

A Dual-mode Optical–electrical Molecular Switching Device

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The triad of compounds **1a**, **1b** and **2** represents a dual-mode molecular switching device for which photochromic and electrochemical properties are mutually regulated and which may form the basis for write–read–erase optoelectronic information handling processes.

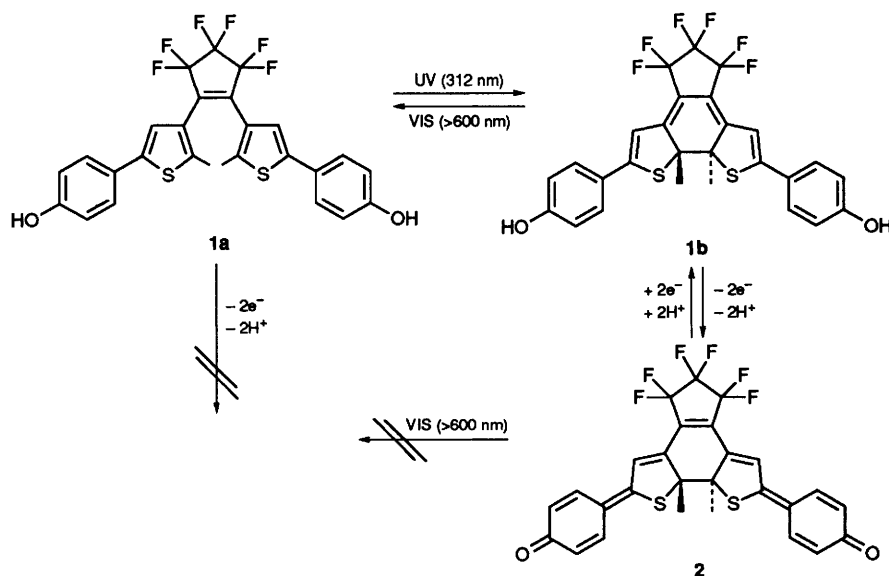
The development of molecular and supramolecular devices¹ requires the realization of molecular components whose physical behaviour (electrical, optical, spectral, *etc.*) may be modulated by external stimulation and which, thus, constitute molecular switches.² Electro-photoswitching of luminescence³ and switched molecular wires⁴ have recently been reported by our groups. Of particular interest are functional units which may be piloted by more than one type of stimulus and may therefore operate at more than a single level. The combination of optical and electrical properties is an attractive approach in that, in principle, it allows for the modulation of electrochemical properties by light and, conversely, of photochemical properties by electrical stimulation within a single component. Chemical transducers consisting of an organic photochrome linked to a redox couple have recently been described.^{5,6} While the interplay of electro- and photo-chemical properties has indeed been observed, only certain states are stable and the properties are often only weakly coupled.

We herein describe a dual-mode switching device based on both photochromic and electrochromic properties which are mutually regulated and are completely integrated within a single structure. The device may be reversibly converted between three states (**1a**, **1b** and **2**) which are all stable and exhibit very distinct absorption spectra. Moreover, it constitutes a two-level switch in which electrical behaviour is controlled in an ‘on–off’ fashion by light and the photochromism is likewise regulated electrochemically. The photoconversion features are based on those of the extensively studied dithienylethene compounds.⁷

The synthesis of the bisphenol photochrome **1a** is outlined in Scheme 1. Dibromide **4** was prepared from 2-methylthiophene by a previously described method.⁸ Although palladium-catalysed aryl–thienyl couplings proceeding *via* thienylzinc or -lithium intermediates are well established,⁹ attempts to couple protected 4-bromophenols and dibromide **4** failed to provide the desired products. Compound **6** (mp 106 °C) could, however, be obtained by the coupling of boronic acid **5** and dibromide **4** employing Pd(PPh₃)₄ in aqueous medium.^{4,10}

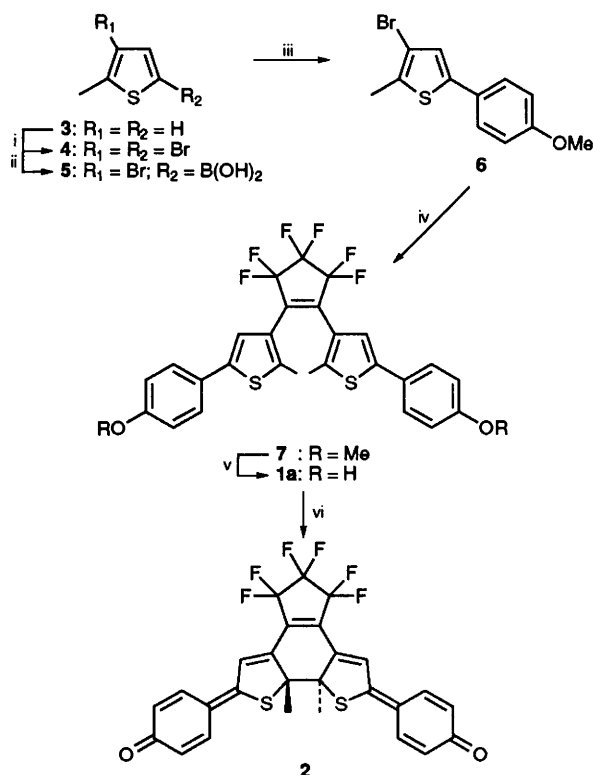
The modest yield of 50% appears to be due to the further coupling of boronic acid and bromide **6** during the later stages of the reaction. Lithiation of the anisidylthiophene **6** followed by the addition of perfluorocyclopentene according to the described method¹¹ afforded the diarylethene **7** (mp 143 °C) in 90% yield. Subsequent demethylation using boron tribromide gave, quantitatively, the target molecule **1a** in the open form as a colourless powder (mp 118–120 °C, decomp.). The quinonoid compound **2** was synthesized by photochemically converting **1a** to its deep-blue closed form **1b** in acetonitrile, followed by the addition of excess potassium ferricyanide and aqueous potassium hydroxide. The extended quinone **2** was thus obtained as a shiny, black–violet solid exhibiting a characteristic IR band at 1620 cm⁻¹.

The photochemical properties of compound **1a** are in line with the remarkable photochromism demonstrated for diarylethenes of this type.⁷ Photocyclization of the colourless open form **1a** was monitored directly by NMR and electronic spectroscopy methods. Irradiation of a solution (1.25 × 10⁻⁵ mol dm⁻³, CD₃CN) of **1a** in a 5 mm NMR tube with ultraviolet light (312 nm) quickly resulted in the appearance of a deep-blue colour and absorption bands at 590 and 340 nm due to the generation of the closed isomer **1b**. The conversion at the photostationary state was determined to be >98% by NMR. The photocyclization could also be effected by irradiation at 365 nm with a photostationary state of 90% conversion to the coloured form. Once cyclized, the solutions were cleanly decolourized by exposure to visible light of >600 nm. While photochemical closure of **1b** could also be carried out at 254 nm, it was found that an additional process ensued resulting in the appearance of bands at 534 and 386 nm, corresponding to the formation of the quinonoid form **2** which does not open by irradiation with visible light (>600 nm). Thus, molecule **1b** may be either reversibly converted into **1a** or irreversibly oxidized to **2** depending on the irradiation wavelength. Fig. 1 shows the absorption spectra of the three species **1a**, **1b** and **2**. The very high interconversion efficiency, like those found earlier for related systems,⁴ may be a result of the respective



quantum yields for the cyclization and ring opening processes, as well as of favourable conformational features. In addition, the closed forms **1b** and **2** are thermally stable in solution at room temperature (unchanged after two weeks; work at higher temperatures in progress), and **2** is also photochemically stable (<2% change after 8 h of irradiation at >600 nm).

The light-triggered switching capacity of the system was demonstrated by cyclic voltammetry carried out in acetonitrile (Fig. 2). Whereas the open form **1a** is electrochemically inert within the -1 to +1 V domain, the closed isomer **1b**, which is an extended hydroquinone, presents a reversible bielectronic oxidation wave at +735 mV (with respect to SCE) corresponding to the formation of the quinonoid form **2**.[‡] The redox process was also studied in the opposite sense. The cyclic



Scheme 1 Reagents and conditions: i, Br_2 , AcOH (74%); ii, BuLi, THF then $(\text{BuO})_3\text{B}$ (78%); iii, 4-bromoanisole, Na_2CO_3 , H_2O , THF, $\text{Pd}(\text{PPh}_3)_4$ (50%); iv, BuLi, THF, C_5F_8 , -78°C (90%); v, BBR_3 , CH_2Cl_2 (quant.); vi, irradiation at 312 nm, MeCN, $\text{K}_3\text{Fe}(\text{CN})_6$, 0.1 mol dm^{-3} KOH (54%)

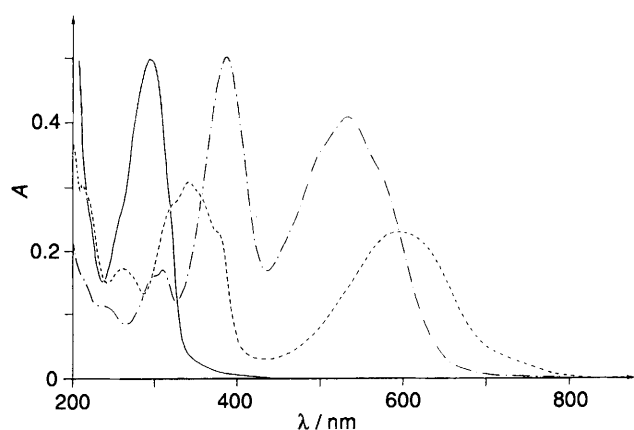


Fig. 1 Electronic absorption spectra of compounds **1a** (full line), **1b** (dashed line) and extended quinone **2** (partially dashed line) ($1.25 \times 10^{-5} \text{ mol dm}^{-3}$ in MeCN). $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$): **1a**: 293 (40000); **1b**: 590 (18300), 340 (24300); **2**: 534 (32800), 386 (40400)

voltammogram of synthetic **2** presents a reversible two-electron reduction wave at -180 mV (SCE). This value is comparable with those obtained for similar extended quinones.¹² Finally, unequivocal proof of multiple interconversion was offered by the following experiment. A solution of quinone **2** prepared chemically ($3.5 \times 10^{-5} \text{ mol dm}^{-3}$, acetonitrile) was reduced coulometrically to the bisphenol **1b**, accompanied by the expected colour change from violet to blue. The absorption spectrum of the solution corresponded to that of **1b** obtained by the photocyclization of **1a**. The same solution was then decolourized with visible light (>600 nm) and, finally, recycled to **1b** by irradiation at 312 nm.

The present study clearly demonstrates the two-level switching capacity of the system. Photochemically, **1** may be reversibly transformed between thermally stable states which are either electrically inert (**1a**) or active (**1b** which may be reversibly oxidized to **2**) within the -1 to $+1 \text{ V}$ range. In a complementary fashion, the device may be electrochemically interconverted between the hydroquinone form (**1b**), which exhibits photochromic properties (interconversion between **1a** and **1b**), and the quinonoid species **2** which is photochemically stable. Furthermore, the photooxidation of **1b** at 254 nm represents a means of directly transforming **1a** into **2**.

The special features of the three species are, in principle, well suited as the basis for an optical memory system¹³ with non-destructive write-read-erase capacity (see also ref. 7a). After photochemical writing with UV light (**1a** \rightarrow **1b**), the information may be 'safeguarded' by an electrical process (**1b** \rightarrow **2**). It may then be read many times and finally, after electroreductive unlocking (**2** \rightarrow **1b**), the information may be erased with visible light (**1b** \rightarrow **1a**). The safeguarding step also results in amplification considering that the quinonoid form

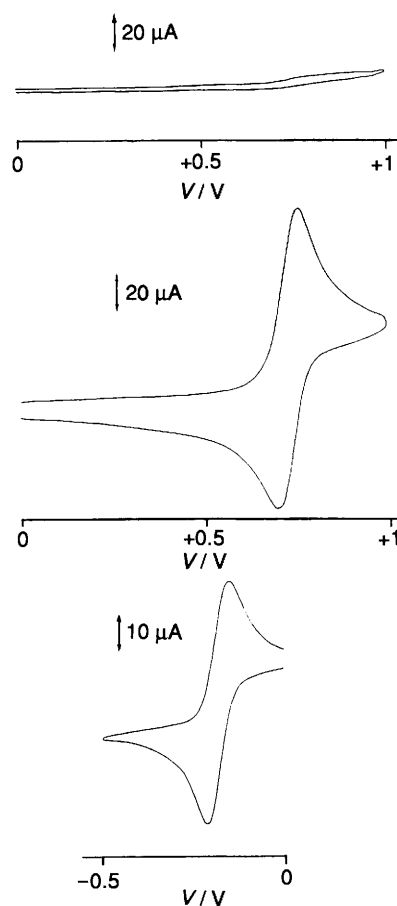


Fig. 2 Cyclic voltammograms determined for compounds **1a** (top), **1b** (centre) and **2** (bottom) in MeCN. ($10^{-3} \text{ mol dm}^{-3}$; supporting electrolyte $0.1 \text{ mol dm}^{-3} \text{ NBu}_4\text{BF}_4$)

absorbs approximately twice as strongly as **1b**. Furthermore, since the longest wavelength bands of **1b** and **2** overlap, reading may be done with either the same visible light as that used to erase or, for higher sensitivity, at the absorption maximum of **2** (534 nm). This represents an EDRAW (erase direct read after write) process as compared to the usual WORM (write once read many) process.

At the macroscopic level, substances of the type described here may be of much interest as materials for reversible information storage. At the microscopic level, they represent optically and electrically addressable, dual-mode molecular switching devices.

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Footnotes

† UPR No. 285 of the CNRS.

‡ Such electrochemical behaviour may be related to the redox properties of a switched molecular wire model based on the same class of compounds,⁴ and of those of another type of electroactive photochromic substances.⁶

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