A new redox-tunable near-IR dye based on a trinuclear ruthenium(II) complex of hexahydroxytriphenylene

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The complex $[\{Ru(bipy)_2\}_3(\mu^3\text{-}L)]^{3+}$ (H_6L = hexahydroxytriphenylene), in which the tris-dioxolene bridging ligand is formally in the tris-semiquinone oxidation state [sq,sq,sq], undergoes three reversible ligand-centred oxidations to the [q,q,q] state (q = quinone); it exhibits very strong NIR absorption arising from Ru → L charge transfer whose maximum wavelength may be tuned over a wide range according to oxidation state.

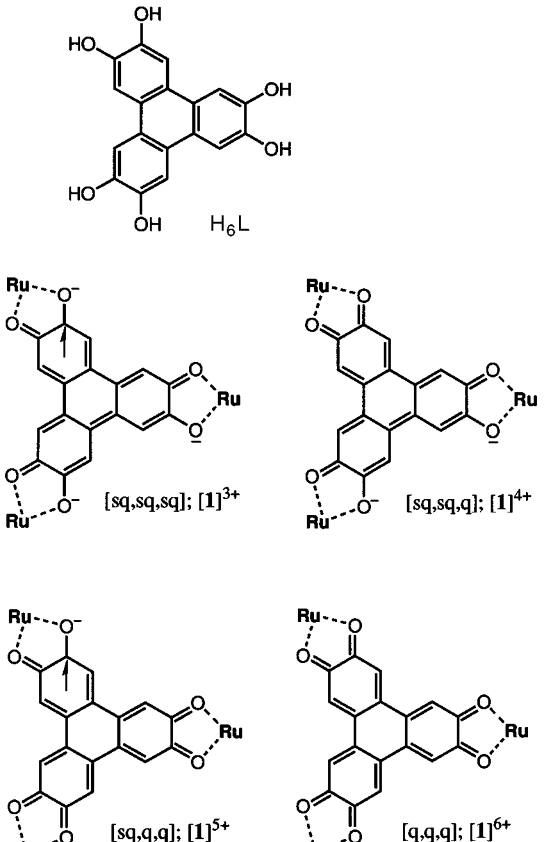
Compounds which absorb light strongly in the near IR (NIR) region of the spectrum have numerous potential applications, including (i) optical data storage devices, in which reading and writing is performed by diode lasers; (ii) Q-switching of lasers, whereby continuous low-energy output in the NIR region is converted to very short, intense bursts; and (iii) photodynamic therapy, which takes advantage of the relative transparency of living tissue to NIR radiation.[1] Prominent examples of such compounds include nickel(II)–dithiolene complexes[2] and extended quinones.[3] If the strong NIR absorption is not permanent but may be switched on by some external perturbation, then the compound is of additional interest as a switchable electrochromic dye; such compounds are relatively rare.[4]

The simple complex $[Ru(bipy)_2(sq)]^+$ (bipy = 2,2′-bipyridine; sq = 1,2-benzosemiquinone monoanion) is of potential interest in this regard, having a NIR transition at about 900 nm (ε *ca.* 10^4 dm^3 mol^{-1} cm^{-1}) arising from a $Ru[d_\pi] \rightarrow sq(\pi^*)$ MLCT process.[5] It undergoes ligand-centred redox behaviour, being oxidised to $[Ru(bipy)_2(q)]^{2+}$ (q = 1,2-benzoquinone) and reduced to $[Ru(bipy)_2(cat)]$ (cat = catecholate dianion), in both of which forms this NIR transition is absent.[5] We have recently been interested in the electrochemical and spectroscopic properties of dinuclear complexes in which two such Ru(II) fragments are linked by bridging ligands containing two dioxolene termini.[6] We describe here the synthesis, electrochemical and UV–VIS–NIR properties of $[\{Ru(bipy)_2\}_3(\mu\text{–}L)]^{n+}$ ($\mathbf{1}^{n+}$, n = 3–6) in which three such redox-active Ru(II) fragments are linked in a triangular array by the bridging ligand hexahydroxytriphenylene (H_6L).[7] Spectroelectrochemical analysis in four oxidation states reveals an exceptionally strong absorbance in the NIR region which may be tuned over a wide range according to oxidation state.

Reaction of hexahydroxytriphenylene[7] with 3 equiv. of $[Ru(bipy)_2(OH_2)_2]^{2+}$ (ref. 8) in refluxing ethanol–water–KOH at reflux in air for 2 h, followed by precipitation of the complex with NH_4PF_6 and chromatographic purification (alumina; CH_2Cl_2–MeOH, 19 : 1 v/v), afforded in 50% yield $[\mathbf{1}][PF_6]_3$ (Scheme 1) as a black solid. Characterisation was on the basis of FAB mass spectrometry [m/z 1848 {70%, $M - PF_6$}, 1703 {100%, $M - 2PF_6$}] and a satisfactory elemental analysis. The +3 charge implies that each of the three dioxolene fragments is in the semiquinone oxidation level (denoted sq-sq-sq) following synthesis in air, which is to be expected.[5,6] Individual $\{Ru(bipy)_2(sq)\}^+$ units have one unpaired electron on the semiquinone ligand, but when two such units are linked in a *para* substitution pattern by a suitable conjugated bridge, the two electrons pair up to give diamagnetic dinuclear complexes with formation of an additional π-bond resulting in a quinonoidal bridging ligand.[6] In $[\mathbf{1}]^{3+}$ any two of the semiquinone sites can be spin-paired, resulting in a monoradical.†

Cyclic and square-wave voltammetry of $[\mathbf{1}][PF_6]_3$ was performed in MeCN. If each dioxolene site showed the expected cat/sq and sq/q interconversions characteristic of mononuclear $[Ru(bipy)_2(sq)]^+$ then we would expect to see six redox processes linking seven oxidation states of the bridging ligand ranging from [cat,cat,cat] to [q,q,q]. Six waves were indeed observed, whose potentials (from a square-wave voltammogram) are +0.66, +0.36, −0.03, −0.43, −0.70 and −0.97 V *vs.* ferrocene–ferrocenium. The approximately constant and quite substantial spacing between these redox potentials is to be expected given the proximity of the dioxolene sites to one another.[6] Of these six processes only the first four appeared fully reversible (equal cathodic and anodic peak currents, ΔE_p 60–80 mV) by cyclic voltammetry using a Pt-wire working electrode (Fig. 1); the two processes at most negative potentials showed stripping peaks on the return waves, characteristic of absorption on the Pt electrode surface after generation of the [cat,sq,sq] and more reduced oxidation states. Despite this it is apparent that all seven oxidation states are in principle accessible.

We therefore subjected $[\mathbf{1}][PF_6]_3$ to a spectroelectrochemical study in an OTTLE cell (MeCN, −30 °C) spanning the oxidation states sq,sq,sq ($\mathbf{1}^{3+}$), sq,sq,q ($\mathbf{1}^{4+}$), sq,q,q ($\mathbf{1}^{5+}$) and q,q,q ($\mathbf{1}^{6+}$). For all three interconversions clean isosbestic points



Scheme 1 **Ru** ≡ $\{Ru(bipy)_2\}^{2+}$.

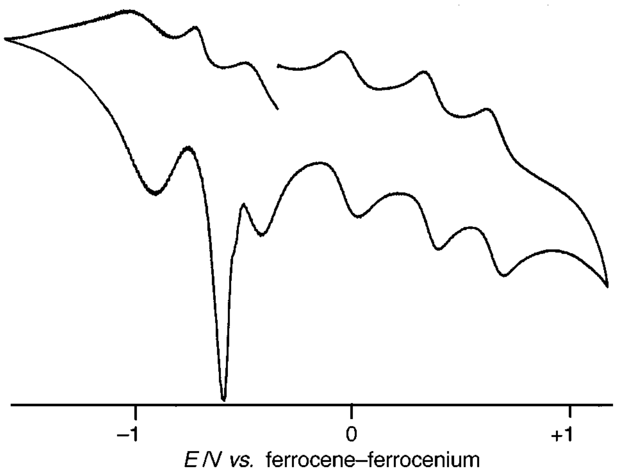


Fig. 1 Cyclic voltammogram of [**1**]$^{3+}$ in MeCN, showing the stepwise interconversions between the [cat,cat,cat] and [q,q,q] states of the bridging ligand. Only the three most positive processes, from [sq,sq,sq] to [q,q,q], are fully reversible at a Pt electrode.

were observed, and after the final oxidation to [**1**]$^{6+}$, re-reduction regenerated exactly the spectrum of the starting [**1**]$^{3+}$. The results (Fig. 2) show that (i) the redox chemistry is indeed ligand-centred, and (ii) the complex has exceptionally strong absorption in the near-IR region whose absorption maximum varies monotonically with oxidation state. It is helpful to recall that for mononuclear [Ru(bipy)$_2$(sq)]$^+$, the MLCT transition at 900 nm shifts to *ca.* 640 nm on oxidation to [Ru(bipy)$_2$(q)]$^{2+}$.[5] For [**1**]$^{3+}$, the MLCT transition involving the delocalised [sq,sq,sq] bridging ligand occurs at 1170 nm (ε = 40 000 dm^3 mol^{-1} cm^{-1}). As the ligand is oxidised in steps to the [sq,sq, q], then [sq,q,q] and finally [q,q,q] oxidation states this absorption maximum moves in steps to 1083 (ε = 74 000), 909 (ε = 32 000) and finally 759 nm (ε = 50 000 dm^3 mol^{-1} cm^{-1}). The 'mixed-valence' [sq,sq,q] and [sq,q,q] states must therefore be delocalised, because a single transition at a 'weighted average' position occurs in each case rather than two separate transitions characteristic of distinct sq and q sites in the bridging ligand. These transitions are remarkably intense and broad: the absorption coefficients of 32 000–74 000 dm^3 mol^{-1} cm^{-1} are comparable to those of commercially useful NIR dyes,[1,2] and the lower-energy three transitions have long low-energy tails (extending to 1700 nm and over) such that in these oxidation states the molecule is effectively a panchromatic NIR absorber. This complex therefore shows an unusual combination of very strong NIR absorbance and tunability of the absorption maximum over a wide range using four readily accessible oxidation states.

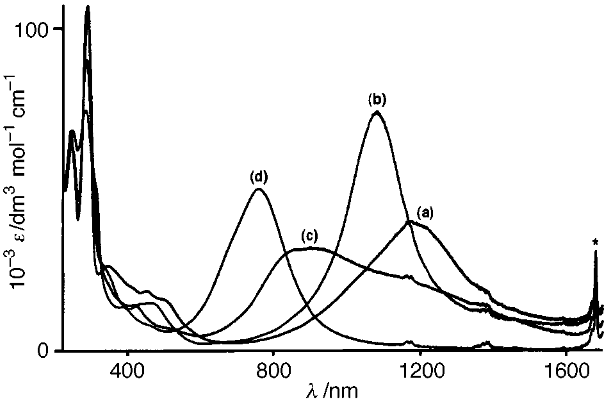


Fig. 2 Electronic spectra of (a) [**1**]$^{3+}$, (b) [**1**]$^{4+}$, (c) [**1**]$^{5+}$ and (d) [**1**]$^{6+}$ (MeCN, −30 °C); * denotes a solvent-based IR overtone.

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Notes and references

† That [**1**][PF$_6$]$_3$ is a monoradical and not a triradical was confirmed both experimentally and theoretically. An EPR spectrum (frozen MeCN solution, 77 K) has a near-symmetric signal at g = 2.017 characteristic of a semiquinone-based monoradical with no evidence for Δm_s = 2 or Δm_s = 3 transitions. A MOPAC calculation on [L]$^{3-}$ in the [sq,sq,sq] state showed that the three frontier orbitals involved in conversion between the [cat,cat,cat] and [q,q,q] states are non-degenerate, such that the [sq,sq,sq] state (as well as the [sq,q,q] and [sq,cat,cat] states) are monoradicals, whilst the others are diamagnetic, as in Scheme 1.

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