Electrochemical Control of Bridging Ligand Conformation in a Binuclear Complex—A Possible Basis for a Molecular Switch

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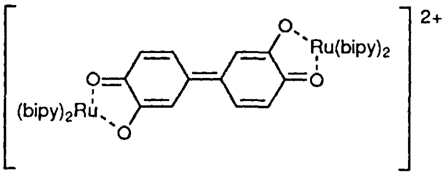
Reaction of the binucleating bridging ligands 3,3',4,4'-tetrahydroxybiphenyl (H_4L^1) or 3,3'',4,4''-tetrahydroxy-*p*-terphenyl (H_4L^2) with 2 equivalents of [Ru(bipy)$_2$Cl$_2$]·2H$_2$O (bipy = 2,2'-bipyridine) results in the formation of binuclear complexes [{Ru(bipy)$_2$}(μ-L){Ru(bipy)$_2$}]$^{2+}$ **1** (L = L^1) and **2** (L = L^2) in which the ligand L^{4-} has been oxidized to the semiquinone (sq) form L^{2-}. In each complex the co-ordinated catecholate fragment (cat) may be oxidised reversibly to the semiquinone and quinone (q) redox states, giving the five-membered redox series cat–cat, cat–sq, sq–sq, sq–q and q–q for the bridging ligands. In the sq–sq state the bridging ligands are necessarily planar due to the presence of double bonds between the aromatic rings; in the cat–cat and q–q states there is formally no double-bond character between the aromatic rings and they are free to adopt a twisted conformation. Spectroelectrochemical measurements confirm that in the cat–cat and q–q states, **1** and **2** behave approximately like their mononuclear counterparts [Ru(bipy)$_2$(cat)] and [Ru(bipy)$_2$(bq)]$^{2+}$ [H$_2$cat = catechol (benzene-1,2-diol); bq = *o*-benzoquinone]; for **1**, the results also show that in the mixed-valence sq–q and sq–cat oxidation states the two halves of the ligand are electronically equivalent (*i.e.* valence delocalised), which is best explained by the bridging ligand retaining the planar conformation of the sq–sq state. The change from planar to twisted therefore occurs at the extremes of the redox series, on formation of the cat–cat and q–q oxidation states. This control of bridging ligand conformation with oxidation state may form the basis for a molecular switch.

The challenge facing synthetic chemistry in the area of molecular electronics is to prepare molecules with specific, well-defined functions (*e.g.* wire, switch, diode); controlled assembly of selected components into 'supramolecular' species will then permit the preparation of nanometre-sized devices with sophisticated electronic properties.[1] Molecular wires permit either long-distance electron transfer or interaction between remote components.[2] A more sophisticated function is that of a switch, which is a molecular wire with the additional property that its state of conductivity may be varied, reversibly and controllably, by some external mechanism such as photochemical isomerism[3] or metal-ion binding.[4,5]

We describe herein the preparation, electrochemical and spectroelectrochemical properties of the binuclear complexes **1** and **2**, based on the bis-catechol ligands 3,3',4,4'-tetrahydroxybiphenyl (H_4L^1) and 3,3'',4,4''-tetrahydroxy-*p*-terphenyl (H_4L^2), in which the oxidation state of the bridging ligands may be varied reversibly over a five-member redox series. When co-ordinated to a Ru(bipy)$_2^{2+}$ fragment (bipy = 2,2'-bipyridine) each catecholate (cat) group may be oxidised in reversible, one-electron steps to a semiquinone (sq) and then a quinone (q).[6] The bridging ligands can therefore in principle exist in five oxidation states (Scheme 1, L^1 system) which we denote cat–cat, cat–sq, sq–sq, sq–q and q–q and are related by one-electron transfers. In the sq–sq state the pairing of the odd electrons of the semiquinone radicals constrains the ligands to be planar by forming double bonds between the aromatic rings.[7] In the extreme cat–cat and q–q states there is no double bond between the rings and they are free to rotate to the extent permitted by steric hindrance and other external factors; the dihedral twist angle of biphenyls has been estimated to be about 45° in the gas phase but only 32° in solution,[8] and in the solid state crystal-packing forces can reduce the dihedral angle further.[9]



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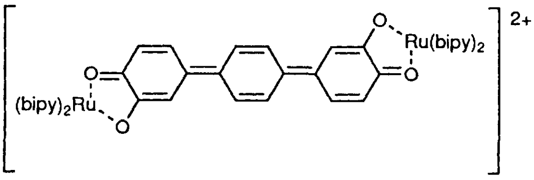

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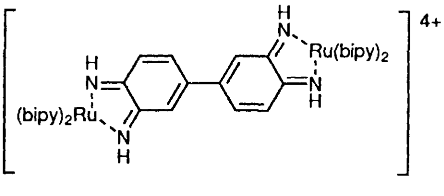
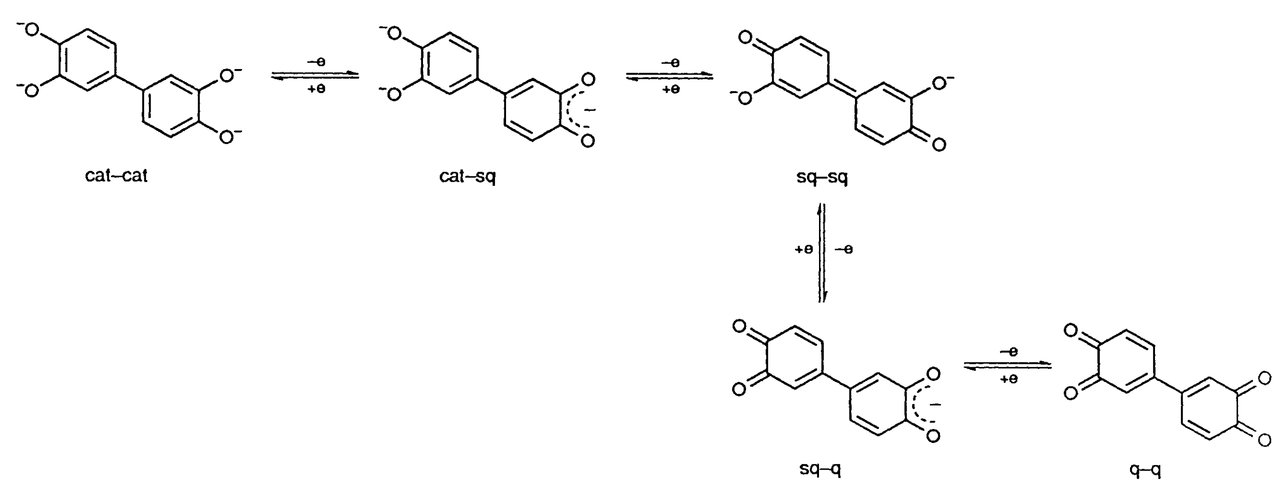


3

The geometry of the intermediate cat–sq and sq–q states is not, at the outset, clear.

Changing the redox level of the bridging ligands will therefore affect both the degree of conjugation in the bridge and the twist angle of the polyphenylene chain. Since the dihedral angle is



Scheme 1

known to affect rates of electron-transfer through molecular wires containing biphenyl groups,[10] the ability to control this parameter electrochemically would clearly be useful and would form the basis of a molecular switch. In the same vein a spectroelectrochemical study of the similar complex **3** was reported recently;[11] the properties of **1** and **2** described here show some significant differences from those of **3**.

Experimental

Instrumentation used for the spectroscopic, electrochemical and spectroelectrochemical measurements has been described elsewhere.[12] Reagents were purchased from Aldrich and used as received. Reaction solvents were, where necessary, dried by standard methods before use.

Syntheses.—3,3′,4,4′-*Tetramethoxybiphenyl*. This compound was prepared in 70% yield by homocoupling of 4-bromoveratrole with a nickel(0) catalyst in thf exactly according to a published procedure[13] and purified by chromatography on SiO_2 with CH_2Cl_2 as eluent. The ^1H NMR and mass spectroscopic properties for the compound prepared this way were identical to those reported earlier.[14]

3,3″,4,4″-*Tetramethoxy*-p-*terphenyl*. A solution of 3,4-$(MeO)_2C_6H_3MgBr$ [prepared by reaction of 4-bromoveratrole (2.38 g, 11 mmol) and Mg turnings (0.3 g, 12 mmol) in thf (15 cm^3) at 40 °C for 4 h] was added by syringe to a stirred solution of 1,4-dibromobenzene (1.18 g, 5 mmol) and $[Ni(PPh_3)_2Cl_2]$ (0.2 g, 0.3 mmol) in thf (thf = tetrahydrofuran) (15 cm^3) at 0 °C under N_2. After stirring overnight at room temperature a mixture of EtOH (5 cm^3) and concentrated HCl (12 mol dm^{-3}, 0.5 cm^3) was added; the mixture was stirred in air until the dark colour of the reaction mixture had disappeared. After addition of aqueous ethanol (10 cm^3, 1 : 1) the crystalline white solid was filtered off, washed with aqueous ethanol (1 : 1) and dried *in vacuo*. Yield: 50–60%. ^1H NMR (270 MHz, $CDCl_3$): δ 3.93 (6 H, s, OCH_3), 3.96 (6 H, s, OCH_3), 6.96 (2 H, d, J = 8.1 Hz, H^5, $H^{5''}$), 7.20 (4 H, m, H^2, $H^{2''}$, H^6, $H^{6''}$), 7.62 (4 H, s, central phenyl ring). Mass spectrum (electron impact, EI): m/z 350 (M^+, 100%) (Found: C, 75.2; H, 6.5. Calc. for $C_{22}H_{22}O_4$: C, 75.4; H, 6.3%).

Demethylation of the above materials to give H_4L^1 and H_4L^2 respectively was accomplished in 70–80% yield with 5 equivalents of BBr_3 in CH_2Cl_2 for 1 h under N_2 according to a published procedure.[15] After allowing the reaction mixture to warm to *ca*. −20 °C, addition of water precipitated the products which were filtered off, washed with cold water and dried. The ligand H_4L^1 is a white solid; H_4L^2 is white when freshly precipitated but adopts a grey-purple tinge on drying, possibly due to a slight degree of oxidation.

Data for 3,3′,4,4′-tetrahydroxybiphenyl (H_4L^1). ^1H NMR (270 MHz, CD_3OD): δ 6.81 (2 H, d, J = 8.2, H^6, $H^{6'}$), 6.88 (2 H, dd, J = 8.2, 2.0, H^5, $H^{5'}$) and 6.99 (2 H, d, J = 2.0 Hz, H^2, $H^{2'}$). Mass spectrum (EI): m/z 218 (M^+, 100%) (Found: C, 65.6; H, 4.6. Calc. for $C_{12}H_{10}O_4$: C, 66.1; H, 4.6%).

Data for 3,3″,4,4″-tetrahydroxy-*p*-terphenyl (H_4L^2). ^1H NMR (270 MHz, CD_3OD): δ 6.88 (2 H, d, J = 8.1 Hz, H^6, $H^{6''}$), 7.03 (2 H, dd, J = 8.1, 2.2, H^5, $H^{5''}$), 7.13 (2 H, d, J = 2.2 Hz) and 7.58 (4 H, s, central phenyl ring). Mass spectrum (EI): m/z 294 (M^+, 100%) (Found: C, 69.1; H, 5.3. Calc. for $C_{18}H_{14}O_4{\cdot}H_2O$: C, 69.2; H, 5.1%).

Complex **1** was prepared by reaction of H_4L^1 (0.055 g, 0.25 mmol) with $[Ru(bipy)_2Cl_2]{\cdot}2H_2O$ (0.27 g, 0.52 mmol) and KOH (*ca*. 0.2 g, excess) in EtOH (20 cm^3) at reflux under N_2 for 3 h. Aqueous NH_4PF_6 was then added and the mixture concentrated to give a dark suspension, which was extracted with several portions of CH_2Cl_2 which were then combined, dried and evaporated. The product was purified on a 2 mm thick SiO_2 PLC plate (Merck, article 5717) with a mixture of MeCN (100 cm^3), water (6 cm^3) and saturated aqueous NH_4PF_6 (4 cm^3) as eluent, followed by recrystallisation from CH_2Cl_2–hexane to give **1** in 50–60% yield. Mass spectrum (fast atom bombardment, FAB): m/z 1332 (**1**, 1), 1187 (**1** − PF_6, 20) and 1042 (**1** − $2PF_6$, 25%) (Found: C, 44.5; H, 2.6; N, 8.0. Calc. for $C_{52}H_{38}F_{12}N_8O_4P_2Ru_2{\cdot}CH_2Cl_2$: C, 44.9; H, 2.8; N, 7.9%).

Complex **2** was prepared similarly (30–40% yield) and recrystallised from CH_2Cl_2–hexane. Mass spectrum (FAB): m/z 1263 (**2** − PF_6, 60) and 1118 (**2** − $2PF_6$, 40%) (Found: C, 45.4; H, 3.0; N, 7.5. Calc. for $C_{58}H_{42}F_{12}N_8O_4P_2Ru_2{\cdot}2CH_2Cl_2$: C, 45.7; H, 2.9; N, 7.1%.)

Results and Discussion

Synthesis of Ligands and Complexes.—3,3′,4,4′-Tetramethoxybiphenyl has been prepared previously by an Ullman coupling of 4-iodoveratrole,[14] and we also found that coupling of 4-bromoveratrole using a nickel(0) catalyst in thf was a satisfactory method.[13] 3,3″,4,4″-Tetramethoxy-*p*-terphenyl was previously prepared in low yield by a mixed Ullman coupling of 1,4-diiodobenzene and 4-iodoveratrole;[7] we obtained better yields (up to 60%) by the more directed reaction of 3,4-$(MeO)_2C_6H_3MgBr$ with 1,4-dibromobenzene in thf, in the presence of $[Ni(PPh_3)_2Cl_2]$ as coupling catalyst. The two ligands were then prepared by demethylation of the appropriate tetramethoxypolyphenyls with BBr_3.[15] The ^1H NMR spectra and EI mass spectra confirm the structures. Repeatable elemental analyses indicate that H_4L^2 is associated with one molecule of H_2O despite drying at 80 °C.

The new complexes **1** and **2** were prepared by reaction of 2 equivalents of $[Ru(bipy)_2Cl_2]{\cdot}2H_2O$ with the appropriate

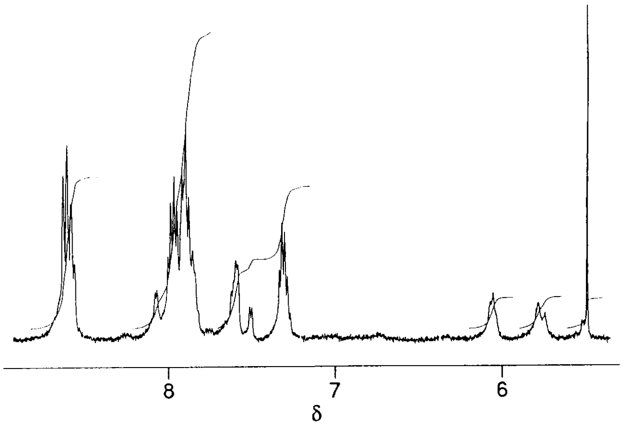


Fig. 1 270 MHz ^1H NMR spectrum of **1** in CD_3CN

ligand in ethanolic KOH at reflux (initial attempts to use methanol rather than ethanol as the reaction solvent resulted primarily in formation of $[\{Ru(bipy)_2\}_2(\mu\text{-}OMe)_2][PF_6]_2$ by direct reaction of $[Ru(bipy)_2Cl_2]\cdot 2H_2O$ with deprotonated solvent).[16] During aerobic work-up of **1** and **2** the bridging ligands oxidise to the sq–sq state, resulting in dicationic complexes which were isolated as their hexafluorophosphate salts. They are diamagnetic, confirming that the two semiquinone fragments have coupled.

The formulations of the complexes were confirmed by FAB mass spectrometry, which in each case shows peaks corresponding to the mass of the binuclear cation with 0 or 1 associated PF_6^- ions. In addition the ^1H NMR spectra show the expected numbers of protons; for example the spectrum of **1** (Fig. 1) shows 32 bipyridyl protons in three groups (the integrals correspond to two sets of 8 protons and one set of 16 protons), and, at lower chemical shifts, three signals each of intensity 2 H corresponding to the protons of L^1. The low chemical shifts of these three signals confirm that the bridging ligand is no longer aromatic.

Electrochemistry.—The cyclic and square-wave voltammograms of **1** in CH_2Cl_2 are shown in Fig. 2. Four reversible, one-electron (ΔE_p = 90–100 mV; $i_{pa} = i_{pc}$) waves occur at -1.04, -0.70, $+0.06$ and $+0.38$ V *vs.* the ferrocene–ferrocenium couple. These are ligand-based,[6] comprising two oxidations to give the sq–q and q–q states and two reductions to give the cat–sq and cat–cat states. That the first oxidation and first reduction are one-electron processes was confirmed coulometrically. Complex **1** therefore exhibits a five-member redox series, with every component accessible by electrolysis at the appropriate potential. The separation between the pairs of redox processes, 0.32 V for the oxidations and 0.34 V for the reductions, indicates a strong electronic interaction between the two halves of L^1. Ru^{II}–Ru^{III} couples might be expected at high positive potential by analogy with mononuclear $[Ru(bipy)_2(bsq)]^+$ (bsq = *o*-benzosemiquinone),[6] but these were not observed within the solvent window we employed.

The cyclic and square-wave voltammograms of **2** (Fig. 3) show two broad waves, centred at -0.40 and $+0.15$ V *vs.* ferrocene–ferrocenium, which correspond to two closely-spaced reductions and two closely-spaced oxidations respectively. In this case the electronic interaction between the two halves of the bridging ligand is sufficiently small to prevent clear resolution of all four processes. The mixed-valence sq–q and sq–cat states of **2** cannot therefore be prepared electrolytically, but the fully reduced cat–cat and fully oxidised q–q states are accessible. The smaller separation between the first oxidation and the first reduction potentials of **2** compared to **1** indicates that the highest-occupied–lowest-unoccupied molecular orbital (HOMO–LUMO) gap of the sq–sq bridging ligand is smaller, which is to be expected considering the greater extent of the conjugated π system.

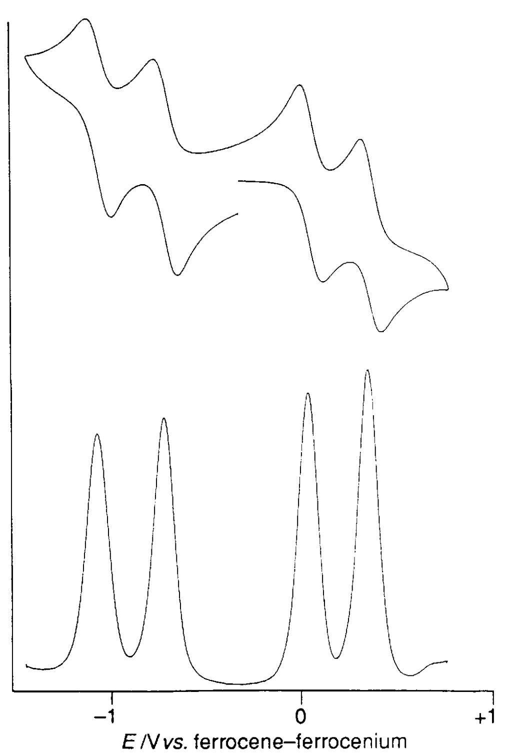


Fig. 2 Cyclic and square-wave voltammograms of **1** in CH_2Cl_2–0.1 mol dm^{-3} NBu_4PF_6 at a platinum-bead electrode with a scan-rate of 0.2 V s^{-1}

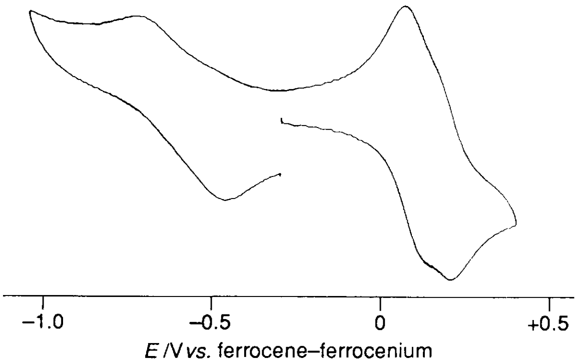


Fig. 3 Cyclic voltammogram of **2** in CH_2Cl_2–0.1 mol dm^{-3} NBu_4PF_6 at a platinum-bead electrode with a scan-rate of 0.2 V s^{-1}

UV/VIS Spectroscopy.—A UV/VIS/near-IR spectroelectrochemical study of **1** shows that the interaction between the two halves of **1** may be controlled according to the oxidation state of the bridging ligand. Spectra for all five oxidation states are summarised in Table 1. All show the $Ru(d_\pi) \rightarrow bipy(\pi^*)$ transitions whose energies smoothly increase with increasing ligand oxidation state. Assuming that changing the oxidation state of the bridging ligand does not significantly affect the energies of the bipy(π*) levels, this indicates that the filled $Ru(d_\pi)$ orbitals are steadily being lowered in energy by an increasingly favourable interaction with the bridging ligand as it becomes a better π acceptor. The spectrum of **1**(cat–cat) is similar to (but more intense than) that of the mononuclear analogue $[Ru(bipy)_2(cat)]$ [H_2cat = catechol (benzene-1,2-diol)],[6] indicating that **1**(cat–cat) is behaving approximately as two non-interacting components. Likewise, the $Ru(d_\pi) \rightarrow bipy(\pi^*)$ metal-to-ligand charge transfer (m.l.c.t.) transitions of **1**(q–q) are similar to those of $[Ru(bipy)_2(bq)]^{2+}$ (bq = *o*-benzoquinone) apart from having higher intensities. The $Ru(d_\pi) \rightarrow q$ m.l.c.t. band of **1**(q–q) however is red-shifted by 2300 cm^{-1} compared to $[Ru(bipy)_2(bq)]^{2+}$, indicating that the

Table 1 Electronic spectra of **1** and **2** in all accessible oxidation states of the bridging ligands; the data for the series $[Ru(bipy)_2L]^{n+}$ (L = cat, bsq, bq) are included for comparison

λ_{max}/nm (10^{-3} ε/dm^3 mol^{-1} cm^{-1})

$[Ru(bipy)_2L]^{n+}$		**1**		**2**	Assignment[a]
L = cat	725 (sh)[b]	725 (sh)[b]	(cat–cat)	725 (sh)[b]	cat→bipy(π*)
	621 (9.0)	618 (17)		613 (10)	Ru(d$_\pi$)→bipy(π*)
	377 (9.9)	376 (35)		400 (22)	Ru(d$_\pi$)→bipy(π*)
	348 (9.9)				
		830 (6)	(sq–cat)		Unknown
		560 (16)			Ru(d$_\pi$)→bipy(π*)
		442 (26)			(sq–cat)→bipy(π*)
		365 (25)			Ru(d$_\pi$)→bipy(π*)
L = bsq	880 (14)	1080 (37)	(sq–sq)	980 (38)	Ru(d$_\pi$)→sq + ligand π→π*
	485 (6.2)	507 (15)		478 (15)	Ru(d$_\pi$)→bipy(π*)
	346 (8.8)	345 (22)		335 (28)	Ru(d$_\pi$)→bipy(π*)
		1225 (37)	(sq–q)		Ru(d$_\pi$)→(sq–q)
		730 (4)			Unknown
		430 (11)			Ru(d$_\pi$)→bipy(π*)
		340 (22)			Ru(d$_\pi$)→bipy(π*)
L = bq	639 (13)	750 (30)	(q–q)	766 (36)	Ru(d$_\pi$)→q
	364 (5.3)	388 (13)		400 (sh)[b]	Ru(d$_\pi$)→bipy(π*)
		315 (sh)[b]		320 (sh)[b]	Ru(d$_\pi$)→bipy(π*)

[a] Assignments based on ref. 6. [b] sh = Shoulder; some of these were not well resolved so the measurements of their positions will have a larger degree of error associated with them than the other peaks.

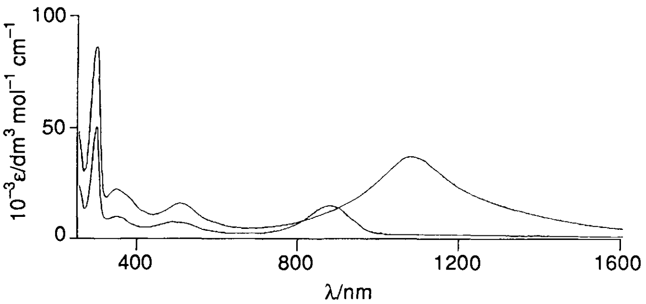


Fig. 4 Electronic spectra of $[Ru(bipy)_2(bsq)][PF_6]$ (upper trace) and **1** (sq–sq) (lower trace) in CH_2Cl_2 at the same concentration

(q–q) ligand is a better electron acceptor than an isolated quinone, but its oscillator strength—as expected—has approximately doubled.

The spectrum of **1**(sq–sq) contains a very intense and broad band (Fig. 4) in the region characteristic of a Ru(d$_\pi$)→sq m.l.c.t., red-shifted by 2100 cm^{-1} from $[Ru(bipy)_2(bsq)]^+$;[6] again, therefore, the bridging ligand in **1**(sq–sq) is a better electron-acceptor than bsq alone. However this band has an oscillator strength of *four* times that of the Ru(d$_\pi$)→sq band of $[Ru(bipy)_2(bsq)]^+$. This we believe is due to the presence of an overlapping intra-ligand π→π* transition, which is to be expected from the electrochemical properties. The separation of 0.76 V between the first ligand-based oxidation and reduction for **1**(sq–sq) indicates that the HOMO–LUMO separation is *ca.* 6100 cm^{-1}, (λ_{max} = 1631 nm). However the increased internuclear distances in the excited state, arising from population of an antibonding orbital, mean that the transition will result in vibrational as well as electronic excitation and will therefore be substantially blue-shifted (in **3**, for example, this π→π* transition occurs at 1176 nm although the 0.62 V separation between the orbitals involved gives λ_{max} = 2000 nm for excitation from the HOMO directly to the LUMO). The broad 1080 nm band therefore incorporates both Ru(d$_\pi$)→sq and intra-ligand π→π* processes, which explains both its unexpectedly large oscillator strength and also its slight asymmetry and long tail on the low-energy side.

Fig. 5 displays the electronic spectra recorded during the successive sq–sq→sq–q and sq–q→q–q oxidations of **1**. The sq–q mixed-valence state may be considered to exist in two extreme forms. The two ligating termini may be identical structurally and electronically, with each terminus being half way between the sq and q states; in this case there would be partial double-bond character between the rings, and although we have no structural evidence it is reasonable to assume that delocalisation of the single unpaired electron between the two termini would be optimised by a planar conformation. Alternatively the two termini may be structurally and electronically distinct (*i.e.* valence localised) due to twisting at the central C–C bond.[17] During the first oxidation to the sq–q state, the Ru(d$_\pi$)→sq m.l.c.t. band at 1080 nm disappears and is replaced by a band of similar intensity at 1225 nm. This is only consistent with the sq–q ligand remaining planar but becoming more electron deficient and hence having lower orbital energies, so the new band is a charge transfer from Ru(d$_\pi$) levels to a molecular orbital spanning the whole mixed-valence sq–q ligand. If the bridging ligand were valence localised in the sq–q state, the spectrum would be approximately a composite of the mononuclear fragments with separate Ru(d$_\pi$)→sq and Ru(d$_\pi$)→q m.l.c.t. bands, which clearly is not the case; there is no absorption in the region characteristic of Ru(d$_\pi$)→q transitions in this spectrum. This is in direct contrast to the behaviour of **3** in the sq–q state, where separate m.l.c.t. bands from Ru(d$_\pi$) to the sq and q fragments of the bridging ligand appear together with an intra-ligand sq→q intervalence charge transfer (i.v.c.t) band, indicating that the complex comprises valence-localised mononuclear components with some electronic coupling between them.[11]

During the second oxidation, to **1**(q–q), the 1225 nm band disappears and is replaced by a Ru(d$_\pi$)→q m.l.c.t. band at 750 nm which is similar to that of mononuclear $[Ru(bipy)_2(bq)]^{2+}$. The two components of the complex have become essentially decoupled, which we suggest is due to a change in the conformation of the bridging ligand initiated by removal of double-bond character between the rings; the λ_{max} value of 750 nm suggests that the ligand LUMO is essentially that of an isolated quinone perturbed by the presence of an electron-accepting substituent, which accounts for the red-shift of this band compared to $[Ru(bipy)_2(bq)]^{2+}$.

Similar behaviour occurs on stepwise one-electron reduc-

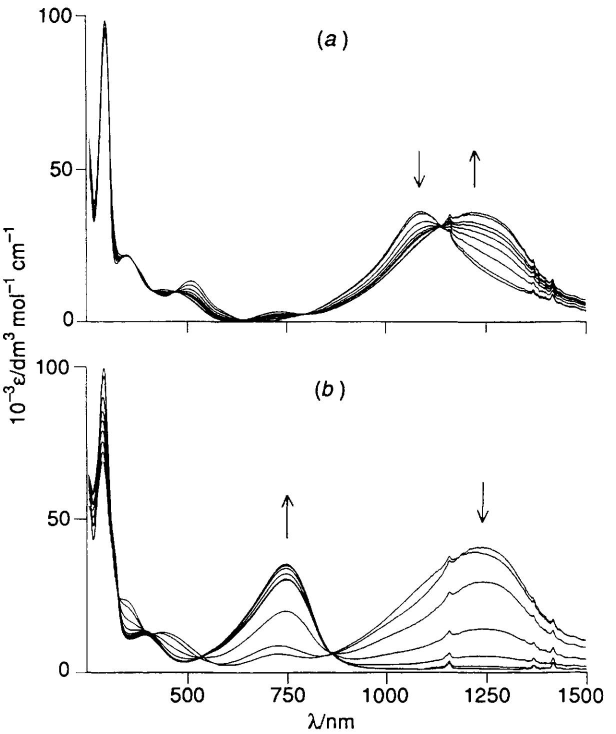


Fig. 5 Successive electronic spectra recorded during the electrochemical oxidations of (*a*) **1**(sq–sq) to **1**(sq–q), and (*b*) **1**(sq–q) to **1**(q–q) in CH$_2$Cl$_2$ in an OTTLE cell

tions (Fig. 6). During the sq–sq→sq–cat reduction, the Ru(d_π)→sq m.l.c.t band disappears, with a new transition appearing at 442 nm. We assign this to a (sq–cat)→bipy(π^*) process from a molecular orbital spanning the whole bridging ligand, which is now acting as an electron donor rather than an electron acceptor. Separate Ru(d_π)→sq and cat→bipy(π^*) transitions are not in evidence. On further reduction to **1**(cat–cat), the bridging ligand becomes more electron rich, raising the energy of its orbitals nearer to the bipy(π^*) levels. The cat→bipy(π^*) transition is accordingly red-shifted to 725 nm, and is now characteristic of uncoupled mononuclear species. As with the sq–q state, the mixed-valence sq–cat state appears to be delocalised and therefore, we suggest, planar; subsequent decoupling of the components is therefore associated with the second electron-transfer step. The chemical reversibility of all of the electrochemical processes, and the stability of **1** in all oxidation states, was confirmed by the presence of isosbestic points during each redox change and the fact that when the complex was finally returned to the starting sq–sq level its spectrum had not changed. This is in contrast to **3** which slowly decomposed on attempted reduction to the sq–sq and lower oxidation states.[11]

For **2** the mixed-valence states are not electrochemically accessible so only the cat–cat, sq–sq and q–q states could be examined; their spectra are summarised in Table 1. As for **1**, the cat–cat and q–q states are similar to those of their mononuclear counterparts apart from their greater intensity and the red-shift of the Ru(d_π)→q m.l.c.t. band in the binuclear complex; in these complexes the two components may be considered as separate and non- (or weakly) interacting. In the sq–sq state, the large oscillator strength of the peak at 980 nm is also likely to be due to superposition of both Ru(d_π)→(sq–sq) and ligand-based $\pi\rightarrow\pi^*$ processes. Again, in CH$_2$Cl$_2$ all oxidation states appear to be chemically stable as indicated by the reproducibility of the electronic spectrum of **2**(sq–sq) after being fully oxidised, fully reduced and then returned to the sq–sq state. Isosbestic points did not occur during these redox processes since two closely-spaced one-electron transfers were involved.

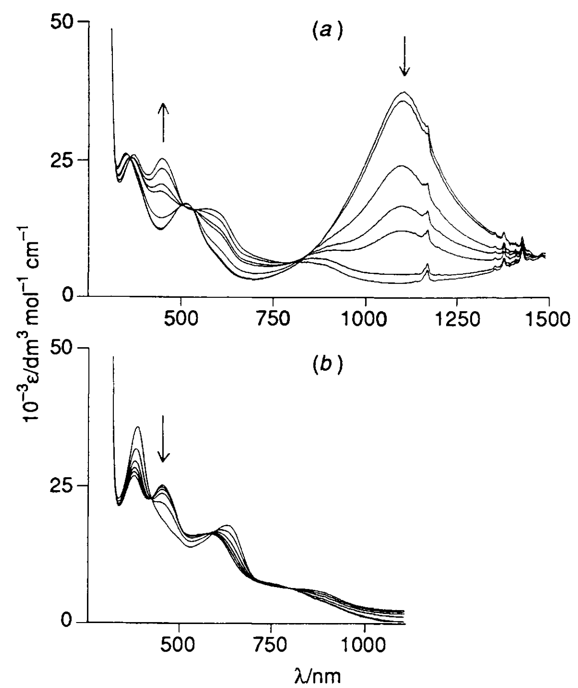


Fig. 6 Successive electronic spectra recorded during the electrochemical reductions of (*a*) **1**(sq–sq) to **1**(sq–cat), and (*b*) **1**(sq–cat) to **1**(cat–cat) in CH$_2$Cl$_2$ in an OTTLE cell

Conclusions.—Complex **1** displays some of the essential features of a molecular switch. It is necessarily planar in the sq–sq state; the electronic spectra clearly demonstrate the delocalised nature of the mixed-valence states, which suggests that they retain a planar conformation. For the successive one-electron oxidations and successive one-electron reductions, the decoupling of the two components, presumably caused by a change in ligand conformation, appears to be associated with the second step in each case.

References

1 *Molecular Electronic Devices*, ed. F L. Carter, Marcel Dekker, New York, 1982; *Molecular Electronic Devices*, eds. F. L. Carter, R. E. Siatkowsky and H. Woltjien, North Holland, Amsterdam, 1988; K. E. Drexler, *Engines of Creation*, Fourth Estate, London, 1990; K. E. Drexler, *Nanosystems: Molecular Machinery, Manufacturing, and Computation*, Wiley, New York, 1992. *Molecular Electronics*, ed. G. J. Ashwell, Wiley, Chichester, 1992; J.-M. Lehn, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 1304; J. S. Miller, *Adv. Mater.*, 1990, **2**, 378, 495, 601.

2 S. Woitellier, J.-P. Launay and C. W. Spangler, *Inorg. Chem.*, 1989, **28**, 758; J. A. Thomas, C. J. Jones, J. A. McCleverty, D. Collison, F. E. Mabbs, C. J. Harding and M. G. Hutchings, *J. Chem. Soc., Chem. Commun.*, 1992, 1796; S. Kugimiya, T. Lazrak, M. Blanchard-Desce and J.-M. Lehn, *J. Chem. Soc., Chem. Commun.*, 1991, 1179; M. J. Crossley and P. L. Burn, *J. Chem. Soc., Chem. Commun.*, 1991, 1569; J. M. Tour, R. Wu and J. S. Schumm, *J. Am. Chem. Soc.*, 1991, **113**, 7064.

3 F. Vögtle, W. M. Müller, U. Müller, M. Bauer and K. Rissanen, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1295; S. L. Gilat, S. H. Kawai and J.-M. Lehn, *J. Chem. Soc., Chem. Commun.*, 1993, 1439; T. Saika, T. Iyoda, K. Honda and T. Shimidzu, *J. Chem. Soc., Chem. Commun.*, 1992, 591; A. K. Newell and J. H. P. Utley, *J. Chem. Soc., Chem. Commun.*, 1992, 800; W. L. Mock and J. Pierpont, *J. Chem. Soc., Chem. Commun.*, 1990, 1509 and refs. therein; M. V. Alfimov and S. P. Gromov, in *Supramolecular Chemistry*, NATO ASI Series, Kluwer Academic Publishers, Dordrecht, 1992, p. 343; S. Shinkai and O. Manabe, *Top. Curr. Chem.*, 1984, **121**, 67.

4 A. Gourdon, *New. J. Chem.*, 1992, **16**, 953.

5 J. Rebek, jun., *Acc. Chem. Res.*, 1984, **17**, 258.

6 M. Haga, E. S. Dodsworth and A. B. P. Lever, *Inorg. Chem.*, 1986, **25**, 447.

7 L. Horner and K.-H. Weber, *Chem. Ber.*, 1967, **100**, 2842.

8 V. J. Eaton and D. Steele, *J. Chem. Soc., Faraday Trans. 2*, 1973, 1601.

9 C. P. Brock and R. P. Minton, *J. Am. Chem. Soc.*, 1989, **111**, 4586.

10 A. Helms, D. Heiler and G. McLendon, *J. Am. Chem. Soc.*, 1992, **114**, 6227; A. Helms, D. Heiler and G. McLendon, *J. Am. Chem. Soc.*, 1991, **113**, 4325.

11 P. R. Auburn and A. B. P. Lever, *Inorg. Chem.*, 1990, **29**, 2553.

12 M. D. Ward, *J. Chem. Soc., Dalton Trans.*, 1993, 1321; S. L. McWhinnie, S. M. Charsley, C. J. Jones, J. A. McCleverty and L. J. Yellowlees, *J. Chem. Soc., Dalton Trans.*, 1993, 413.

13 M. Iyoda, H. Otsuka, K. Sato, N. Nisato and M. Oda, *Bull. Chem. Soc. Jpn.*, 1990, **63**, 80.

14 T. Yamato, C. Hideshima, K. Suehiro, M. Tashiro, G. K. Suraya Pradesh and G. A. Olah, *J. Org. Chem.*, 1991, **56**, 6248.

15 J. F. W. McOmie, M. L. Watts and D. E. West, *Tetrahedron*, 1968, **24**, 2289.

16 D. A. Bardwell, J. C. Jeffery, L. Joulié and M. D. Ward, *J. Chem. Soc., Dalton Trans.*, 1993, 2255.

17 J. Almlöf, *Chem. Phys.*, 1974, **6**, 135.

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