

## 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<sup>II</sup>(trpy)(diphosph)L]<sup>n+</sup> (trpy = 2,2',2''-terpyridine and diphosph is, e.g., Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>)} 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<sup>6</sup> low-spin transition-metal com-

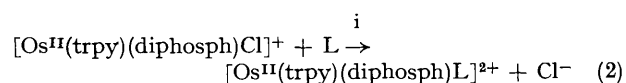
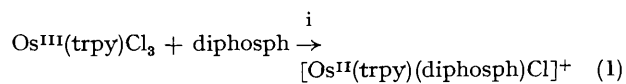
plexes of the polypyridine ligands 2,2'-bipyridine (bpy) and 1,10-phenanthroline (phen) is common.<sup>1</sup> However, complexes of the closely related 2,2',2''-terpyridine (trpy) ligand either exhibit weak or no luminescence in fluid solutions at room temperature.<sup>2†</sup> Where data are available for MLCT-based luminescence, e.g. Ru(trpy)<sub>2</sub><sup>2+</sup><sup>2</sup> and Os(trpy)<sub>2</sub><sup>2+</sup>,<sup>3</sup> and for d-d luminescence, e.g. Cr(trpy)<sub>2</sub><sup>2+</sup>,<sup>4</sup> excited-state lifetimes have been found to be short (typically less than 100 ns).<sup>‡</sup> It has been suggested that the lack of luminescence is due to extremely rapid non-radiative processes. The origins of

† An apparent exception is an Ir<sup>III</sup>-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)<sub>2</sub><sup>2+</sup> complex (tsite = 4,4',4''-triphenyl-2,2',2''-terpyridine) with  $\tau$  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<sup>5</sup> 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.<sup>6</sup>

We have prepared a series of mixed-ligand, monoterpyridine complexes of Os<sup>II</sup> which contain strong-field chelating ligands such as *cis*-Ph<sub>2</sub>PCH=CHPh<sub>2</sub> (dppe) and Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub> (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



Reagents: i, Heat, H<sub>2</sub>O-ethylene glycol.

material Os<sup>III</sup>(trpy)Cl<sub>3</sub>.<sup>7</sup> Purification of the products, which were isolated as PF<sub>6</sub><sup>-</sup> salts, was achieved by non-aqueous chromatographic methods which have been previously described.<sup>8</sup>

That the emission is π\*(trpy) → dπ(Os) in character is suggested by the earlier assignment made for Os(trpy)<sub>2</sub><sup>2+</sup>.<sup>3</sup> 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<sub>1/2</sub>(Os<sup>III/II</sup>) - E<sub>1/2</sub>(trpy/trpy)] (see the Table). It should be noted, however, that the emission for [Os(trpy)(dppe)CO]<sup>2+</sup> could be ligand-localized, π\* → π, since the luminescence maximum of the complex is nearly co-incidental with that for the π\* → π phosphorescence from [trpy<sup>+</sup>].<sup>9</sup> The Figure shows typical absorption and emission spectra for two of the new complexes.

Estimations of excited-state redox potentials for the complexes have been made from spectral data using the procedure suggested by Balzani *et al.*<sup>1b</sup> (see the Table). A comparison of potentials of the excited states as oxidants, M<sup>II\*</sup> + e → M<sup>I</sup>, between [Os(trpy)(dppm)<sub>2</sub><sup>2+</sup>]<sup>\*</sup> (1.10 V), which contains both chelate and monodentate dppm-ligands,

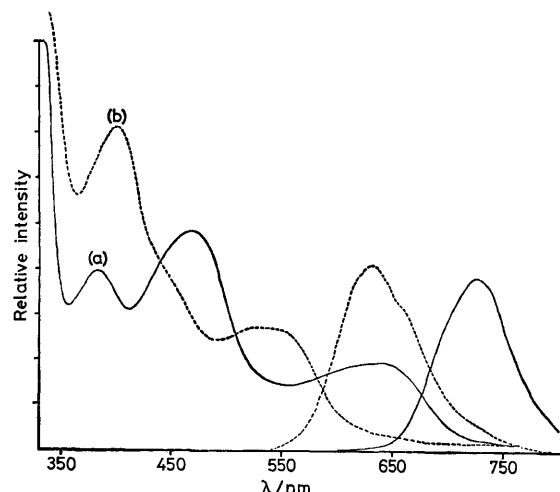
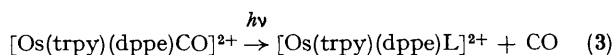


FIGURE. Absorption and emission spectra of (a) [Os(trpy)(dppm)Cl](PF<sub>6</sub>) and (b) [Os(trpy)(dppe)MeCN](PF<sub>6</sub>)<sub>2</sub>, taken in an oxygen-saturated MeCN solution at room temperature.

and [Ru(bpy)<sub>3</sub><sup>2+</sup>]<sup>\*</sup> (0.80 V)<sup>10</sup> 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<sup>II</sup> complexes shown in the Table, except the chloro-complexes [Os(trpy)(diphosph)Cl]<sup>+</sup>, are photolabile, as shown in equation (3).



Photochemical substitution is not an important reaction for related complexes of the type (phen)<sub>2</sub>OsL<sub>2</sub><sup>2+</sup> or (bpy)<sub>2</sub>-OsL<sub>2</sub><sup>2+</sup>.<sup>1a,11</sup> This observation suggests a possible origin for the relatively short-lived excited-state lifetimes found for trpy-complexes (at least for Ru<sup>II</sup> and Os<sup>II</sup>). For Ru(bpy)<sub>3</sub><sup>2+</sup> photosubstitution appears to occur from a d-d state which is thermally accessible after population of the low-energy MLCT excited-states.<sup>12</sup> For the trpy-complexes the symmetry is lower and significant deviations in ligand-metal-ligand angles compared with the angles of an octahedron exist.<sup>6,13</sup> One effect of the ligand-imposed distortion from octahedral symmetry is a mixing of the e<sub>g</sub>- and t<sub>2g</sub>-type d-orbitals. Mixing of e<sub>g</sub>-t<sub>2g</sub> orbitals could lead to the

TABLE. Spectral and electrochemical properties of the (trpy)Os<sup>III</sup> complexes.

(trpy)OsR, R	E <sub>1/2</sub> <sup>ox</sup> /V <sup>a,b</sup>	E <sub>1/2</sub> <sup>red</sup> /V <sup>a,c</sup>	λ <sub>abs</sub> /nm <sup>d</sup>	λ <sub>em</sub> /nm <sup>d</sup>	τ <sub>o</sub> /ns <sup>e</sup>	E <sub>ox</sub> <sup>*</sup> /V <sup>f</sup>	E <sub>red</sub> <sup>*</sup> /V <sup>g</sup>
(Ph <sub>2</sub> PCH=CHPh <sub>2</sub> )Cl <sup>+</sup>	0.96	-1.18	624	712	101	+0.66	-0.88
(Ph <sub>2</sub> PCH <sub>2</sub> PPh <sub>2</sub> )Cl <sup>+</sup>	0.93	-1.18	632	725	99	+0.65	-0.89
(Ph <sub>2</sub> PCH=CHPh <sub>2</sub> )py <sup>2+</sup>	+1.41	-0.99	570	653	455	+1.01	-0.56
(Ph <sub>2</sub> PCH=CHPh <sub>2</sub> )MeCN <sup>2+</sup>	+1.43	-1.01	553	629	43	+1.06	-0.64
(Ph <sub>2</sub> PCH <sub>2</sub> PPh <sub>2</sub> ) <sup>2+</sup>	+1.70 <sup>c</sup> , 1.42	-0.99	409	622	768	+1.10	-0.39
(Ph <sub>2</sub> PCH=CHPh <sub>2</sub> )CO <sup>2+</sup> <sup>h</sup>	> 1.9	-0.95	1	529	26	+1.49	< -0.54

<sup>a</sup> Measured in MeCN solution with 0.1M tetraethylammonium perchlorate as supporting electrolyte. <sup>b</sup> Reversible potential; E<sub>1/2</sub> = (E<sub>p,a</sub> + E<sub>p,c</sub>)/2. <sup>c</sup> Irreversible peak potential at half current, E<sub>p/2</sub>. <sup>d</sup> Measured in MeCN solution, air saturated; the wavelength is of maximum absorption or emission. <sup>e</sup> Measured in MeCN solution, N<sub>2</sub> saturated. <sup>f</sup> 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<sup>II\*</sup> + e → M<sup>I</sup>. <sup>g</sup> As in footnote f; the potential refers to: M<sup>III</sup> + e → M<sup>II\*</sup>. <sup>h</sup> ν(CO) in a KBr pellet is found at 1996 cm<sup>-1</sup>; footnote b does not apply. <sup>i</sup> No distinct visible absorption maximum.

§ 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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