Photo- and electro-chromism of diarylethene modified ITO electrodes - towards molecular based read-write-erase information storage
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Published in:
Chemical Communications

DOI:
10.1039/b608502d

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2006

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):

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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 hold considerable potential in the development of molecular electronic and optoelectronic memory devices. Amongst the many photochromic molecular systems reported, spiropyrans, azobenzenes and dithienylethenes 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, IR, Raman spectroscopy etc.) is required, to read the state of the switch non-destructively. Recently, we 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 with methyl-4-bromobenzoate, followed by alkaline hydrolysis of the methyl ester. Subsequently 5 was converted to 1 and 2 by coupling with 3-aminopropyl-triethoxysilane and n-propylamine, respectively (Scheme 3).

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

The general strategy employed for immobilisation of 1 on ITO electrode surfaces is summarized in Scheme 4. The ITO electrodes were activated by a procedure, described by Markovich et al. The treatment did not affect, significantly, the electrochemical properties or the hydrophobicity of the surface (see ESI). Diarylethene 1 was immobilised on the activated ITO surface in toluene at reflux for 24 h to give 1-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 1-ITO).
Cyclic voltammetry of 1o-ITO in 0.1 M TBAPF₆–CH₂Cl₂ 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 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 V s⁻¹) and for 1c-ITO \( E_{p,a} - E_{p,c} < 59 \) mV at 0.1 V s⁻¹. Coulometric analysis of the 1o-ITO redox wave yields a surface density of the diarylthene 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 \( \sim 0.45 \) 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 diarylthene 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 (λ₃12nm 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 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(CF₃SO₃) 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. 2b). Moreover, the contact angle of ITO

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Fig. 1  Cyclic voltammetry of (a) 2o (inset cyclic voltammetry of 2c) and (b) 1o-ITO at 0.1 V s⁻¹ in CH₂Cl₂ (0.1 M TBAPF₆).

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.

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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, 1c⁻-ITO at 0.38 V. In 0.1 M TBAPF₆–CH₂Cl₂ at 2 V s⁻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(CF₃SO₃)-CH₂Cl₂, scan rate 2 V s⁻¹.
glass after the four cycles with TBA(CF$_3$SO$_3$) as electrolyte showed only a modest change from 80° to 70°. In addition, the use of TBA(CF$_3$SO$_3$) 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.

The authors thank the University of Groningen (Ubbio Emmanuel scholarship J.A.), the NRSC-C program (W.R.B.) and the Koerber Foundation (Hamburg, Germany, N.K.) for financial support. We thank Dr. Johan Hjelm (Riso National Laboratory, Denmark) for suggestions and discussions.

Notes and references