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Electronic coupling and photochemical stability of *O*,*N* bound mononuclear Ru(II) and Os(II) – Hydroquinone complexes

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Abstract

The synthesis, spectroscopic and electrochemical characterisation of a series of optically tuneable, ruthenium (II) and osmium (II) polypyridyl complexes, *O*,*N* coordinated to electroactive donor ligand, bis-2,5-(2-benzoxazolyl)-hydroquinone (bbhq) is described. The complexes exhibit a rich optical spectroscopy which can be controlled through the redox state of the metal and bbhq ligand. The influence of both the metal and counter-ligand identity on the optical properties of these hydroquinone-based complexes is addressed.

Regardless of the identity of metal or counter-ligand, it is the bbhq which is the site of the most facile oxidation and hydroquinone, semiquinone (bbsq) and quinone (bbq) can be generated electrochemically. In each instance, the semiquinone is strongly stabilised with respect to disproportionation, reflected in large stability constants for this moiety. The levels of orbital mixing between metal and ligand are discussed on the basis of the optical properties of the complex and the nature of the metal and counter-ligand. In addition, we address, for the first time, the effect of metal and counter-ligand on the photostability, of Ru(II) and Os(II) hydroquinone bound complexes. We find that like other ruthenium (II) complexes containing strong σ-bonding ligands, the $M(bpy)_2$ containing complexes are photostable, but the $[Ru(biq)_2(bbhq)]^+$ complex is relatively photolabile.

Keywords: Ruthenium compounds; Spectroelectrochemistry; Quinone; Hydroquinone; Non-innocent ligands; Electronic spectroscopy

1. Introduction

The ability to rationally tune the optical properties of redox and photoactive metal complexes across the visible and NIR spectrum is of significant value across a wide range of applications from solar sensitizers to biological probes to electrochromics. There are relatively few compounds whose absorbance extends to the NIR and which are in addition, easily optically tuned. Important examples include Ru(II) polypyridyl complexes which incorporate anionic oxygen donor ligands such as catechols or phenolates. Such complexes have been demonstrated to show very rich optical spectroscopy, the wavelengths of which, can be controlled by altering the redox state of the donor ligand or the metal [1]. For example, in such complexes when the oxygen donor ligand is in a reduced state, these complexes exhibit MLCT Ru(II)–L–L(π*) (where L–L represents for example, 2,2-bipyridyl) transitions upon which are imposed the much less common inter-ligand charge transfer ILCT transitions which can frequently extend to the NIR [2]. Oxidation of a hydroquinone or catechol ligand may result in additional new MLCT transitions to ligand SOMO states, again, these absorbances frequently extend well into the NIR spectral region [3].

Quinone/hydroquinone based ruthenium and osmium complexes have been demonstrated to exhibit significant mixing of metal and ligand orbitals of the non-innocent ligand and the extent of mixing is inherently dependent on the oxidation state of the ligand [4]. Almost invariably, the quinone state is shown to mix best, due most likely to the low-lying π* orbitals of this species [5,6].

Altering the nature of the counter ligand to change the acceptor levels in quinone/hydroquinone based ruthenium

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and osmium complexes, for example from bipyridine to biquinoline, should permit tuning of both the ILCT and MLCT transitions. Indeed we recently demonstrated such optical tuning occurs in ruthenium and osmium complexes containing phenolate donors [3]. In these complexes, the metal, principally, was the first site of oxidation, and so in this report we extend these studies to identify the effect of altering metal and counter ligand identity on the optical properties of a hydroquinone complex, where the states can be further tuned by oxidation of the non-innocent hydroquinone ligand. In addition, we address, for the first time, the effect of metal and counter-ligand on the photostability, of the Ru(II) and Os(II) hydroquinone bound complexes. Ultimate application of these materials as sensitizers or in electrochromics requires that they exhibit photochemical stability. We anticipated that they would be reasonably stable given the strong σ-donor nature of the anionic hydroquinone ligand and indeed find that compared to $[Ru(bpy)_3]^{2+}$ they are photochemically stable, however this stability is particularly dependent on the π-acceptor ability of the counter-ligand.

2. Experimental

2.1. Materials

D_8-bpy was synthesised according to published methods (Supplementary data). Dichloride complexes, *cis*-$Ru(bpy)_2Cl_2$, $Ru(d_8\text{-}bpy)_2Cl_2$, $Os(bpy)_2Cl_2$, $Ru(d_8\text{-}bpy)_2Cl_2$, *cis*-$Ru(biq)_2Cl_2$, where bpy is 2,2-bipyridine and biq is 2,2-biquinoline, were synthesised according to standard techniques [7–9]. Bis-2,5-(2-benzoxazolyl)-hydroquinone (bbhq) was synthesised according to the method described by Mordzinski and Grabowski et al. [10–12]. All reagents, purchased from Sigma–Aldrich, were used as received.

2.2. Metal complexes

2.2.1. $[Ru(bpy)_2(bbhq)](PF_6)$

Bbhq (352 mg, 93 mmol) was dissolved in ethanol/water (3:1 v/v, 60 cm^3). This solution was heated and adjusted to pH 10.96, with conc. NaOH. $[Ru(bpy)_2Cl_2] \cdot 2H_2O$ (500 mg, 1.03 mmol) dissolved in ethanol/water (1:1 v/v, 40 cm^3) was added slowly over 30 min. The mixture was heated under reflux for 7.5 h after which time the brown solution was reduced in volume by rotary evaporation to approximately 10 cm^3. The complex was re-dissolved in methanol/dichloromethane/water and several drops of saturated aqueous NH_4PF_6 were subsequently added to the solution. The resulting brown precipitate was collected by vacuum filtration. Yield (65.64%). *Anal.* Calc. for $RuC_{40}H_{27}N_6O_4PF_6$: C, 53.28; H, 3.02; N, 9.32. Found: C, 53.32; H, 3.04; N, 9.0%.

2.2.2. $[Os(bpy)_2(bbhq)](PF_6)$

$[Os(bpy)_2(bbhq)](PF_6)$ was synthesised as described for $[Ru(bpy)_2(bbhq)](PF_6)$. Bbhq (184 mg, 48 mmol) was dissolved in ethanol/water (3:1 v/v, 60 cm^3). This solution was heated and adjusted as for $[Ru(bpy)_2(bbhq)](PF_6)$. $[Os(bpy)_2Cl_2] \cdot 2H_2O$ (250 mg, 44 mmol) was used in this case. The resulting dark brown precipitate was collected by vacuum filtration. Yield (53.49%). *Anal.* Calc. for $OsC_{40}H_{27}N_6O_4PF_6 \cdot 2.5H_2O$: C, 46.42; H, 3.12; N, 8.12. Found: C, 46.32; H, 2.71; N, 8.00%.

2.2.3. $[Ru(biq)_2(bbhq)](PF_6)$

$[Ru(biq)_2(bbhq)](PF_6)$ was synthesised as described for $[M(bpy)_2(bbhq)](PF_6)$. Bbhq (278 mg, 73 mmol) and $[Ru(biq)_2Cl_2] \cdot 2H_2O$ (450 mg, 66 mmol) was used. The resulting green precipitate was collected by vacuum filtration. Yield (50.92%). *Anal.* Calc. for $RuC_{56}H_{35}N_6O_4PF_6$: C, 60.06; H, 3.33; N, 7.63. Found: C, 59.22; H, 3.73; N, 8.04%.

All complexes were purified by column chromatography on neutral alumina using methanol as mobile phase. All bbhq complexes were columned at least three times to ensure purity, which was confirmed using HPLC.

3. Physical measurements

High performance liquid chromatography (HPLC) was performed on a Shimadzu liquid chromatograph LC-10AD HPLC pump using a Waters 2487 dual wavelength absorbance detector. A 20 μl injector loop and a cation exchange column partisil SCX radial PAK cartridge were employed. The detection wavelength was 280 nm and mobile phase was 80:20 (v/v) acetonitrile:water containing 0.1 mol dm^{-3} lithium perchlorate. The flow rate was set at 2 ml/min.

Proton NMR spectra were obtained using a Bruker AC 400 or Varian 200 MHz spectrometer. Measurements were carried out in d_3-acetonitrile or d_6-DMSO. Peak positions are relative to TMS (σ, 0 ppm) and solvent peaks.

Electronic absorption spectra were measured using a Shimadzu 3500 UV–Vis/NIR spectrophotometer or a Perkin–Elmer lambda 900 UV–Vis/NIR spectrometer. Spectra were deconvoluted into Gaussians using standard iterative algorithms [13].

Cyclic voltammetry was carried out using a CH instruments Model 660 or 602a electrochemical workstation and a scan rate of 100 mV s^{-1} was used unless otherwise stated. Electrochemical studies were conducted in high purity HPLC grade solvents, dried over molecular sieves; 0.1 mol dm^{-3} tetraethylammonium tetrafluoroborate ($TEABF_4$) was used as the supporting electrolyte. A three-electrode system was used with a non-aqueous Ag/Ag^+ electrode. The working electrode was a 3 mm diameter teflon shrouded glassy carbon and a platinum wire was used as the auxiliary electrode. All solutions were degassed using nitrogen gas, and a blanket of nitrogen was maintained over the solution during all experiments. The unreactive redox couple Fc^+/Fc ($E^0 = 0.312$ V vs. Ag/Ag^+) was employed as an internal standard [14].