

NEW PHOTOCHROMIC MATERIALS

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Abstract

The aim of this work was the synthesis and study of photochromic compounds with new properties. Five dithienylethene type compounds (**1a-3a** and **1b-2b**) were synthesized and studied. They can reversibly interconvert between two thermally stable forms, an open and a closed one, by using light of different wavelengths as triggers.

Compounds **2** and **3** represent oligothiophenes endowed with a photoactivated switch and in view of their potential use as switched oligothiophenes they are of special interest in molecular electronic devices. In addition, both forms of **1b** and **2b** present absorption bands whose excitation gives very large differences in fluorescence between the two forms with very little effect on the opening/closing state, a feature of interest for optical memory data systems.

1 INTRODUCTION

The development of *molecular electronic devices* such as rectifiers, transistors, switches, photodiodes and molecular wires requires the design of functional components capable of handling electrons and is of central importance in supramolecular chemistry [1]. As switches can be considered systems that allow the reversible modulation of a given physical property, like conjugation, by an external trigger. The insertion into a polyenic path of such a functional unit (switch) which interrupts or establishes electronic conjugation (Figure 1) may be used to turn "ON" or "OFF" properties dependent on this conjugation (optical or/and electrical).

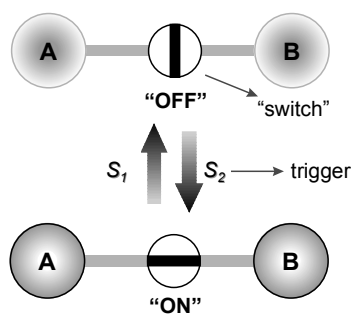


Figure 1: Schematic representation of a switching conjugated system.

Especially *light driven molecular switches* have been subject of a considerable amount of work [2]. Different wavelengths of light are used as external triggers and two distinct stages **I** and **II** (Figure 2) are obtained as result.

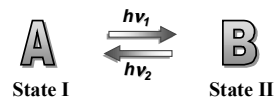


Figure 2: Light driven bistable systems.

Photochromism is defined as a reversible transformation in a chemical species between two forms having different absorption spectra by photoirradiation. The bistability of organic photochromic compounds is of special interest for optical data memory systems (photon-mode erasable optical recording media) [3]. Numerous other uses have also been explored with encouraging results. They can be classified into three main categories: **a)** applications concerning single molecules [2,4,5] (switching recognition, transportation, fluorescence, non-linear optical properties, chirality and catalysis) **b)** applications concerning polymers [2,6,7] (switching of colours, conductivity, viscosity, liquid crystallinity, gelation, solubility, dendritic structure, etc.) and finally **c)** applications concerning biological molecules [8] (photoswitching of peptide helicity, membrane permeability, enzyme activity, and bilayer stability).

In the case of optical storage memory systems, the interest of photochromic compounds is based on the fact that photon-mode recording has certain advantages over the heat-mode, regarding resolution speed of writing and multiplex recording capability [3,6]. Also, fatigue due to material movement is eliminated. Despite these advantages, photochromic molecules still await practical applications. The reason is that they must fulfill many requirements such as: i) low photofatigue (can be cycled many times without loss of performance), ii) archival storage capability (thermal stability), iii) sensitivity to the diode laser (650-830 nm), iv) high quantum yields and v) non destructive read-out capability.

Among the various photochromic systems [2] (azobenzenes, stilbenes, fulgides, spiropyrans, azulenes, etc.) diarylethenes, notably perfluoro-cyclopentene bis-thien-3-yl systems (Figure 3) have been shown to exhibit excellent properties such as thermal and chemical stability, as well as remarkable fatigue resistance [3,6]. Examples showing fatigue resistance to a number of cycles as high as $1,3 \times 10^4$ have been reported [6]. They are especially well-suited as "light driven molecular switches" since irradiation at well separated wavelengths can be used to interconvert them reversibly between an open (non-conjugated or "OFF") and a closed (conjugated or "ON") form.

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[#] This work has been performed in the years 1993-1995, under the supervision of Prof. J.-M. Lehn at the laboratory of College de France "Chimie des Interactions Moléculaires" 11, place Marcelin Berthelot - 75005 Paris, France.

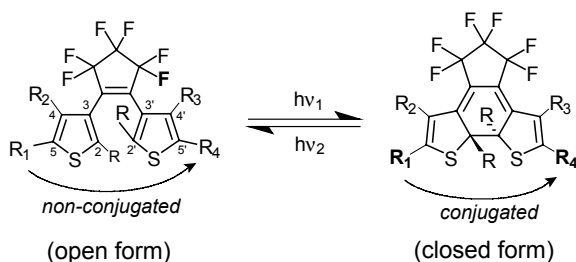
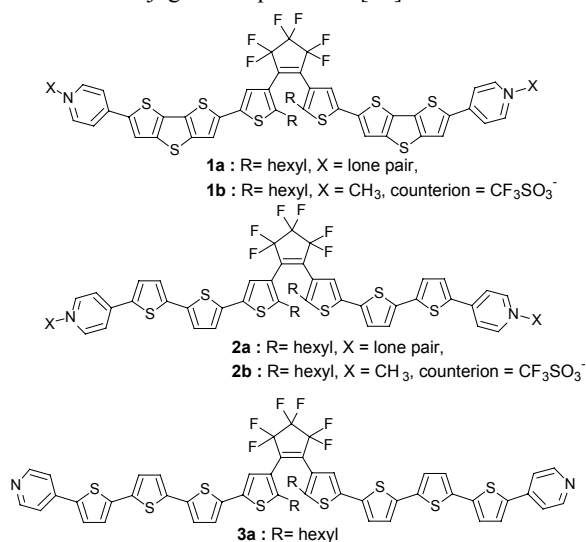


Figure 3: The bis-thien-3-yl-perfluorocyclopentene photochromic system.

In spite of the large number of diarylethene type compounds that have been synthesized until now and their good photochromic properties only very few examples [9] propose a solution to the problem of the non destructive read-out capability. Thus, any attempt to get information related to the state of the switch “ON” or “OFF” results to undesirable change of the information (the switch state is altered by the action of the reading method). A solution to this problem can be molecules which present not only absorption bands active to the opening closing procedure but also present additional bands inactive to the switching action. Reading in this case could be easily effected by irradiation of these inactive bands. Unfortunately, the examples that have been described so far, do not show such properties.

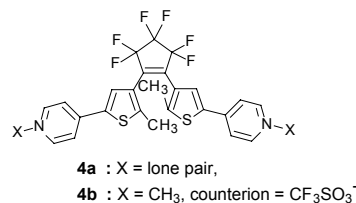
An approach to address this problem is to synthesize molecules that their Uv-vis spectra will be more complex. One way to realize this is to integrate into the molecular design many conjugated double bonds. In that way, the practical problem of sensitivity to the photodiode laser [6] can also be solved since the existence of many double bonds in conjugation will cause a red shift of the absorption bands. Of course the absorption bands of the two forms open-closed must remain well separated. In summary, in this work the synthesis and study of molecules (**1-3**, Scheme 1) having many double bonds switchable conjugated is presented [10].



Scheme 1: Compounds **1-3**.

2 DESIGN

The structure of molecules **1-3** is based on the simpler molecule **4** (Scheme 2) which has shown to exhibit excellent photochromic properties [5,11].



Scheme 2: Compound **4**.

Between the two forms open and closed of molecules **1-4** a number of differences concerning structural, electronic, optical, and oxidation properties are present. This permits a variety of interconversion modes to be highly integrated into a single molecule and so, explore the possibility to construct advanced, multi-functional, high density molecular electronic devices.

For example, molecule **4b** is interesting for two type of applications: a) in the optical memory systems, as a bistable system with good photochromic properties and b) in molecular electronics. The interest to the last area arises from the fact that molecule **4b** combines the features of a **light triggered electron switch** [5,12]. Particularly, two terminal electroactive [13] pyridinium groups have been placed in positions 5 and 5' (Figure 3) so that the “communication” (transport of electrons) between these two groups can be switched “OFF” or “ON” in the open and closed form, respectively. Indeed, the experimental data provide evidence that in the closed form the two positive charges are conjugated since reduction is significantly facilitated. Thus, the closed form can be reversibly reduced at -0,23 V while the open one shows no reduction up to -1.0 V.

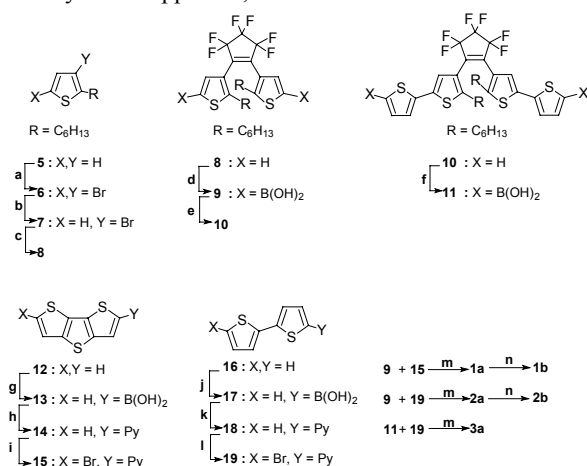
Molecules **1-3** combine the same features as molecule **4** while at the same time oligothiophene derivatives have been introduced in between the central switching unit and the two electrochemically active pyridinium groups. Therefore it is expected to act as **photoswitchable molecular wires**.

In addition, these molecules might have interest in the area of electronics. It is known that conjugated oligomers provide insight into the more complex properties of the corresponding polymers. Also investigations of the chemical stability and conductivity of modified or non-modified oligothiophenes show that their properties are interesting for use as electronic materials as well as for the development of conducting polymers [14]. The two states of molecules **1-3** are very different regarding the number of thiophenes that are conjugated. So, it is expected that the electronic properties like conductivity will be very different between the two forms.

3 SYNTHESIS

Attempts to synthesize compounds **1-3** according to the literature method [15] were not successful because of solubility and selectivity problems. Therefore, the synthesis of the target compounds **1-3** was carried out by a

new synthetic approach, shown in Scheme 3.



Scheme 3: Pathways for the synthesis of compounds **1a-b**, **2a-b**, **3a**. Reagents and conditions: a) Br₂ (CHCl₃/AcOH); b) 1. BuLi (Et₂O); 2. MeOH; c) 1. BuLi (THF); 2. C₅F₈; d) 1. BuLi/ TMEDA (pentane-THF); 2. B(n-OBu)₃; e) 2-Bromo-thiophene/Pd(PPh₃)₄ (THF/ aq. Na₂CO₃); f) 1. BuLi (Et₂O); 2. B(n-OBu)₃; g) 1. BuLi (Et₂O); 2. B(n-OBu)₃; h) 4-Bromo-pyridine:HCl/Pd(PPh₃)₄ (THF/aq. Na₂CO₃); i) Br₂ (CHCl₃/AcOH); j) 1. BuLi (Et₂O); 2. B(n-OBu)₃; k) 4-Bromo-pyridine:HCl/ Pd(PPh₃)₄ (THF/aq. Na₂CO₃); l) Br₂ (CHCl₃/AcOH); m) Pd(PPh₃)₄ (THF/aq. Na₂CO₃); n) CF₃SO₃CH₃ (CH₂Cl₂).

This new approach is of general application and has certain advantages over the previous one. Firstly, the key compound **9** gives access to more complex switch molecules with fewer steps and simultaneously allows the use as final step of a well known, usually high-yield reaction, namely palladium catalyzed carbon-carbon bond formation. Secondly, it is not necessary for the end groups, which are to be attached to the central switch unit, to be inert against carbanions or to bear the unstable boronic acid group. The only requirement is to bear a halogen at the position of connection. More experimental details can be found in reference [10].

4 PROPERTIES

4.1 Physical Properties

Compounds **1a-3a** are soluble (unlike unsubstituted oligothiophenes [16]) in many common organic solvents like chloroform (CHCl₃), dichloromethane (CH₂Cl₂), acetone, tetrahydrofuran (THF), higher alcohols, and even to some extent in hexane. The solubility decreases in the order **2a** > **1a** > **3a**. On the other hand, compounds **1b** and **2b** carrying two positive charges, are insoluble in solvents of low or medium polarity like hexane CHCl₃, CH₂Cl₂, acetone, but are moderately soluble in high polarity solvents like acetonitrile (CH₃CN), dimethyl sulfoxide (DMSO), dimethyl formamide (DMF) and methanol (MeOH).

With respect to photostability, compounds **1a-2a** and **1b-2b** show no decomposition when exposed to daylight

or oxygen for 2-3 days, but an inert atmosphere (N₂) was always used during irradiation experiments. After 10 opening-closing photocycles no change in the UV spectra can be found. The open and closed forms are thermally stable at room temperature for periods of more than 10 days.

4.2 Photochromic Properties

The photochromic properties were studied by irradiating solutions of compounds **1a-3a** and **1b-2b** in benzene and methanol respectively. In both cases the concentration was $\sim 1 \times 10^{-5}$ M.

In molecules **1-3** the methyl groups in positions 2 and 2' (Figure 3) have been replaced by hexyl groups. The effect of this replacement to the opening-closing process was explored. It was found that although the longer n-hexyl chains are bulkier than methyls, not only improve greatly the solubility but enhance also the switching properties: i) the absorption maxima are shifted to longer wavelengths (24-30 nm red-shift for the closed form), ii) the separation between the peaks of open and closed forms is increased. Also no change was observed to the photostationary state [17] for all compounds tested.

In general, irradiation of the absorption bands of each form (open or closed) leads to conversion to the other form (figure 4). The most important absorption bands of the Uv-vis spectra of the open and closed forms of compounds **1a-3a** and **1b-2b** are shown in Tables 1 and 2 respectively; the complete Uv-vis spectra of compounds **2a** and **1b** are shown in figure 4 and 5 respectively.

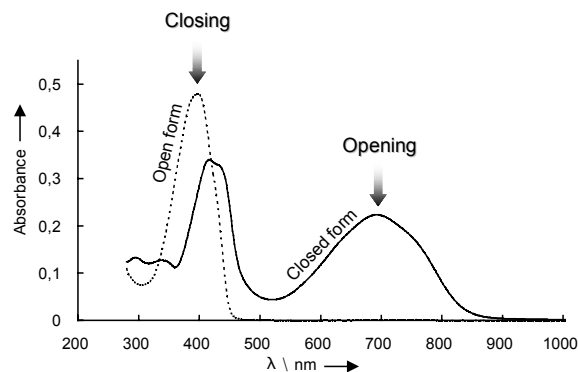


Figure 4: UV-vis absorption spectrum of the open and closed forms of compound **2a** in benzene solution.

Table 1: Uv-vis absorption λ_{\max} values (nm) of compounds **1a**, **2a** and **3a** in benzene.

Open forms			Closed forms		
1a	2a	3a	1a	2a	3a
395	398	420	426	417	440
			701	692	701

Table 2: Uv-vis absorption λ_{max} (nm) and ϵ ($\text{M}^{-1}\text{cm}^{-1}$; in parenthesis) values of the open and closed forms of compounds **1b** and **2b** in methanol.

Open forms		Closed forms	
1b	2b	1b	2b
261	261	246	253
(25400)	(32700)	(23250)	(23000)
329	333	454	440
(21700)	(21500)	(78900)	(67600)
459	451	704	698
(92800)	(80500)	(41000)	(37500)

The non methylated compounds **1a-3a** have similar photochromic properties but different from those of the methylated compounds **1b** and **2b**. In the case of **1a-3a** no UV light is necessary to obtain the closed forms but photoswitching between the two forms, open and closed, can be achieved by irradiation with two different wavelengths of the visible region. In particular, the open forms can be generated by irradiation of the closed forms at a wavelength >600 nm while subsequent irradiation of the open forms at a wavelength <450 -500 nm leads again to the closed forms. Both transformations were quantitative (according to $^1\text{H-NMR}$ at 200 MHz).

On the other hand, the methylated compounds **1b** and **2b**, display remarkably different behaviour. Methylation of the pyridine groups in **1a-2a**, affects mainly the absorption bands of the open forms causing a 50-65 nm red shift of λ_{max} while the λ_{max} of the closed forms are red shifted only 4-6 nm (Tables 1 and 2). Also, when the closed forms are irradiated at $\lambda > 600$ nm they open quantitatively, but even prolonged irradiation of the intense absorption bands of the open forms at 400-500 nm does not give the closed forms. Conversion to the closed forms (in $\sim 92\%$ yield in both cases) can only be achieved by irradiation of the relatively small absorption bands at $\lambda_{\text{max}} = 329$ nm and 333 nm for **1b** and **2b** respectively. In order to confirm that these correspond to photostationary states [17], solutions of the closed forms of **1b** and **2b** were irradiated at 365 nm and 312 nm respectively, giving opening to a maximum conversion around 8%.

The closed forms of **1b** and **2b** also present strong absorption bands in the 400-500 nm domain. As in the case of the open forms these bands give only little conversion, so that after 30 min of irradiation at 400-500 nm only a 3-5% opening is observed (Table 3).

Compounds **1a-3a** exist in the closed form in the daylight while **1b-2b** are in the open form. There is an important bathochromic shift of the λ_{max} (36-118 nm) of the absorption bands of compounds **1a-3a** and **1b-2b** in comparison with the simpler compounds **4a** and **4b** respectively. Thus, the λ_{max} (closed forms) for all compounds **1-3** are in the range of 690-705 nm. It has been already pointed out that this bathochromic shift is important from the viewpoint of practical applications (sensitivity to the diode laser).

Table 3: Interconversion between the open and closed forms. Proportion (%) of final form after 30 min of irradiation in MeOH.

Irradiation wavelength	Open --> Closed		Closed --> Open	
	1b	2b	1b	2b
312 nm	91.5	91 ^[18]	----	7
365 nm	92	85	7-8	----
400-500 nm	<0.5	0	5	3
>610 nm	0	0	98	95 ^[19]

Comparison between the rates of conversion to the closed forms for **1b** and **2b** using three commercial UV lamps at 254 nm, 312 nm, and 365 nm demonstrates that irradiation at 365 nm and 312 nm gives always significantly faster closing than irradiation at 254 nm. This shows that the absorption bands at $\lambda = 329$ nm and 333 nm for **1b** and **2b** respectively are the most active bands for conversion to the closed forms. In general, **1b** appears to undergo somewhat faster opening closing interconversions than **2b**, irradiated under similar conditions, at 312 nm, 365 nm, 400-500 nm or >600 nm (Table 3). For the non-methylated compounds **1a-3a** the order is **1a** \geq **2a** $>$ **3a**.

4.2 Fluorescence Properties

It was shown that for both **1b** and **2b** the absorption bands at ~ 300 nm can be used for the closing process while those at ~ 700 nm for the opening one (Table 3). The presence of the absorption bands around 400-500 nm which affect only little or not at all the state of conversion is of great interest in optical data memory systems since they propose a new solution to the problem of non-destructive read-out. Unfortunately, the difference between the absorption coefficients of the closed and open forms in **1b** and **2b** is small (Table 2) from practical point of view. Therefore, other properties related to these bands were explored.

Fluorescence was found to be of a particular interest. Indeed, the open forms of both **1b** and **2b** present strongly emissions at 589 nm and 611 nm, respectively when excited in the 400-500 nm region. In contrast, the closed forms display only a very weak fluorescence (less than 3% of the open ones Figure 5).

Although no inactive absorption bands are found in the UV-vis absorption spectra of the non-methylated compounds **1a-3a**, their fluorescence properties follow the same pattern with those of the methylated ones **1b** and **2b**. Thus, in the case of **1a** a large change in fluorescence is observed between open and closed forms. It is not possible at present to determine which structural and/or conjugation effects are responsible for this dramatic change in fluorescence.

4.2 Electrochemical Properties

The closed forms of compounds **1b** and **2b** present the features of molecular wires, namely an extended conjugated polyenic chain for electron transfer fitted with terminal electroactive pyridinium groups for reversible electron exchange.

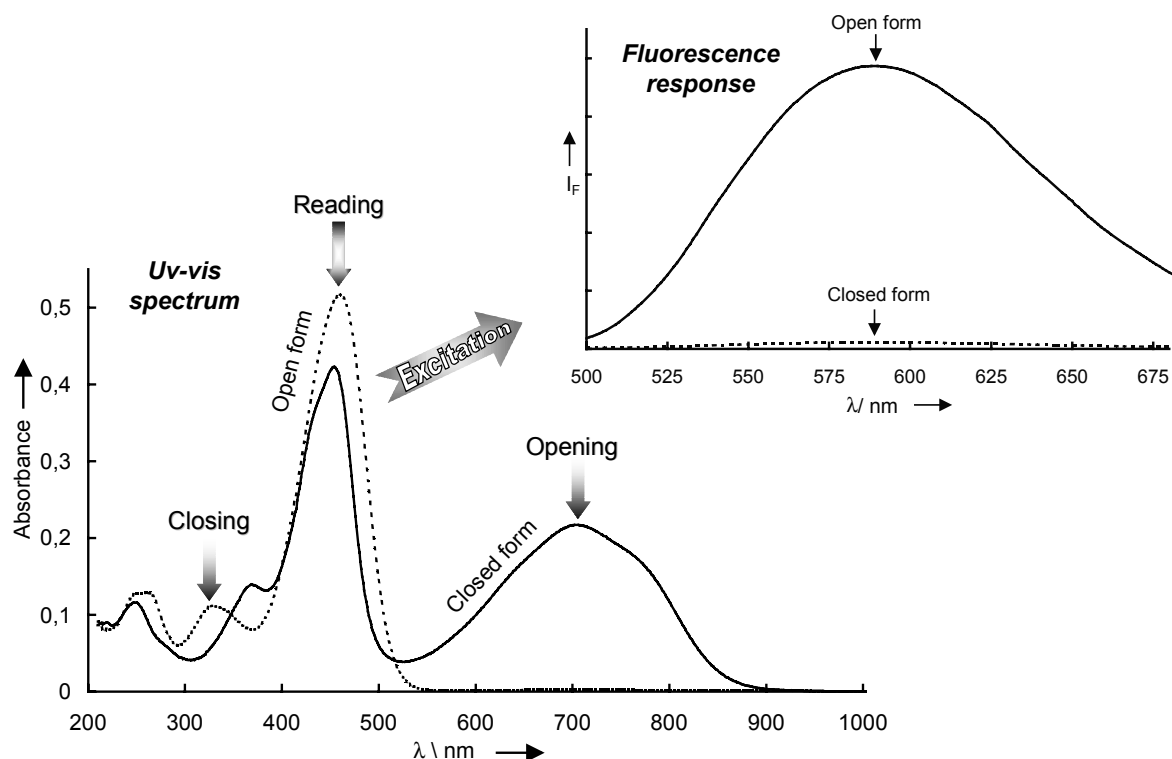


Figure 5: UV-vis absorption and fluorescence spectra (excitation at 455 nm) of the open and closed forms of compound **1b** in methanol solution.

Cyclic voltammetry experiments in DMSO were performed in order to study the electrochemical properties of these compounds. Both **1b** and **2b** gave similar voltammograms but different from those of the molecule **4b**. Whereas the open form of compound **4b** is reduced irreversibly at -1.01 V, those of **1b** and **2b** are reduced reversibly at -0.98 V and -1.01 V respectively, probably due to the stabilizing effect of the additional thiophene units on the radical formed (Table 4).

Table 4: Cyclic voltammetry data. Redox potentials (vs. SCE) for compounds **1b**, **2b**, **1a**, **4a** and **4b** in DMSO (0.1 M $n\text{-Bu}_4\text{N}^+\text{PPh}_6^-$).

Comp.	Form	$E_{\text{oxidation}}$	$E_{\text{reduction}}$
4a ^[20]	open	--	-1.78 ^[21]
	closed	1.13 ^[21]	-0.90 ^[21]
4b	open	--	-1.01 ^[21]
	closed	--	-0.27
1b	open	--	-0.98
	closed	0.79 ^[22]	-0.68 ^[21]
2b	open	--	-1.01
	closed	1.03 ^[22]	-0.68 ^[21]
1a ^[20]	closed	0.78	-0.99 ^[21]

For the closed form of **4b** a reversible reduction wave at -0.27 V was observed, whereas compounds **1b** and **2b** (closed forms) display a non-reversible reduction at a

potential around -0.68 V. The more negative value can be attributed to the donor properties of the additional thiophene groups. Replacement of the condensed thiophene rings in the closed form of compound **1b** by linear connected ones in compound **2b** does not change the electrochemical behaviour.

Surprisingly, the non-methylated compound **1a** showed an electrochemical behavior towards a switchable molecular wire since the fully conjugated closed form can be oxidized reversibly at 0.78V (Figure 6).

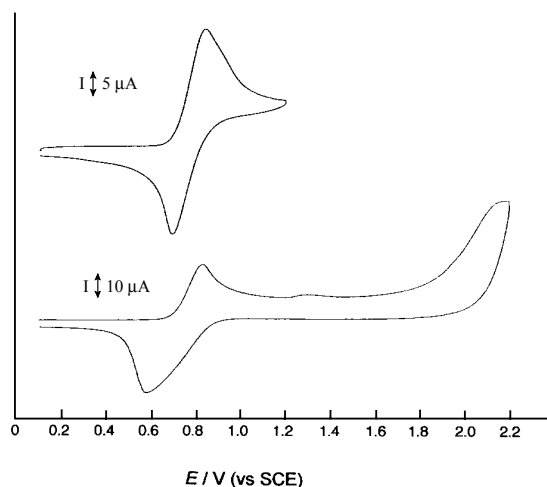


Figure 6: Cyclic voltammogram for the oxidation of the closed form of compound **1a**; scanning rate = 100mVs⁻¹.

5 CONCLUSION

Compounds **1b** and **2b** represent interesting examples for optical memory systems since they propose a new solution to the destructive read out problem. Particularly, they display absorption bands around 400-500 nm of very little activity relating to the switching action while at the same time excitation of them results in a very large difference on the fluorescence response between the two forms.

The voltammograms of the open and closed forms show large differences that represent the different level of conjugation. Such changes represent a photocontrol of electrochemical properties in a photoswitched molecular wire fashion. They are of special significance in the case of the elongated compounds **2** and **3**, whose closed forms correspond respectively to about six and eight conjugated thiophene units, in view of the interest of oligothiophenes as materials for molecular electronic devices.

6 ACKNOWLEDGMENTS

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- [17] As photostationary state for a particular wavelength of irradiation is described as the equilibrium ratio between the two forms.
- [18] At t = 35 min, conversion = 92-93 %.
- [19] At t = 40 min, conversion > 98%.
- [20] In CH₂Cl₂ (0.1 M n-Bu₄N⁺ClO₄⁻).
- [21] Irreversible.
- [22] Quasi-reversible.