A Dual-Mode Molecular Switching Device: Bisphenolic Diarylethenes with Integrated Photochromic and Electrochromic Properties

Stephen H. Kawai, Sylvain L. Gilat, Rachel Ponsinet and Jean-Marie Lehn*

Dedicated to Professor George Just on the occasion of his 65th birthday

Abstract: The bisphenolic dithienylethene molecules **1a** and **1b** were synthesized in overall yields of 45% from 4-bromoanisole and 44% from 2,6-di-*tert*-butyl-4-iodophenol, respectively. The corresponding extended quinones **3a** and **3b** were also prepared. Photochemical studies showed that compounds **1** are photochromic; the open forms **1** could be converted with UV light of 312 nm to the closed coloured forms **2** with photostationary states lying at essentially complete conversion (>98%). The **1a–2a** system was found to exhibit good resistance to photofatigue and thermal stability for both photoisomers. Cyclic voltammetry studies involving the **2**/**3** couples showed that whereas **2b** undergoes irreversible oxidation at + 0.85 V (vs. SCE in THF), the hydroquinone **2a** is reversibly oxidized at an $E_{1/2}$ of + 0.72 V (in MeCN, quasi-reversibly in THF at + 0.81 V); this reflects the differences in deprotonation behaviour of the generated QH_2^{2+} species. The large difference in oxidation potential between **1a** and **2a** allows the photochemical switching of redox properties. In a complementary fashion, redox switching of the photochromic properties within the **2a–3a** pair is possible since **3a** is stable to visible light. Owing to this unique behaviour, the triad consisting of **1–3a** represents a novel molecular device with mutually regulating photo- and electrochromic behaviour. In addition, the ability to interconvert between the three stable states makes the system well-suited as the basis for an optical memory system with multiple storage and nondestructive readout capacity through a write-lock-read-unlock-erase cycle.

Keywords
diarylethenes · electrochromes · molecular devices · optical memory · photochromes

Introduction

There is much interest in molecular switching processes[1] as they are crucial to the realization of devices that operate at the molecular and supramolecular levels.[2] Varied approaches have been used in designing bistable systems whose physical behaviour can be modulated by an external stimulus. We have recently described molecular devices whose luminescent properties can be switched electrochemically,[3] as well as a series of switchable systems for which conjugation-dependent (electron-conduction, nonlinear optical) behaviour is triggered with light.[4, 5]

To a large extent, the molecular switches described to date operate in a single level or mode with the controlling stimulus reversibly modulating or, at best, regulating a second property in an "on–off" manner. A more complex type of switching capacity is exhibited by dual-mode systems combining two reversible processes that can be addressed by means of two different stimuli (Fig. 1a). Chemical transducers of this type have been reported, all of which combine photochromic and electrochromic properties in such a way that light and redox reactions may be employed to effect reversible conversions between an array of states. Examples of such systems include anthroquinone-incorporating azobenzene,[6] stilbene[7] and dihydroazulene-type[8] photochromes. Dihydroazulenes bearing dicyanovinyl[9] and other electroactive groups[10] have also been described. Shortcomings of these systems are the instability of certain states and the fact that the two properties, which are often dependent on structurally separate components within the molecules, are only weakly coupled.

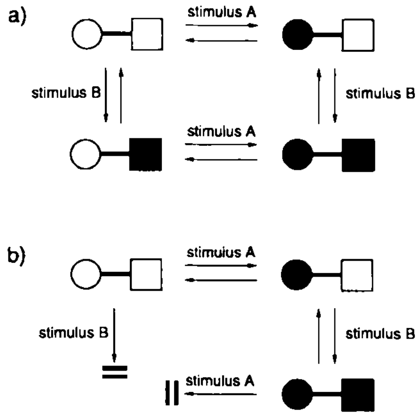

Fig. 1. Schematic representations of dual-mode switching devices: a) a chemical transducer for which the different stimuli A and B can be used to interconvert the device within an array of states; b) an integrated system for which the stimuli A and B mutually control each other's effect.

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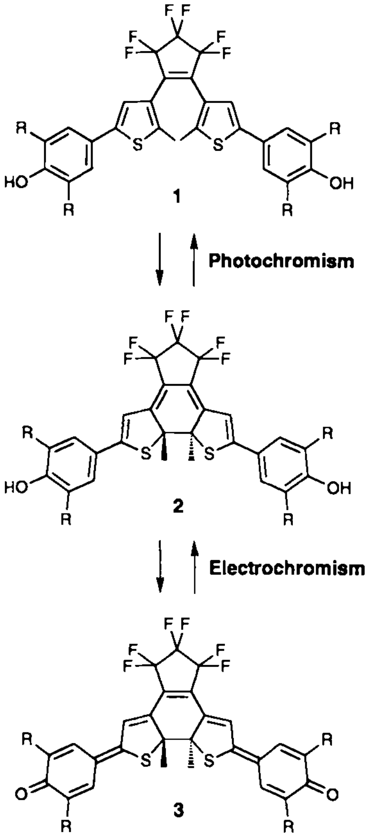
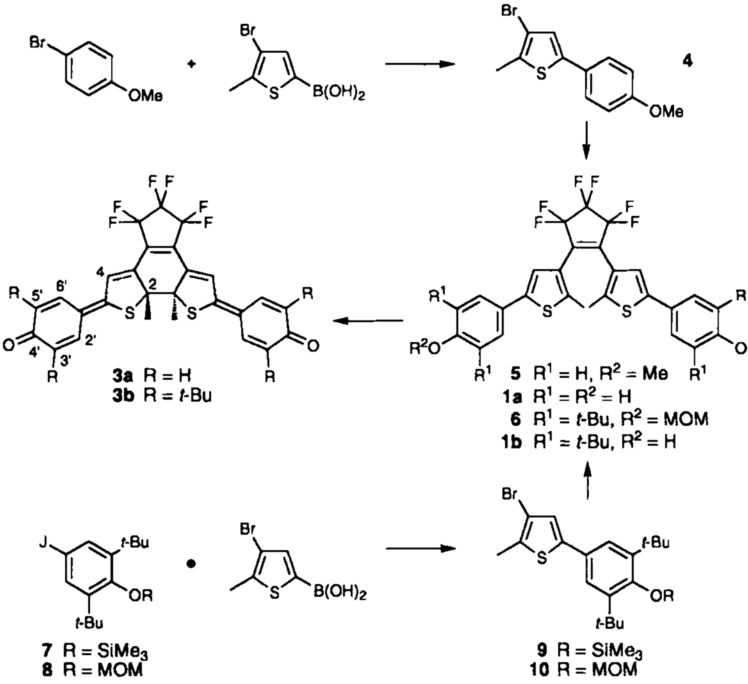


Scheme 1. Photo- and electrochemical interconversions between open 1, closed 2 and quinonoid 3 forms.

We herein describe a molecular switching device whose unique behaviour is well-suited to form the basis of a medium for erasable optical data storage exhibiting nondestructive readout capacity. In this system, photochromic and electrochromic properties are mutually regulating in a manner depicted in Figure 1 b, owing to the fact that the structural features responsible for them are tightly integrated within a single molecular architecture. The device (Scheme 1) consists of the three components 1, 2 and 3, which all exhibit good stability unless exposed to the specific stimulus required to interconvert them, namely, light of a particular frequency or an applied potential.



Scheme 2. Synthesis of the bisphenolic dithienylethenes and of the corresponding extended quinones.

Results and Discussion

Synthesis: The target molecules were prepared according to Scheme 2. Initial attempts to carry out the palladium(0)-catalyzed cross-coupling[11] of 4-bromoanisole and 2-methyl-3,5-dibromothiophene[12] via organolithium or organozinc intermediates[13] failed to give the desired anisylthiophene 4, regardless of the lithium or zinc derivative employed. Only small quantities of the 2,2'-dithiophene were, at times, produced. Similar results were also obtained using *O*-silylated derivatives of 4-bromophenol. The aryl–aryl bond could, however, be formed through the coupling[14] of 3-bromo-2-methylthiophene-5-boronic acid[4,15] and 4-bromoanisole using Pd(PPh$_3$)$_4$. The modest yield of 50% is likely to be due to the further coupling of bromide 4 and unreacted boronic acid. Evidence for the much greater reactivity of 4 compared to bromoanisole is provided by the fact that only slight traces of the desired product are obtained after prolonged reaction times.

Abstract in French: *Les dithiényléthènes photochromes 1a et 1b, substitués par des groupements phénols, et les quinones allongées correspondantes 3a et 3b ont été synthétisés. Les formes ouvertes 1 peuvent être complètement (>98%) cyclisées par irradiation UV en formes fermées colorées 2. Le système 1a–2a présente une bonne résistance à la photofatigue et une bonne stabilité thermique. La différence de réversibilité dans l'oxydation de 2a et 2b indique une différence de comportement dans la déprotonation de l'espèce QH_2^{2+} générée. Les propriétés rédox du couple 1a–2a peuvent être modulées photochimiquement du fait de l'écart important entre leur potentiel d'oxydation. De même, 3a étant insensible à l'irradiation par la lumière visible, la modulation électrochimique des propriétés photochromes est possible pour le système 2a–3a. La triade 1–3a constitue ainsi un nouveau composant moléculaire intégrant des fonctions photo- et électrochimiques mutuellement régulées qui pourrait former la base d'une mémoire optique permettant le stockage multiple et la lecture sans destruction d'informations selon la séquence écrire-verrouiller-lire-déverrouiller-effacer.*

The lithiation of bromothiophene 4 in tetrahydrofuran, followed by the addition of perfluorocylopentene, according to the published method,[16,17] afforded the bisanisyl photochrome 5 in 90% yield, which was subsequently demethylated with boron tribromide in dichloromethane. By carrying out the reaction, workup and chromatography in the dark, the target molecule 1a could be quantitatively obtained in its open form as a white powder. The extended quinone 3a was prepared by irradiating a series of 5 mm NMR tubes containing solutions of 1a in acetonitrile, with UV light of 312 nm. Aqueous potassium ferricyanide and potassium hydroxide were then added to the combined solutions of the resulting photochrome in its cyclized form; an immediate change in colour from blue to red-violet was observed. After workup and chromatographic purification, the intensely coloured quinonoid compound 3a was obtained as a violet-black solid. The ^{1}H NMR spectrum of 3a exhibits the anticipated nonequivalency of the oxocyclohexadienylidene protons; the H-2' signal is 0.17 ppm upfield of that of H-6', presumably due to shielding by the thiophene sulphur. A characteristic IR band at 1620 cm^{-1} was also observed for the carbonyl group.

The diarylethene 1b was prepared in a similar manner to 1a. Since it had been reported that phenolic methyl groups in such *tert*-butylated systems were difficult to cleave, we proceeded from the known silyl ether 7.[18] The Suzuki coupling[14] of 7 and boronic acid provided the arylthiophene 9 in 68% yield, accompanied by desilylated product. Treatment of 9 with *n*-

butyllithium followed by the addition of perfluorocyclopentene, however, repeatedly yielded the starting bromide. It was found that, even at ambient temperature, the lithium–halogen exchange does not occur. This may be due to competing deprotonation of the silyl methyl group to yield an α-stabilized lithio species, which occurs much more rapidly than attack at the bromine.

Few protecting groups are suitable for highly hindered phenols; in this case, it would also have to be stable in the presence of butyllithium. Methoxymethyl ether (MOM) seemed to be the best candidate. Attempts to introduce the MOM group by the usual methods failed. Finally, 2,6-di-*tert*-butyl-4-iodophenol[19] was deprotonated with *n*-butyllithium in tetrahydrofuran followed by the addition of chloromethyl methyl ether to afford the MOM-protected phenol **8** in 60% yield. The subsequent Pd^0-catalyzed coupling to the boronic acid gave an excellent yield (92%) of the arylthiophene **10**. In a model study, the molecule was treated with one equivalent of *n*-butyllithium at −78 °C, which, after the addition of methanol, yielded the debrominated product; this demonstrated that the lithium–halogen exchange proceeds smoothly for this system. Thus, **10** was condensed with perfluorocyclopentene in the usual manner to give photochrome **6**, which was not isolated, but hydrolysed directly. Removal of the MOM groups required stirring a solution of diether **6** in 1:4 concentrated hydrochloric acid/tetrahydrofuran for 2.5 days at room temperature. After workup and chromatography, the target system **1b** was obtained as a colourless foam in 79% yield from **8**. Unlike the case for the quinonoid compound **3a** which, after workup, yielded a mixture consisting essentially of product and uncyclized photochrome, the ferricyanide oxidation of **2b** generated by the UV irradiation of **1b** gave many coloured products. After partial purification by chromatography, the resulting violet glass was triturated with acetonitrile to afford the tetra(*tert*-butylated) quinone **3b** as a black powder in 27% yield.

Photochemical Properties: The photochromism of diarylethenes, involving light-induced electrocyclization and ring opening, has been known for several decades.[20] However, it is only recently that thiophene-derived systems,[17, 21, 22] notably those based on perfluorocyclopentene,[17, 22] have been demonstrated to exhibit especially pronounced photochromic behaviour. In most cases, both open and cyclized forms are thermally stable and photochemical interconversion may be repeatedly carried out without loss of activity.

The photocyclization of the bisphenol photochrome **1a** was monitored simultaneously by both proton NMR and UV methods. Irradiation of a colourless solution of **1a** in deuterated acetonitrile with UV light of 312 nm resulted immediately in a deep blue colour. The reaction was easily monitored by the appearance of new NMR signals (see Table 1) corresponding to the cyclized form **2a**. At the end of the reaction, no trace of the open isomer could be observed (>98% cyclization at the photostationary state). The photocyclization was followed by UV spectroscopy by diluting aliquots of the NMR sample. The irradiation resulted in the disappearance of an absorption band at 293 nm corresponding to **1a**, and the appearance of a complex band at 340 nm and a broad absorption band centred in the visible region at 590 nm, corresponding to the cyclized isomer **2a**. A clean isosbestic point was recorded at 318 nm (Fig. 2).

Table 1. ^{1}H NMR (200 MHz) and absorption spectral data for compounds **1–3**.

	^{1}H NMR chemical shifts, δ/ppm 2″	3″	5″	6″	4′	Me	OH	UV/Vis, λ_{max}/nm ($\varepsilon \times 10^{-4}$/cm^{-1}M^{-1})
1a [a]	6.89	7.49	7.49	6.89	7.27	2.20	7.20	293 (3.8)
2a [a]	6.93	7.59	7.59	6.93	7.62	2.21	6.74	340 (2.5), 590 (1.8)
3a [b]	7.37	6.54	6.46	7.54	7.46	1.78		386 (4.0), 534 (3.3)
1b [c]	7.31			7.31	7.08	2.01	5.30	296 (4.0) 296 (4.2) [d]
2b [c]	7.40			7.40	6.57	2.14	5.65	361 (2.4), 597 (1.9) 365 (2.6), 598 (2.1) [d]
3b [b]	7.09			7.23	7.38	1.76		395 (4.7), 554 (4.0) [d]

[a] In CD_3CN. [b] In $CDCl_3$. [c] In CD_2Cl_2, *tert*-butyl signals at δ = 1.44 and 1.42 for **1b** and **2b**, respectively. [d] In tetrahydrofuran.

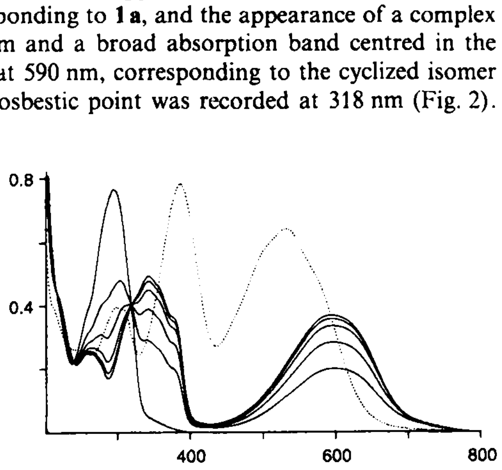


Fig. 2. Changes in the absorption spectrum during the photochemical conversion of **1a** to **2a**; spectra of **1a** before and after six successive irradiations of 2 s duration at 312 nm (——); absorption spectrum of **3a** (·····) (2.0 × 10^{-5} M in MeCN).

The colourless open form could then be regenerated by irradiation with visible (red) light of λ > 600 nm. The colouration reaction could also be effected with UV light of 365 nm with a photostationary state at 90% cyclization. Finally, the photofatigue resistance of the **1a–2a** pair was evaluated by alternating irradiation with UV and visible light. After ten colouration–decolouration cycles, less than 1% decomposition (oxidation to the corresponding quinonoid form **3a**) was observed.

The thermal stability of the coloured forms of dithienylethene photochromes is well established,[21–24] and the present system exhibits similar features. A solution of **2a** in acetonitrile was found to be stable at ambient temperature in the dark for over two weeks. After over a month, very slight traces of what was most likely the quinone **3a** were detected by NMR; however, no open isomer was observed. At 60 °C in acetonitrile solution, clean thermal decolouration to the open-ring form **1a** (isosbestic point at 318 nm) was found to occur with a half-life of slightly under a week (167 h).

The analogous *tert*-butylated system **1b** was studied in a similar fashion. Attempts to carry out the photocyclization from **1b** to **2b** in chloroform, acetonitrile or DMF failed to give clean results. In the more polar solvents, the colourless solutions initially turned blue, then rapidly turned pink and then greyish yellow upon continued irradiation at 312 nm. Clean photocyclization was, however, achieved in dichloromethane (as well as in THF), which made it possible to perform the NMR–UV experiment described above. Again, the closed form was produced in essentially quantitative yield (>98%) by irradiation, as measured by proton NMR. The process was monitored by the decrease in the absorption band at 296 nm (open form **1b**) and the appearance and increase in absorptions centred at 361 and 597 nm; the latter is responsible for the deep blue colour of the cyclized dye **2b**. A clean isosbestic point was observed at 324 nm (Fig. 3).

Electrochemical Properties: The electrochemical properties of molecules **1a** and **2a** were studied by cyclic voltammetry (Table 2). Initial measurements were carried out in anhydrous

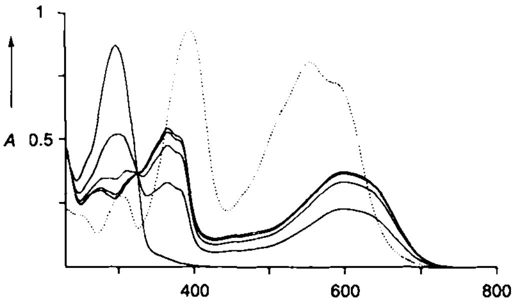


Fig. 3. Changes in the absorption spectrum during the photochemical conversion of **1b** to **2b**; spectra of **1b** before and after five successive irradiations of 2 s duration at 312 nm (——); absorption spectrum of **3a** (·····) (2.0×10^{-5} M in THF).

acetonitrile and the results are shown in Figure 4. The open form **1a** is electrochemically inert within the −1.4 to +1 V range and undergoes irreversible oxidation and reduction processes at +1.20 and −1.56 V, respectively (all potentials given with respect to SCE). The same sample was then irradiated with UV light directly in the electrochemical cell; this resulted in complete conversion to **2a** as verified spectrophotometrically. In its closed state, which may be viewed as an extended hydroquinone, the molecule undergoes a reversible (Fig. 7a), bielectronic oxidation at a half-wave potential of + 0.72 V. The quinonoid form **3a** exhibited a clearly reversible, two-electron reduction wave at a half-wave potential of −0.18 V (Table 3).

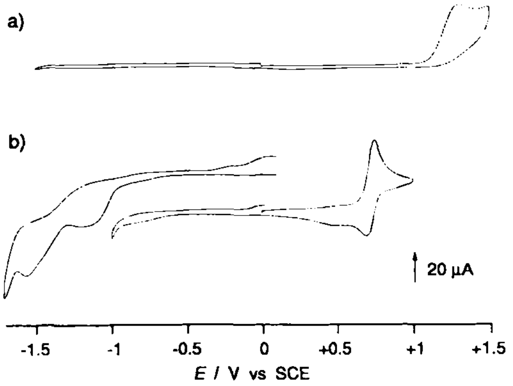


Fig. 4. Cyclic voltammograms of a) **1a** and b) **2a** (10^{-3} M in anhydrous MeCN, 0.1 M $n\mathrm{Bu_4NBF_4}$, scan rate: 100 $\mathrm{mV\,s^{-1}}$).

Table 3. Electrochemical data for quinonoid compounds **3** [a].

Compound	Solvent	E_{pa}^{red1}	E_{pc}^{red1}	ΔE^1	$E_{1/2}^{red1}$	E_{pa}^{red2}	E_{pc}^{red2}	ΔE^2	$E_{1/2}^{red2}$
3a	MeCN [b]	−0.21	−0.15	0.06	− 0.18	–	–	–	–
3a	THF [c]	−0.22	0.00	0.22	− 0.11	–	–	–	–
3b	THF [c]	−0.37	−0.15	0.22	− 0.26	−0.68	−0.47	0.21	−0.56

[a] Cyclic voltammetry in anhydrous solvent, 10^{-3} M, scan rate 100 $\mathrm{mV\,s^{-1}}$, 20 °C, under Ar, data given in V vs. SCE. [b] 0.1 M $n\mathrm{Bu_4NBF_4}$. [c] 0.1 M $n\mathrm{Bu_4NClO_4}$.

Similar experiments were carried out for the analogous *tert*-butylated system **1**–**3b**. It is known that the introduction of the bulky groups into the quinonoid structure often results in the separation of two normally coalesced reduction waves. Interconversion with the **2b**/**3b** redox couple would, therefore, be expected to proceed via a stable and observable semi-quinonoid species, adding a further element to the multi-mode switching properties of the device. Electrochemical measurements could not be performed in acetonitrile for two reasons: the low solubility of quinone **3b** in this solvent ($<10^{-7}$ M) and the fact that photocyclization from **1b** to **2b** could not be carried out cleanly, as mentioned above. Both photochemical and electrochemical processes could, however, be studied in tetrahydrofuran (THF). The cyclic voltammograms of the photochromic pair are shown in Figures 5a and 5b. The open bisphenol **1b** is inert within the −1.6 to + 0.85 V range in anhydrous solvent. After clean cyclization to **2b**, carried out in the electrochemical cell by irradiation at 312 nm, two irreversible oxidative process occur at + 0.85 and + 0.96 V.

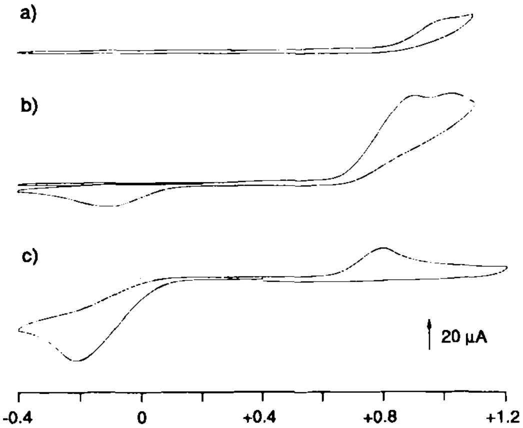


Fig. 5. Cyclic voltammograms of a) **1b** and b) **2b** in THF, and c) **3b** in THF/2% TFA (10^{-3} M in anhydrous solvent, 0.1 M $n\mathrm{Bu_4NClO_4}$, scan rate: 100 $\mathrm{mV\,s^{-1}}$).

Table 2. Electrochemical data for compounds **1** and **2** [a].

Compound	Solvent [b]	$E^{oxidation}$/V						$E^{reduction}$/V				
		$E\mathrm{pa}^1$	$E\mathrm{pc}^1$	ΔE^1	$E^1_{1/2}$	$E\mathrm{pa}^2$	$E\mathrm{pa}^3$	$E\mathrm{pc}^1$	$E\mathrm{pc}^2$	$E\mathrm{pc}^3$	$E\mathrm{pc}^4$	$E\mathrm{pc}^5$
1a	MeCN	+1.20	–	–	–	–	–	−1.56	–	–	–	–
	THF	+1.5	–	–	–	–	–	−1.8	–	–	–	–
1b	THF	+0.97	–	–	–	+1.46	–	−1.8	–	–	–	–
2a	MeCN	+0.75	+0.68	0.07	+0.72 [c]	+1.06	+1.82	−1.12	−1.54	−1.69	–	–
	MeCN/H_2O	+0.66	+0.60	0.06	+0.63 [c]	+1.05	+1.68	−1.11	−1.46	−1.67	−1.98	− 2.12
	THF	+0.93	+0.68	0.25	+0.81 [d]	+1.24	+1.5	−1.34	−1.7	–	–	–
	THF/H_2O	+0.72	+0.48	0.24	+0.60 [d]	+1.1	+1.9	−1.19	−1.61	−1.82	–	–
2b	THF	+0.85	–	–	–	+0.96	–	−1.37	−1.83	–	–	–

[a] Cyclic voltammetry with predistilled solvents, 10^{-3} M, scan rate 100 $\mathrm{mV\,s^{-1}}$, 20 °C, under Ar, all potentials vs. SCE; irreversible process unless otherwise indicated. [b] 0.1 M $n\mathrm{Bu_4NBF_4}$ for MeCN and MeCN/H_2O; 0.1 M $n\mathrm{Bu_4NClO_4}$ for THF and THF/H_2O. [c] Reversible, bielectronic. [d] Quasi-reversible, bielectronic.

The cyclic voltammogram of quinonoid **3b** in THF is shown in Figure 6a. As anticipated, two reversible, monoelectronic waves with half-wave potentials of −0.26 and −0.56 V were recorded, corresponding to the stepwise reduction of the system via the semiquinone. To permit comparison with these values, the measurements involving quinone **3a** were also carried out in anhydrous THF (Fig. 6b). In this solvent, a quasi-reversible bielectronic reduction occured at a half-wave potential of −0.11 V. This less negative value, compared to **3b**, is expected for a system lacking the electron-donating alkyl substituents. The data obtained for these systems also fall in line with those reported for a fairly large number of recently described[25] extended quinones incorporating sulphur-containing nuclei. These include *p*-diphenoquinone analogues extended by one[18, 26] or up to four[27] dihydrothiophenediylidene units, as well as a system incorporating a dihydrodithiapentalenediylidene.[28]

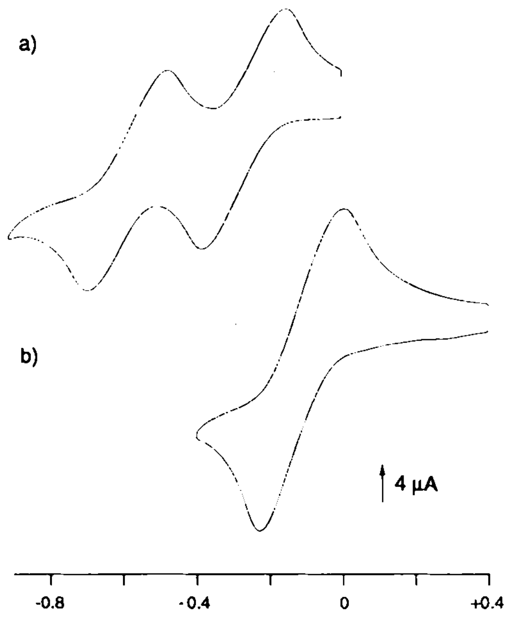


Fig. 6. Cyclic voltammograms of a) **3b** and b) **3a** (10^{-3} M in anhydrous THF, 0.1 M $n\mathrm{Bu_4NClO_4}$, scan rate: 100 mV s^{-1}).

Unlike these straightforward results obtained for the extended quinones **3**, those described above for the oxidation of the hydroquinone forms **2** raised a number of questions and led us to carry out more detailed studies. Of particular concern was the question of why, in the case of **2a**, the oxidation process is reversible, whereas it is irreversible for the *tert*-butylated analogue **2b**. In organic solvents, simple quinones are generally reduced in successive reversible one-electron waves to the dianion (i.e., $Q \rightleftharpoons Q^{\bullet -} \rightleftharpoons Q^{2-}$). Thus, the processes shown in Figure 6 correspond to the reversible reductions of **3** to closed photochromes **2** as the bisphenolates. The oxidation of hydroquinones, however, is complicated by the fact that protons are normally lost in the process shown in Equation (a), which

$$QH_2 \rightleftharpoons Q + 2H^+ + 2e^- \tag{a}$$

renders it irreversible.[29] While this is no doubt the case for hydroquinone **2b**, the apparent reversibility of the oxidation of **2a** implies that the diprotonated quinone QH_2^{2+} does not, at least not entirely, lose its protons before the reverse potential sweep.

More detailed studies of the reduced forms **2** were undertaken to clarify this, as well as to resolve certain problems of reproducibility. Furthermore, while a large amount of data exists for the reduction of quinones,[30] much less work has been carried out for the complementary oxidation of the hydroquinonoids, especially in the case of extended systems. As can be seen in Figure 4b, the return potential sweep following the oxidation of **2a** exhibits a small wave or "shoulder" following the E_{pa}. Initial results employing deoxygenated, but not predried, solvent did not always present this feature. Figure 7a shows the voltammogram of **2a** in anhydrous MeCN at different scan rates. The peak potentials E_{pc} and E_{pa} are clearly unaffected, consistent with a reversible redox process. The shoulder, however, becomes relatively more intense at slower scan rates. This suggests the partial intervention of a chemical reaction such as deprotonation. The experiment was then repeated in MeCN containing 2% water (Fig. 7b). Here, the reversible process is much cleaner, lacking the small wave on the return sweep. Finally, the experiment was carried out in anhydrous THF since this solvent would have to be employed to allow for comparison with results obtained for **2b** (Fig. 7c). In this case, the oxidation is quasi-reversible as shown by the dependence of the E_{pc} and E_{pa} values on the scan rate. The half-wave potential remains unchanged at + 0.81 V.

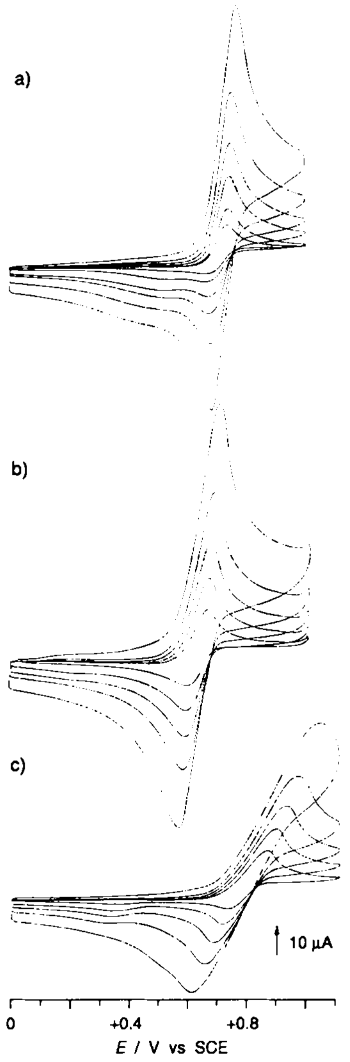


Fig. 7. Cyclic voltammograms of **2a** at scan rates of 500, 200, 100, 50 and 20 mV s^{-1} in a) anhydrous MeCN, b) MeCN/2% H_2O and c) anhydrous THF (10^{-3} M, 0.1 M $n\mathrm{Bu_4NBF_4}$ in MeCN, or $n\mathrm{Bu_4NClO_4}$ in THF).

A feature of the cyclic voltammogram of closed form **2b** (Fig. 5b) is the appearance of a wave at −0.10 V on the return potential sweep. This behaviour is typical for simple quinones in aprotic media and results from the reduction of the monoprotonated QH^+ species. The cyclic voltammogram (Fig. 5c) of the corresponding quinone **3b** in THF containing 2% trifluoroacetic acid (TFA) also shows a similar reduction process at −0.21 V, which corresponds to the QH^+ wave. These results indicate that **2b** indeed behaves like simple hydroquinones, with the oxidation being accompanied by deprotonation of the generated species.

A similar series of experiments were carried out for compounds **1**–**3a** in anhydrous THF (Fig. 8). In the open form **1a**, no oxidation is observed up to +1 V, whereas, as mentionned

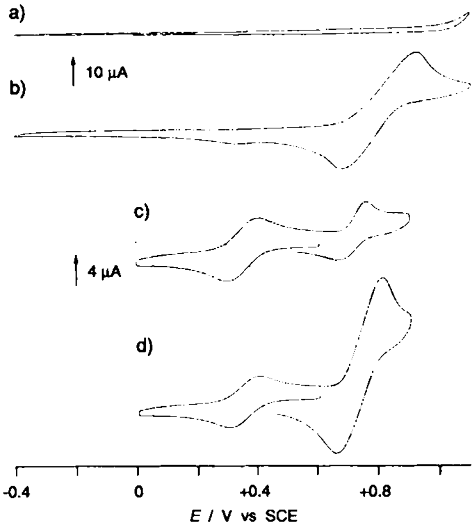


Fig. 8. Cyclic voltammograms of a) **1a** and b) **2a** in THF, c) **3a** in THF/2% TFA, and d) **2a** added to (c) (10^{-3} M in anhydrous solvent, 0.1 M $n\mathrm{Bu_4NClO_4}$, scan rate: 100 mVs^{-1}).

above, **2a** is quasi-reversibly oxidized at a half-wave potential of + 0.81 V. The experiment involving the quinone **3a** was then also carried out in THF containing 2% TFA. As shown in Figure 8c, when the voltage is swept downward from + 0.6 V, a reversible reduction process at + 0.35 V is observed (E_{pa} = + 0.30 V) corresponding to the reduction of the QH^+ species. A second reversible process is observed at + 0.71 V on the return positive sweep. This may correspond to the oxidation of a small amount of **2a** generated by the reduction of the monoprotonated quinone and subsequent deprotonation of the resulting monoprotonated hydroquinone form. When a small volume of solution containing hydroquinone **2a** was added to the cell and the measurement repeated (Fig. 8d), the QH^+ wave at + 0.35 V remained unchanged, while a large wave appeared at + 0.73 V (E_{pc} = + 0.81 V, E_{pa} = + 0.66 V), which must correspond to the oxidation of the added photochrome.

The fact that the QH^+ wave, observed in the above preprotonation study involving **3a**, is not seen or is only weakly present in the oxidation of **2a** further indicates that the resulting QH_2^{2+} species retains its protons, to be reduced back to **2a** on the reverse potential sweep. The reasons why **2a** and **2b** behave differently in this respect remain to be explained.

Dual-Mode Switching: Thus far, the photochromic and electrochromic properties of the present systems have been dealt with separately. Of key interest, however, is the manner in which the two types of behaviour are tightly coupled, each capable of contolling the other.

In the case of the device comprised of **1–3a**, the redox properties of the system can clearly be controlled photochemically in an "on–off" manner: When in the open form (**1a**), the molecule is electrochemically inert within the −1 to +1 V domain, whereas the photocyclized hydroquinonoid isomer **2a** is cleanly and reversibly oxidized at + 0.72 V in MeCN. The resistance of this system to photofatigue (described above) allows it to be switched repeatedly in this fashion.

The system is also designed such that the photochromic properties are dependent on the oxidation state within the **2a**–**3a** couple. The stability of the quinonoid form **3a** was therefore examined. The molecule is very stable in the solid state, remaining unchanged after over a year at ambient temperature. A high degree of chemical stability was also observed in solution at room temperature. When **3a** was heated to 60 °C in MeCN, slow decomposition to unidentifiable products occurred with a first-order half-life of 13 h for the decrease in the lowest energy absorption band. What is most important for our purposes is that quinone **3a** be photochemically stable. Irradiation of a MeCN solution of the dye with red light of $\lambda > 600$ nm for 8 h resulted in less than a 2% decrease in absorbance at its λ_{max}. A nonnegligible fraction of this loss is likely to be due to heating of the sample at later stages of the irradiation period. Under comparable conditions, the closed form **2a** is completely decolourized within 10 min. Thus, in its reduced hydroquinone form **2a**, the system is photochromic, while oxidation to the quinone **3a** can be used to effectively block photochemical decolouration.

Having established that complementary switching of photo- and electrochromic behaviour is indeed possible for this system, we performed the following experiment to clearly demonstrate the two-level interconversion properties. A solution of chemically prepared quinone **3a** in acetonitrile was reduced coulometrically to **2a**, and the anticipated colour change from red-violet to blue was observed. Apart from being a demonstration of electrochromism, the results confirmed the bielectronic nature of the process, since two equivalents of electrons were consumed. The sample of **2a** was then decolourized to **1a** with red light, which was then photocyclized by UV irradiation to regenerate the blue closed form.

Finally, a clear demonstration of the remarkable interconversion properties of the system is offered by the following: A solution of open photochrome **1a** in acetonitrile was photocyclized by irradiation at 312 nm. The resulting blue solution of **2a** was then coulometrically oxidized at +1 V to the red-violet quinone **3a**. The sample was then reconverted back to the hydroquinonoid form, again coulometrically, and the resulting blue solution of **2a** decolourized with visible light of wavelength above 600 nm to return, finally, back to the original, colourless open state **1a**. UV spectra were taken after each step of this full cycle and are presented in Figure 9 (compare with Fig. 2; the decrease in absorbance is due to dilution during the electrolytic steps).

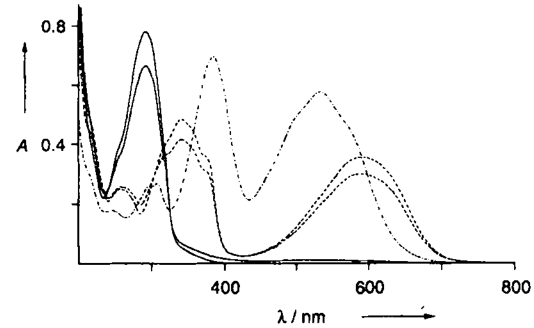


Fig. 9. Absorption spectra of **1–3a** during photo- and electrochemical interconversions: initial sample of **1a** (150 mL solution of 2×10^{-5} M concentration in anhydrous MeCN containing 0.1 M $n\mathrm{Bu_4NBF_4}$) (——); after irradiation at 312 nm for 7 min to give **2a** (−−−); after coulometric oxidation at + 1 V to give **3a** (-·-·-); after coulometric reduction at − 0.8 V to give **2a** (−−−); and after irradiation at $\lambda > 600$ nm for 10 min to give **1a** (——) (decrease in absorbance due to dilution during the electrolytic steps).

It was hoped that the properties of the analogous tetra(*tert*-butylated) series **1–3b** would also permit this type of dual-mode switching behaviour with the additional feature of a stable radical (semiquinone) species. However, a number of problems are inherent in this system. While the open form **1b** could be cleanly

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photocyclized to the closed isomer **2b**, the difference in their respective oxidation potentials is very small. In other words, oxidation of **2b** to **3b** cannot be effected without modification of the open form **1b**. In addition, the coloured photoisomer **2b** does not exhibit the degree of stability observed for **2a**. After five colouration–decolouration cycles, a 17% decrease in absorbance of the cyclized form was observed. Thus, although the semiquinone form was observed in these studies (by reduction of **3b**, Fig. 6), it is not readily accessible from **1b**.

Conclusion

The results obtained for compounds **1–3a** are summarized in Figure 10. At the microscopic level, the system clearly behaves as a dual-mode optical–electrical molecular switching device according to Figure 1 b, in which all three states are stable species. Furthermore, on the macroscopic level, the spectral and redox properties are very well suited to form the basis of an erasable optical data storage system[21c, 24, 31] with nondestructive readout capacity as depicted in Figure 11. While photochemical writing and erasing may be carried out as for any photochrome-based system, the redox behaviour of **2a** allows for the written data to be safeguarded or "locked" by oxidation to the quinonoid form **3a**. Not only does this prevent erasing during the "read" process with visible light, but it also represents an amplification of the stored data, since the quinone **3a** absorbs approximately twice as strongly as the coloured, photochromic form **2a**. A reduction process would then be used to "unlock" the information and permit subsequent photochemical erasing. The complete process is thus a five-step write-lock-read-unlock-erase cycle. Such a system is also of interest in that it allows for both "deep" and "shallow" memory modes within the same medium, since "locked" data would remain unaffected during the course of writing and erasing of temporarily stored information based solely on the photochromic forms of the device.

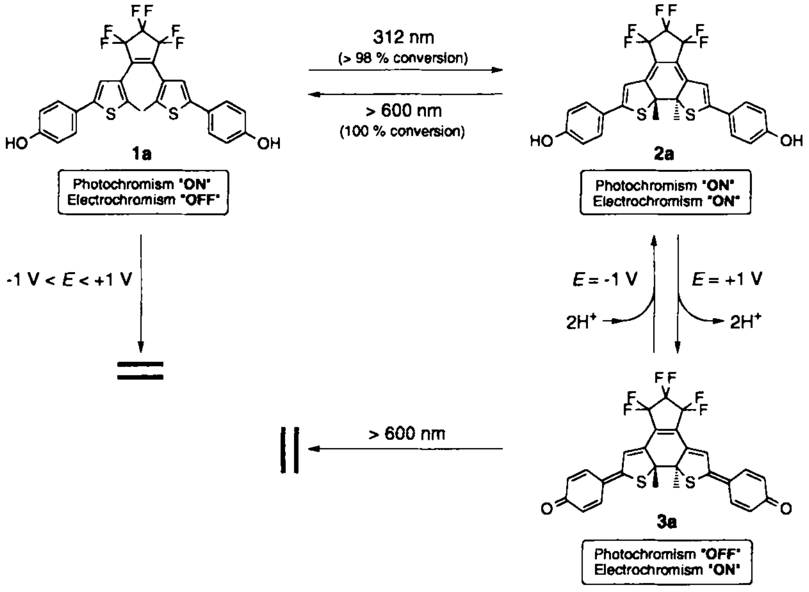

Fig. 10. Schematic representation of dual-mode switching and interconversion properties of **1–3a**.

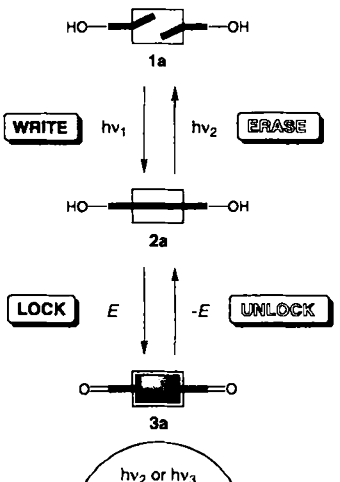

Fig. 11. Schematic representation of an erasable optical memory system with nondestructive readout capacity based on the photo- and electrochromic properties of compounds **1–3a**.

Experimental Section

General Methods: Starting materials were commercially available (Aldrich) and were used without further purification. Perfluorocyclopentene was purchased from Heraeus (Karlsruhe) or was obtained from Rhône-Poulenc. Tetrahydrofuran, dichloromethane and acetonitrile were distilled under nitrogen over lithium aluminium hydride, phosphorus pentoxide and calcium hydride, respectively. Thin-layer chromatography was performed using Kieselgel 60 F_{254} aluminium-backed plates (0.2 mm thickness) and visualized by UV. Kieselgel 60 (Merck 230–400 mesh) silica gel was employed for flash-column chromatography.

Melting points were determined on an Electrothermal 1A9100 digital apparatus and are uncorrected. NMR spectra were recorded on a Bruker AM200SY spectrometer. ^{1}H NMR spectra were obtained at 200.13 MHz, and the chemical shifts are given in ppm with respect to the residual proton signals of deuterated chloroform, dichloromethane and tetrahydrofuran, assigned values of $\delta = 7.26$, 5.32 and 1.85, respectively. Proton-decoupled ^{13}C NMR spectra were recorded at 50.33 MHz, and the chemical shifts are given with respect to the $CDCl_3$ or CD_3OD signals, assigned values of $\delta = 76.9$ and 49.0, respectively. IR spectra were obtained on a Perkin-Elmer 297IR instrument. UV/Vis absorption spectra were recorded on Perkin-Elmer 554 and Beckman DU640 spectrophotometers with spectrograde solvents. UV irradiations were performed with VL6LC (6 W) lamps. These are standard lamps used for visualizing TLC plates (intensity at 15 cm from filter: 610 $\mu W cm^{-2}$ at 312 and 365 nm). The emission is broad with a spike at 312 nm and 365 nm, respectively. For visible irradiations, light from a 300 W tungsten source was passed through a red filter (600 nm), and the samples were placed in a glass chamber maintained at 20 °C. Elemental analyses were performed by the Service Régional de Microanalyse, Université P. & M. Curie (Paris) or the Service Central d'Analyse CNRS (Vernaison). Mass spectra were measured at the Centre de Spectrométrie, Université de Paris VI.

5-(4′-Methoxyphenyl)-3-bromo-2-methylthiophene (4): Aqueous sodium carbonate (20% w/w, 45 mL) and tetrahydrofuran (45 mL) were added to 3-bromo-2-methylthiophene-5-boronic acid (7.00 g, 31.7 mmol), and 4-bromoanisole (6.0 mL, 48 mmol) was then added to the mixture which, upon rapid stirring, separated into two homogeneous phases. Tetrakis(triphenylphosphine)palladium(0) (1.65 g, 1.43 mmol) was then added to the reaction, which was refluxed under a nitrogen atmosphere. After 2.5 h, the reaction was cooled, extracted with diethyl ether (500 + 300 mL) and washed with saturated aqueous sodium bicarbonate (500 mL) and water (1 L). The combined ether phases were then dried ($MgSO_4$), filtered and evaporated in vacuo. The crude product, a yellowish solid, was chromatographed over silica gel (hexane/dichloromethane = 2:1) to yield a slightly yellow solid, which was triturated with hexane, filtered and washed twice with cold hexane. The procedure was repeated for the residue obtained after evaporation of the filtrate. The combined solids were then dried in vacuo. The thiophene **4** was obtained as a colourless, crystalline solid (4.49 g; 50%): M.p. 106 °C; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 2.40$ (s, 3H; 2-CH_3), 3.83 (s, 3H; OCH_3), 6.90 (A of AA′BB′, J(app.) = 8.9 Hz, 2H; H-2′,6′), 6.98 (s, 1H; H-4), 7.43 (B of AA′BB′, J(app.) = 8.9 Hz, 2H; H-3′,5′); ^{13}C NMR (50.33 MHz, $CDCl_3$): $\delta = 14.61$ (2-CH_3), 55.21 (OCH_3), 109.48 (C-3), 114.20 (C-3′,5′), 124.31 (C-4), 126.24 (C-1′), 126.50 (C-2′,6′), 132.38 (C-5), 140.96 (C-2), 159.27 (C-4′); MS (CI, NH_3): m/z (%): 285/283 (29) $[M + H^+]$, 284/282 (100/90) $[M^+]$, 269/267 (26/24) $[M^+ - CH_3]$, 204 (11) $[M + H^+ - Br]$, 81 (37), 69 (34); $C_{12}H_{11}BrOS$ (283.18): calcd C 50.90, H 3.92; found C 51.06, H 3.83.

1,2-Bis-[5′-(4″-methoxyphenyl)-2′-methylthien-3′-yl]perfluorocyclopentene (5): n-Butyllithium (2.7 mL, 2.5 M in hexane, 6.7 mmol) was added to a stirred solution of bromothiophene **4** (1.80 g, 6.36 mmol) in freshly distilled tetrahydrofuran (50 mL) at −78 °C under a nitrogen atmosphere. After 45 min, perfluorocyclopentene (384 µL, 2.86 mmol) was added to the reaction (through cooled syringe) which was stirred in the dark. After an additional 2 h of stirring at −78 °C, the reaction was allowed to warm to ambient temperature and was then extracted with diethyl ether (400 + 200 mL) and washed with hydrochloric acid (1.2 N, 400 mL) and water (400 mL). All operations were carried out, as much as possible, in the dark. The combined ether layers were then dried (MgSO$_4$), filtered and evaporated in vacuo. The resulting reddish syrup was chromatographed over silica gel (hexane/dichloromethane = 2:1) to yield the bisanisyl photochrome **5** as a slightly blue, amorphous solid (1.49 g, 90%). An analytical sample was obtained as a pale blue powder by trituration with hexane, filtration and drying in vacuo: M.p. 143 °C; ^{1}H NMR (200 MHz, CDCl$_3$): δ = 1.95 (s, 6H; 2′-CH$_3$), 3.84 (s, 6H; OCH$_3$), 6.91 (A of AA′BB′, *J*(app) = 8.8 Hz, 4H; H-2″,6″), 7.16 (s, 2H; H-4′), 7.47 (B of AA′BB′, *J*(app) = 8.8 Hz, 4H; H-3″,5″); ^{13}C NMR (50.33 MHz, CDCl$_3$): δ = 14.34 (2′-CH$_3$), 55.29 (OCH$_3$), 114.36 (C-3″,5″), 121.33 (C-4′), 125.70 (C-3′), 126.20 (C-1″), 126.84 (C-2″,6″), 140.16 (C-2′), 142.05 (C-5′), 159.48 (C-4″); MS (CI, NH$_3$): *m/z* (%) 581 (100) [*M* + H$^+$], 257 (12); $C_{29}H_{22}F_6O_2S_2$ (580.60): calcd C 59.99, H 3.82, found C 60.08, H 3.84.

1,2-Bis-[5′-(4″-hydroxyphenyl)-2′-methylthien-3′-yl]-perfluorocyclopentene (1a): Boron tribromide (73 µL, 0.78 mmol) was added to a stirred solution of photochrome **5** (226 mg, 0.39 mmol) in freshly distilled dichloromethane (5 mL) under a nitrogen atmosphere, and the reaction was stirred at ambient temperature in the dark. After 6.5 h, the reaction was extracted with dichloromethane (60 + 20 mL) and washed with water (2 × 40 mL). The combined organic phases were then dried (MgSO$_4$), filtered and evaporated in vacuo. The bisphenol **1a** was thus obtained as a slightly violet solid (214 mg, quantitative). An analytical sample was obtained as a white powder by trituration with dichloromethane, filtration and drying in vacuo: M.p. 118–120 °C (decomp.); ^{1}H NMR (200 MHz, CDCl$_3$): δ = 1.94 (s, 6H; 2′-CH$_3$), 4.94 (s, 2H; OH, exchangeable), 6.85 (A of AA′BB′, *J*(app) = 8.7 Hz, 4H; H-2″,6″), 7.15 (s, 2H; H-4′), 7.42 (B of AA′BB′, *J*(app) = 8.7 Hz, 4H; H-3″,5″); ^{13}C NMR (50.33 MHz, CD$_3$OD): δ = 14.44 (2′-CH$_3$), 116.87 (C-3″,5″), 121.91 (C-4′), 126.22 (C-3′), 126.81 (C-1″), 127.97 (C-2″,6″), 141.20 (C-2′), 144.33 (C-5′), 158.86 (C-4″); MS (CI, NH$_3$): *m/z* (%): 553 (45) [*M* + H$^+$], 552 (100) [*M*$^+$], 537 (23), 536 (25), 522 (13), 405 (5); $C_{27}H_{18}F_6O_2S_2$ (552.55): calcd C 58.69, H 3.28, found C 58.60, H 3.31.

Chemical Oxidation of 1a: A solution of bisphenol **1a** (50 mg, 0.090 mmol) in acetonitrile (10 mL) was divided into five 5 mm NMR tubes which were irradiated with UV light (312 nm). After 0.5 h, the resulting deep blue solutions were emptied into a round-bottom flask and the tubes rinsed with acetonitrile (5 mL in total). Potassium ferricyanide (500 mg, 1.50 mmol) was then added to the rapidly stirred solution of the cyclized photochrome followed by aqueous potassium hydroxide (0.1 M, 1.2 mL), which was slowly added dropwise. The reaction was then stirred at ambient temperature, protected from light. After 2 h, the wine-coloured reaction mixture was extracted with dichloromethane (80 + 40 mL) and washed with water (2 × 150 mL). The combined organic phases were dried (Na$_2$SO$_4$), filtered and evaporated in vacuo. The crude product, a violet solid, was then chromatographed over silica gel (dichloromethane/acetonitrile = 5:1, and then pure acetonitrile) to afford the quinonoid compound **3a** as a violet-black powder (27 mg, 54%): M.p. > 300 °C; ^{1}H NMR (200 MHz, CDCl$_3$): δ = 1.78 (s, 6H; 2-CH$_3$), 6.46 (dd, ^3J(H5′,H6′) = 9.9 Hz, ^4J(H5′,H3′) = 1.8 Hz, 2H; H-5′), 6.54 (dd, ^3J(H3′,H2′) = 9.7 Hz, ^4J(H3′,H5′) = 1.8 Hz, 2H; H-3′), 7.37 (dd, ^3J(H2′,H3′) = 9.7 Hz, ^4J(H2′,H6′) = 2.7 Hz, 2H; H-2′), 7.46 (s, 2H; H-4), 7.54 (dd, ^3J(H6′,H5′) = 9.9 Hz, ^4J(H6′,H2′) = 2.7 Hz, 2H; H-6′); ^{13}C NMR (50.33 MHz, CDCl$_3$): δ = 26.41 (2-CH$_3$), 70.92 (C-2), 127.05 (2C, C-1′ and 6′), 129.06 (C-4), 130.00 (C-2′), 132.45 (C-3′), 135.15 (C-5′), 146.01 (C-3), 158.35 (C-5), 186.63 (C-4′); IR (Nujol): $\tilde{\nu}$ = 1620 cm^{-1} (C=O).

***O*-Methoxymethyl-2,6-di-*tert*-butyl-4-iodophenol (8)**: *n*-Butyllithium (12.1 mL, 1.5 M in hexane, 18.1 mmol) was added over 15 min to a stirred solution of 2,6-di-*tert*-butyl-4-iodophenol (6.00 g, 18.1 mmol) in anhydrous tetrahydrofuran (30 mL) at −78 °C under a nitrogen atmosphere. After 5 min, chloromethyl methyl ether (2.7 mL, 36 mmol) was added to the reaction, which was allowed to warm to ambient temperature. After 2.5 h, the solution was extracted with diethyl ether (2 × 100 mL) and washed with saturated aqueous sodium bicarbonate (100 mL) and water (100 mL). The combined ether phases were then dried (Na$_2$SO$_4$), filtered and evaporated in vacuo. The crude product, a brown syrup, was chromatographed over silica gel (hexane) to afford the MOM-protected phenol **8** as a pale yellow syrup, which crystallized overnight (4.10 g, 60%): M.p. 70–71 °C; ^{1}H NMR (200 MHz, CDCl$_3$): δ = 1.41 (s, 18H; C(CH$_3$)$_3$), 3.64 (s, 3H; OCH$_3$), 4.88 (s, 2H; OCH$_2$O), 7.52 (s, 2H; H-3,5); ^{13}C NMR (50.33 MHz, CDCl$_3$): δ = 31.76 (C(*C*H$_3$)$_3$), 35.69 (*C*(CH$_3$)$_3$), 57.20 (OCH$_3$), 88.57 (C-4), 100.66 (OCH$_2$O), 135.63 (C-3,5), 146.98 (C-2,6), 154.55 (C-1); $C_{16}H_{25}O_2I$ (376.28): calcd C 51.07, H 6.70; found C 51.16, H 6.70.

3-Bromo-5-(*O*-methoxymethyl-3′,5′-di-*tert*-butyl-4′-hydroxyphenyl)-2-methylthiophene (10): A solution of iodide **8** (2.61 g, 6.95 mmol) in tetrahydrofuran (14 mL) was added to a solution of 3-bromo-2-methylthiophene-5-boronic acid (1.69 g, 7.64 mmol) in aqueous sodium carbonate (14 mL, 20% w/w). Two homogeneous phases were formed. Tetrakis(triphenylphosphine)palladium(0) (241 mg, 0.208 mmol) was then added and the reaction was refluxed under a nitrogen atmosphere. After 1.5 h the reaction was cooled, extracted with diethyl ether (2 × 100 mL) and washed with saturated aqueous sodium bicarbonate (200 mL) and water (200 mL). The combined ether phases were then dried (Na$_2$SO$_4$), filtered and evaporated in vacuo to yield a brown syrup. This was chromatographed over silica gel (hexane/dichloromethane = 5:1) to give the arylthiophene **10** as a pale yellow syrup (2.73 g, 92%): ^{1}H NMR (200 MHz, CDCl$_3$): δ = 1.48 (s, 18H; C(CH$_3$)$_3$), 2.42 (s, 3H; 2-CH$_3$), 3.67 (s, 3H; OCH$_3$), 4.94 (s, 2H; OCH$_2$O), 7.02 (s, 1H; H-4), 7.41 (s, 2H; H-2′,6′); ^{13}C NMR (50.33 MHz, CDCl$_3$): δ = 14.67 (2-CH$_3$), 31.88 (C(*C*H$_3$)$_3$), 35.77 (*C*(CH$_3$)$_3$), 57.17 (OCH$_3$), 100.62 (OCH$_2$O), 109.51 (C-3), 123.85 (C-2′,6′), 124.85 (C-4), 126.39 (C-1′), 132.77 (C-5), 141.82 (C-2), 144.95 (C-3′,5′), 154.49 (C-4′).

1,2-Bis-[5′-(3″,5″-di-*tert*-butyl-4″-hydroxyphenyl)-2′-methylthien-3′-yl]perfluorocyclopentene (1b): *n*-Butyllithium (1.35 mL, 1.5 M in hexane, 2.02 mmol) was added to a stirred solution of bromothiophene **10** (800 mg, 1.88 mmol) in freshly distilled tetrahydrofuran (15 mL) at −78 °C under a nitrogen atmosphere. After 40 min, perfluorocyclopentene (384 µL, 2.86 mmol) was added to the reaction by means of a cooled syringe, and the reaction kept in the dark. After an additional 2 h of stirring at −78 °C, the reaction was allowed to warm to ambient temperature and was then extracted with diethyl ether (2 × 100 mL) and washed with water (2 × 200 mL). The combined ether layers were dried (Na$_2$SO$_4$), filtered and evaporated in vacuo. The resulting orange solid, consisting primarily of the MOM-protected photochrome **6**, was used without further purification: ^{1}H NMR (200 MHz, CDCl$_3$): δ = 1.47 (s, 36H; C(CH$_3$)$_3$), 2.01 (s, 6H; 2′-CH$_3$), 3.66 (s, 6H; OCH$_3$), 4.91 (s, 4H; OCH$_2$O), 7.12 (s, 2H; H-4′), 7.39 (s, 4H; H-2″,6″).

The crude product obtained above was dissolved in tetrahydrofuran (12 mL), and concentrated hydrochloric acid (3 mL) was then added. After being stirring in the dark at ambient temperature for 2.5 d, the reaction was poured into water (300 mL), extracted with diethyl ether (150 + 100 mL) and washed with saturated aqueous sodium bicarbonate (100 mL). The combined ether layers were then dried (Na$_2$SO$_4$), filtered and evaporated in vacuo to give a brown syrup. Chromatography over silica gel (hexane/dichloromethane = 5:1) yielded the *tert*-butylated photochrome **1b** as a colourless foam (497 mg, 79% from **10**): ^{1}H NMR (200 MHz, CDCl$_3$): δ = 1.46 (s, 36H; C(CH$_3$)$_3$), 2.00 (s, 6H; 2′-CH$_3$), 5.30 (s, 2H, exchangeable: OH), 7.08 (s, 2H; H-4′), 7.32 (s, 4H; H-2″,6″); ^{13}C NMR (50.33 MHz, CDCl$_3$): δ = 14.37 (2′-CH$_3$), 30.15 (C(*C*H$_3$)$_3$), 34.32 (*C*(CH$_3$)$_3$), 121.06 (C′-4), 122.61 (C-2″,6″), 124.90 (C-1″), 125.65 (C-3′), 136.50 (C-3″,5″), 139.76 (C-2′), 143.31 (C-5′), 153.85 (C-4″); $C_{43}H_{50}O_2S_2F_6$ (776.98): calcd C 66.47, H 6.49; found C 66.73, H 6.71.

Photocyclization and Oxidation of (1b): A solution of bisphenol **1b** (135 mg) in acetonitrile (20 mL) was irradiated with UV light (312 nm) for 2 h; this resulted in a deep blue solution. Aqueous potassium hydroxide (0.1 M, 2 mL) and potassium ferricyanide (1.50 g) were then added, and the mixture was stirred at ambient temperature in the dark. After 10 h, the reaction was extracted with dichloromethane (80 + 40 mL) and washed with water (2 × 150 mL). The combined organic phases were dried (Na$_2$SO$_4$), filtered and evaporated, and the crude product was chromatographed over silica gel (hexanes/dichloromethane = 3:1) to afford a reddish-black glass. This material was then triturated with acetonitrile and the resulting solid filtered and washed with additional solvent to yield the quinonoid compound **3b** as a black powder (36 mg, 27%): M.p. 234–236 °C (decomposes to a reddish syrup); ^{1}H NMR (200 MHz, CDCl$_3$): δ = 1.34 (s, 36H; C(*C*H$_3$)$_3$), 1.76 (s, 6H; 2-CH$_3$), 7.09 (d, ^4J(H2′,H6′) = 2.4 Hz, 2H; H-2′), 7.23 (d, ^3J(H6′,H2′) = 2.4 Hz, 2H; H-6′), 7.38 (s, 2H; H-4); ^{13}C NMR (50.33 MHz, CDCl$_3$): δ = 26.70 (2-CH$_3$), 29.47 and 29.51 (C(*C*H$_3$)$_3$), 35.36 and 35.69 (*C*(CH$_3$)$_3$), 69.90 (C-2), 125.20 (C-6′), 127.63 (C-1′), 128.55 (C-2′), 128.75 (C-4), 143.96 (C-3), 146.73 (C-3′), 150.26 (C-5′), 154.01 (C-5), 185.93 (C-4′); IR (KBr): $\tilde{\nu}$ = 1600 cm^{-1} (C=O).

Electrochemistry: Cyclic voltammetry was performed using a standard three-electrode configuration with a glassy carbon (3 mm diameter disk) working electrode, a platinum wire counter electrode and a Saturated Calomel Electrode (SCE) equipped with a double fritted sheild as the reference electrode. A Princeton 362 scanning potentiostat was used and the results were recorded on an Ifalec 1F-3802 recorder. All experiments were performed under argon at 20 °C (thermostated) in freshly distilled solvents that had been previously saturated with argon. The surface of the working electrode was polished before each measurement. The electrolytes used were $n\mathrm{Bu_4N\,BF_4}$ and $n\mathrm{Bu_4N\,ClO_4}$ for experiments carried out in acetonitrile and tetrahydrofuran, respectively. Solutions of 3 or 5 mL containing compounds **1**, **2** or **3** at 10^{-3} M concentration and 0.1 M in electrolyte were employed. Closed forms **2** were prepared in situ by irradiating solutions of **1** in the electrochemical cell with 312 nm light at 20 °C using two lamps. Attainment of the photostationary state (i.e., > 98% cyclization) was verified by measurement of the UV spectra. The apparatus was placed in a simple cardboard box to protect solutions from ambient light.

For coulometry experiments, a 5 m platinum wire (0.25 mm diameter) working electrode, a platinum wire counter electrode and an SCE reference electrode were employed at electrolytic potentials of +1 V and −0.8 V. The reactions were carried out in a 250 mL beaker fitted with a plastic lid under a current of argon. The entire apparatus was protected from ambient light throughout all experiments.

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