# Photo- and electro-chromism of diarylethene modified ITO electrodes—towards molecular based read–write–erase information storage†

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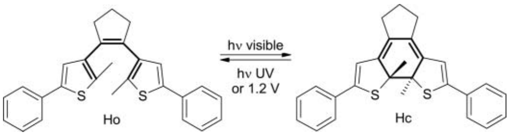
**Molecular memory devices based on dithienylethene switch modified ITO electrodes undergo reversible ring opening/closing both photo- and electro-chemically with non-destructive electrochemical readout.**

Self assembled monolayers of molecular switches[1] hold considerable potential in the development of molecular electronic[2] and optoelectronic memory devices.[3] Amongst the many photochromic molecular systems reported, spiropyrans,[4,5] azobenzenes,[6,7] and dithienylethenes[8] have demonstrated their applicability as photoswitchable molecular systems for immobilisation on surfaces due to their excellent photochemical characteristics, which can be tuned by synthetic modification. However, the development of practical read/write memory devices depends, ultimately, on additional functions other than the molecular switching 'write/erase' function (*e.g.* photochromism). That is, to achieve a read/write memory device a secondary physical signal (electrochemistry,[9,10] IR,[11] Raman spectroscopy[12] *etc.*) is required, to read the state of the switch non-destructively.[13] Recently, we[10] have reported that dithienylethenes such as **Ho** can undergo an electrocyclic ring closure to form **Hc**, *via* electrochemical oxidation and subsequent reduction, in addition to the well-known photoswitching (Scheme 1).

Here we report the first chemisorbed diarylethene based molecular switch monolayers on ITO electrodes. The immobilised switch can undergo multi-cyclic ring-opening and ring-closing reactions both electrochemically and photochemically and, importantly, the state of the modified surface can be read 'non-destructively' by electrochemical means (Scheme 2).

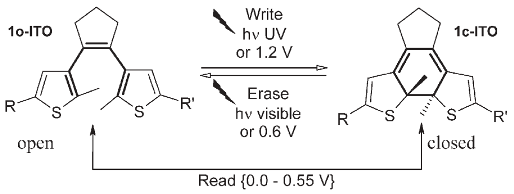
Diarylethene **5** was prepared *via* Suzuki coupling of **3**[14] with methyl-4-bromobenzoate, followed by alkaline hydrolysis of the methyl ester. Subsequently **5** was converted to **1o** and **2o** by coupling with 3-aminopropyl-triethoxysilane and *n*-propylamine, respectively (Scheme 3).



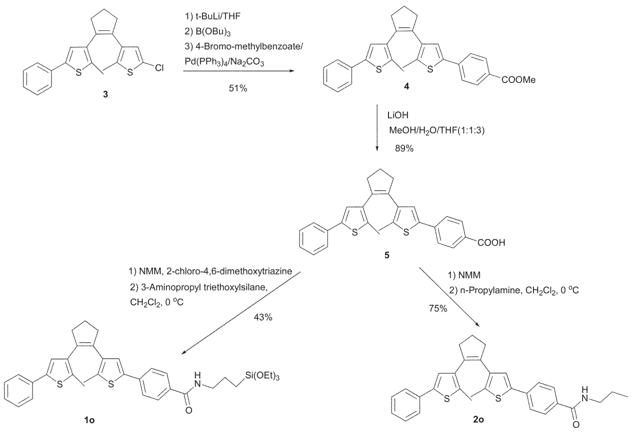
**Scheme 1** Photochemical/electrochemical switching of **Ho/Hc**.

As for **Ho**,[14] **2o** undergoes efficient photochemical ring closing and opening in solution upon irradiation with 312 nm and >400 nm light, respectively. The redox chemistry of **2o** is characterised by an irreversible oxidation at $E_{p,a}$ = 1.15 V [*vs.* SCE] leading to oxidative ring closure to $\mathbf{2c}^{2+}$, which can then be reduced, first to $\mathbf{2c}^{+}$ at 0.78 V and finally **2c** at 0.42 V (Fig. 1a).

The general strategy employed[15] for immobilisation of **1o** on ITO electrode surfaces is summarized in Scheme 4. The ITO electrodes were activated by a procedure, described by Markovich *et al.*[16] The treatment did not affect, significantly, the electrochemical properties or the hydrophobicity of the surface (see ESI).† Diarylethene **1o** was immobilised on the activated ITO surface in toluene at reflux for 24 h to give **1o-ITO** (Scheme 4). The increase in surface hydrophobicity upon immobilisation was confirmed by contact angle measurement, with the contact angle changing from 30° (for the activated ITO surface) to 80° (for **1o-ITO**).[7]



**Scheme 2** Write–Read–Erase system based on the photochemical/electrochemical switching of **1o-ITO** to **1c-ITO**.



**Scheme 3** Synthesis of **1o** and **2o**.

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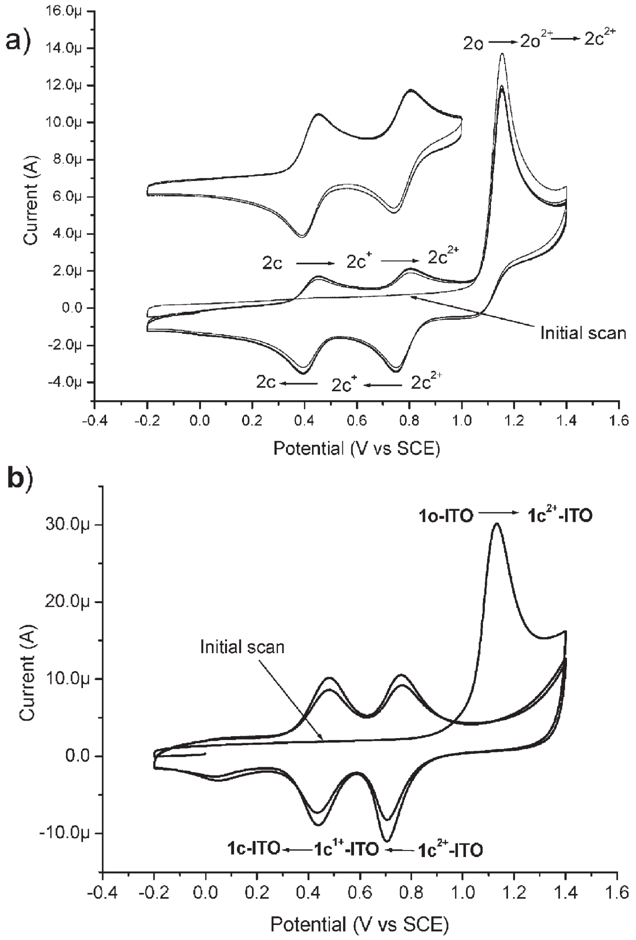
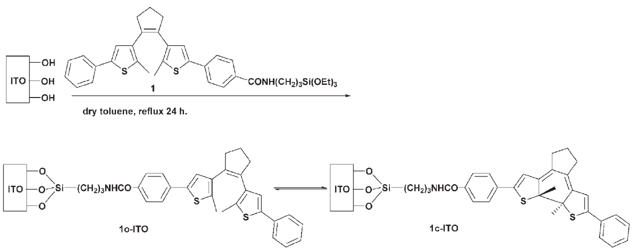


**Fig. 1** Cyclic voltammetry of (a) **2o** (inset cyclic voltammetry of **2c**) and (b) **1o-ITO** at 0.1 $Vs^{-1}$ in $CH_2Cl_2$ (0.1 M $TBAPF_6$).



**Scheme 4** Covalent attachment of **1o** on an ITO electrode surface (to form **1o-ITO**), which subsequently can be switched reversibly to **1c-ITO** either photo- or electrochemically.

Cyclic voltammetry of **1o-ITO** in 0.1 M $TBAPF_6$–$CH_2Cl_2$ shows an irreversible oxidation wave at 1.10 V [**1o-ITO→1c$^{2+}$-ITO**], which gives rise to two reversible redox waves at 0.73 and 0.46 V *vs.* SCE [**1c$^{2+}$-ITO→1c$^{1+}$-ITO→1c-ITO**] (Fig. 1b). Essentially the cyclic voltammetry of **1o-ITO/1c-ITO** is equivalent to that observed for **2o/2c** in solution, however, as is expected for a modified surface the intensity of the Faradaic current is directly dependent on the scan rate (0.5–10 $Vs^{-1}$) and for **1c-ITO** $E_{p,a} - E_{p,c} < 59$ mV at 0.1 $Vs^{-1}$.† Coulometric analysis of the **1o-ITO** redox wave yields a surface density of the diarylethene on the electrode surface of $5.5 \times 10^{-11}$ mol $cm^{-2}$; the roughness factor of **1o-ITO** is estimated as 1.2 by atomic force microscopy.† No change in the separation of the anodic and cathodic peak potentials centred at ~0.45 V was observed indicating that at the experimental timescales (*i.e.* maximum scan rate) employed in the present study electron transfer (ET) kinetics are not rate limiting. The lower limit for the $k_{ET}$ from the electrode to the diarylethene units in the monolayer can be set to 10 $s^{-1}$ based on the highest scan rate employed (10 V $s^{-1}$).

The cyclic voltammogram of the **1o-ITO** shows no Faradaic processes from −0.2 to 0.6 V (Fig. 2a). Irradiation of **1o-ITO** ($\lambda_{312nm}$ for 5 min) results in photocyclisation of **1o-ITO** to **1c-ITO** (Fig. 2a) and the appearance of a reversible redox wave at 0.45 V, *i.e.* the first oxidation of **1c-ITO**. Irradiation of the electrode with $\lambda > 420$ nm, for 30 min sees a complete loss in the redox process at 0.45 V, *i.e.* restoration of **1o-ITO**. This process can be continued over several cycles of photochemical switching of the monolayer between the states **1o-ITO** and **1c-ITO**, however it is apparent that with each cycle the signal in the closed state diminishes considerably (Fig. 2b). In addition the contact angle of the surface decreases from 80° before irradiation to 58° after the four cycles. The decrease in the intensity of the redox wave of **1c-ITO** over several cycles can be attributed to instability of the anchoring silyl group[17] of the dithienylethene switch on the surface due to the liberation of $F^-$ from the supporting electrolyte, rather than any inherent electrochemical instability of **1c**. Indeed, this instability can be circumvented by using $TBA(CF_3SO_3)$ as the supporting electrolyte. The decrease in intensity of the first oxidation wave of **1c-ITO** was not observed over four photochemical 'close–open–close' cycles (Fig 3 and ESI†). Moreover, the contact angle of ITO

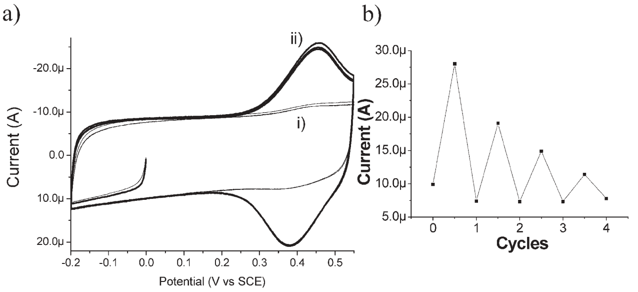


**Fig. 2** (a) Cyclic voltammetry of (i) **1o-ITO** and (ii) **1c-ITO** (formed after irradiation of **1o-ITO** at 312 nm for 5 min). (b) Repetitive photochemical switching of **1o-ITO** to **1c-ITO**, $I_{p,c}$ at 0.38 V. In 0.1 M $TBAPF_6$–$CH_2Cl_2$ at 2 $Vs^{-1}$. For Cyclic Voltammetry at 0.1 V $s^{-1}$ see ESI.†

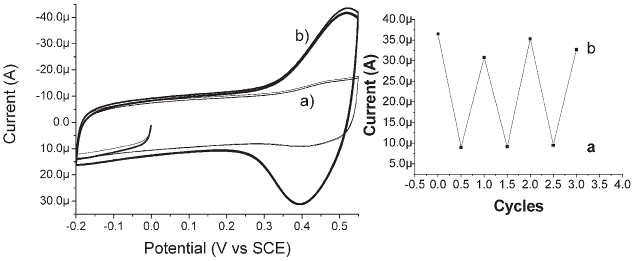


**Fig. 3** Left: Cyclic voltammetry of (a) **1o-ITO** and (b) **1c-ITO** after irradiation at 312 nm for 5 min. Right: Repetitive photochemical switching of **1o-ITO** to **1c-ITO**, in 0.1 M $TBA(CF_3SO_3)$–$CH_2Cl_2$, scan rate 2 V $s^{-1}$.

glass after the four cycles with TBA($CF_3SO_3$) as electrolyte showed only a modest change from 80° to 70°. In addition, the use of TBA($CF_3SO_3$) allows for oxidative ring opening of **1c-ITO** by cycling at scan rates $< 1$ V $s^{-1}$, between 0 and 0.5 V *vs.* SCE† without loss in surface coverage.

The electrochemical/photochemical properties of the diarylethene modified ITO electrodes reveal a robust system, where redox and/or optical switching allows for write–read–erase function (Scheme 2). The open form **1o-ITO** can act as an information recording interface. The information is 'written' either photochemically or electrochemically (*i.e.* to produce the closed form **1c-ITO**) and the information stored can be erased subsequently by either photochemical or electrochemical conversion from **1c-ITO** to **1o-ITO**. The information is 'read out' non-destructively by monitoring the reversible first oxidation of the closed form electrochemically in the potential interval of 0.0 to 0.5 V as shown in Scheme 2 and Fig. 3. In the same potential window the open form **1o-ITO** is electrochemically inert.

In summary, the present communication demonstrates that robust immobilisation of monolayers of dithienylethene switches can be achieved on non-metallic conductive interfaces, without loss of functionality. Furthermore the ability to drive ring-opening and closing reactions oxidatively provides increased functionality to these photochromic surfaces and a basis for read–write–erase systems.

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