

Light-triggered Electrical and Optical Switching Devices

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

Chimie des Interactions Moléculaires, Collège de France, 11 place Marcelin Berthelot, 75005 Paris, France†

The functional photoswitchable systems **1–3** and **12–15** display pronounced photochromic properties; the bis-pyridinium derivative **1** represents a prototype of a switched molecular wire which may be converted from an open unconjugated form to a closed electron-conducting state.

The design of switching devices, allowing for the reversible modulation of a given physical property by means of an external trigger, is of basic importance for the development of molecular and supramolecular devices.¹ This concerns, in particular, the ability to switch on and off an electrical or optical signal by means of light of two different frequencies.

Bis-pyridinium polyenes, the caroviologens,² may be considered as prototypes of molecular wires allowing electron flow to take place,³ and push-pull polyenes present very pronounced non-linear optical properties.⁴ The combination of these components with an externally triggered switching process could lead to electro-photo or opto-photo switches. This may, in principle, be achieved by inserting into the polyenic path a bistable 'on/off' unit which establishes or interrupts the electronic conjugation by reversible interconversion between a closed and an open state (Fig. 1).

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We report here the design, synthesis and properties of the symmetrical **1** and non-symmetrical **2** species which represent prototypes of switchable molecular wires displaying light-triggered reversible changes in electrical and optical properties.

1,2-Diarylethenes,^{5,6-8} namely those bearing two thiophene-derived groups⁶⁻⁸ whose photochromic properties have been extensively studied, appeared particularly well suited for our purposes. Indeed, compounds of this type undergo a reversible electrocyclic interconversion between a conjugated closed (on) and an unconjugated open (off) state under irradiation at well separated wavelengths, with high quantum yield and, for perfluorocyclopentene-derived molecules in particular, with marked resistance to photofatigue.⁸

Compounds **1** and **2** were synthesized according to Scheme 1. 2-Methylthiophene **4** was brominated in acetic acid⁹ yielding the 2,4-dibromide **5** (oil, 74%), which was subsequently lithiated and reacted with tri-*n*-butyl borate¹⁰ to afford the boronic acid **6** (m.p. 230 °C, decomp.; 78%). The palladium-catalysed coupling¹¹ of **6** and 4-bromopyridine yielded the pyridyl thiophene **7** (m.p. 83 °C; 84%). Coupling of **7** with perfluorocyclopentene according to the described method¹² [in tetrahydrofuran (THF)] gave the bis-pyridyl compound **3** (m.p. 181 °C; 67%). Methylation of **3** yielded the bis-pyridinium species **1** as the trifluoromethanesulfonate (triflate) salt (m.p. 157–159.5 °C; 98%).

Bromination of 5-methylthiophene-2-carbaldehyde **8** in acetic acid afforded **9** as a single regioisomer (m.p. 58 °C;

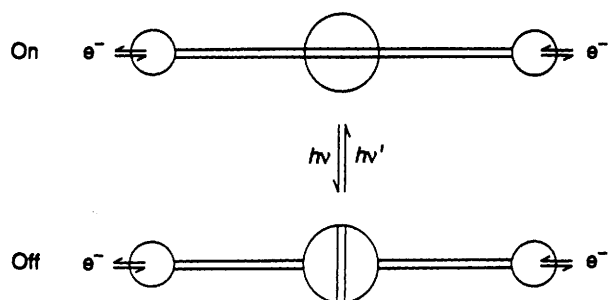
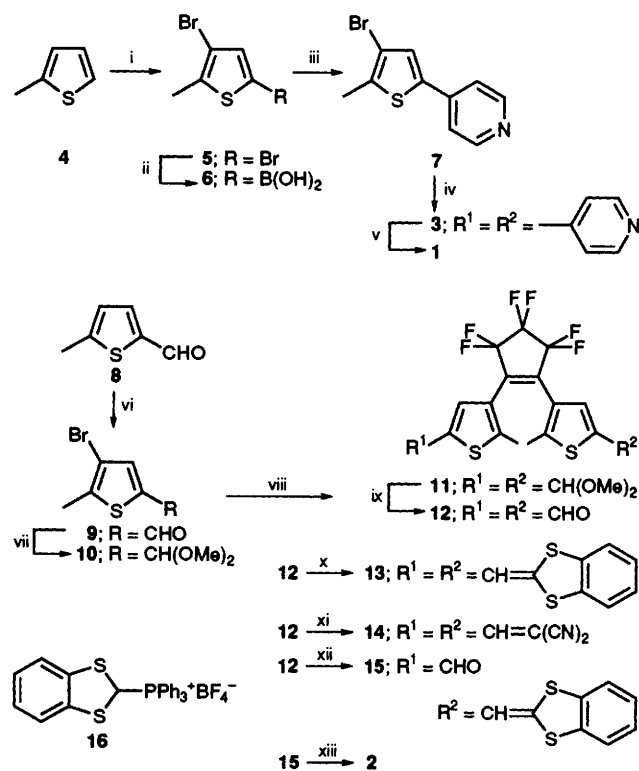


Fig. 1 Schematic representation of the open (bottom) and closed (top) states of a switched molecular wire consisting of a polyconjugated chain, two terminal electron exchanging groups and a central on/off switching unit

74%). The carbonyl group was protected as the dimethyl acetal **10** (oil; 97%) prior to coupling with the fluorinated ring to give the bis-acetal **11** (syrup; 56%) which was hydrolysed to give the key dialdehyde **12** (m.p. 182 °C; 93%). Wittig¹³ and Knoevenagel¹⁴ condensations (employing respectively phosphonium salt **16** and malonodinitrile) were used to transform **12** to the symmetrical compounds **13** and **14** (m.p. 225–226 °C,

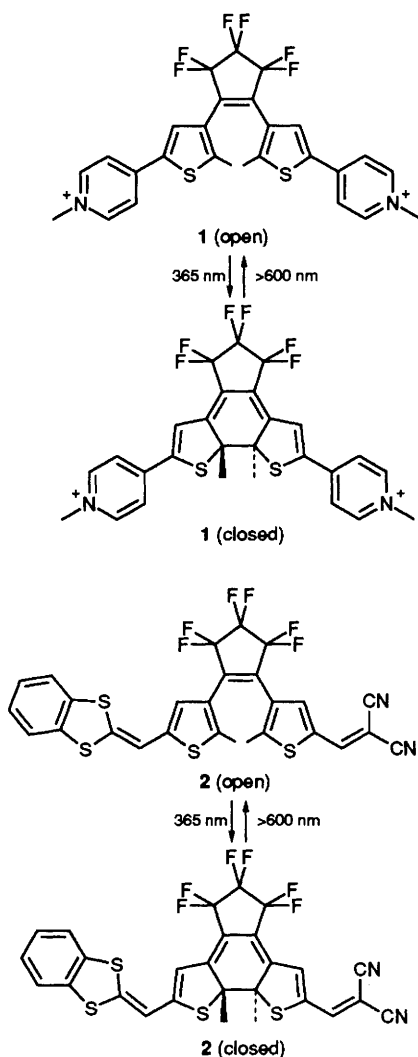


Scheme 1 Reagents and conditions: i, Br₂, AcOH; ii, BuⁿLi, Et₂O, -78 °C, (BuⁿO)₄B, NaOH, HCl; iii, 4-bromopyridine·HCl, Pd⁰(PPh₃)₄ (3 mol %), Na₂CO₃, H₂O, THF, reflux; iv, BuⁿLi, THF, perfluorocyclopentene, -78 °C room temp.; v, MeOTf, CH₂Cl₂; vi, as i; vii, TsOH, MeOH, reflux; viii, as iv in Et₂O; ix, TsOH, THF, H₂O; x, **16** (2 equiv.), CH₂Cl₂, NaOH, H₂O; xi, CH₂(CN)₂ (2 equiv.), piperidine (cat.), EtOH, reflux; xii, as x using 1 equiv. of **16**; xiii, as xi using 1 equiv. of CH₂(CN)₂. Tf = CF₃SO₂; Ts = *p*-MeC₆H₄SO₂.

Table 1 Photochemical and spectral data for the open and closed forms of compounds 1–3 and 12–15

Compound (form)	R ¹ , R ²	λ _{max} /nm (ε × 10 ⁻³)	Δλ _{max} /nm	Solvent	Conversion ^a (%)	¹ H NMR data		
						2-Thiophene CH ₃	CH=	4-Thiophene CH
1 (open)	PyMe ⁺ OTf ⁻	352 (46)	310	CD ₃ CN	>99.5	2.13	4.26 ^b	8.07
(closed)		662 (16)				2.34	4.34 ^b	7.37
2 (open)	Benzodithia C=CH,	354 (40)	474	C ₆ D ₆	>99.5	1.50, 1.35	6.17, 6.16	6.80, 6.77
(closed)	CH=C(CN) ₂	828 (23)				1.97, 1.91	5.90, 5.77	5.89, 5.80
3 (open)	Py	300 (32)	292	C ₆ D ₆	81	1.57	—	7.29
(closed)		592 (14)				1.99	—	6.55
(open)		304 (35)	288	CD ₂ Cl ₂	>98	2.00	—	7.51
(closed)		592 (14)				2.22	—	6.85
12 (open)	CHO	296 (19)	328	C ₆ D ₆	40	1.19	9.20	7.01
(closed)		624 (8.0)				1.70	8.89	5.99
(open)		263 (30)	361	CD ₂ Cl ₂ ^c	>98	2.02	9.83	7.74
(closed)		624 (7.2)				2.20	9.86	6.97
13 (open)	Benzodithia C=CH	350 (50)	363	C ₆ D ₆	>99.5	1.71	6.17	6.90
(closed)		713 (29)				2.18	5.98	5.87
14 (open)	CH=C(CN) ₂	361 (40)	368	C ₆ D ₆	>98	1.54	6.11	6.78
(closed)		729 (14)				1.58	5.65	5.70
15 (open)	Benzodithia C=CH,	350 (26)	351	C ₆ D ₆	>99.5	1.42, 1.52	6.14, 9.24	6.6–6.8 ^d
(closed)	CHO	701 (20)				1.98, 2.03	5.79, 9.09	5.82, 6.28

^a Photostationary state for irradiation at 365 nm. ^b Signal of *N*-Me groups. ^c Irradiation at 254 nm. ^d Hidden by the signals of the aromatic protons.



Scheme 2 Photochemical interconversion of compounds **1** and **2** between open and closed forms

decomp.; 82% and m.p. 207–209 °C; 86%), respectively. Finally, reaction of **12** with 1 equiv. of **16** afforded a mixture of mono-adduct **15** (m.p. 193 °C, 60%) and **13** which were easily separated by chromatography. The former was then condensed with malonodinitrile to yield the unsymmetrical compound **2** (m.p. 183–185 °C; 94%). All new compounds had spectral (^1H ^{13}C NMR, mass) and microanalytical properties in agreement with their structures.

Molecules **1–3** and **12–15** exhibit remarkable photochromism, in line with that described for related compounds.^{6–8} Irradiation of the open forms **1–3** and **12–15** with 365 nm light resulted in (Table 1): (i) almost total conversion (>98–99%) to the corresponding closed forms (Scheme 2, Fig. 2); (ii) very large shifts, $\Delta\lambda_{\text{max}}$, of the absorptions (in excess of 300 nm) towards longer wavelengths, (iii) λ_{max} values located well into the red, or even into the infrared, and high absorption coefficients for the closed forms. The push–pull substance **2** is particularly remarkable, displaying $\lambda_{\text{max}}(\text{closed}) = 828$ nm and $\Delta\lambda_{\text{max}} = 474$ nm. All three features presented by **1–3** and **12–15** are notably more pronounced than those of the related substances described earlier (typically: 30–70% conversion, $\lambda_{\text{max}} = 500–600$ nm, $\Delta\lambda_{\text{max}} = 100–250$ nm).^{6–8} The rate of thermal opening of the closed forms back to the open forms of **1–3**, **12–15** is markedly dependent on the nature of the substituents. Photochemical opening has been achieved ($\geq 90\%$) by irradiation with visible light above 600 nm.

The nearly total open-to-closed conversions for **1–3** and **12–15** may result from the fact that the rotational interconver-

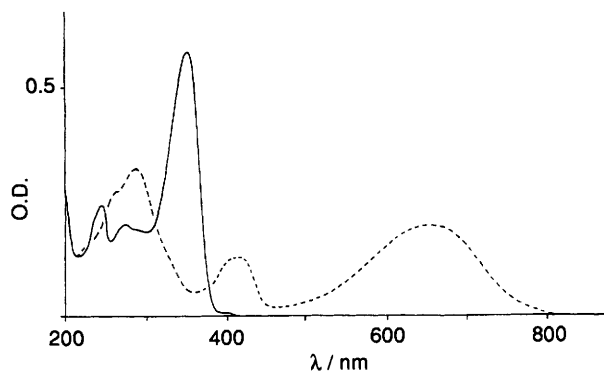


Fig. 2 Electronic absorption spectra of the open (full line) and closed (dashed line) forms of compound **1**; the conversion of the former to the latter was effected by irradiation of the solution at 365 nm; solvent: MeCN

sion of the open forms of these substances between anti-parallel (where cyclisation can occur), and parallel (where cyclisation cannot occur) orientations of the thiophene rings may take place with little hindrance, whereas it is strongly hindered in the case of the reported compounds in which the thiophene rings are fully substituted.^{6–8} Low-temperature ^1H NMR measurements (down to -70 °C in CH_2Cl_2) did not allow the observation of the two conformers for compound **12**.

The high λ_{max} and ϵ values are due to the extended conjugation present in the closed forms. From a practical standpoint, such red-shifted absorptions are of critical importance in the context of optical memory systems, since they allow for the use of a diode laser (780–830 nm) to effect the reverse photoreaction to the open forms.

Of major significance for the goal of the present study was the determination of the electrochemical properties of the open and closed forms of the bis-pyridinium compound **1**. Cyclic voltammetry (in MeCN) indicated that whereas no electrochemical process occurs for the open form of **1** in the +0.6 to -0.6 V region, a clearly reversible and mono-electronic reduction wave was observed for the closed form at a potential $E_{1/2} = -230$ mV vs. standard calomel electrode (SCE) (Fig. 3). This value is considerably less negative than those determined for methylviologen (-460 mV vs. SCE¹⁵) and for bis-pyridinium polyenes;² this might result from the presence of the strongly electron-attractive $-\text{CF}_2\text{CF}_2-$ unit. More detailed electrochemical studies are underway.

Thus, **1**(open) behaves like two isolated pyridinium groups, whereas **1**(closed) presents the features of two conjugated ones with electron delocalisation in the reduced state. The latter form may be considered as a shortened version of the caroviologen molecular wires^{2,3} or an extended version of methylviologen. Compound **1** indeed represents a prototype of a switchable molecular wire in which electron flow may occur in the closed state, on/off switching being triggered by an external factor, namely, irradiation with light of two well-separated frequencies. Such a function is of basic interest for the development of molecular electronic devices.

With respect to optical properties, the push–pull substance **2** in the closed form (as well as the other compounds, but to a lesser degree) may, on the basis of the data obtained for push–pull polyenes (ref. 4 and references cited therein), be expected to display pronounced nonlinear optical features. Thus, **2** represents an entry into a class of substances operating as a two-level optical system with reversible changes in absorption and nonlinear features. Such studies are underway.

Finally, one may point out that photochromic substances such as those studied here may be considered to present molecular hysteresis characteristics since interconversion of the bistable substances (open and closed forms) follows a different pathway when the irradiation frequency is swept either up or down the wavelength scale.

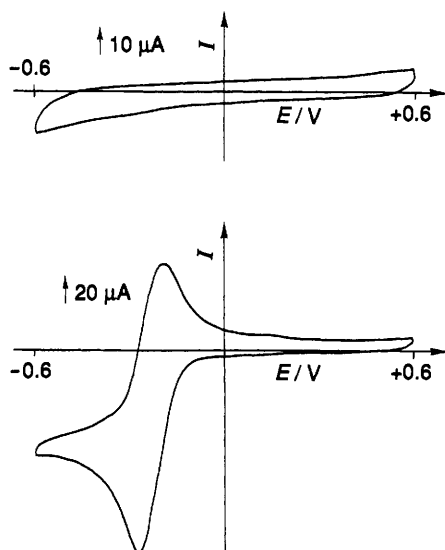


Fig. 3 Cyclic voltammograms determined for the open (top) and closed (bottom) forms of compound **1** in MeCN (1 mmol l⁻¹; supporting electrolyte 0.1 mol l⁻¹ NBu₄BF₄)

It is clear that compounds based on the same principles as the present ones and bearing various functional features (metal complexes, ionizable groups, energy and electron transfer units) may be devised, thus allowing for the reversible switching of a variety of physicochemical properties and providing entries into semiochemistry,^{1b} the chemistry of molecular signalling processes.

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