rightarrow M^{I}$. [g] As in footnote f; the potential refers to: $M^{III} + e \rightarrow M^{II*}$. [h] ν(CO) in a KBr pellet is found at 1996 cm^{-1}; footnote b does not apply. [i] No distinct visible absorption maximum.

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§ Satisfactory elemental analyses were obtained for the new complexes.

stabilization of a photolabile d–d state so that significant thermal population can occur from the emitting MLCT-states. A low-energy d–d state would explain both the photosubstitution and lifetime shortening observed for the trpy-complexes.

An alternative possibility is that e_g–t_{2g} orbital-mixing imparts substantial d–d character to the low-energy CT states, in which case both emission and photosubstitution have the same origin.

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