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## “Electrical” Behavior of Photochromic Compounds

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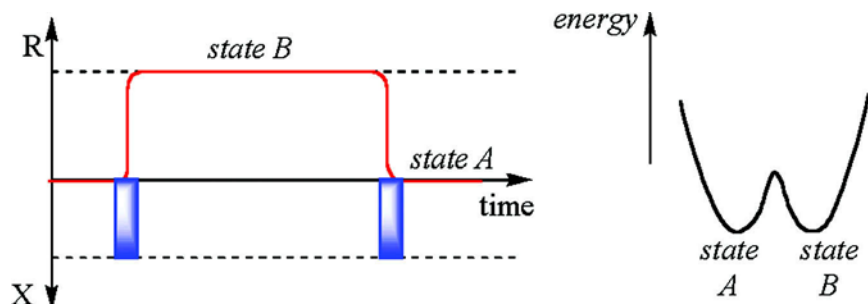
*Dithienylethylene unit have been incorporated in a molecular wire. Incorporated in a Self Assembled Monolayer and tested by Scanning Tunnelling Microscopy, the molecule has been shown to have a blinking contrast. Redox properties of model compounds have been explored in order to explain this feature: all molecules can be oxidized and the resulting radical cations may undergo ring closure or opening depending on its substituents.*

**Keywords:** dithienylethylene; electrochemistry; photochromism, switch molecular electronics, scanning tunneling microscopy

One of the simplest molecular device of Molecular Electronics is a “bis-table switch”, a three terminal device for which a perturbation (input X) is used only to trigger a state exchange: the output R indicating only if state A or B is obtained (Fig. 1) [1].

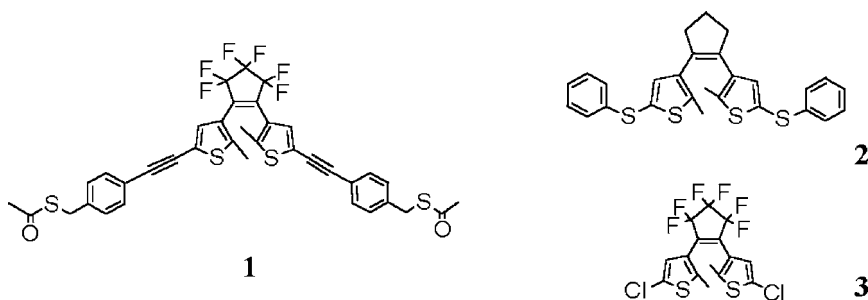
We gratefully acknowledge Prof. I. Gallardo, *Universitat Autònoma de Barcelona*, for electrochemical instrumentation, Mrs C. Viala for recording the NMR spectra. We also thank the “Ministerio de Educación, Cultura y Deporte” of Spain for the award of a post-doctoral grant (G.G.), the MENRST for fellowships (C.H., N.B.), and CNRS for a grant (AC-Nano, *POEM*)

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**FIGURE 1** A “bistable switch”.

The two isomeric forms, interconverted by light-induced electrocyclic reactions, of photochromic dyes, are typical of a “bistable” compound. Furthermore, the large HOMO-LUMO gap variation accompanying the ring closure makes them attractive units for current switching. Known for their high stability, the photochromic dithienylethylene derivatives offer several advantages: high symmetry of both forms, and a polyene-type for the “ring-closed” one. Numerous examples have been proposed as control unit for molecular devices [2,3], and to our knowledge only one single molecule study have been performed, in broken junctions [4]. Scanning Tunneling Microscopy is a convenient way to address specifically this issue, but, since the molecule is then submitted to an electron flow, electrochemical properties of these compounds should also be taken in account. Indeed, recent reports indicate that ring-closure or -opening could be induced for the dithienylethene family by oxidation [3–6]. As a starting point we have selected very simple structures of the



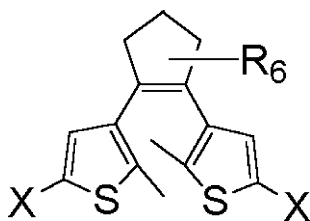
**FIGURE 2** Compounds studied in the present article.

“molecular wire” type, or for electrochemical studies, bearing a trimethylene or a perfluorotrimethylene lateral cycle (Fig. 2).

We wish here to present our preliminary results in this domain.

## EXPERIMENTAL

Synthetic details will be given elsewhere. Briefly, all compounds were obtained from the appropriate dihalo photochrome precursor (Scheme below).

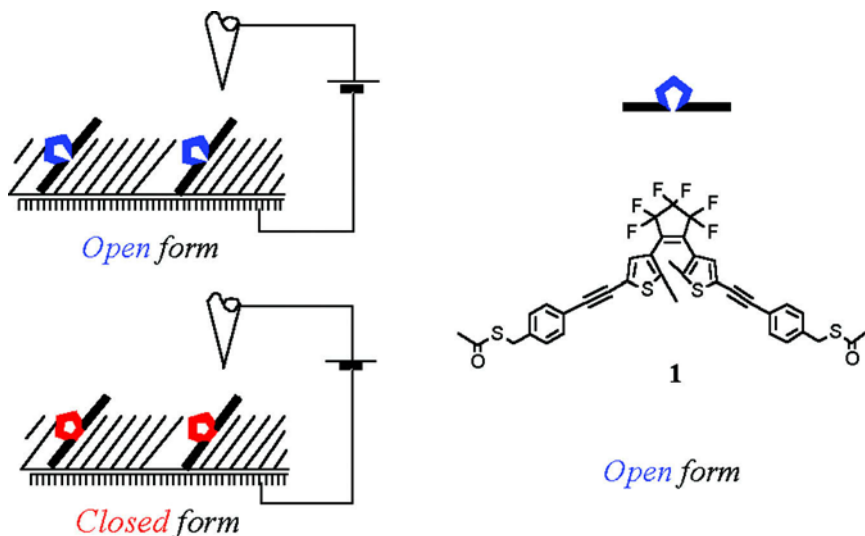


### SCHEME

Thus, **1** was prepared by a Sonogashira coupling from the known diiodide (R : F, X : I) [3], while compound **2** was obtained by lithiation of the described dichloride (R : H) [7] followed by trapping by diphenyldisulfide. Compound **3** was prepared following literature procedure [7]. Photochemical isomerisation was achieved using a TLC UV-lamp, and the resulting mixture of closed and open isomers was assayed by electrochemistry. Electrochemical behaviour was tested in oxidation by cyclic voltammetry (MeCN, 0,1 M N(nBu)<sub>4</sub>PF<sub>6</sub>, glassy C, SCE., 1V/s) or by coulometry (platinum grid working electrode). Mixed SAM were prepared by exposure of gold substrate to solutions of the thioacetate **1** and n-octanethiol in dichloromethane; their surface was explored by STM in air, with very small current (<5 pA) in order not to destroy the SAM with the tip.

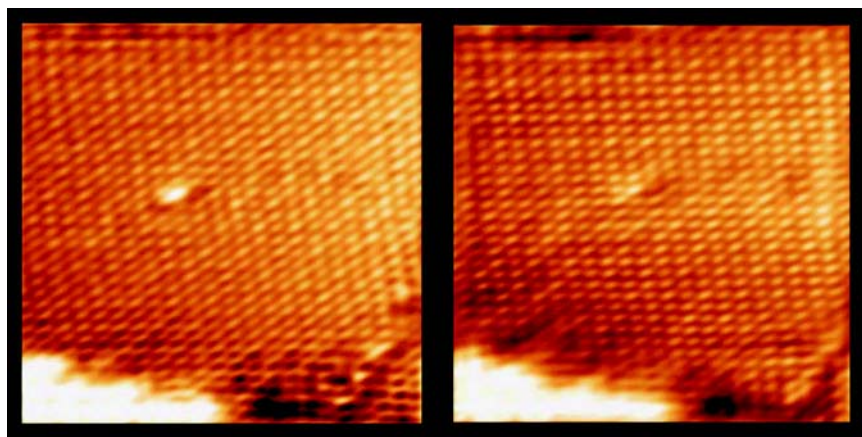
## Self Assembled Monolayers

The highly oriented Mixed Self-Assembled Monolayers medium has been commonly proposed in the making of molecular devices [8]. Since it provides a “chemical like” environment to its components, fragile molecules can be studied as long as they dissolve in it, but, being only weakly conductive, they are difficult to image by STM, because it implies the detection of very low currents. Our first goal was to study

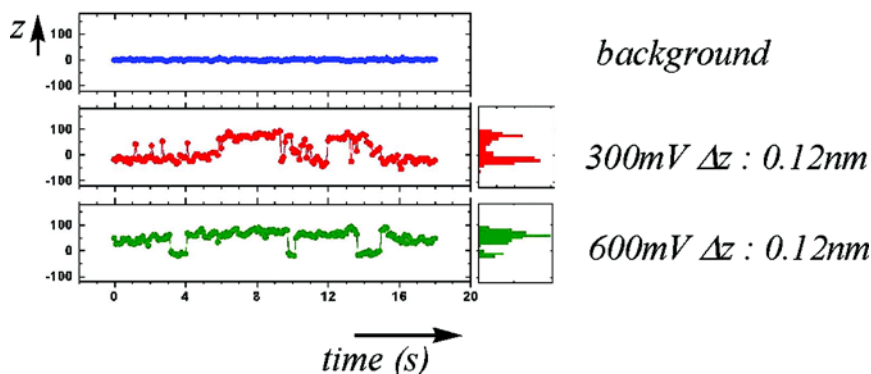


**FIGURE 3** Schematic view of the proposed STM experiments.

the difference of conductance (electronic transparency) between two generated *ex-situ* photoisomers of a molecular wire containing the dithienylethene unit (Fig. 3).



**FIGURE 4** Blinking of a photochrome in a n-octanethiol SAM (Scale 12.8 × 12.8 nm, I : 3pA, Bias voltage 800 mV).



**FIGURE 5** Tip's altitude *vs.* time as a function of the bias voltage.

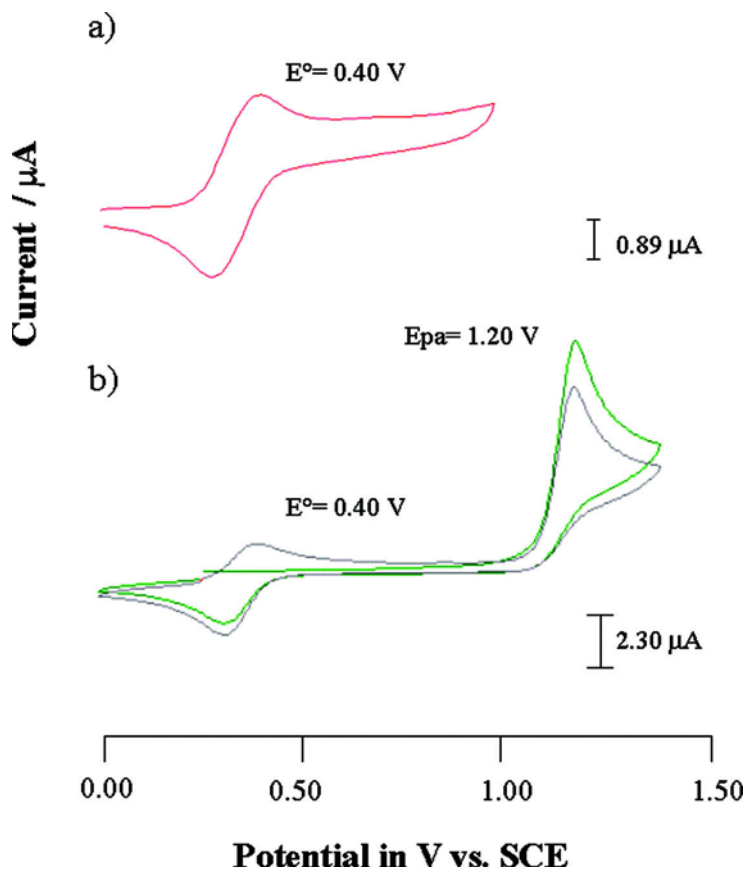
A molecule such as **1** was expected to bind to a gold surface by one of its thiomethyl groups. By comparison to SAM of pure n-octanethiol, molecule **1** (open isomer) was found to be partly soluble in octanethiol, leading to demixed domains, and bright defects in the "octanethiol-rich areas" were attributed to the (more transparent than n-octanethiol) isolated molecules of **1** (Fig. 4). More surprising was the fact that the contrast was found to be fluctuating at room temperature over minute time scale (Fig. 5).

Contrast blinking of an adsorbate is known to occur in SAM under STM conditions [9,10], and various explanations have been proposed, namely intramolecular conformation dynamics, a gold-sulfur bond fluctuation, and also an artifact such as disruption of the SAM by the tip itself.

In the present case, the reproducible blinking of the molecule was found to be bias voltage dependent. This fact was attributed to a chemical reaction. Although a current induced isomerisation is tempting, we investigated the possible oxidation of the molecule in these conditions since a simple change of electronic configuration may also lead to a different contrast.

## Electrochemical Behavior

As expected for both model compounds **2** and **3**, the closed isomer is always easier to oxidize than the open one, however, the strongly electron withdrawing perfluorotrimethylene substituent shifts all potentials anodically. Thus, compound **3**'s oxidation wave (irreversible) is centered at 1.99 V *vs.* SCE : its oxidized ring-opened form is therefore a strong oxidizer.



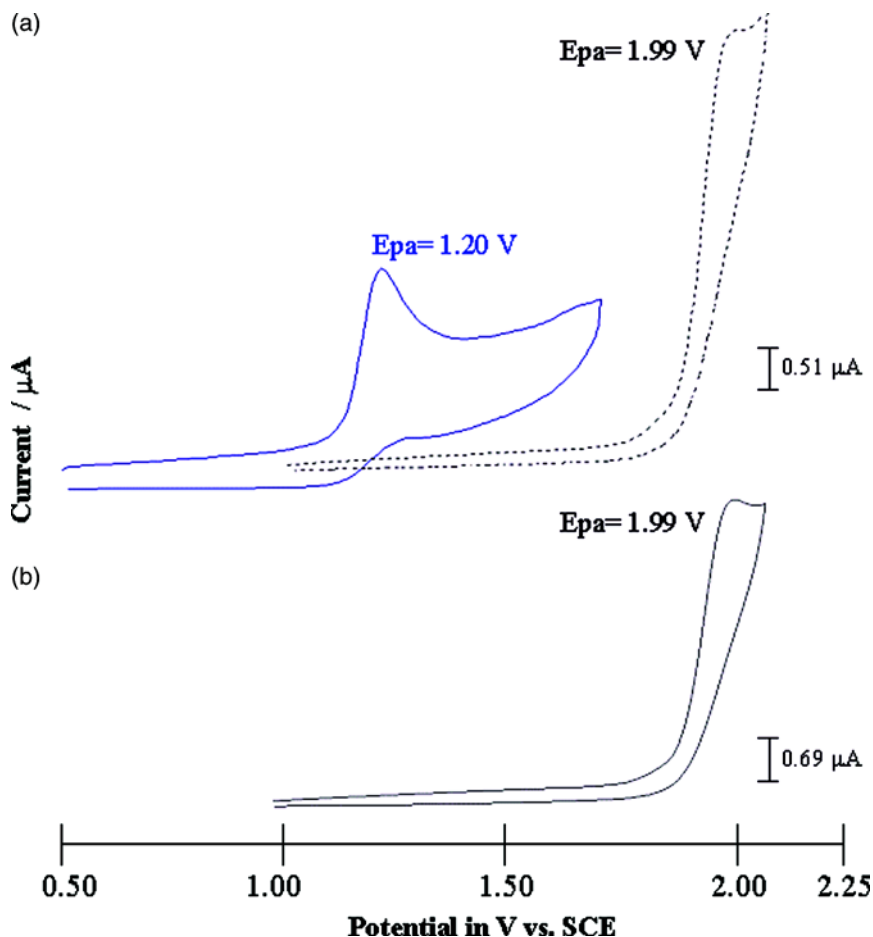
**FIGURE 6** a) CV of **2c** (0.45 mM). b) CV of **2o** (1.35 mM). Scan range: 1.00/0.00/ + 1.50/0.00 V (two cycles).

Cyclic voltammetry analysis of compound **2** reveals that while the ring-closed isomer **2c** shows reversible oxidation wave at  $0.40\text{ V vs. SCE}$ , the ring-open isomer **2o** shows an irreversible oxidation wave at  $E_{\text{pa}} = 1.20\text{ V}$  respectively (Fig. 6).

Careful cyclic voltammetry analysis reveals that the irreversible oxidation wave of the ring-open isomer (ca.  $1.20\text{ V vs. SCE}$ ) on the first anodic scan, is followed by a reduction wave on the cathodic scan. The expected anodic counterpart is obtained on the second cycle giving a reversible wave centered on a redox potential value of  $0.40\text{ V vs. SCE}$ .

This  $E^\circ$  value corresponds to the standard oxidation potential of **2c**. A radically different behavior was observed for the fluorinated





**FIGURE 7** a) CV of **3c** (1.10 mM). Solid line: Before electrolysis. Dotted line: After exhaustive electrolysis at 1.30 V vs. SCE. b) CV of **3o** (1.10 mM).

compound **3** since its closed isomer **3c** was shown to undergo an *irreversible* oxidation wave at  $E_{\text{pa}} = 1.20\text{ V}$  (Fig. 7a, solid line).

When controlled potential electrolysis of **3c** at 1.30 V was performed, the original red-pink color was discharged within minutes. Cyclic voltammetry, UV-Vis absorption spectroscopy since the closed isomer presents a characteristic band at 508 nm, and thin layer chromatography analysis of the resulting solution show that the ring-open isomer **3o** is the only product obtained (Fig. 7a, dotted line).

No specific substituent at the sigma bond locus are thus required to promote ring opening or closure (as opposed to ref. [5a]), but it is found to depend strongly on the inductive effect of the saturated branch and also on the a substituent on the thiophene rings. Remarkably, this phenomenon occurs on very simple molecule and extension to larger one is underway.

## CONCLUSION

Dithienylethene photochromes present a rich “electrical” behavior either in STM imaging or in electrochemistry. Rather easily oxidized, it is thus possible that their “ionized forms” may contribute to their electrical properties. Furthermore, depending on the substituent, the ionized photochromic core can undergo analogous reaction to their photochemical one. Work is in progress to examine the possible correlation between the two phenomena, either by electrochemistry on larger compound, or by calculation.

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