

Ruthenium and Osmium Complexes of 2,2' : 6',2''-Terpyridine Covalently Linked to Electron Acceptor and Electron Donor Groups

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2,2' : 6',2''-Terpyridine ligands have been modified so as to bear an electron acceptor or an electron donor group; efficient intramolecular vectorial electron transfer has been shown to occur in an osmium complex from its metal-to-ligand charge transfer excited state.

Several examples of chromophores attached to an electroactive quencher have been described, leading to directed charge transfer. Besides porphyrin systems bearing an electron acceptor,¹ devices based on metal-to-ligand charge transfer (MLCT) excited states have recently been proposed.²⁻⁵ A

particularly promising extension is that of ternary systems consisting of a photoactive centre (PC) linked to both an electron acceptor (A) and an electron donor (D).⁶⁻⁸ Strict control over the geometry of the system is necessary in order to avoid intramolecular recombination between D⁺ and A⁻

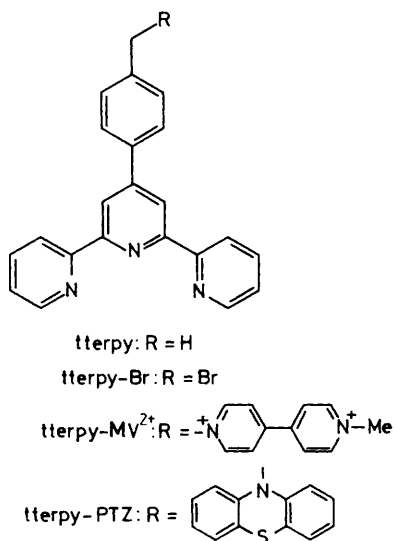
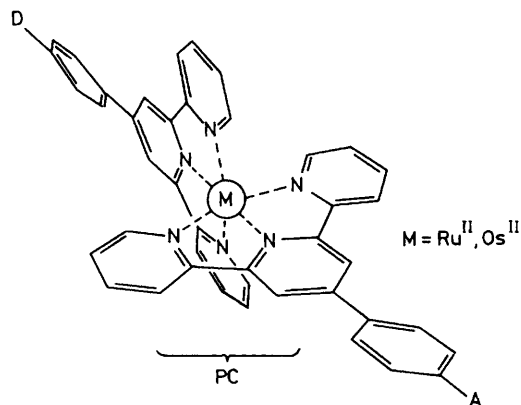


Figure 1

after photoinduced charge separation. Tris-2,2'-bipyridine complexes cannot easily be modified to afford a linear disposition of D, PC, and A,⁸ whereas the geometry of bis-terpy complexes⁹ seems to be ideally adapted to a vectorial electron transfer leading to D⁺-PC-A⁻ (Figure 1). In addition, 2,2':6',2''-terpyridine (terpy) derivatives bearing an aromatic ring at the central position 4' are readily accessible¹⁰ and some ruthenium(II) or, better, osmium(II) complexes of terpy have recently been described as electron transfer agents in their MLCT excited state.¹¹



We now report the synthesis of terpy ligands covalently linked either to an *N,N'*-dialkyl-4,4'-bipyridinium group (A) or to a phenothiazine ring (D) as well as the preparation (PF₆⁻ salts) and electro- and photo-chemical properties of several of their ruthenium(II) and osmium(II) complexes.

The ligands and tterpy-Br were synthesized by a modified literature method.^{10c-d} tterpy-MV²⁺ (MV²⁺ = *N,N'*-dimethyl-4,4'-bipyridinium²⁺) was obtained from tterpy-Br and *N*-methyl-(4-pyridyl)-pyridinium iodide (60% yield, refluxing ethanol for a week). tterpy-PTZ (PTZ = 10-methylphenothiazine) was made by the reaction of tterpy-Br with the sodium salt of phenothiazine anion (tetrahydrofuran, room temperature overnight, 60% yield).

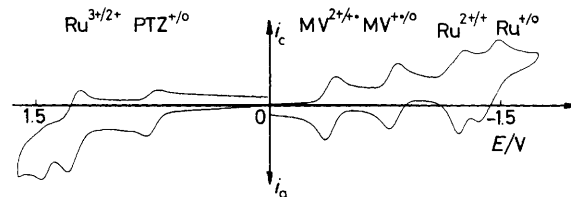


Figure 2. Cyclic voltammogram of [Ru(tterpy-MV²⁺)(tterpy-PTZ)]⁴⁺ in MeCN/0.1 M Bu₄NClO₄ at a glassy carbon electrode; scan rate = 100 mV s⁻¹. The ruthenium oxidation states I and 0 are only formal.

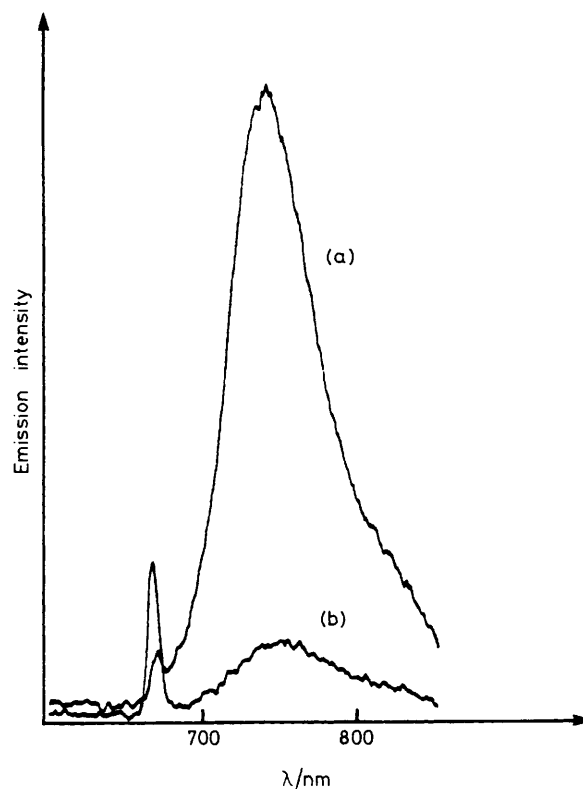


Figure 3. Emission spectra in degassed MeCN at room temperature. (a) Os(tterpy)₂²⁺, (b) [Os(tterpy)(tterpy-MV²⁺)]⁴⁺. Excitation wavelength = 667 nm (sharp peak in spectrum b); each complex is 5.0 × 10⁻⁵ M.

The reference complexes M(tterpy)₂²⁺ (M = Ru, Os) were prepared from MCl₃·3H₂O and tterpy in refluxing ethylene glycol in 63 and 70% yield respectively. [Ru(tterpy)(tterpy-MV²⁺)]⁴⁺ and the triad [Ru(tterpy-MV²⁺)(tterpy-PTZ)]⁴⁺ were obtained following a statistical method by the reaction of a 1:1 mixture of the ligands (tterpy + tterpy-MV²⁺ or tterpy-MV²⁺ + tterpy-PTZ) with a stoichiometric amount of ruthenium blue¹² (refluxing MeOH) in 25 and 5% yield respectively. The diads [Os(tterpy)(tterpy-MV²⁺)]⁴⁺ and Os(tterpy)(tterpy-PTZ) were synthesized from Os(tterpy)Cl₃ in the presence of stoichiometric amounts of the corresponding ligand (tterpy-MV²⁺ or tterpy-PTZ; ethanol/H₂O/triethylamine 90:9:1 under reflux) in 30 and 56% yield respectively. The complexes prepared were purified by column chromatography (silica, 0.1 M KNO₃ in MeCN/H₂O 10:1 as eluant).

All new compounds have been characterized by u.v.-visible and ¹H n.m.r. spectroscopy (200 MHz). They gave satisfactory elemental analyses.

Table 1. Redox potentials of osmium complexes.^a

	Os ^{III} /Os ^{II}	PTZ ⁺ /PTZ ⁰	MV ²⁺ /MV ⁺	MV ⁺ /MV ⁰	Os ^{II} /Os ^I ^b	Os ^I /Os ⁰ ^b
Os(terpy) ₂ ²⁺	+0.90	—	—	—	-1.20	-1.45
[Os(terpy)(terpy-MV ²⁺)] ⁴⁺	+0.90	—	-0.35	-0.75	-1.20	-1.45
Os(terpy)(terpy-PTZ) ²⁺	+0.90	+0.75	—	—	-1.20	-1.45

^a Cyclic voltammetry measurements on glassy carbon as working electrode in MeCN, V vs. standard calomel electrode (SCE); Bu₄NClO₄ (0.1 M) as supporting electrolyte; scan rate = 100 mV s⁻¹. ^b The osmium oxidation states I and 0 are only formal.

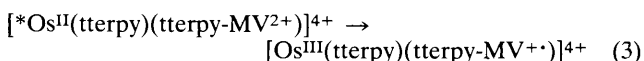
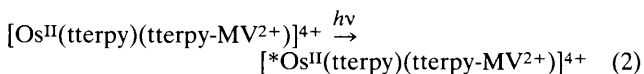
The fast atom bombardment (FAB) mass spectrum of [Ru(terpy-MV²⁺)(terpy-PTZ)]⁴⁺ was also measured and was consistent with the structure of the complex. The cyclic voltammogram of the compound is represented in Figure 2. It shows clearly all the redox processes localized on the various electroactive components. Unfortunately, bis-terpy ruthenium(II) and analogous complexes are non-emissive at room temperature¹³ so that comparative studies require detailed photophysical analysis.¹⁴

The electrochemical properties of the three osmium complexes reported are presented in Table 1.

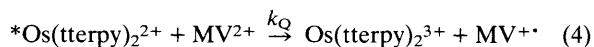
As for the ternary ruthenium complex [Ru(terpy-MV²⁺)(terpy-PTZ)]⁴⁺, each electroactive component of the complexes of Table 1 corresponds to a distinct one-electron redox process at a potential similar to that of the corresponding isolated species: MV²⁺, Os(terpy)₂²⁺, or PTZ (A-PC-D). Noteworthy is the fact that the MLCT excited state of the bis-terpyridine derivative Os^{II} complex is sufficiently reducing to transfer an electron to the accepting part (MV²⁺) of terpy-MV²⁺.¹¹ In addition the trivalent osmium complex should readily be reduced by the donor subunit (PTZ) of terpy-PTZ.

Evidence for photoinduced intramolecular electron transfer within the binary compound Os(terpy)(terpy-PTZ)²⁺ was obtained by emission measurements. The emission spectra of Os(terpy)₂²⁺ and [Os(terpy)(terpy-MV²⁺)]⁴⁺ are depicted in Figure 3.

The emission quantum yield for Os(terpy)₂²⁺ is 10 times larger than that for [Os(terpy)(terpy-MV²⁺)]⁴⁺. In view of the redox potential value of the Os^{III}*/Os^{II} couple for analogous complexes,¹¹ the intramolecular quenching reaction is due to electron transfer [reactions (2) and (3)].



For comparison purposes, the bimolecular quenching reaction (4) of *Os(terpy)₂²⁺ by MV²⁺ was studied in MeCN. Stern-Volmer plots gave a k_Q value of 5 × 10⁸ dm³ mol⁻¹ s⁻¹ [assuming an excited state lifetime for *Os(terpy)₂²⁺ of 300 ns^{11,14}].



In fact, the intermolecular deactivation contribution to the quenching process observed for [Os(terpy)(terpy-MV²⁺)]⁴⁺ is negligible under the conditions of Figure 2. The efficient electron transfer observed within the binary compound [Os^{II}(terpy)(terpy-MV²⁺)]⁴⁺ indicates that the hypothetical triad species [Os^{II}(terpy)(terpy-PTZ)]⁴⁺ may undergo interesting photoinduced intramolecular charge separation.

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