

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

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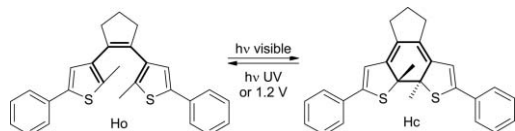
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Molecular memory devices based on dithienylethene switch modified ITO electrodes undergo reversible ring opening/closing both photo- and electro-chemically with non-destructive electrochemical readout.

Self assembled monolayers of molecular switches¹ hold considerable potential in the development of molecular electronic² and optoelectronic memory devices.³ Amongst the many photochromic molecular systems reported, spiropyrans,^{4,5} azobenzenes,^{6,7} and dithienylethenes⁸ have demonstrated their applicability as photo-switchable 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 spectroscopy¹² etc.) is required, to read the state of the switch non-destructively.¹³ Recently, we¹⁰ 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



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

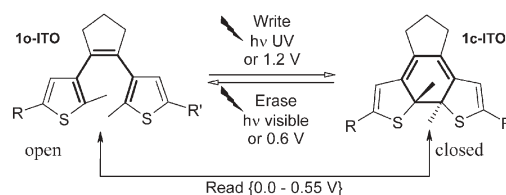
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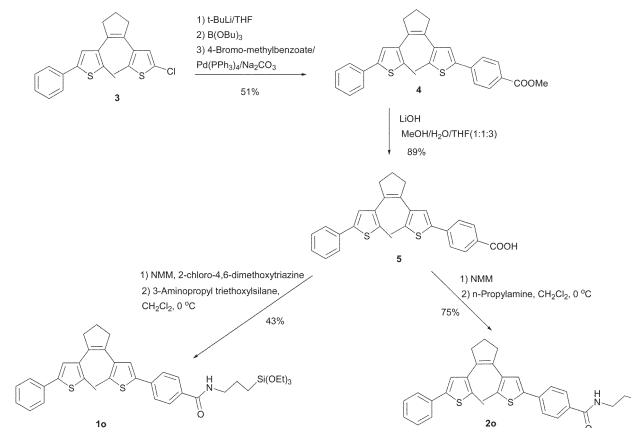
coupling with 3-aminopropyl-triethoxysilane and *n*-propylamine, respectively (Scheme 3).

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 $E_{p,ox} = 1.15$ V [vs. SCE] leading to oxidative ring closure to **2c**²⁺, which can then be reduced, first to **2c**⁺ at 0.78 V and finally **2c** at 0.42 V (Fig. 1a).

The general strategy employed¹⁵ 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**.

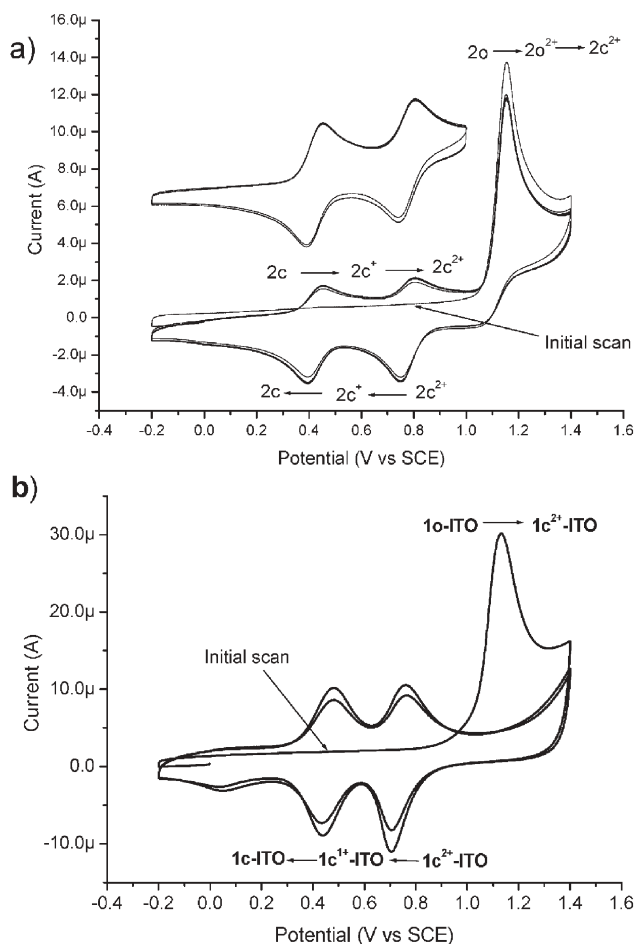
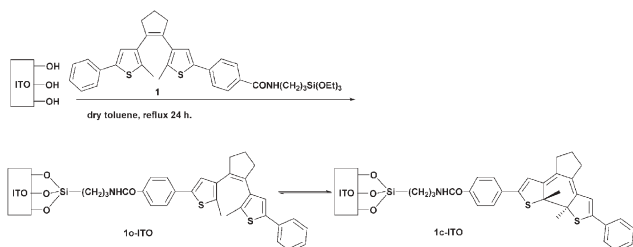


Fig. 1 Cyclic voltammery of (a) **2o** (inset cyclic voltammery of **2c**) and (b) **1o-ITO** at 0.1 Vs^{-1} in CH_2Cl_2 (0.1 M TBAPF_6).



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 voltammery of **1o-ITO** in $0.1 \text{ M TBAPF}_6\text{-CH}_2\text{Cl}_2$ shows an irreversible oxidation wave at 1.10 V [**1o-ITO**→**1c²⁺-ITO**], which gives rise to two reversible redox waves at 0.73 and 0.46 V vs. SCE [**1c²⁺-ITO**→**1c¹⁺-ITO**→**1c-ITO**] (Fig. 1b). Essentially the cyclic voltammery 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 ($0.5\text{--}10 \text{ Vs}^{-1}$) and for **1c-ITO** $E_{\text{p,a}} - E_{\text{p,c}} < 59 \text{ mV}$ 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 $5.5 \times 10^{-11} \text{ mol cm}^{-2}$; 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 $\sim 0.45 \text{ V}$ 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** ($\lambda_{312\text{nm}}$ 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 $\lambda > 420 \text{ nm}$, 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 group¹⁷ 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 $\text{TBA}(\text{CF}_3\text{SO}_3)$ 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

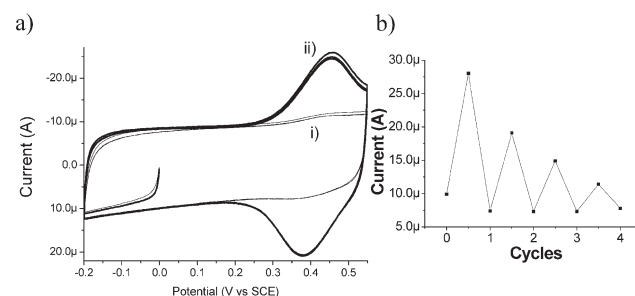


Fig. 2 (a) Cyclic voltammery of (i) **1o-ITO** and (ii) **1c-ITO** (formed after irradiation of **1o-ITO** at 312 nm for 5 min). (b) Repetitive photochemical switching of **1o-ITO** to **1c-ITO**, $I_{\text{p,c}}$ at 0.38 V . In $0.1 \text{ M TBAPF}_6\text{-CH}_2\text{Cl}_2$ at 2 Vs^{-1} . For Cyclic Voltammery at 0.1 V s^{-1} see ESI.†

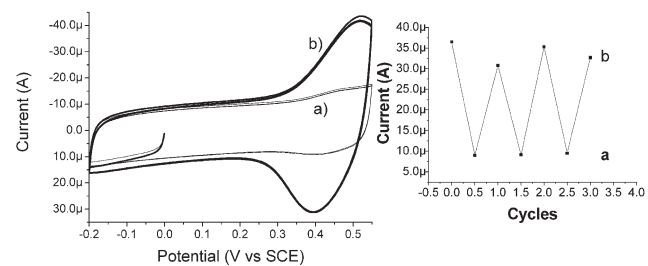


Fig. 3 Left: Cyclic voltammery of (a) **1o-ITO** and (b) **1c-ITO** after irradiation at 312 nm for 5 min . Right: Repetitive photochemical switching of **1o-ITO** to **1c-ITO**, in $0.1 \text{ M TBA}(\text{CF}_3\text{SO}_3)\text{-CH}_2\text{Cl}_2$, scan rate 2 V s^{-1} .

glass after the four cycles with TBA(CF₃SO₃) as electrolyte showed only a modest change from 80° to 70°. In addition, the use of TBA(CF₃SO₃) 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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