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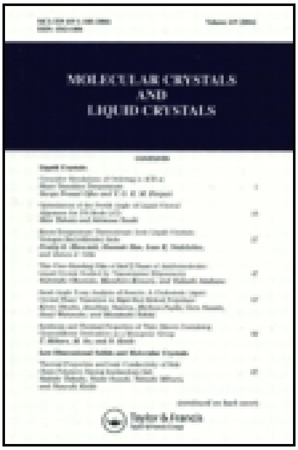

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Light-Triggered Electrical and Optical Switches

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Version of record first published: 24 Sep 2006.

To cite this article: Sylvain L. Gilat , Stephen H. Kawai & Jean-Marie Lehn (1994): Light-Triggered Electrical and Optical Switches, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 246:1, 323-326

To link to this article: http://dx.doi.org/10.1080/10587259408037837

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Mol. Cryst. Liq. Cryst. 1994, Vol. 246, pp. 323–326
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Printed in the United States of America

LIGHT-TRIGGERED ELECTRICAL AND OPTICAL SWITCHES

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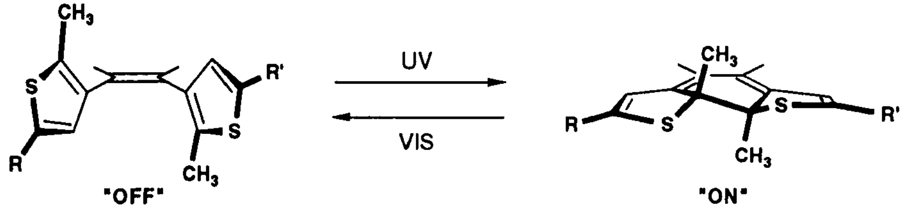
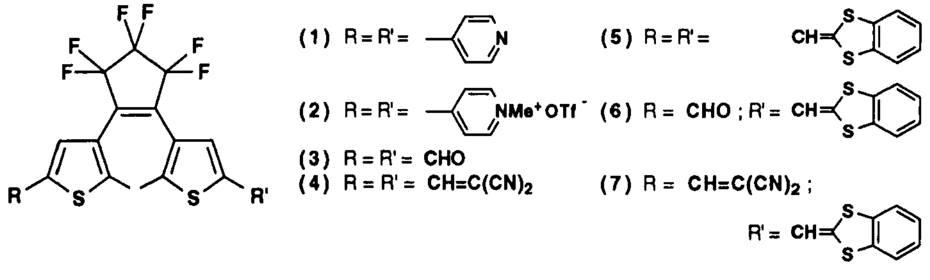
Abstract The protochromic properties of *bis*-thien-3-yl ethene-derived "switches", as well as the electrochemical properties of a prototype "switchable" molecular wire, are described.

The electron conduction and non-linear optical properties of *bis*-pyridinium polyenes[1,2] (caroviologens) and push-pull polyenes[3], respectively, are dependent on the electronic conjugation between the functional groups situated at the extremities of the polyolefinic chains. The incorporation of a photochromic "switching unit" capable of reversibly interrupting or establishing this conjugation would allow for the modulation of these properties by light. Diarylethenes, notably thiophene-derived systems[4,5], are especially well-suited for this purpose in that irradiation with light of well-separated wavelengths can effectively interconvert them between isomers in which the heterocycles are either conjugated ("on") or unconjugated ("off").



"OFF"
(open form)

"ON"
(closed form)



With the goal of developping such switchable devices, a series of *bis*-thien-3-yl ethenes **1-7** bearing an array of e⁻-donating, e⁻-withdrawing and redox groups was prepared. Full details of the synthesis of these compounds will be published elsewhere.

Compounds **1-7** all exhibit remarkable photochromic properties. Photochemical cyclizations from the open to closed forms were carried out by irradiating solutions of open isomers with UV light (365 nm, or 254 nm in the case of **3**) in 5 mm NMR tubes. Aliquots were removed and diluted for the measurement of UV spectra throughout the course of each photocyclization. In this way, the reactions could be monitored directly using both ^{1}H-NMR and UV methods (Figures 1 and 2).

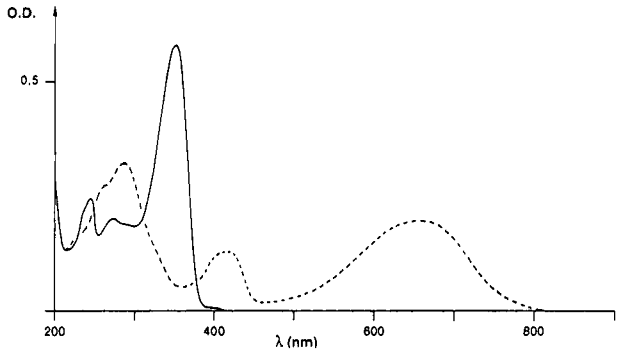


FIGURE 1 UV spectra of **2** prior to irradiation (i.e. open form):[—]; and at the photostationary state under irradiation at 365 nm (>99,5 % conversion):[- - -]. (1,25 x 10^{-5} M / CH_3CN).

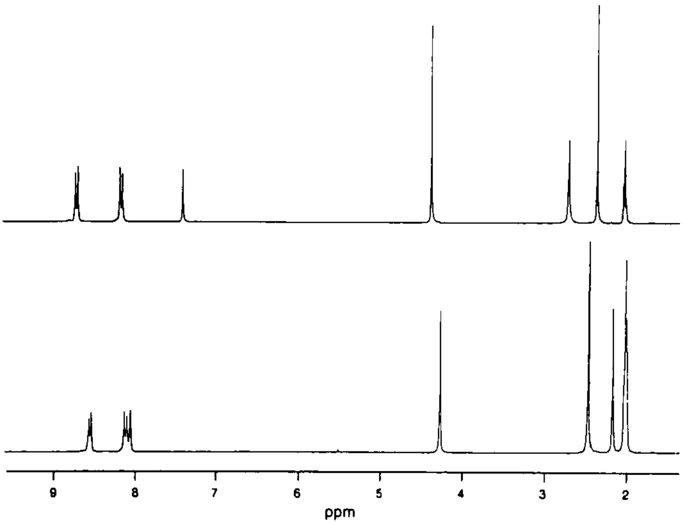


FIGURE 2 200 MHz ^{1}H-NMR spectra of **2(open)** [top] and **2(closed)** [bottom] in CD_3CN.

The results (Table 1) show that, unlike previously described compounds of this type, the present systems may essentially be fully converted (>98 %) from the open to closed forms. Once cyclized, the intensely-colored closed isomers were reopened (>90 %) by irradiation with visible (red) light of greater than 600 nm. Such high degree of interconversion is necessary for an "on/off"-type switching function. The results also reveal that the absorption maxima of the closed isomers are highly shifted (large $\Delta\lambda_{max}$) towards, and even into, the IR region; this is important in the context of optical memory systems.

TABLE I Photochemical and spectral data for compounds **1**-**7**.

Compound (form)	λ_{max} / nm ($\varepsilon \times 10^{-3}$)	$\Delta\lambda_{max}$ / nm	Solvent	Conversion[a]
1 (open) (closed)	304 (35) 592 (14)	288	CD_2Cl_2	>98 %
2 (open) (closed)	352 (46) 662 (16)	310	CD_3CN	>99,5 %
3 (open) (closed)	263 (30) 624 (7,2)	361	CD_2Cl_2	>98 %[b]
4 (open) (closed)	361 (40) 729 (14)	368	C_6D_6	>98 %
5 (open) (closed)	350 (50) 713 (29)	363	C_6D_6	>99,5 %
6 (open) (closed)	350 (26) 701 (20)	351	C_6D_6	>99,5 %
7 (open) (closed)	354 (40) 828 (23)	474	C_6D_6	>99,5 %

[a] Percent conversion at the photostationary state under irradiation at 365 nm.
[b] Irradiation at 254 nm.

Of central importance to this study was the determination of the electrochemical properties of the two forms of the *bis*-pyridinium compound **2**. Cyclic voltammetry (Figure 3) showed that whereas no electrochemical process occurs for **2**(**open**) within the -0,6 to +0,6 V domain, a reversible reduction wave is observed at $E_{1/2}$ = -250 mV versus SCE for **2**(**closed**). The monoelectronic nature of the reduction was confirmed by coulometry. Thus, while **2(open)** behaves as isolated pyridinium groups, **2(closed)** exhibits the properties of two which are conjugated. These results are a clear demonstration of the switching function; compound **2** represents a prototype "switchable" molecular wire through which electron flow may be controlled in an "on/off" fashion by light.

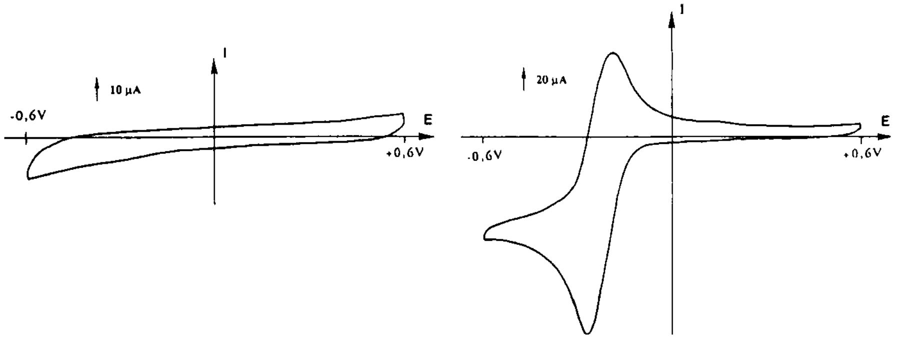


FIGURE 3 Cyclic voltammograms of **2(open)** [left] and **2(closed)** [right]. (1 mM in acetonitrile / 0,1 M n-Bu_4N BF_4 / under Ar / 20°C. Photocyclization was carried out in the electrochemical cell.)

The unsymmetrical compound **7**, which bears strong electron-donating and -withdrawing substituents, displays the greatest spectral change upon photocyclization (a $\Delta\lambda_{max}$ of 474 nm and an absorption well into the IR). Its closed form, structurally analogous to a push-pull polyene, exhibits considerable solvatochromism and is anticipated to possess pronounced non-linear optical properties. Thus, molecule **7** represents an entry into photo-switchable optical devices. These studies are presently underway as well as the elaboration of related light-triggered systems.

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