Light-Triggered Molecular Devices: Photochemical Switching of Optical and Electrochemical Properties in Molecular Wire Type Diarylethene Species

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

Abstract: Organic photochromic systems represent a starting point for the elaboration of light-triggered molecular switching devices. The novel bispyridinium and bispyridine compounds $\mathbf{1}^{2+}$ and **6** were synthesized as their uncyclized isomers from 3,5-dibromo-2-methylthiophene in overall yields of 43 and 44%, respectively. The diarylethene photochromes **2** and **10**–**13**, substituted with electron donors and acceptors, were prepared from 5-methylthiophene-2-carboxaldehyde in 21–32% overall yield. All of the compounds were found to exhibit pronounced photochromic properties. Irradiation with UV light resulted in essentially complete photocyclization of the open forms to the intensely coloured closed isomers which could, in turn, be reconverted back to the open state with visible light of $\lambda > 600$ nm. The absorption maxima of the described compounds in their closed forms are shifted far towards, and even into, the near-IR region. Whereas no thermochromic properties were observed for the open isomers, the rates of thermal decolouration of the cyclized forms was found to be highly dependent on the nature of the substituents on the thiophene rings. It was demonstrated that reversible photochemical interconversion between the two photochromic states could be used to effectively switch a number of physical properties. Thus, the molecules $\mathbf{1}^{2+}$ and **12** represent two kinds of redox switches, the former in reduction and the latter in oxidation, in which electron conduction is switched on in the closed state and off in the open state. Compound **12** may also be considered to be a photoswitchable analogue of tetrathiafulvalene type substances. On the other hand, compound **2** displays a marked increase in nonlinear optical activity on conversion from the open to the closed form. Such systems are prototypes of photoswitchable molecular wires where electron conduction and push–pull interaction can be reversibly modulated by an external stimulus, namely, irradiation by light.

Keywords
diarylethenes · molecular devices · nonlinear optics · photochromes · redox switches ·

Introduction

The ability to modulate a given physical property by means of an external trigger is of central importance to the development of molecular and supramolecular devices.[1, 2] Owing to this fact, an ever increasing effort is presently being directed towards the design of dynamic molecular systems for use as switching devices that can undergo reversible changes between different states. To date, a variety of systems has been described[3, 4] for which a particular stimulus can be used to activate or modulate a second physical property and which fall into the category of molecular switches. In this context, photochromic organic compounds[5] are of particular interest since they represent a starting point for the design of bi or oligo stable molecules whose behaviour can be controlled by light.

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Terminally functionalized polyenes have long been the subject of investigation in our laboratory. Much of this work has focused on their pronounced nonlinear optical properties; symmetrically substituted systems have high cubic hyperpolarizabilities and donor–acceptor compounds exhibit marked second-harmonic generation capacities.[6] Bispyridinium polyenes (caroviologens) have been studied and shown to function as molecular wires, capable of conducting electrons across bilayer membranes into which they are incorporated.[7] The respective behaviours of all of these systems rely on the electronic conjugation between the functional groups situated at the extremities of the polyolefinic chains. The incorporation of an appropriate photochromic switching unit capable of reversibly interrupting or establishing this conjugation would, therefore, permit reversible modulation of the properties through irradiation at selected frequencies as depicted in Figure 1. In principle, any type of physical behaviour dependent on the electronic communication between the end groups A and B can be controlled photochemically in such a system.

Diarylethenes,[8–15] notably thiophene-derived systems,[11–15] are especially well-suited as switching units since irradiation with light of well-separated wavelengths can interconvert them between isomers in which the heterocycles are

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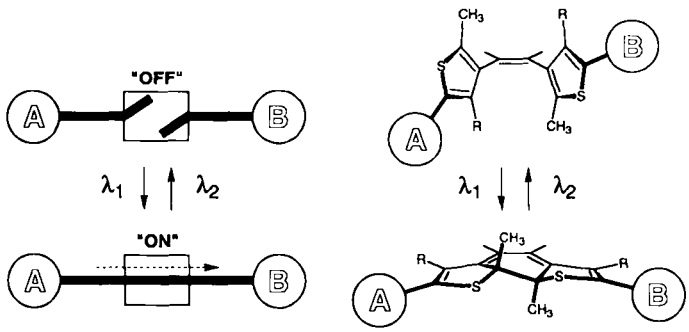

Fig. 1. Left: Principle of a photo-controlled molecular switching device based on functional units A and B joined by a polyconjugated pathway, which incorporates a light-sensitive switching unit. Right: Open and closed forms of a dithienylethene-based device corresponding to the "off" and "on" states, respectively.

either conjugated (closed or "on" state) or nonconjugated (open or "off" state), as shown in Figure 1. Moreover, bis(thien-3-yl) derivatives of perfluorocyclopentene[14-16] have been shown to exhibit excellent thermal stability for both forms and a marked resistance towards photofatigue. Furthermore, their preparation is relatively straightforward.

In the present work, we describe the synthesis and the characterization of a series of novel diarylethene-based molecular switches bearing electron donor, acceptor and electroactive substituents. The pronounced photochromic properties of the molecules are also described. The key systems, the bispyridinium compound $\mathbf{1}^{2+}$ and the nonsymmetrical push–pull photochrome **2**, are switchable molecular devices whose electron conduction and nonlinear optical properties, respectively, can be controlled by light (Figure 2).

Abstract in French: *Les nouveaux dithiényléthènes substitués par des groupements pyridinium ($\mathbf{1}^{2+}$), pyridine (**6**) et donneur/accepteur d'électrons (**2** et **10–13**) présentent des propriétés photochromes prononcées. L'irradiation UV induit la cyclisation réversible (par la lumière visible) et complète (>98%) des formes ouvertes incolores en formes fermées colorées. La vitesse d'ouverture thermique des formes fermées dépend de la nature des substituants. L'interconversion réversible permet la modulation de certaines propriétés physiques: $\mathbf{1}^{2+}$ et **12** représentent deux types de commutateurs rédox (en réduction et en oxydation) où la conjugaison électronique est effective dans l'état fermé et interrompue dans l'état ouvert. D'autre part, l'activité en optique non-linéaire du composé **2** peut être augmentée de manière importante par photocyclisation. De tels systèmes constituent des prototypes de fils moléculaires photocommutables où la conduction électronique et l'interaction donneur-accepteur peuvent être réversiblement modulées par un stimulus extérieur, l'irradiation par la lumière.*

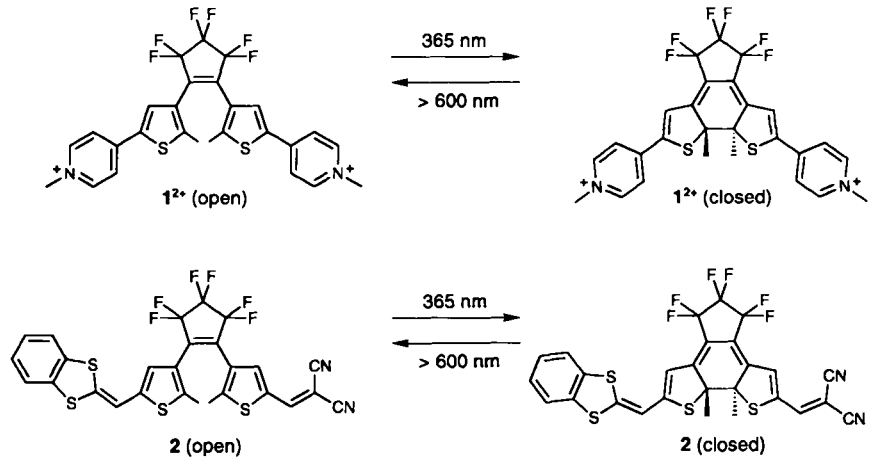

Fig. 2. Photochemical interconversion of compounds $\mathbf{1}^{2+}$ and **2** between their open and closed forms. Electronic communication between the donor and acceptor groups (i.e., intramolecular charge transfer) and between the electroactive pyridinium termini is only possible in the latter state.

Results And Discussion

Synthesis: The synthesis of the photochromes $\mathbf{1}^{2+}$ and **6** is shown in Scheme 1. The known dibromide **3** was prepared from 2-methylthiophene by a described method.[17] It was then lithiated and treated with tri-*n*-butylborate[18] to give the thiopheneboronic acid **4** as a white powder in 78% yield. The palladium-catalysed Suzuki coupling[19] of **4** and 4-bromopyridine in aqueous base containing tetrahydrofuran gave the pyridylthiophene **5** in 84% yield. The previously described[14, 20] coupling to perfluorocyclopentene, carried out in tetrahydrofuran for reasons of solubility, afforded the bispyridyl photochrome **6**. Finally, treatment of **6** with methyl trifluoromethanesulfonate in dichloromethane resulted in the precipitation of the bispyridinium species $\mathbf{1}^{2+}$ as its triflate salt in a yield of 93%.

The photochromic diarylethenes **2** and **10–13** were synthesized as outlined in Scheme 2. Although the literature suggests otherwise,[17] the bromination of 5-methylthiophene-2-carboxaldehyde in acetic acid proceeds smoothly without the use of aluminium trichloride to yield bromide **7** as a single regioisomer in 74% yield. The carbonyl group was subsequently protected as the dimethyl acetal according to standard methodology;[21] **8** was obtained as an oil in 97% yield. The latter was treated with *n*-butyllithium in diethyl ether, and the resulting orange 3-lithium salt coupled with perfluorocyclopentene according to the standard method, which afforded the diacetal photochrome **9** in a yield of 56%. Subsequent hydrolysis in wet tetrahydro-

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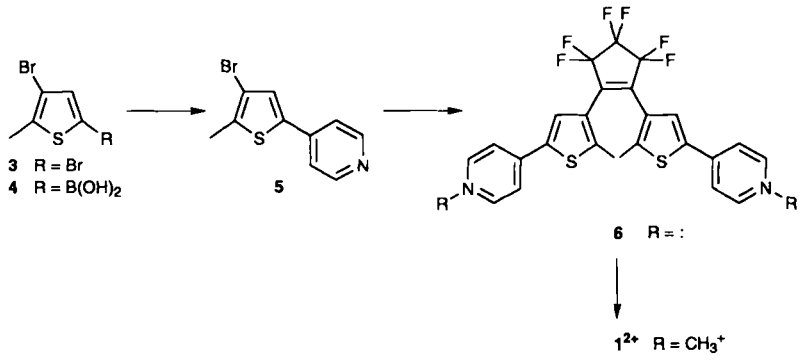
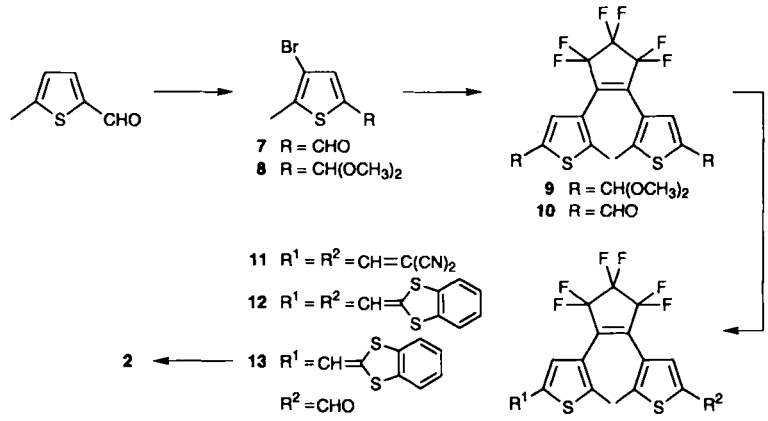


Scheme 1. Synthesis of dithienylethene photochromes 1^{2+} (as its triflate salt) and **6**.



Scheme 2. Synthesis of dithienylethene photochromes **2** and **10**–**13**.

furan containing *p*-toluenesulfonic acid provided the key dialdehyde intermediate **10** in 93% yield. Slow evaporation of a chloroform solution of the dialdehyde afforded crystals suitable for X-ray analysis.[22]

The Knoevenagel[23] condensation of **10** and malonodinitrile in absolute ethanol containing a catalytic amount of piperidine gave the bis-acceptor substituted compound **11** as pale yellow crystals in 86% yield. The Wittig[24] condensation of **10** with two equivalents of 2-triphenylphosphonio-1,3-benzodithiole tetrafluoroborate in a two-phase (dichloromethane/50% aqueous sodium hydroxide) system cleanly afforded the bis-donor substituted molecule **12** as a yellow powder in 82% yield. The reaction carried out with a single equivalent of phosphonium salt afforded the mono-adduct **13** which could be easily isolated in 60% yield by chromatographic separation from the bis-adduct **12**. Monoaldehyde **13** was then condensed with malonodinitrile in the usual manner to give an 89% yield of the unsymmetrical push–pull compound **2** as an orange powder.

For all manipulations involving the bis(thienyl)-cyclopentenes, including workup and chromatographic purification, care was taken to protect the compounds from light. In this way, the products were isolated exclusively as the uncyclized isomers. All of the present molecules exhibit a very high degree of chemical stability. Even after over a year at 5 °C (in the dark), no decomposition of the open forms had occurred.

Photochromic Properties:

Photocyclizations: Photochemical cyclizations from the open to the closed forms were followed directly by both ^{1}H NMR and UV spectroscopy. NMR tubes containing solutions of open isomers were irradiated with UV light of 365 nm (or 254 nm in the case of **10**). After measured irradiation times, aliquots were removed and diluted for the recording of UV spectra. The conversions to the deeply coloured cyclized forms were easily followed by the relative integrals of corresponding pairs of proton signals for the two isomers. The chemical shift data for both open and closed isomers of all of the compounds studied are given in Table 1. Certain trends are apparent: photocyclization results in a considerable upfield shift (of up to 1 ppm) of the thiophene proton signal in all cases; a less pronounced downfield shift is also observed for the methyl singlets.

Table 1. ^{1}H NMR chemical shift data (200 MHz) for open and closed forms of compounds 1^{2+}, **2**, **6** and **10**–**13** [a].

Compound	(form)	Thiophene CH_3	CH=	Thiophene CH	Aromatic protons	
1^{2+}	(open) [b]	2.13	4.26 [c]	8.07	8.11 (J = 7.0) [e]	8.55 (J = 7.0) [e]
	(closed) [b]	2.34	4.34 [c]	7.37	8.12 (J = 6.9) [e]	8.67 (J = 6.9) [e]
2	(open)	1.50/1.35	6.17/6.16	6.80/6.77	6.59–6.67 (m, 2H)	6.69–6.78 (m, 2H)
	(closed)	1.97/1.91	5.90/5.77	5.89/5.80	6.59–6.67 (m, 2H)	6.72–6.78 (m, 2H)
6	(open)	1.57	–	7.29	6.81 (J = 6.1) [e]	8.46 (J = 6.1) [e]
	(closed)	1.99	–	6.55	6.61 (J = 6.1) [e]	8.42 (J = 6.1) [e]
	(open) [d]	2.00	–	7.51	7.43 (J = 6.2) [e]	8.58 (J = 6.2) [e]
	(closed) [d]	2.22	–	6.85	7.42 (J = 6.1) [e]	8.67 (J = 6.1) [e]
10	(open)	1.19	9.20	7.01	–	–
	(closed)	1.70	8.89	5.99	–	–
	(open) [d]	2.02	9.83	7.74	–	–
	(closed) [d]	2.20	9.86	6.97	–	–
11	(open)	1.54	6.11	6.78	–	–
	(closed)	1.58	5.65	5.70	–	–
12	(open)	1.71	6.17	6.90	6.54–6.66 (m, 4H)	6.68–6.78 (m, 4H)
	(closed)	2.18	5.98	5.87	6.55–6.71 (m, 8H)	
13	(open)	1.42/1.52	6.14/9.24	6.6–6.8	6.58–6.66 (m, 2H)	6.69–6.80 (m, 2H)
	(closed)	1.98/2.03	5.79/9.09	5.82/6.28	6.56–6.68 (m, 4H)	

[a] In C_6D_6 unless otherwise indicated. [b] In CD_3CN. [c] *N*-methyl signal. [d] In CD_2Cl_2. [e] AA'BB' system, apparent coupling constants given.

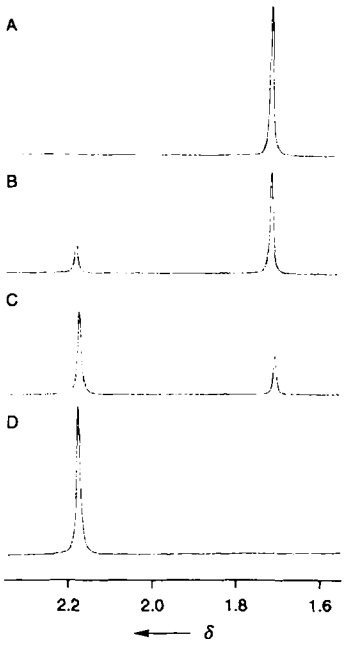


Fig. 3. Details of the 200 MHz ^{1}H NMR spectra of **12** (1.25×10^{-3} M in [D_6]benzene) showing the changes in the thiophene methyl group signals throughout the course of irradiation at 365 nm: A: prior to irradiation (open form), B: after 30 s (23% conversion), C: after 3.5 min (71%), D: after 15 min (>99.5% closed form).

The spectra shown in Figures 3 and 4 for compound **12** are typical of the results obtained for these experiments. In the cases where the photostationary state was essentially at complete transformation to the cyclized form, the extent of conversion was determined, when possible, by comparing the intensities of the ^{13}C satellite peaks of the closed form with that of any remaining corresponding signal of the open isomer. When the former was clearly greater, a conversion of >99.5% was recorded. Otherwise, direct comparison of the peak integrals for the two forms was used. When the remaining open isomer could not be detected and comparison with the satellite peak was not possible, a conservative value of >98% was noted. In no instance was any decomposition observed by NMR, and the superimposed UV spectra obtained through the course of irradiation exhibited clean isosbestic points in all cases.

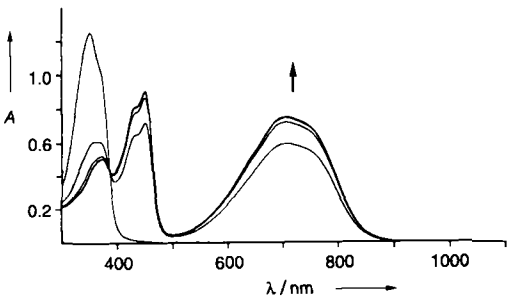


Fig. 4. Evolution of the absorption spectrum of **12** upon irradiation of the open form at 365 nm (2.5×10^{-5} M in benzene, 5 successive irradiations of 2 s duration in a 10 mm cuvette).

The results of the photocyclization experiments are given in Table 2. They clearly show that the present systems exhibit very pronounced photochromic properties, in particular compared to previously described bis(thienyl)ethene compounds. UV irradiation results in virtually total conversion to the closed state (>98%) in all cases. Moreover, the absorption maxima of the coloured forms are located well into the red, and even the infrared, region and have high molar extinction coefficients (see Figs. 4 and 7). Also noteworthy are the very large shifts in absorption maxima ($\Delta\lambda_{max}$) in the order of 300 nm observed upon photocyclization. Previously described compounds of this type typically exhibit photostationary states at 30–70% conversion, absorption maxima for closed coloured forms in the 500–600 nm range and $\Delta\lambda_{max}$ values of about 100–250 nm.

Table 2. Photochemical and spectral data for the open and closed forms of compounds $\mathbf{1}^{2+}$, **2**, **6** and **10**–**13**

Compound (form)		Thiophene substituents	Solvent	λ_{max}/nm ($\varepsilon \times 10^{-3}$/cm^{-1} M^{-1})	$\Delta\lambda_{max}$/nm	% Conversion [a]
$\mathbf{1}^{2+}$	(open)	4-pyMe$^+$TfO$^-$	CD_3CN	352 (46)	310	>99.5%
	(closed)			662 (16)		
2	(open)	CH= benzodithiole;	C_6D_6	354 (40)	474	>99.5%
	(closed)	CH=C(CN)$_2$		828 (23)		
6	(open)	4-py	C_6D_6	300 (32)	292	81%
	(closed)			592 (14)		
	(open)		CD_2Cl_2	304 (35)	288	>98%
	(closed)			592 (14)		
10	(open)	CHO	C_6D_6	296 (19)	328	40%
	(closed)			624 (8.0)		
	(open)		CD_2Cl_2 [b]	263 (30)	356	>98%
	(closed)			619 (7.2)		
11	(open)	CH=C(CN)$_2$	C_6D_6	361 (40)	366	>98%
	(closed)			727 (14)		
12	(open)	CH= benzodithiole	C_6D_6	350 (50)	363	>99.5%
	(closed)			713 (29)		
13	(open)	CH= benzodithiole;	C_6D_6	350 (26)	352	>99.5%
	(closed)	CHO		702 (20)		

[a] Photostationary state under irradiation at 365 nm. [b] Irradiation at 254 nm.

The fact that the present compounds can be fully converted to their cyclized isomers is of great importance since it allows a complete "on/off"-type switching function. This indicates that the quantum yield for cyclization must be much higher than that for ring opening. The results obtained for the present molecules are in marked contrast to the extent of conversion displayed by related bis(thienyl)ethenes, which are generally much lower and vary widely from system to system. This difference may be related to the fact that the 4-positions of the thiophene rings are unsubstituted in the present molecules, whereas all previously described systems either bear 4-methyl groups or are benzothiophene derivatives. In the latter compounds, an unfavorable steric interaction arises between the substituent and the allylic fluorine atoms upon photocyclization, which affects the nature of the transition state for cyclization and also increases the energy of the closed isomer relative to the open one. This may account, at least in part, for a lower quantum yield ratio $\Phi_{(open \rightarrow closed)}:\Phi_{(closed \rightarrow open)}$ as compared to the 4-unsubstituted photochromes (for which the steric factor is absent). The relative quantum yields should be affected by the difference in electronic structure along the cyclization pathway, owing to different rotational angles of the thiophene rings with respect to the perfluorocyclopentene unit in the substituted and unsubstituted compounds. It has also been already reported for adamantylidene furylfulgide[25] as well as for diarylethenes[9c, 9d, 12] that the decolouration quantum yield is affected by the steric crowding within the closed-ring form.

The rotational freedom about the vinylic bonds to the heterocycles, which allows interconversion between parallel and antiparallel conformers[15] of the open form (see Figure 5), is relevent since it reflects the extent of the steric interaction evoked above. Evidence of rapid conformational interconversion or a pronounced preference for one conformer was offered by low-temperature NMR experiments with dialdehyde **10** (in CD_2Cl_2). No change was seen in the proton spectra upon cooling of the sample to −70 °C. This is in marked contrast to results obtained for a benzothiophene-derived system; here both parallel and antiparallel conformers were observed, and equivalent NMR signals only coalesce at 45 °C.[12]

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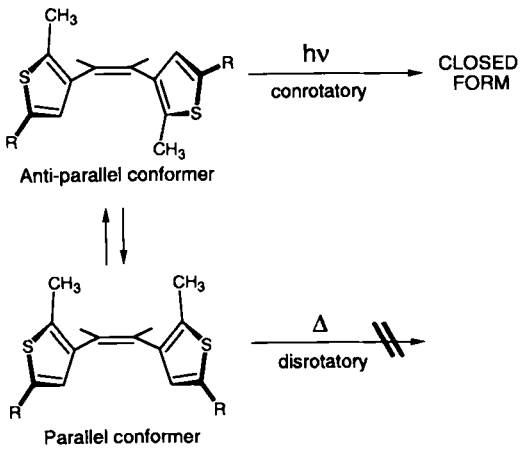

Fig. 5. Interconversion of a dithienylethene between antiparallel and parallel conformers. The allowed thermal process (disrotatory cyclization) is prevented by steric hinderance between methyl groups.

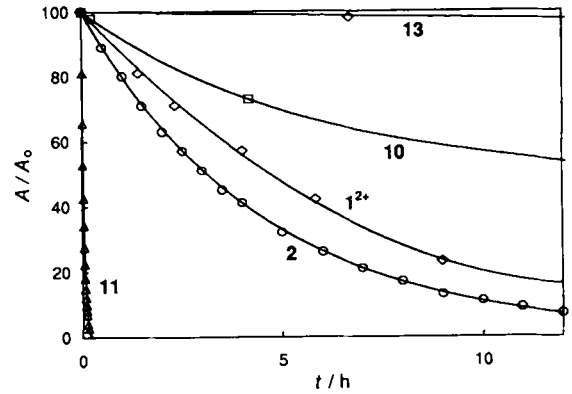

Fig. 6. Variation of the thermal stabilities of the closed photochromic forms. Thermal openings of $\mathbf{1}^{2+}$, **2**, **10**, **11** and **13** monitored by the decrease in absorption (at the λ_{max}) in benzene solution (acetonitrile for $\mathbf{1}^{2+}$) at 60 °C.

Table 3. First order half-lives for the thermal opening of the closed forms of compounds $\mathbf{1}^{2+}$, **2**, **6** and **10–13** [a].

Compound	$t_{1/2}$/min	Compound	$t_{1/2}$/min
$\mathbf{1}^{2+}$	247 [b]	**11**	3.3
2	186	**12**	[c]
6	[c]	**13**	16300 [d]
10	573		

[a] For solutions in benzene at 60 °C in the dark. [b] In acetonitrile. [c] No detectable change after 15 d. [d] Over 11 d.

It should be noted that, in the crystalline state, the dialdehyde **10** exists as the antiparallel conformer with the thiophene rings tilted approximately 45° with respect to the central perfluorinated cycle.[22] Conrotary photocyclization of the antiparallel form is expected to yield the closed form with *trans*-oriented CH_3 groups[10, 15] (see Fig. 1).

Photochemical Opening and Photofatigue: Photochemical decolourations were carried out by irradiating solutions of fully closed isomers with visible (red) light of $\lambda > 600$ nm in a chamber maintained at 20 °C. Clean closed-to-open transformation was observed in all cases, although the time required for complete bleaching varied from system to system. After the determination of the minimal irradiation times required for complete cyclization and >90% photochemical opening (generally in the order of 30 s and 5 min, respectively, except in the case of **12** whose opening requires several hours), ten colouration–decolouration cycles were carried out. With the exception of dialdehyde **10**, no significant decomposition was observed as monitored by any decrease in absorbance at the λ_{max} of the open and/or closed isomers. After ten cycles, a decrease of 8.3% was detected for compound **10**. These results are in line with the remarkable photofatigue resistance reported for previously described perfluorocyclopentene-derived diarylethene systems.[14] It should be noted that cyclization in the other direction towards a closed form with R = H instead of CH_3 (Fig. 1) at the central ring junction would be expected to lead to subsequent irreversible transformation, for instance, to yield an oxidized derivative. This has not been observed with the present compounds in the conditions used.

Thermal Opening: Whereas no thermochromism was observed for the open forms of the molecules studied, it was found that the rate of thermal opening of the closed isomers is highly dependent on the nature of the substituents attached to the switching unit (Fig. 6). Table 3 lists the half-lives for the thermal opening of the molecules $\mathbf{1}^{2+}$, **2**, **6** and **10–13** in benzene solution (acetonitrile in the case of $\mathbf{1}^{2+}$) at 60 °C. Whereas the closed forms of the photochromes bearing electron-donating or weakly attracting substituents (compounds **6** and **12**) exhibit marked thermal stablity (no change after over 2 weeks), the systems substituted with stronger withdrawing groups open at rates that reflect the electron-withdrawing strength of the thiophene functionalities. The tetracyano compound **11** is completely bleached within ten minutes at 60 °C. The much slower rates of opening at room temperature nevertheless permitted physical studies to be carried out on the cyclized isomers without any problems arising from partial decolouration (except in the case of **11**).

It has been proposed that the thermal stability of diarylethene photochromes depends on the aromatic stabilization energy.[10] According to this hypothesis, the destabilization resulting from the loss of aromaticity upon photocyclization is reflected in an increase in the ground-state energy of the closed form, which, in turn, results in thermal instability. The great variation in thermal stability observed for the cyclized forms of the compounds described here is not easily accounted for by this argument and efforts are presently under way to gain a better understanding of this phenomenon. An alternative rationale to explain the observed trend is that the strength of the central carbon–carbon bond, which is cleaved during opening, is a key factor in the thermal process; a cleavage of this type may be facilitated by electroattractive substituents as observed.

Switching Properties—Towards Switchable Molecular Wires: *Photochromism—Switching of Light-Absorption Properties*: Of central importance to this work are the changes in physical properties that can be effected by photochemical switching between the open and closed forms of the present systems. The first and most obvious change reflecting the reversible, light-triggered establishment of conjugation between the two lateral moeities is the observed photochromism, which results from the very large shift in the absorption maximum, as discussed in detail above. This effect is especially pronounced for compound **2** (Fig. 7) whose λ_{max} is shifted from 354 to 828 nm in benzene upon photocyclization; this $\Delta\lambda_{max}$ of 474 nm is the largest difference reported for diarylethenes to date.

From a practical viewpoint, such highly red-shifted absorption maxima are of great interest. Photochromic molecules, notably of the diarylethene class,[9a, 26] have great potential for the

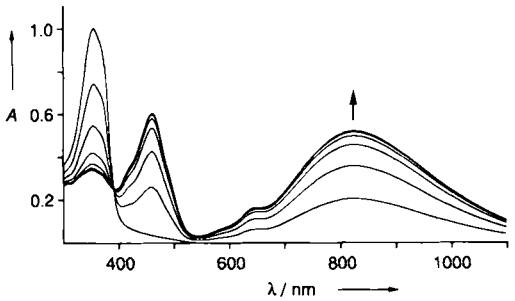

Fig. 7. Evolution of the absorption spectrum of **2** upon irradiation of the open form at 365 nm (2.5×10^{-5} M in benzene, 7 successive irradiations of 5 s duration in a 10 mm cuvette).

development of materials for reversible optical data storage.[27] While the problems of thermal stability and photofatigue have largely been addressed, more difficulty has been encountered in attempting to shift the low-energy band of the coloured forms into the region within which a diode laser may be efficiently employed to effect the decolouration step (700–840 nm). The present compounds **2**, **11**, **12** and **13** all absorb very strongly in this range.

Switching of Redox and Electronic Conduction Properties: The second type of behaviour under photochemical control, in particular for the bispyridinium and bis-donor photochromes, $\mathbf{1}^{2+}$ and **12**, are the electrochemical properties. Viologens are the most extensively studied Weitz-type redox systems; their reversible electron-accepting abilities are of great interest in the context of electrochromic materials and other technological applications.[28] Recent work has focused on extended systems incorporating (poly)olefinic and aromatic spacers between terminal pyridinium groups,[7, 28, 29] which may, in particular, function as a molecular wire.[7] Likewise, the system $\mathbf{1}^{2+}$ in its closed state is an extended analogue of methylviologen. One would therefore expect a substantial difference in the redox features of the photochrome in its open and cyclized forms and that it might therefore function as a switchable molecular wire.

The electrochemical properties of $\mathbf{1}^{2+}$ were studied by cyclic voltammetry, and the results are shown in Figure 8.[3b] In the open state, the photochrome is electrochemically inert within the -0.9 and $+1.6$ V domain (all potentials vs. saturated calomel electrode, SCE); an irreversible process occurs at -1.04 V, which no doubt corresponds to the reduction of the isolated pyridinium groups (Fig. 8a). The closed $\mathbf{1}^{2+}$ isomer was then generated in situ by irradiating the solution in the electrochemical cell with 365 nm light; cyclization was quantitative as verified spectrophotometrically. The voltammogram of the resulting coloured form (Fig. 8b) exhibits a reversible one-electron wave at a half-wave potential of -0.23 V corresponding to the reduction of $\mathbf{1}^{2+}$ (closed) to the $\mathbf{1}^{\bullet+}$ radical cation. In addition, a second irreversible reduction occurs at -1.47 V and an irreversible oxidation at $+1.37$ V. The large shift in E_{red} towards a much less negative potential upon photochemical closure of the system is a result of conjugation being established between the two positively charged electroactive termini.

While the shift described above is easily understood, two aspects of the electrochemical behaviour of $\mathbf{1}^{2+}$ (closed) are, however, somewhat surprising when examined in the context of extended viologens in general: the monoelectronic nature of the reduction (i.e., reduction to $\mathbf{1}^{\bullet+}$ rather than **1**) and the relatively low potential at which it occurs. Under comparable conditions, methylviologen undergoes two successive one-electron reductions ($MV^{2+} \rightarrow MV^{\bullet+} \rightarrow MV$) at half-wave potentials of -0.43 and -0.85 V.[29b] Separation of the pyridinium groups by conjugated spacers results in both a shift of the E_{red} values to more negative values and coalescence of the waves for vinylogues incorporating two or more double bonds.[29b] Even though coulommetry measurements carried out at a potential of -0.6 V for $\mathbf{1}^{2+}$ (closed) indicated that the reduction at -0.23 V was monoelectronic, a second experiment was performed to confirm this fact. Figure 8c shows the voltammogram of a 1:1 mixture of $\mathbf{1}^{2+}$ (closed) and ferrocene (known to undergo a monoelectronic oxidation to ferricinium) in acetonitrile; this clearly confirms the one-electron nature of the reduction in the former. The low E_{red} value for $\mathbf{1}^{2+}$ (closed) may perhaps be related to the presence of the electron-withdrawing CF_2 groups in the system. However, the reasons why the second reduction ($\mathbf{1}^{\bullet+} \rightarrow \mathbf{1}$) occurs at such a negative potential are still not known. Nevertheless, it is clear that only the cyclized form of $\mathbf{1}^{2+}$ is electrochemically active at potentials between -0.9 and -0.3 V and that the reversible addition of an electron is photochemically controlled.

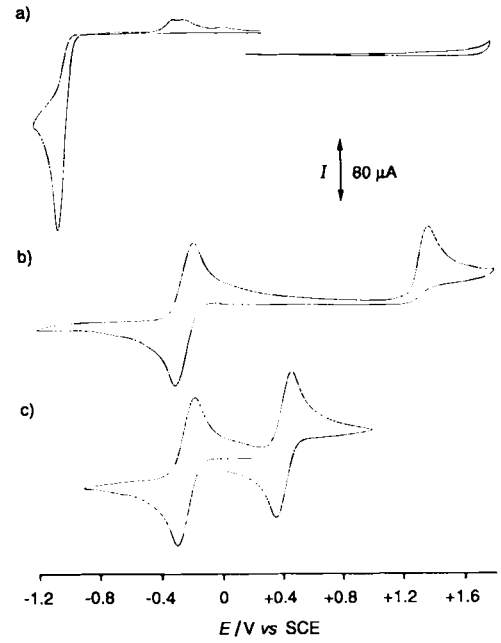

Fig. 8. Cyclic voltammograms of a) $\mathbf{1}^{2+}$ (open), b) $\mathbf{1}^{2+}$ (closed) and c) $\mathbf{1}^{2+}$ (closed) and 1 equiv ferrocene (10^{-3} M in acetonitrile, 0.1 M nBu$_4$NBF$_4$, scan rate 100 mV s^{-1}, reference electrode: saturated calomel electrode).

The redox behaviour of a second system, the bis-donor photochrome **12**, was also investigated. The discovery that the TTF–TCNQ charge-transfer complex exhibits electrical conductivity has stimulated intense activity directed towards the synthesis and study of new electron-donor molecules for organic metals.[30] The plethora of systems based on TTF include dibenzotetrathiafulvalene (DBTTF) and conjugationally extended analogues thereof.[31, 29b] In this context, compound **12** is of particular interest in that it represents a photoswitchable DBTTF analogue.[32]

The cyclic voltammograms of **12** are presented in Figure 9. In its open state, the molecule is inert towards reduction (up to -1.8 V) and undergoes a quasi-reversible monoelectronic oxidation process at $+0.90$ V (Fig. 9, top); the reduction of the generated species is not under diffusion control. The same sample was then photocyclized in the electrochemical cell by UV irradiation at 365 nm. The cyclic voltammogram of **12** in its closed form (Fig. 9, bottom) exhibits a reversible bielectronic oxidation wave at a half-wave potential of $+0.34$ V. This value is in line with results reported for DBTTF and its extended

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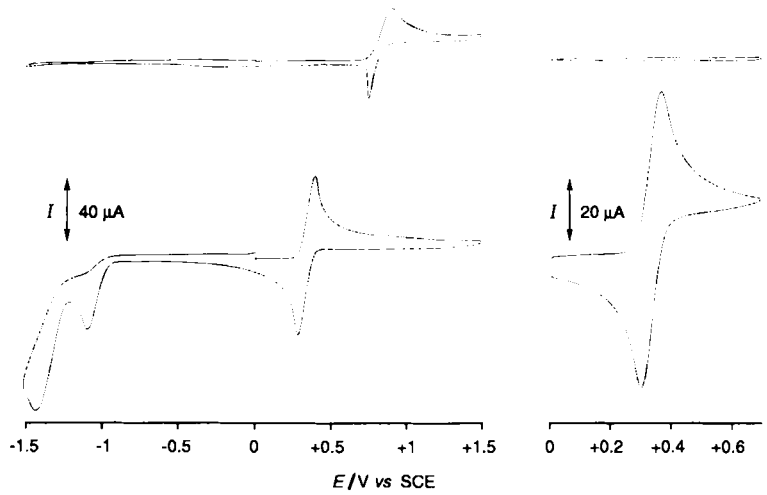

Fig. 9. Cyclic voltammograms of **12**(open) (top) and **12**(closed) (bottom) (10^{-3} M in dichloromethane, 0.1 M nBu$_4$NClO$_4$, scan rate 100 mVs^{-1}, reference electrode: saturated calomel electrode).

vinylogues; in these compounds, increasing the length of the conjugated pathway results in coalescence of two monoelectronic processes at a less positive potential.[33] It is noteworthy that in the voltammogram of the closed form, no oxidation is observed at around + 0.90 V; this indicates that cyclization was close to quantitative (also verified spectrophotometrically). Moreover, we routinely carried out the CV experiments at various scan rates (up to 500 Vs^{-1}) and with repeated cycles. If some ring opening had occurred, one would expect that cycling between 0 and +1 V would result in the appearance of a wave for the open form. This was not the case. Otherwise, compound **12**(closed) exhibits two irreversible reduction waves at peak potentials of −1.09 and −1.41 V.

Thus, compounds $\mathbf{1}^{2+}$ and **12** represent prototype switchable molecular wires whose electrochemical behaviour is highly dependent on the photochromic state and which operate through reversible reduction and oxidation processes, respectively.[34] The above results are also of importance in that they offer a further illustration of the great difference in the extent of electronic conjugation in the two photoisomeric states.

Switching of Nonlinear Optical Properties: The third type of photo-controlled behaviour in the present systems is the second-order nonlinear optical (NLO) properties of compound **2**. It is well established that a structural arrangement consisting of electron donor and attractor groups separated by a conjugated pathway is required for enhanced second-order molecular nonlinear optical hyperpolarizability (β).[35] Polyenic systems, notably those bearing 1,3-benzodithiole-2-ylidenyl/dicyanomethylidenyl partners,[36] have been extensively studied by our group and shown to be highly efficient in second harmonic generation. Furthermore, "push–pull" systems incorporating thiophene units have also been shown to be very active in this respect.[37]

Considering the obvious structural similarity between **2** in its cyclized form and a push–pull polyene, one would expect the former to exhibit a greater molecular optical nonlinearity than its open photoisomer for which intramolecular charge-transfer between the terminal donor and acceptor units is not possible. The great difference in electronic structure between the two forms manifests itself in a marked change in the solvatochromic properties[38] on switching between **2**(open) and **2**(closed). In the former state, little solvent dependence is observed for the λ_{max}, which varies within 4 nm for spectra obtained in n-hexane, benzene, dichloromethane and DMSO. In its cyclized form, however, the system exhibits pronounced positive solvatochromism; the broad band in the visible region undergoes a large bathochromic shift with increasing solvent polarity (Fig. 10). The 142 nm difference in the absorption maxima, from 778 nm in hexane to 920 nm in DMSO, corresponds to a frequency difference of nearly 2000 cm^{-1}.

To demonstrate the photoswitching of NLO properties for compound **2**, the respective microscopic hyperpolarizabilities of the two forms were determined by EFISH (electric field induced second harmonic) generation measurements.[39] These studies were carried out in toluene solution at a fundamental wavelength of 1.064 μm. In the case of **2**(open), a $\mu\beta(2\omega)$ value of 260×10^{-48} esu was obtained. The sample was then photochemically transformed to its closed state, and the UV spectrum was recorded, verifying that clean photocyclization and a conversion of >97% to the coloured form had taken place. The subsequent EFISH measurement for **2** in its closed state yielded a $\mu\beta(2\omega)$ value of 1100×10^{-48} esu.[40] Thus, compound **2** is indeed a photomodulable optical switch whose second-order nonlinear optical properties can be reversibly modulated by over a factor of four by irradiation at well separated wavelengths.

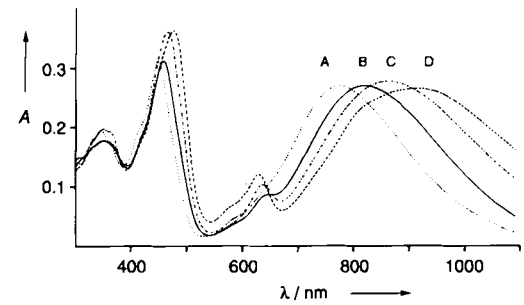

Fig. 10. Absorption spectra of **2**(closed) at 1.25×10^{-5} M in: A: hexane (λ_{max} = 449, 778 nm), B: benzene (459, 828), C: dichloromethane (466, 866), D: DMSO (477, 920).

Conclusion

The results of the present studies clearly demonstrate the suitability of the bis(thienyl)ethene system as a switching unit for light-triggered molecular devices of the type depicted in Figure 1. Many other photo-controlled substances based on this same principle may be imagined. Analogous systems fitted with electroactive (hydroxyphenyl) groups constitute dual-mode molecular switching devices,[3c] and related investigations are presently being carried out involving similar photochromes bearing ionizable groups, metal complexes, and highly extended conjugated systems.

Owing to the strong electron donating and withdrawing nature of some of the substituents chosen for this work, the present compounds also offer an opportunity to gain further insight into the importance of electronic factors on the remarkable properties of this class of photochromes.

Experimental Procedure

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 (UK). Ethyl ether and tetrahydrofuran were distilled from lithium aluminium hydride. Dichloromethane and methanol were distilled from phosphorus pentoxide and magnesium methoxide, respectively. Reactions were monitored by TLC using aluminium-backed Kieselgel 60_{254} plates and visualized by UV light. Flash column chromatography was performed on Kieselgel 60 (230–400 mesh) silica gel. In the case of photochromes, columns were protected from light with aluminium foil.

Melting points were determined on an Electrothermal 1A9100 digital apparatus and are uncorrected. NMR spectra were recorded on a Bruker AM 200 SY instrument. ^1H NMR spectra were obtained at 200.13 MHz with the residual proton signals as reference peaks (assigned chemical shifts at $\delta = 7.26$, 5.32, 7.15, 2.49 and 3.30 for deuterated chloroform, dichloromethane, benzene, DMSO and methanol, respectively). ^{13}C NMR spectra were obtained at 50.33 MHz using the $CDCl_3$ and $[D_6]$DMSO signals, assigned the respective chemical shifts of $\delta = 76.90$ and 39.60, as the reference peaks. UV absorption spectra were recorded on Perkin-Elmer 554 and Beckman DU 640 spectrophotometers, in spectrograde solvents. UV irradiations were performed with standard lamps used for visualizing TLC plates (VL 6 LC; intensity at 15 cm from filter: 400 $\mu W\,cm^{-2}$ at 254 nm and 610 $\mu W\,cm^{-2}$ at 365 nm). Whereas the emission at 254 nm is fairly monochromatic, that at "365 nm" consists of a broad emission band with spike at 365 nm. 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 $\approx 20\,^{\circ}C$. Mass spectrometry was carried out by the Laboratoire de Chimie Organique Structurale 1, ERS 73 (Paris). Elemental analyses were performed by the Service Régional de Microanalyse, Université P. & M. Curie (Paris).

Cyclic voltammetry was performed with a standard three-electrode configuration employing a glassy carbon (3 mm diameter disk) working electrode, a platinum wire counter electrode; the reference electrode was an SCE equipped with a double-fritted sheild. The surface of the working electrode was polished before each measurement. A Princeton 362 scanning potentiostat was employed; the results were recorded on an Ifalec 1F-3802 XY-recorder.

3-Bromo-2-methyl-5-thiopheneboronic acid (4): *n*-Butyllithium (10 M in hexane, 7.4 mL, 74 mmol) was added to a stirred solution of dibromide **3** (18.05 g, 70 mmol) in anhydrous diethyl ether (500 mL) at $-78\,^{\circ}C$ under a nitrogen atmosphere. After 30 min, tri-*n*-butyl borate (28.3 mL, 105 mmol) was added, and the reaction stirred at $-78\,^{\circ}C$ for 4 h and then allowed to warm to ambient temperature. After 15 h, the reaction was shaken with hydrochloric acid (1.2 N, 200 mL), and the ether phase separated and extracted with aqueous sodium hydroxide (1 N, 4 × 50 mL). The combined aqueous phases were then filtered to remove traces of solid, and then acidified to pH = 1 at $0\,^{\circ}C$ with concentrated hydrochloric acid. The resulting precipitate was filtered, washed with hydrochloric acid (10^{-2} M) and dried in vacuo, to yield the boronic acid **4** as a white powder (12.20 g, 78%): M.p. $230\,^{\circ}C$ (dec.); ^1H NMR (200 MHz, $[D_6]$DMSO): $\delta = 2.35$ (s, 3H; CH_3), 7.48 (s, 1H; H-4), 8.33 (s, 2H; OH); ^{13}C NMR (50.33 MHz, $[D_6]$DMSO): $\delta = 14.61$ (CH_3), 109.59 (C-3), 135.85 (C-4), 137.77 and 138.83 (C-2 and C-5); MS (CI, NH_3, neg. ion mode): *m/z* (%): 219/221 (7) $[M-H^+]$, 204/206 (4), 189/191 (4).

3-Bromo-2-methyl-5-(4′-pyridyl)thiophene (5): Tetrahydrofuran (75 mL) and aqueous sodium carbonate (20% w/v, 75 mL) were added to a flask containing boronic acid **4** (9.99 g, 45.0 mmol), 4-bromopyridine hydrochloride (14.59 g, 75 mmol) and *tetrakis*-triphenylphosphine palladium(0) (1.73 g, 1.5 mmol). Two homogeneous phases were formed. The reaction was refluxed under a nitrogen atmosphere for 20 h and then cooled, extracted with chloroform (2 × 200 mL), and washed with brine (200 mL) and water (200 mL). The combined organic phases were dried (Na_2SO_4), filtered, and the filtrate concentrated to about 25 mL and then loaded onto a short column of silica gel. The product was eluted with dichloromethane containing triethylamine (1%) and increasing proportions of acetone. The evaporation of the solvents in vacuo yielded an orange solid. Recrystallization from ethyl acetate afforded pyridylthiophene **5** as colourless crystals (9.55 g, 84%): M.p. $83\,^{\circ}C$; ^1H NMR (200 MHz, $CDCl_3$): $\delta = 2.44$ (s, 3H; CH_3), 7.30 (s, 1H; H-4), 7.36 (A of AA′BB′, *J*(app) = 6.2 Hz, 2H; H-3′,5′), 8.58 (B of AA′BB′, *J*(app) = 6.2 Hz, 2H; H-2′,6′); ^{13}C NMR (50.33 MHz, $CDCl_3$): $\delta = 14.79$ (CH_3), 110.40 (C-3), 118.87 (C-3′,5′), 127.65 (C-4), 136.14 (C-5), 137.61 (C-2), 140.06 (C-4′), 150.20 (C-2′,6′); MS (CI, NH_3): *m/z* (%): 253/255 (97) $[M^+]$, 174 (31) $[M^+-Br]$, 140 (100): $C_{10}H_8NSBr$ (254.14): calcd C 47.26, H 3.17, N 5.51; found C 47.61, H 3.13, N 5.29.

1,2-Bis(2′-methyl-5′-(pyrid-4″-yl)thien-3′-yl)perfluorocyclopentene (6): *n*-Butyllithium (1.6 M in hexane, 12.5 mL, 20 mmol) was slowly added to a stirred solution of bromide **5** (5.08 g, 20 mmol) in freshly distilled tetrahydrofuran (300 mL) at $-78\,^{\circ}C$ under a nitrogen atmosphere. Perfluorocyclopentene (1.3 mL, 10 mmol) was then added (through a cooled syringe) to the deep red solution, which immediately turned green. The reaction was allowed to warm to ambient temperature. After 2 h, hydrochloric acid (1.2 M, 50 mL) was added and, after vigorous stirring, the tetrahydrofuran was removed in vacuo. After neutralization of the acid with aqueous sodium bicarbonate, the product was extracted with dichloromethane (2 × 200 mL) and washed with saturated aqueous sodium bicarbonate (2 × 100 mL). The combined organic extracts were dried (Na_2SO_4), filtered and evaporated in vacuo. The product was chromatographed over alumina (dichloromethane/ethyl acetate = 4:1) to yield a greenish solid. This was recrystallized from ethyl acetate, and the bispyridyl photochrome **6** was obtained as a white powder (3.5 g, 67%): M.p. 181 °C; ^1H NMR (200 MHz, $CDCl_3$): $\delta = 2.00$ (s, 6H; CH_3), 7.41 (A of AA′BB′, *J*(app) = 6.2 Hz, 4H; H-3″,5″), 7.48 (s, 2H; H-4′), 8.61 (B of AA′BB′, *J*(app) = 6.2 Hz, 4H, H-2″,6″); ^{13}C NMR (50.33 MHz, $CDCl_3$): $\delta = 14.53$ (CH_3), 119.41 (C-3″,5″), 124.63 (C-4′), 126.05 (C-3′), 139.27 and 139.97 (C-2′ and 5′), 143.42 (C-4″), 150.42 (C-2″,6″); MS (CI, NH_3): *m/z* (%): 522 (75) $[M^+]$, 502 (27) $[M^+-HF]$, 482 (4) $[M^+-2HF]$, 172 (100); $C_{25}H_{16}N_2S_2F_6$ (522.52): calcd C 57.47, H 3.09, N 5.36; found C 57.79, H 3.40, N 5.03.

1,2-Bis(2′-methyl-5′-(*N*-methylpyrid-4″-yl)-thien-3′-yl)perfluorocyclopentene bistrifluoromethanesulfonate (1^{2+}): To a stirred solution of bispyridine **6** (313 mg, 0.60 mmol) in dry dichloromethane (10 mL) was added methyl trifluoromethanesulfonate (200 mL, 1.8 mmol). The reaction was stirred at ambient temperature in the dark under a nitrogen atmosphere. After 24 h, the resulting suspension was filtered, the solid washed repeatedly with dichloromethane and then dried in vacuo. The bispyridinium triflate $\mathbf{1^{2+}}$ was obtained as a white powder (474 mg, 93%): M.p. 157–159.5 °C; ^1H NMR (200 MHz, CD_3OD): $\delta = 2.16$ (s, 6H; CH_3), 4.32 (s, 6H; N^+CH_3), 8.15 (s, 2H; H-4′), 8.23 (apparent d, *J*(app) = 6.9 Hz, 4H; H-3″,5″), 8.75 (d, *J*(app) = 6.9 Hz, 4H; H-2″,H-6″); $C_{29}H_{22}N_2O_6S_4F_6 \cdot H_2O$ (868.74): calcd C 40.09, H 2.78, N 3.22; found C 39.81, H 2.68, N 3.21.

3-Bromo-2-methyl-5-thiophenecarboxaldehyde (7): A solution of bromine (3.7 mL, 72 mmol) in glacial acetic acid (30 mL) was added dropwise over 7 h to a stirred solution of 5-methylthiophene-2-carboxaldehyde (7.57 g, 60.0 mmol) in glacial acetic acid (50 mL). After 36 h of stirring in the dark at ambient temperature, the reaction was carefully added to a solution of sodium carbonate (210 g) in water (1.3 L). The product was then extracted with diethyl ether (500 + 200 mL) and washed with aqueous sodium bicarbonate (5% w/v, 500 mL). The combined ether phases were dried (Na_2SO_4), filtered and evaporated in vacuo to yield a yellow solid. Chromatography over silica gel (dichloromethane/hexane = 2:1) afforded the bromothiophene **7** as a slightly yellow, crystalline solid (9.10 g, 74%). An analytical sample was obtained by recrystallization from *n*-hexane: M.p. 58 °C; ^1H NMR (200 MHz, $CDCl_3$): $\delta = 2.43$ (s, 3H; CH_3), 7.53 (s, 1H; H-4), 9.72 (s, 1H; CHO); ^{13}C NMR (50.33 MHz, $CDCl_3$): $\delta = 15.59$ (2-CH_3), 110.96 (C-3), 138.20 (C-4), 139.99 (C-2), 145.35 (C-5), 181.05 (C=O); MS (CI, NH_3): *m/z* (%) 239/241 (89) $[M + NH_3 + NH_4^+]$, 222/224 (100) $[M + NH_4^+]$, 175/177 (3) $[MH^+-CH_2O]$; C_6H_5OSBr (205.07): calcd C 35.14, H 2.46; found C 35.23, H 2.41.

3-Bromo-2-methyl-5-thiophenecarboxaldehyde dimethyl acetal (8): Aldehyde **7** (7.65 g, 37.3 mmol) was suspended in anhydrous methanol (45 mL). Upon adding *p*-toluenesulfonic acid (60 mg, cat.) and trimethyl orthoformate (5.7 mL, 52 mmol), the reaction became homogeneous. The reaction was refluxed under a nitrogen atmosphere for 3 h and then cooled, extracted with diethyl ether (300 + 100 mL) and washed with aqueous sodium bicarbonate (5% w/v, 2 × 500 mL). The combined ether layers were then dried (Na_2SO_4), filtered and evaporated in vacuo to yield a yellow oil. Chromatography over silica gel (hexane/dichloromethane = 3:1) afforded acetal **8** as a slightly yellow oil (9.07 g, 97%): ^1H NMR (200 MHz, $CDCl_3$): $\delta = 2.36$ (s, 3H; CH_3), 3.33 (s, 6H; OCH_3), 5.50 (s, 1H; $CH(OCH_3)_2$), 6.86 (s, 1H; H-4); ^{13}C NMR (50.33 MHz, $CDCl_3$): $\delta = 14.54$ (2-CH_3), 52.36 (OCH_3), 99.37 ($C(OCH_3)_2$), 106.30 (C-3), 127.94 (C-4), 134.50 (C-5), 138.31 (C-2); MS (CI, NH_3): *m/z* (%): 285/287 (3) $[M + NH_3 + NH_4^+]$, 268/270 (2) $[M + NH_4^+]$, 219/221 (100) $[MH^+-CH_3OH]$, 204/206 (4).

The acetals **8** and **9** were difficult to purify (partial hydrolysis to the corresponding aldehydes **7** and **10** during chromatography), and the reactions were therefore taken through to compound **10**, which was fully characterized.

1,2-Bis(5′-formyl-2′-methylthien-3′-yl)perfluorocyclopentene (10): Ethyl ether (300 mL) was distilled directly into a flask containing bromide **8** (7.96 g, 31.7 mmol) and the resulting solution cooled to $-78\,^{\circ}C$ under a nitrogen atmosphere. *n*-Butyllithium (10 M in hexane, 3.3 mL, 33 mmol) was then slowly added over 10 min, followed by perfluorocyclopentene (2.0 mL, 14.9 mmol, added through cooled syringe), and the reaction stirred for 30 min at $-78\,^{\circ}C$, after which time the reaction was allowed to warm to ambient temperature. After an additional 2 h, the reaction was diluted with diethyl ether (300 mL), washed with dilute hydrochloric acid (1% v/v, 500 mL), saturated aqueous sodium bicarbonate (500 mL) and aqueous sodium bicarbonate (2% w/v, 500 mL), and reextracted with diethyl ether (300 mL). The combined ether phases were then dried ($MgSO_4$), filtered and evaporated in vacuo to yield a yellow-brown syrup. Chromatography over silica gel (dichloromethane/hexanes = 1:1 to 6:1) afforded the diacetal **9** as a slightly yellow syrup (4.35 g, 56%). Mixed fractions containing monoacetal and dialdehyde **10** were also obtained, accounting for an additional 6% yield: ^1H NMR (200 MHz, $CDCl_3$): $\delta = 1.87$ (s, 6H; CH_3), 3.33 (s, 12H; OCH_3), 5.54 (s, 2H; $CH(OCH_3)_2$), 7.01 (s, 2H; H-4′); MS (CI, NH_3): *m/z* (%): 517 (58) $[MH^+]$, 516 (100) $[M^+]$, 496 (19).

The diacetal **9** (691 mg, 1.34 mmol) was dissolved in tetrahydrofuran (6.0 mL), and *p*-toluenesulfonic acid (40 mg) and water (300 mL) were then added. After stirring at ambient temperature for 3 h, the reaction was extracted with dichloromethane (2 × 50 mL) and washed with saturated aqueous sodium bicarbonate (100 mL) and

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water (100 mL). The combined organic phases were dried (Na_2SO_4), filtered and evaporated in vacuo to yield a yellow solid. This was triturated with a mixed solvent consisting of dichloromethane, *n*-hexane and diethyl ether (20:20:1 by volume), and pure dialdehyde **10** was obtained as a white powder (422 mg, 93%). A crystalline product was obtained by recrystallization from dichloromethane/*n*-hexane: M.p. 182 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.02 (s, 6H; CH_3), 7.73 (s, 2H; H-4'), 9.84 (s, 2H; CHO); ^{13}C NMR (50.33 MHz, $CDCl_3$): δ = 15.21 (2'-CH_3), 125.77 (C-4'), 135.34 (C-3'), 142.19 (C-2'), 151.33 (C-5'), 181.49 (C=O), 110.1, 115.7, 136.5 (3 × m, cyclopentene ring); MS (CI, NH_3): *m/z* (%): 424 (100) [M^+], 404 (66) [M^+ − HF], 384 (5) [M^+ − 2HF]; $C_{17}H_{10}F_6O_2S_2$ (424.38): calcd C 48.11, H 2.38; found C 48.35, H 2.35.

1,2-Bis[5'-(2'',2''-dicyanoethenyl)-2'-methylthien-3'-yl]perfluorocyclopentene (11): Dialdehyde **10** (64 mg, 0.15 mmol) was suspended in absolute ethanol (1.5 mL) containing malonodinitrile (20 mg, 0.303 mmol) and a catalytic amount of piperidine (2 drops of a stock solution of 1 drop amine in 2 mL absolute ethanol) was then added. The reaction was heated to reflux under a nitrogen atmosphere. This resulted in the dissolution of the remaining solid within 10 min. After 3 h, the homogeneous, brown solution was cooled and the solvent removed in vacuo. Trituration of the crude product in methanol resulted in the formation of pale yellow crystals of tetranitrile **11**, which were filtered and dried in vacuo (68 mg, 86%): M.p. 207–209 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.14 (s, 6H; CH_3), 7.64 (s, 2H; H-4'), 7.77 (s, 2H; C=CH); MS (CI, NH_3): *m/z* (%): 520 (100) [M^+], 470 (27), 450 (20), 424 (14); $C_{23}H_{10}F_6N_4S_2$ (520.47): calcd C 53.08, H 1.94, N 10.76; found C 53.42, H 1.96, N 10.94.

1,2-Bis[5'-(1'',3''-benzodithiole-2''-ylidenylmethyl)-2'-methylthien-3'-yl]perfluorocyclopentene (12): Dichloromethane (1.0 mL) was added to dialdehyde **10** (50 mg, 0.118 mmol) and 2-triphenylphosphonio-1,3-benzodithiole tetrafluoroborate (118 mg, 0.236 mmol). A pale yellow suspension was formed. Upon addition of aqueous sodium hydroxide (50% w/w, 1.0 mL), two clear phases appeared, which were vigorously stirred at ambient temperature. After 3 h, the orange emulsion was extracted with dichloromethane (2 × 25 mL) and washed with water (3 × 80 mL). The combined organic phases were then dried (Na_2SO_4), filtered and evaporated in vacuo to yield a green-yellow semi-solid. Chromatography over silica gel (dichloromethane/hexane = 2:1) afforded the diadduct **12** as a yellow solid (67 mg, 82%). An analytical sample was obtained by recrystallization from methanol: M.p. 225–226 °C (decomp.), darkens at 215 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.98 (s, 6H; CH_3), 6.63 (s, 2H; C=CH), 6.88 (s, 2H; H-4'), 7.04–7.18 (m, 4H; aromatics), 7.20–7.33 (m, 4H; aromatics); MS (CI, NH_3): *m/z* (%) 696 (4) [M^+], 590 (6), 560 (9), 292 (60), 172 (100); (FAB-nitrobenzyl alcohol): *m/z* (%) 696 (100) [M^+]; $C_{31}H_{18}F_6S_6$ (696.83): calcd C 53.43, H 2.60; found C 53.62, H 2.68.

1-[5'-(1'',3''-Benzodithiole-2''-ylidenylmethyl)-2'-methylthien-3'-yl]-2-[5'''-formyl-2'''-methylthien-3'''-yl]perfluorocyclopentene (13): Aqueous sodium hydroxide (50% w/w, 3 mL) was added to a suspension of dialdehyde **10** (300 mg, 0.707 mmol) and 2-triphenylphosphonio-1,3-benzodithiole tetrafluoroborate (354 mg, 0.707 mmol) in dichloromethane (3.5 mL). The reaction was carried out and worked up in a manner identical to that described for the preparation of **12** above. The crude yellow semi-solid thus obtained was chromatographed over silica gel (dichloromethane/hexane = 3:1) to yield the diadduct **12** (215 mg) and the desired monoadduct **13** (yellow foam, 237 mg, 60%). An analytical sample of yellow crystals was obtained by recrystallization from dichloromethane/*n*-hexane: M.p. 193 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.96 (s, 3H; 2'''-CH_3), 2.03 (s, 3H; 2'-CH_3), 6.61 (s, 1H; C=CH), 6.84 (s, 1H; H-4'), 7.10-7.32 (m, 4H; aromatics), 7.77 (s, 1H; H-4'''), 9.86 (s, 1H; CHO); MS (CI, NH_3): *m/z* (%): 561 (100) [MH^+], 531 (5) [$MH^+ - CH_2O$], 394 (4), 209 (6), 153 (8); (FAB-nitrobenzyl alcohol): *m/z* (%): 560 (100) [M^+]; $C_{24}H_{14}S_4OF_6$ (560.60): calcd C 51.42, H 2.52; found C 51.40, H 2.37.

1-[5'-(1'',3''-benzodithiole-2''-ylidenylmethyl)-2'-methylthien-3'-yl]-2-[5'''-(2'''',2''''-dicyanoethenyl)-2'''-methylthien-3'''-yl]perfluorocyclopentene (2): Monoaldehyde **13** (250 mg, 0.446 mmol) was suspended in absolute ethanol (5 mL) containing malonodinitrile (34 mg, 0.510 mmol), and a catalytic amount of piperidine (8 drops of a stock solution of 1 drop amine in 2 mL absolute ethanol) was then added. The reaction was heated to reflux under a nitrogen atmosphere, and the remaining solid dissolved within 10 min. After 3 h, the homogeneous, brown solution was cooled and the solvent removed in vacuo. This crude product was purified by chromatography over silica gel (dichloromethane/*n*-hexane = 3:2 to 4:1), which afforded the unsymmetrical photochrome **2** as an orange solid (254 mg, 94%). An analytical sample was obtained by recrystallization from dichloromethane/*n*-hexane, which yielded an orange powder: M.p. 183–185 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.96 (s, 3H; 2'''-CH_3), 2.09 (s, 3H; 2'-CH_3), 6.62 (s, 1H; 5'-CH), 6.82 (s, 1H; H-4'), 7.10–7.35 (m, 4H; aromatics), 7.67 (s, 1H; H-4'''), 7.80 (s, 1H; H-1''''); MS (FAB-nitrobenzyl alcohol): *m/z* (%): 608 (100) [M^+]; $C_{27}H_{14}S_4N_2F_6$ (608.65): calcd C 53.28, H 2.32, N 4.60; found C 53.21, H 2.15, N 4.44.

Photocyclizations: A solution of the open form of the photochrome (1.25×10^{-3} M, deuterated solvent) was placed in a 5 mm quartz NMR tube after an aliquot was diluted 100-fold (1.25×10^{-5} M, corresponding nondeuterated, spectrograde solvent) for measurement of the UV spectrum of the uncyclized form. After recording of the 200 MHz ^{1}H NMR spectrum of the uncyclized isomer, the sample tube was irradiated using two UV lamps with light of either 254 or 365 nm. After measured irradiation times, the ^{1}H NMR spectrum was obtained, and an aliquot diluted for recording of the UV spectrum. This was repeated until the photostationary state was attained. Care was taken to prevent exposure of the irradiated samples to ambient light. The ratio of the isomers was obtained by integration of all well-resolved pairs of NMR signals corresponding to the cyclized and uncyclized forms. When possible, conversions near 100% were quantitated by the relative intensity of the signal of the remaining uncyclized isomer and the ^{13}C-satellite of the corresponding signal of the cyclized isomer (given an intensity of 0.5% that of the uncoupled peak). Attainment of the photostationary state was verified by prolonged irradiation of the diluted UV samples. Molar extinction coefficients of the cyclized forms were determined by means of plots of the absorbance vs. the concentration of the cyclized isomer obtained by integration of the NMR signals.

Photochemical Opening and Photofatigue: A stirred solution of the open form of the photochrome ($1-2 \times 10^{-5}$ M) was converted to its closed form in a 10 mm cuvette until the photostationary state (> 98% conversion) was attained. The stirred sample was then irradiated using two lamps with visible ($\lambda > 600$ nm) light in a refrigerated glass chamber maintained at 20 °C. Measured periods of irradiation (typically 5 min) were used to determine the minimal time required for at least 90% reconversion to the colourless isomer. Ten colouration–decolouration cycles were then carried out; UV spectra were recorded after each operation. In the case of **12**, for which the decolouration process is relatively slow, the opening step was carried out to ca. 60% conversion.

Thermal Opening: For compounds $\mathbf{1}^{2+}$, **10**, **12**, **13** and **6**, solutions of cyclized isomers in benzene ($\approx 2 \times 10^{-5}$ M; 25 mL, acetonitrile in the case of $\mathbf{1}^{2+}$) were incubated, protected from light, in tightly stoppered glass tubes in a water bath maintained at 60 °C. After measured intervals, the samples were cooled to room temperature, and an aliquot removed to spectrophotometrically monitor the thermal opening by the decrease in absorbance at λ_{max} (closed). In the case of compounds **2** and **11**, the thermal openings in benzene ($\approx 10^{-5}$ M) were monitored directly in the spectrophotometer (decrease in absorption at λ_{max}) in thermostated 10 mm cuvettes connected to a circulating water bath heated to 60 °C.

Cyclic Voltammetry: Cyclic voltammetry experiments were carried out in an oven-dried electrochemical cell at 20 °C under nitrogen using freshly distilled and degassed solvents. For $\mathbf{1}^{2+}$, a solution containing $\mathbf{1}^{2+}$ (open) (5×10^{-3} M) and tetrabutylammonium tetrafluoroborate (0.1 M) in acetonitrile (5 mL) was employed. The sample was irradiated with UV light of 365 nm (two lamps) for 20 min to generate the closed form. Complete conversion to $\mathbf{1}^{2+}$ (closed) was verified by UV spectroscopy prior to further electrochemical measurements. For **12**, a 10^{-3} M solution of photochrome containing tetrabutylammonium perchlorate (0.1 M) in dichloromethane (5 mL) was used and photocyclized in the same manner. Coulommetry was carried out using a 5 m silver wire working electrode, a platinum wire counterelectrode and an SCE reference electrode in a 150 mL solution of $\mathbf{1}^{2+}$ (closed) (10^{-5} mol) in degassed acetonitrile at a potential of −0.6 V.

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