Polynuclear ruthenium-dioxolene complexes as near-infrared electrochromic dyes

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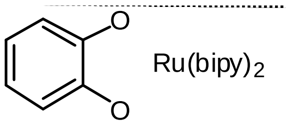
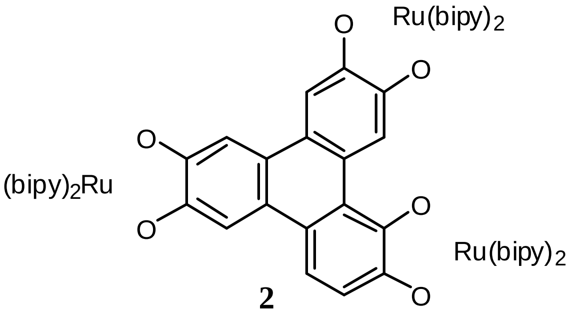
A variety of mononuclear and polynuclear ruthenium-dioxolene complexes have been prepared which show very strong near-infrared (NIR) electrochromism (1,2). These complexes have been characterised in solution by UV/Vis/NIR spectroelectrochemistry; and a sample complex, functionalised with carboxylate anchoring groups, has been attached to an Sb-doped tin oxide surface to make a NIR-active electrochromic window. Representative complexes are **1** and **2** below.



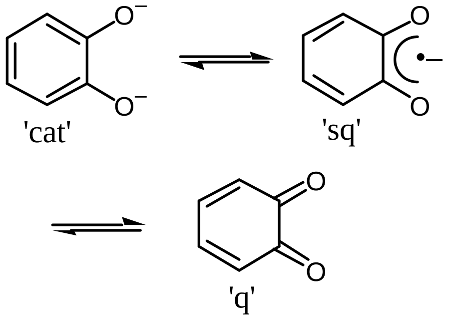
1



2

(bipy = 2,2'-bipyridine)

In the fully reduced forms the dioxolene ligands are in the 'catecholate' oxidation state; ligand-centred oxidation to give semiquinone ('sq') and then quinone ('q') units results in the appearance of intense, low-energy metal-to-ligand charge-transfer transitions (Scheme 1, Fig. 1).



Scheme 1

In the mononuclear complexes the NIR charge-transfer transitions are relatively modest (wavelengths *ca.* 900 nm; extinction coefficients *ca.* 10,000 M^{-1} cm^{-1}). However in the polynuclear complexes, which undergo multiple redox interconversions, the transitions are at lower energy (*ca.*1200 nm) and very intense (extinction coefficients up to 60,000 M^{-1} cm^{-1}). The electrochromic behaviour of complex **2** in charge states +3 to +6 is shown in Figure 1; the charge-transfer transition can be varied smoothly from 760 to 1170 nm.

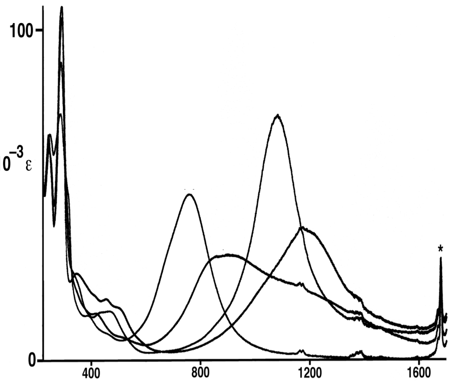


Figure 1: Electrochromic properties of complex 2

Attachment of carboxylate substituents onto the terminal bipyridyl ligands allows these complexes to be anchored onto a metal oxide semiconductor (Sb-doped tin oxide); a prototypical example will be presented which shows reversible modulation of the NIR transmittance of a film on cycling between two oxidation states.

References:

(1) The spectroelectrochemical complexes of mononuclear complexes such as **1** were first reported by Lever *et al:* M. Haga, E. S. Dodsworth and A. B. P. Lever, *Inorg. Chem.*, 1986, **25**, 447.

(2) L. F. Joulié, E. Schatz, M. D. Ward, F. Weber and L. J. Yellowlees, *J. Chem. Soc., Dalton Trans.*, 1994, 799; A. M. Barthram, R. L. Cleary, R. Kowallick and M. D. Ward, *Chem. Commun.*, 1998, 2695; A. M. Barthram and M. D. Ward, *New J. Chem.*, 2000, **24**, 501.