Near-Infrared Electrochromic Window

A Near-Infrared Electrochromic Window Based on an Sb-Doped SnO_2 Electrode Modified with a Ru–Dioxolene Complex**

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Candidate materials for electrochromic devices (e.g. viologens, conducting polymers, metallopolymers, metal oxides), generally exhibit redox states with distinctly different electronic UV/Vis absorption spectra.[1] Compounds that exhibit electrochromism in the near-infrared (NIR) region of the spectrum are much less well-known, despite the considerable technological importance of this region of the spectrum for uses as diverse as medicine (photodynamic therapy), telecommunications (silica-based fiber-optic devices operate in the 1300–1500 nm window), and even applications to aerospace and military camouflage.[2,3] Some conducting polymers have been shown to exhibit NIR electrochromism.[3] The well-known reversible redox activity of transition metal complexes makes them excellent candidates for use as electrochromic materials, although this activity is usually confined to the visible region of the spectrum.[4] We recently described extensive series of both ruthenium-dioxolene and oxo–Mo^{V}–

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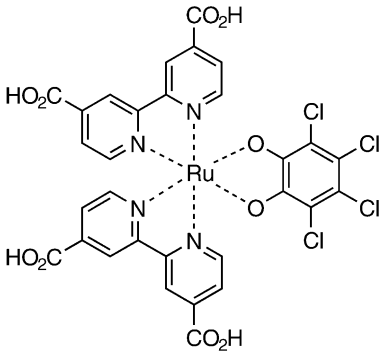
phenolate complexes whose redox activity is associated with the appearance/disappearance of intense NIR charge-transfer transitions.[5] In the case of the Ru–dioxolene systems, the electrochromism is based on the redox activity of the dioxolene ligand: oxidation of this ligand (from its catecholate form to the semiquinone and then quinone forms) results in the appearance of strong MLCT transitions in the NIR region,[5] as first demonstrated by Lever and co-workers.[6] To turn this behavior into a useful device, the electrochromic dyes need to be attached to a solid support for fast switching.

Herein, we describe the preparation and characterization of a NIR electrochromic window based on a conducting glass electrode coated with a thin nanocrystalline film of Sb-doped SnO_2, which is modified with the complex bis(2,2′-bipyridine-4,4′-dicarboxylic acid) (tetrachlorocatecholato)ruthenium(II), complex **1**. This complex is a derivative of $[Ru(bpy)_2(Cl_4cat)]$



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(cat = catecholate), known to show NIR electrochromism,[6] but contains appended carboxylate groups to anchor the complex to a metal oxide surface. Nanocrystalline antimony-doped tin oxide (SnO_2:Sb) electrodes were chosen because they are highly conducting and electrons can tunnel easily in either direction between the adsorbed electroactive species and the SnO_2 conduction band.[7] Compared with TiO_2, SnO_2 is a better electron acceptor as its conduction band is about 0.5 V lower in energy.[8] The behavior of the electrochromic electrode was studied by cyclic voltammetry and spectroelectrochemical methods.

Complex **1** was prepared by the treatment of tetrachlorocatechol with $[Ru(dcbpy)_2Cl_2]$ (dcbpy = 2,2′-bipyridine-4,4′-dicarboxylic acid) in aqueous methanol at reflux, and purified by chromatography on Sephadex-G25 with MeOH.[9,10] The cyclic voltammogram in MeOH/KOH (Figure 1a) shows a chemically reversible catecholate/semiquinone couple at +0.18 V versus SCE, followed at higher potential (+0.94 V) by an irreversible semiquinone/quinone couple. The Ru^{II}/Ru^{III} couple, which is expected at a still more positive potential, was not observed within the accessible potential window.[6] In Figure 1b are the results of a spectroelectrochemical study in water which show the electronic spectra of **1** (no NIR absorption) and electrochemically-generated $[\mathbf{1}]^+$ (showing a transition at 940 nm arising from a $Ru^{II} \rightarrow$semiquinone MLCT transition following oxidation of the dioxolene ligand). These spectroscopic properties are similar to those observed for the noncarboxylated parent complex $[Ru(bpy)_2(Cl_4cat)]$.[6] This complex was then adsorbed from a MeOH/EtOH solution onto an electrode prepared from a layer of nanocrystalline Sb-doped SnO_2 on a transparent, conducting substrate.[11,12]

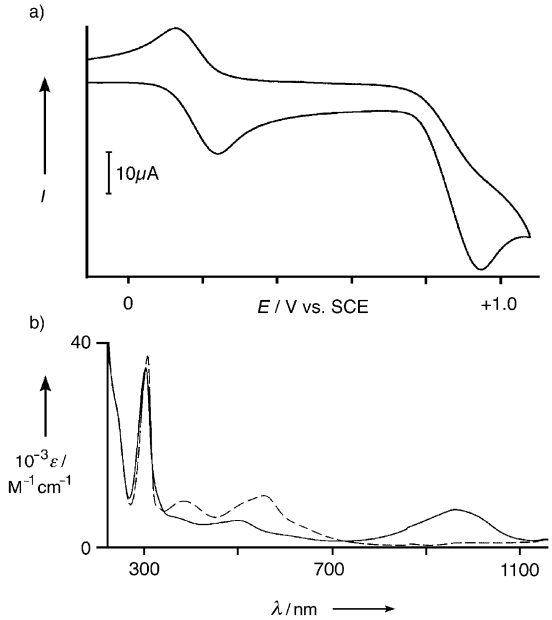

Figure 1. a) Cyclic voltammogram of **1** in MeOH containing 0.01 M KOH at a Pt-bead working electrode (scan rate 0.1 V sec^{-1}). b) Electronic spectra of **1** (•••••) and $[\mathbf{1}]^+$ (——) in water/0.1 M $NaClO_4$ from a spectroelectrochemistry experiment in an OTTLE cell at 293 K.

Figure 2 shows a cyclic voltammogram of the modified electrode recorded at a sweep rate of 10 mV s^{-1}. When the experiment was performed in the absence of the adsorbed dye, only the featureless background charging current typical of highly doped SnO_2:Sb electrodes[13] was observed. It follows that the peaks seen in Figure 2 arise from the oxidation and reduction of the catecholate/semiquinone couple. The electrode is initially blue-gray (catecholate

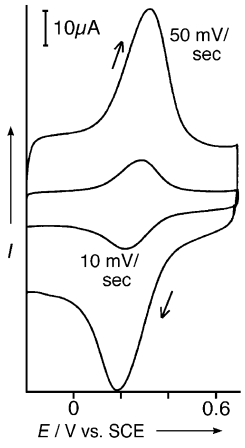

Figure 2. Cyclic voltammograms at 10 mV sec^{-1} and 50 mV sec^{-1} of a porous nanocrystalline Sb-doped SnO_2 film modified with complex **1**; recorded in acetonitrile containing 0.1 M Bu_4NPF_6.

form), changes to pink (semiquinone form) during oxidation, and returns to blue-gray during the reverse sweep. The two peaks observed in the voltammogram are almost symmetric as expected for the case of a thermodynamically ideal surface-attached redox system; the small separation between the two peak potentials may arise from interactions between the species in the densely populated substrate,[14] as well as from the ohmic potential drop in the system.

The changes in the optical transmittance of the film (at two different wavelengths) as a function of applied potential (scanned at 10 $mV\,s^{-1}$) are shown in Figure 3. At 630 nm, the

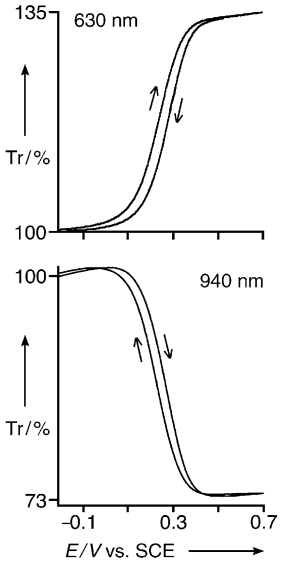

Figure 3. Changes in optical transmittance at 630 and 940 nm of a Sb-doped SnO_2 film modified with complex **1**; recorded with acetonitrile containing 0.1 M Bu_4NPF_6. Sweep rate was 10 mV sec^{-1}. The values have been normalized to the initial transmission at the beginning of the voltage sweep (i.e. in the reduced catecholate form of the dye) in each case.

transmittance increases on oxidation, and decreases (returning to its initial value) on reduction, thus indicating the reversible behavior of the system. The small hysteresis demonstrates the reversibility of the electrochromic couple. At 940 nm, the transmittance of the electrode decreases on the oxidation sweep due to the appearance of the MLCT transition, and decreases (returning to its initial value) during the reductive sweep. The same small hysteresis effect already mentioned was observed. Background optical transmittance experiments at the three wavelengths without the presence of adsorbed **1** showed no significant change of transmittance. In all cases, the changes in transmittance are in agreement with what would be expected on the basis of the spectroelectrochemical properties (Figure 1). It is clear from these results that the reversible ligand-based redox process of **1** provides a good basis for electrochromic systems operating both in the visible and NIR. The extensive redox activity and substantial NIR electrochromism of related dinuclear and trinuclear Ru–dioxolene complexes means that they are very promising candidates for NIR electrochromic windows.

The optical switching speed of the electrochromic layer is determined by the rate of the oxidation/reduction process. The current that flows to the porous electrode is required not only to effect the redox switching but also to charge the electrical double layer of the nanocrystalline SnO_2 support, which has a high surface area, thus resulting in a high background current (Figure 2). The magnitude of the background current indicates that the internal surface area of the porous oxide film is at least 500 times larger than the geometric area. Based on this internal surface area, the charge under the voltammetric peaks can be used to estimate the coverage of the internal surface with the complex as of the order of 10^{13} molecules cm^{-2}, which is consistent with monolayer coverage.[15]

The dynamic electrical and optical properties of the electrochromic layer were also characterized by using a small sinusoidal modulation of the electrode potential. The low-frequency spectroelectrochemical response of the modified electrode could be modeled by a single time constant with a value of about 0.5 s, which means that the window should switch almost completely (98%) in 1.5 seconds. This switching time will be susceptible to improvement, as the time constant is determined predominantly by the series resistance of the conducting glass electrode and the electrolyte solution (80Ω total) and is not determined by the properties of **1**. Consequently, the use of electrode and cell designs that give lower values of series resistance will improve the response time of the electrochromic window.

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[9] A mixture of $[Ru(dcbpy)_2Cl_2]$ (ref. [10]) (50 mg, 75 μmol), tetrachlorocatechol (25 mg, 160 μmol, excess) and KOH (0.1 g in MeOH/water (1:1, 50 cm^3) was heated to reflux for 5 h. After the removal of the solvent in vacuo the residue was dissolved in the minimum volume of MeOH and purified by repeated chromatography on Sephadex-G25, elution with MeOH followed by recrystallisation from MeOH/diethyl ether (yield: ca. 20%). Negative-ion ESMS: *m/z* 416 $\{M - 4\,K^+ + 2H^+\}^{2+}$. The elemental analysis consistently indicated the presence of several molecules of water of crystallization. A typical example is given. Elemental analysis calcd(%) for **1**·7 H_2O: C 32.4, H 2.4, N 5.0% found (%): C 32.2, H 2.2, N 5.0.

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[11] The conductive glass substrate (Libby Owens Ford, F^--doped SnO_2) was cleaned by brushing with Decon 5% solution, rinsing with milli-Q water, immersion for 30 minutes in boiling 2-propanol, rinsing again with milli-Q water and drying in an air stream. The Sb-doped SnO_2 (15% in H_2O colloidal dispersion, Alfa Aesar) was spread over the cleaned glass substrate with a glass rod by using adhesive tape spacers. The geometric area of the film was 1.5 cm^2. The plate was then fired at 450°C for 30 minutes in air. This process was repeated four times to get four layers of SnO_2 and so increase the thickness of the film to around 2–3 microns. The SnO_2 film was then modified by chemisorption of the Ru complex **1** from a MeOH/EtOH solution (3×10^{-4} M) over 20 h, then removed and placed in a horizontal position for homogeneous drying for a few minutes prior to use. Measurements by using this modified electrode were carried out under dinitrogen at room temperature in a three-electrode cell. Pt wire was used as a counter electrode and Ag wire as the reference electrode. The electrolytic solution was dry acetonitrile containing 0.1 M Bu_4NPF_6. A small amount of ferrocene was added to the solution after the measurements and used as an internal standard; the conversion of potential values to the SCE scale was carried out by using published values. (ref. [12]) Optical measurements were performed by illuminating the cell from the substrate side with a light emitting diode at 940 or 630 nm and collecting the transmitted light with a silicon photodetector in a Faraday dark box while taking care to eliminate stray light. The output of the photodetector was connected with a current amplifier. Frequency-resolved measurements were performed at fixed dc potential by using a Solartron 1250 frequency-response analyser. The potential amplitude was 10 mV root mean square in all cases.

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[15] The surface coverage of complex **1** was calculated from the faradaic charge in the cyclic voltammogram. The charge (2 mC) is divided by the estimated internal surface area (500 cm^2) to obtain a charge per unit area of 4 μC cm^{-2}. This corresponds to 4×10^{-11} mol cm^{-2} or 2.4×10^{13} molecules cm^{-2}. This is equivalent to a monolayer if one assumes an area per molecule of 4×10^{-14} cm^2. This is an order of magnitude estimate only as the orientation of the adsorbed molecules is not known; however, the figures look reasonable for monolayer coverage.

