A Covalently Linked Photosensitizer/Electron Acceptor Complex derived from Ruthenium Tris(bipyridine) and Diquat

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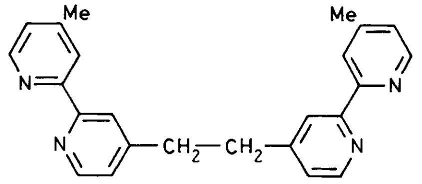
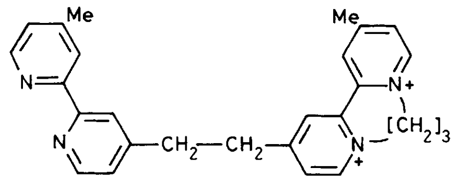
A non-luminescent ruthenium tris(bipyridyl) complex containing a covalently attached diquat electron acceptor has been prepared, and its electrochemical, spectroelectrochemical, and photochemical properties have been investigated.

A dimer of 4,4′-dimethyl-2,2′-bipyridine, (**1**), has been prepared and modified by conversion of one of the linked bipyridines into an *N,N′* bridged diquaternary salt (diquat, DQ), an electron acceptor with properties similar to those of paraquat. By reaction of the resulting ligand, Mebpy-3DQ^{2+}, (**2**), with Ru(bpy)$_2$Cl$_2$ (bpy = 2,2′-bipyridine), the unusual mixed-ligand complex, [Ru(bpy)$_2$(Mebpy-3DQ^{2+})]$^{4+}$, (**3**), has been obtained. Thus, an inert covalent linkage between a ruthenium tris(bipyridyl) photosensitizer and an electron acceptor has been achieved. This complex is nonluminescent; efficient intramolecular electron transfer from the Ru(bpy)$_3$$^{2+}$ excited state to the diquat electron acceptor accounts for the emission quenching.



(**1**)



(**2**)

[Ru(bpy)$_2$(Mebpy-3DQ^{2+})]$^{4+}$

(**3**)

Cyclic voltammograms of (**2**) and (**3**) are shown in Figure 1. The electrochemistry of the ligand (**2**) is characterized by two reversible one-electron reductions, corresponding to reduction of the diquat to its radical cation [$E_{1/2}$ −0.65 V *vs.* saturated calomel electrode (s.c.e.)] then to the neutral species ($E_{1/2}$ −0.89 V). Reduction of the free bipyridine part of (**2**) occurs with $E_{1/2}$ −2.16 V. The shape of the wave and its scan rate dependence indicate an EC mechanism for this bipyridine reduction. For the ruthenium complex (**3**) five

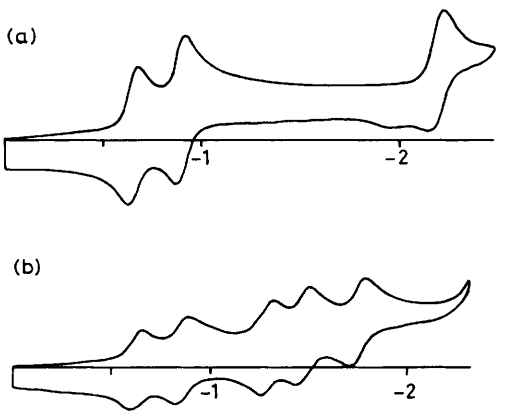


Figure 1. Cyclic voltammograms of (a) $(\mathbf{2})(\mathrm{PF_6})_2$ and (b) $(\mathbf{3})(\mathrm{PF_6})_4$ in dimethylformamide, 0.1 M tetrabutylammonium hexafluorophosphate, glassy carbon electrode. Potentials are *vs.* s.c.e.

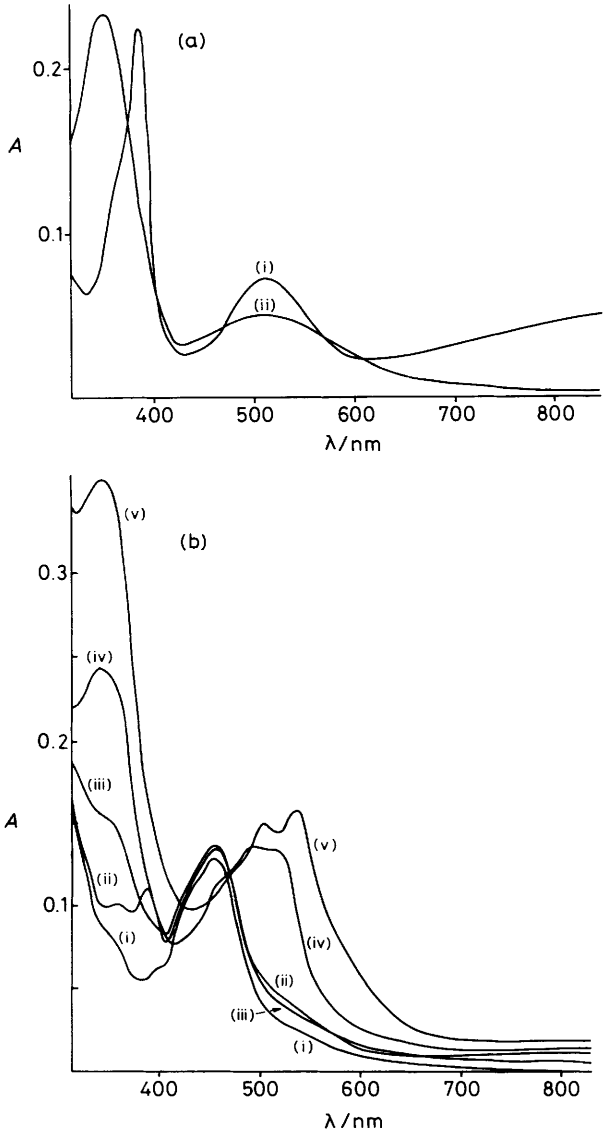


Figure 2. Visible absorption spectra of (a) 3.0×10^{-3} M Mebpy-3DQ^{n+}; (i) $n = 1$ (-0.75 V); (ii) $n = 0$ (-1.40 V). (b) 1.5×10^{-3} M $[\mathrm{Ru(bpy)_2(Mebpy\text{-}3DQ^{n+})}]^{m+}$; (i) $n = 2, m = 4$ (0 V); (ii) $n = 1, m = 3$ (-0.75 V); (iii) $n = 0, m = 2$ (-1.08 V); (iv) $n = 0, m = 1$ (-1.38 V); (v) $n = 0, m = 0$ (-1.64 V).

reversible, one-electron reductions are observed. The diquat reductions are shifted slightly anodically relative to the free ligand (-0.63 and -0.86 V, respectively). The three ruthenium tris(bipyridyl)-based reductions occur at $E_{1/2}$ -1.29, -1.47, and -1.75 V, very close to those values reported for reduction of unsubstituted $\mathrm{Ru(bpy)_3^{2+}}$.[1] The potential of the $\mathrm{Ru^{2+}/Ru^{3+}}$ couple for the mixed ligand complex ($E_{1/2}$ $+1.24$ V) is identical to that reported for $\mathrm{Ru(bpy)_3^{2+}/Ru(bpy)_3^{3+}}$.[1]

Visible absorption spectra of the reduced species of (**2**) and (**3**) were obtained by spectroelectrochemistry using an optically transparent thin layer electrochemical (OTTLE) cell (Figure 2). The diquat radical cation exhibits a sharp absorption at 387 nm (ε 14 500), a broad peak at 514 nm (4 400) and a very broad absorption with $\lambda_{\mathrm{max.}}$ 800 nm. These peaks can be superimposed on the characteristic $\mathrm{Ru(bpy)_3^{2+}}$ spectrum ($\lambda_{\mathrm{max.}}$ 456 nm) in the spectrum of the first one-electron reduction product of (**3**), $[\mathrm{Ru(bpy)_2(Mebpy\text{-}3DQ^{+})}]^{3+}$. Spectra of the reduced species $[\mathrm{Ru(bpy)_2(Mebpy\text{-}3DQ^{0})}]^{+}$ and $[\mathrm{Ru(bpy)_2(Mebpy\text{-}3DQ^{0})}]^{0}$ are very similar to those reported for $\mathrm{Ru(bpy)_3^{+}}$ and $\mathrm{Ru(bpy)_3^{0}}$.[2]

The photochemistry of (**3**) in the presence of triethanolamine, a sacrificial electron donor, has been investigated. Irradiation of a degassed solution of this complex in acetonitrile–water containing triethanolamine (10% by volume) results in spectral changes corresponding to a build-up of the diquat radical cation.† The absorption spectrum of the irradiated sample in the wavelength range 370—800 nm is the same as that of the complex following chemical reduction of the diquat with sodium hydrosulphite. Thus, the reduction of $\mathrm{Ru^{3+}}$ by triethanolamine can compete with the back electron transfer from the diquat radical cation, allowing the reduced diquat to accumulate in solution.

The use of linked electron donor–acceptor molecules is becoming increasingly important in the understanding of electron transfer processes.[3] The system described here promises to be extremely useful owing to the ease with which the properties of the components can be varied. By adding substituents to the bipyridine ligands, varying the length of the diquat carbon bridge, and changing the nature of the bipyridine dimer, it will be possible to tune the redox potentials of the electron donor and acceptor, and to change the distance and orientation between them.

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† Irradiation of the samples was conducted using polychromatic visible light from a standard projector bulb. No attempt was made here to measure efficiencies or quantum yields of the electron transfer quenching process except to note a total lack of luminescence for the complex. Also, neither the free ligand (**2**) nor its tris iron(II) complex produce reduced diquat products when irradiated under identical conditions, thus indicating the necessary role of the $\mathrm{Ru(bpy)_3}$ moiety in $\mathrm{DQ^+}$ product production.