Direct Evidence for Electrochemically Induced, Reversible, Proton Transfer involving a Quinone/Hydroquinone Redox Couple

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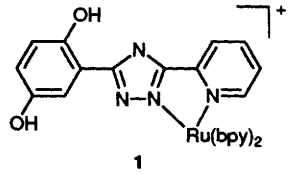
The complex $[Ru(bpy)_2L](PF_6)$ [HL = 3-(2,5-dihydroxyphenyl)-5-(pyridin-2-yl)-1,2,4-triazole], exhibits electrochemically induced proton transfer between the hydroquinone moiety and the triazole; evidence for this phenomenon is derived from electrochemical and spectroelectrochemical experiments, and suggests that the transfer occurs intramolecularly *via* a hydrogen-bridge formation between the hydroquinone and triazole.

The hydroquinone group plays an important role in the natural photosynthetic process, where it is oxidised to quinone. It has been proposed that this process is coupled with a reversible proton transfer to a protein chain.[1–4] Although there are reports of proton transfers involving such groups,[5–7] to our best knowledge there are no reports of hydroquinone based redox reactions involving such a reversible proton transfer where destination and source of the proton is not the solvent. In this communication we report the first example of such a reaction, using a ruthenium based model compound. For the complex $[Ru(bpy)_2L](PF_6)$, **1** [bpy = 2,2′-bipyridine, HL = 3-(2,5-dihydroxyphenyl)-5-(pyridin-2-yl)-1,2,4-triazole] a reversible, electrochemically induced proton transfer reaction occurs from a hydroquinone group to the attached triazole ring.

To obtain complex **1** pure, and in high yield, the hydroxy moieties were protected by acetylation using standard synthetic procedures before complexation. Reaction of this protected ligand with $[Ru(bpy)_2Cl_2]\cdot 2H_2O$ followed by deprotection yields the desired product in good yield.† The structure of **1**, and in particular the coordination of the N^1-triazole atom has been confirmed using ^1H NMR spectroscopy and comparison with analogous complexes of known crystal structure.[8–10] The deprotonated status of the triazole ring, is supported by the λ_{max} value of the lowest energy ^{1}MLCT transition of 475 nm. Protonation of the complex results in a blue shift in λ_{max} to 430 nm.[11–13]

Electrochemical experiments on **1** were carried out in the pH‡ range of 2.0 (0.01 mol dm^{-3} $HClO_4$) to 9.5 (5.0×10^{-5} mol dm^{-3} NH_4OH) in acetonitrile. Using cyclic voltammetry starting from 0 V (*vs.* SCE), and an anodised glassy carbon electrode[14] three oxidation waves are observed (see Fig. 1). Ox1 and Ox2 and their reductive counterparts Red1 and Red2 are assigned to two one-electron reversible redox reactions of the bipyridine ligands.[15] The two oxidations, Ox3



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† Satisfactory elemental analysis was obtained.

‡ The acid or base concentrations present in the different solutions have been defined by the actual amount of acid or base added to the solution and by the pH obtained from a pH meter. Our investigations have shown that these acid and base concentrations correlate very well with the pH measured. While the dissociation behaviour of ammonia in acetonitrile is to our knowledge not known, perchloric acid is known to dissociate fully in this solvent.[16]

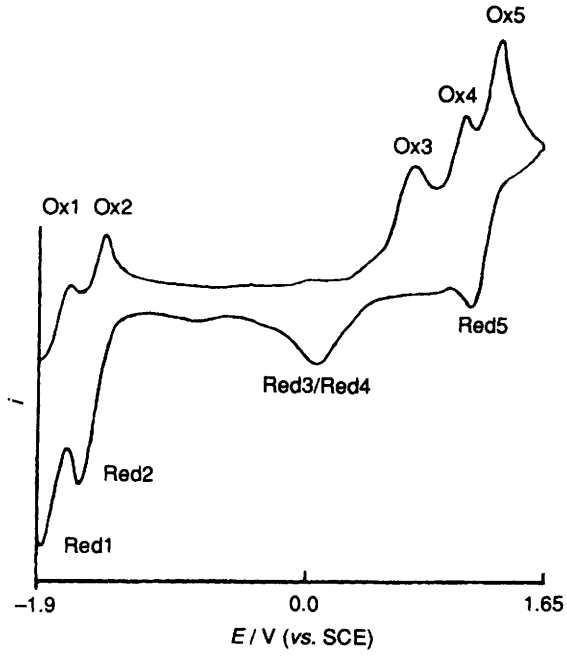


Fig. 1 Cyclic voltammogram of **1**, at pH 7.5 (3×10^{-7} mol dm^{-3} NH_4OH) in acetonitrile containing 0.1 mol dm^{-3} tetraethylammonium perchlorate: working electrode, Teflon shrouded glassy carbon electrode; scan rate, 100 mV s^{-1}

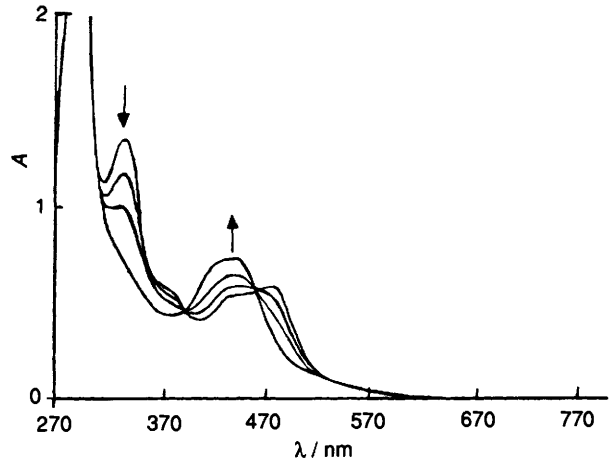
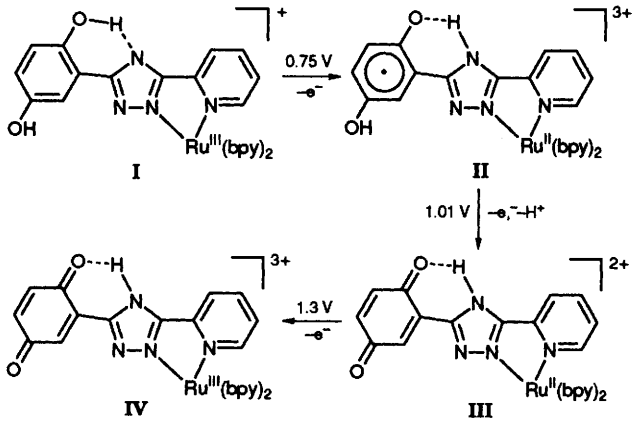


Fig. 2 Spectroelectrochemistry of **1** at pH 7.5, applied potentials, 0, 0.25, 0.50 and 0.7 V



Scheme 1

at 0.74 and Ox4 at 1.01 V are attributed to the two one-electron oxidations of the hydroquinone ring. Such separation of the individual oxidation steps of the hydroquinone has been reported previously, using similarly treated electrodes.[14] Coulometric measurements show that the oxidations Ox3 and Ox4 are associated with a one-electron process each, whereas the associated reduction Red3/Red4, is a two-electron process, coulometry of the redox wave Red3/Red4 was carried out after exhaustive oxidation of the complex. The reversible redox couple Ox5/Red5 ($E_{\frac{1}{2}}$ = 1.18 V) is assigned as the metal-based Ru^{II}/Ru^{III} oxidation by comparison with other similar compounds.[15] The CV of **1** at pH 2 reveals a Ru^{II}/Ru^{III} based reversible oxidation at 1.18 V, corresponding to the protonated complex. At pH 9.5 the complex exhibits two oxidation waves, the first at E = 0.76 V is hydroquinone based, while the second at 0.91 V is assigned to the Ru^{II}/Ru^{III} oxidation of the complex containing a deprotonated triazole ring. These results suggest that the most positive oxidation wave observed in Fig. 1 is the metal based oxidation of the complex containing a protonated triazole ring. However, UV–VIS spectra suggest that the triazole ring in **1** is normally deprotonated in this pH range. This implies that protonation of the triazole ring is occurring as a result of oxidation of the hydroquinone group.

Spectroelectrochemistry yields the most compelling evidence to support this concept of such an electrochemically induced proton transfer process. Upon scanning the applied potentials (in 0.1 V steps, followed by 30 min equilibration) from 0 to 0.90 V (*vs.* Ag/AgCl) between pH 5 (1×10^{-5} mol dm^{-3} $HClO_4$) and 8 (1×10^{-6} mol dm^{-3} NH_4OH) there is a gradual blue shift of the band at 475 to 430 nm in the absorbance spectrum of **1** (see Fig. 2). Hence, the triazole is gradually protonated with increasing potential. This situation is reversible over the potential range employed.

The proton transfer process is independent of pH within the range studied. In neutral methanol and aqueous solutions the CV of the metal centred oxidation corresponded to the complex containing the deprotonated triazole. Presumably in such media the solvent interferes with the proton transfer process, by accepting the released proton.

The first hydroquinone oxidation is accompanied by proton transfer to the triazole ring, as observed from spectroelectrochemistry at potentials as low as 0.45 V. Oxidation of the hydroquinone species is then completed at a potential of 1.0 V, yielding the quinone species (**III**). Further scanning of the potential to 1.3 V leads to complete oxidation of the Ru^{II} centre (**IV**), as manifested by the disappearance of the typical Ru^{II} polypyridyl ^{1}MLCT bands. Since the process is pH independent in the range studied the protonation of the triazole ring is unlikely to be simply a manifestation of increased acidity of the solution caused by release of protons as a result of the oxidation of the hydroquinone group. Furthermore, it was found that the pK_a of **1** is about 2.6 in acetonitrile, since, the concentration of the ruthenium complex ranges from *ca.* 2×10^{-4} mol dm^{-3} for spectroelectrochemical to about 1×10^{-3} mol dm^{-3} for electrochemical experiments, so a change to pH 2.6 (2.5×10^{-3} mol dm^{-3} H^+) clearly can not occur in the early stages of hydroquinone oxidation when proton transfer is observed.

The basis of this facile reversible proton transfer process in **1** may be hydrogen bonding between the hydroquinone moiety and the adjacent triazole ring, making the proton transfer intramolecular. Such a hydrogen bridge is observed for the complex $[Ru(bpy)_2L']^+$, where L′ represents the phenol analogue of the hydroquinone ligand, hydrogen bonding between the phenol group and N^4 of the triazole ring is observed, with an N–O bond distance of 2.62 Å.[8]

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