

Understanding Electrochromic Processes Initiated by Dithienylcyclopentene Cation-Radicals

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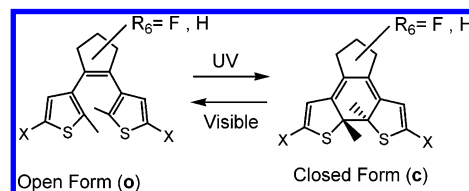
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Simple photochromic dithienylethylenes with either a perfluoro or a perhydro cyclopentene ring, and a variety of substituents (chlorine, iodine, trimethylsilyl, phenylthio, aldehyde, carboxylic acid, and ethynylanisyl), have been prepared and their electrochemical behavior was explored by cyclic voltammetry. All dithienylethylenes present two-electron irreversible oxidation waves in their open form, but the cation-radical of the open isomers can follow two different reaction pathways: dimerization or ring closure, whereas the halogen derivatives follow a dimerization mechanism, the presence of donor groups, such as the phenylthio-substituted compound, promote an efficient oxidative ring closure following an ECE/DISP mechanism. Electrochromic properties are also found in the corresponding ring-closed isomers. Depending on the substituents on the thiophene ring, and the perfluoro or perhydro cyclopentene ring, open isomers can be obtained from oxidation (chemical or electrochemical) of the corresponding ring-closed isomers via an EC mechanism. This reaction pathway is favored by the presence of electron-withdrawing groups in the molecule. For all these compounds, closed or open, the oxidation lies between 0.8 and 1.5 V vs SCE, and provokes a permanent modification of the color, even after an oxidation–reduction cycle. This could be qualified as “electrochromism with memory”. On the other hand, the ring-closed electron-rich isomers ($E^\circ < 0.8$ V), which show reversible waves at the cation-radical or even dication level, give rise to “true electrochromism”, for which no structural changes are observed. The experimental study was completed by theoretical calculations at the DFT level, using B3LYP density functional, which gave information on the total energy, the geometry, and the electronic structures of several representative compounds, either in the neutral form or in the cation-radical state. These results are important for the potential design of photochromic systems, such as three-state conjugated systems and photoelectrical molecular switching devices.

Introduction

The development of photochromic compounds is a steadily growing field due to new possible applications of this class of dyes.¹ Indeed, the reversible photochemical isomerization of the dye molecules can lead to global changes in the bulk material properties (UV–vis–IR absorption spectrum,² but also refractive index,² and liquid crystal properties^{2,3}), or trigger a mechanical deformation, from reorientation to a matter transfer that could be used for various purposes from computing technology (data storage)^{2,4} to astronomy (active filters).⁵ More intriguing is the possible use of these compounds as molecular switches for data processing at the nanometric scale.⁶ Recently, examples have been published of a controlled fluorescence of a single lumiphore grafted to a photochromic unit,⁷ and a disruption of a magnetic interaction between two radical centers.⁸ Our research has shown the possibility of switching “on” or “off” of an intramolecular electron transfer.⁹ It has also been envisioned to eventually control an electrical current with such compounds. In this latter perspective, the large gap change between the highest occupied molecular orbital and the lowest unoccupied molecular orbital (HOMO–LUMO) resulting from the isomerization is expected to deeply modify the global

SCHEME 1



conductance of the molecule. For such a purpose, the dithienylethylene structure is particularly attractive since it is highly symmetrical, can be highly fatigue-resistant, and presents a P-type photochromism.¹⁰ However, recent reports indicate that some members of this family of compounds present a redox behavior, which leads to the opening of a thermal route to their isomerization.¹¹ Thus, mastering such a feature is of prime importance in the field of molecular electronics.

The dithienylethylene chromophore can be seen as the association of two basic components: aromatic thienyl groups and a hexatriene subunit (Scheme 2). While the electrochemistry of the first component is well documented,¹² the redox properties of the photoactive core are rather unknown. A similar observation can be made about the ring-closed isomer. The electrochemical behavior of the isomer should be related to oligoenes since it can be understood as the fusion of a cyclohexadiene with a sulfur-stoppered octatetraene (Scheme 2).

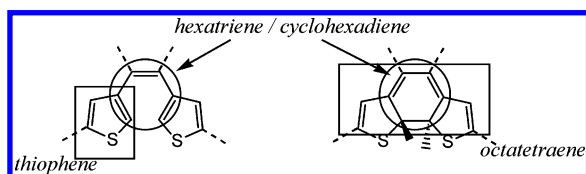
Pericyclic-like reactions using open-shell reactants were described several decades ago.¹³ Examples are the [2+2] and

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SCHEME 2



the [4+2] cyclizations; the cation-radical opening of cyclobutane ("cycloreversion") is a proposed mechanism for the DNA repairing enzyme (photolyase), and several examples show that some Diels–Alder reactions are accelerated when cation-radicals are involved as intermediates.¹⁴ Unfortunately, very little experimental data are available on the electrocyclic hexatriene/cyclohexadiene reaction, and only recently was a theoretical exploration of the possible reaction paths for the simplest hydrocarbon, namely hexatriene, published.¹⁵

These types of reactions immediately raise a simple question: does the oxidation to a cation-radical promote a reactivity of the photochemical type or of the thermal type? Several other points can also be considered: Is there a specific substituent pattern to promote an electrochemical ring-opening or closure? In the latter case, is this reaction a "thiophene-like" reaction, involving the dimerization of two radical species? Eventually, if such reactions are due to a transient cation-radical, is it this intermediate's equilibrium geometry that makes the bond-breaking or creation so efficient?

Since charged, open-shell species are invoked, it is natural to think of an electrochemical approach to study this problem. It is possible to generate the reactive species and study the transformation of these types of intermediates at the same time. One of the most convenient techniques for performing these studies is cyclic voltammetry. This technique allows access to the features of the *electrochemical* process; moreover, it can provide crucial kinetic data, such as the reaction order, for

establishing the nature of *chemical* processes linked to the electron transfer.¹⁶

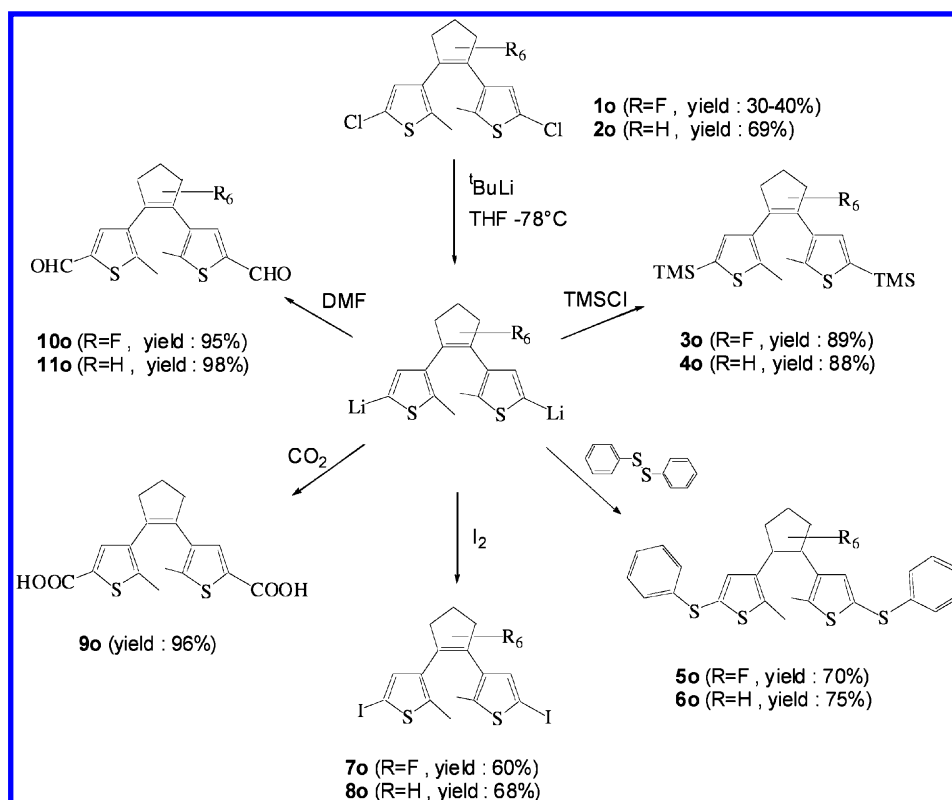
To get reaction trends, we have prepared a bank of compounds in which the substituent of the α position (C5) of the thiophene ring has been systematically varied. This was made possible by the extensive use of a "building block approach", recently described in the literature,¹⁷ which uses a dichloro-substituted intermediate as a starting point. The general behavior was found to be extremely rich and dependent on the electronic nature of the substituent. To understand the general trends, the experimental study was completed with theoretical calculations using the DFT method at the B3LYP level, which gave information on the total energy, the geometry, and the electronic structures of several representative compounds, either in the neutral form or in the cation-radical state.

Results and Discussion

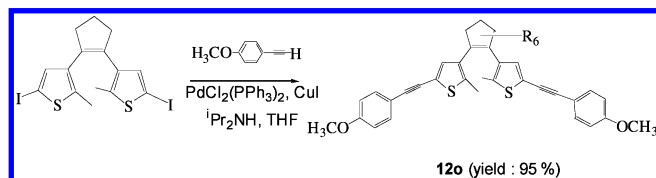
Syntheses of All Compounds. Syntheses of all compounds were based on the systematic use of dichloro starting materials, **1o**, carrying a perfluorinated side chain, or **2o**, with a hydrocarbon chain. Such precursors were shown in the past to be a convenient source of the photochromic unit, being prepared either by a conventional nucleophilic fluorine substitution of perfluorocyclopentene by 2-chloro-4-lithio-5-methylthiophene or, for its hydrocarbon counterpart, by an intramolecular McMurry reaction. For the latter, a moderate improvement was achieved by adding an excess (i.e. 3.5 equiv) of TMSCl to the reaction mixture.¹⁸ The efficient chlorine–lithium exchange^{17,19,20} produces variously substituted compounds in good to high yields, from electron-withdrawing substituents (i.e. aldehyde), to donating compounds, such as the previously unknown phenylthioethers, **5o** and **6o** (Scheme 3).

In the case of compound **9o**, by changing the addition order,^{20b} the yield was improved from 88% to 96% (inverse

SCHEME 3



SCHEME 4



addition of the photochromic dilithium to a CO₂ saturated THF solution results in a quantitative formation of the diacid) (Scheme 3).

Other interesting intermediates are the diiodo compounds **7o** and **8o** that could be used in palladium-catalyzed ethynylation reaction.^{9,21} Compound **7o** reacted with anisylacetylene, and thus, it was converted into a longer molecule, **12o**, in a mostly quantitative yield (Scheme 4).

The colored and closed isomers were obtained by photoisomerization irradiating with UV light.²² No attempts were made to determine the related quantum yields. All compounds were purified and characterized using standard organic chemistry techniques.

As expected, the colors of the closed isomers spanned a wide range of hues: the fluorinated series always ranged from blue to purple, while the hydrogen series mostly ranged from yellow to orange. A remarkable change, due to the extension of conjugation, was observed for the long, conjugated anisyl compound, **12o** closed (deep blue), while its closed precursor (diiodo) was yellow. In the last column of Table 1, the maximum absorption wavelengths as well as the extinction absorption coefficients for all the compounds studied in this paper are given.

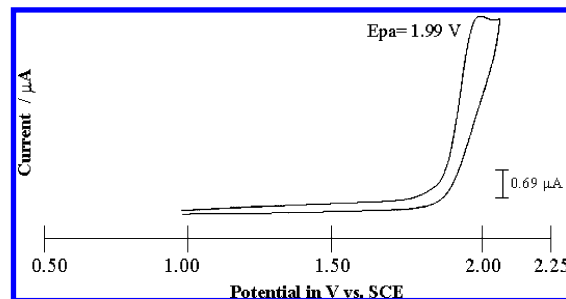


Figure 1. Cyclic voltammetry (CV) of **1o** (1.10 mM) in ACN + 0.1 M *n*-Bu₄NPF₆. Scan range: 1.00/2.10/1.00 V. Working electrode: glassy carbon electrode (0.5 mm diameter). Scan rate = 1 V·s⁻¹.

Daylight was found to be sufficient to promote the cycloreversion for most of the compounds.

Electrochemical Results

General Presentation of Electrochemical Behavior in Microelectrolysis (CV). Cyclic voltammograms were recorded for all compounds (**1–12**). As expected, all of the compounds underwent a redox oxidative processes. It is interesting to find the presence of at least one irreversible wave for the corresponding closed or open isomer. We have focused our efforts on disclosing the nature of the chemical reaction linked to the electron transfer.

A typical cyclic voltammogram is given in Figure 1. Oxidation standard potential values (*E*^o) for the compounds that show reversible waves are depicted in Table 1. Anodic peak potentials values are given for compounds that show irreversible

TABLE 1: Electrochemical and Optical Data of Dithienylcyclopentene Derivatives

compound ^a	epa (V vs. SCE) ^b (0.1 V·s ⁻¹)	Δ <i>E</i> _p (mV) ^b (0.1 V·s ⁻¹)	<i>N</i> (no. e ⁻) ^b	λ _{max} /nm (ε/10 ³ cm ⁻¹ M ⁻¹) ^c
Cyclopentene Ring				
2	2o 1.34	48	2	240(19.0) ^c
-Cl	2c <i>E</i> ^o = 0.67	48	1	444(1.2) ^c
8	8o 1.31	48	2	361(17.8)
-I	8c <i>E</i> ^o = 0.66		1	463(1.3)
4	4o 1.20	46	1.6	248(3.2)
-Si(CH ₃) ₃	4c <i>E</i> ^o = 0.44	59	1	468(0.3)
12	12o 1.18	44	2	337(25.7)
-CH≡CHPhOCH ₃	12c <i>E</i> ^o = 0.52 ^f	53	1	541(9.7)
6	6o 1.16	44	2	246(21.2)
-SPh	6c <i>E</i> ^o = 0.40 ^g	74	1	490(5.1)
11	11o 1.46	48	2	280(41.0) ^c
-CHO	11c 0.98 (rev at 2 V·s ⁻¹ <i>E</i> ^o = 0.93 V)	68	1	580(14.7) ^c
9^e	9o 1.42	46	2	252(29.7)
-COOH	9c 0.85 (rev at 5 V·s ⁻¹ <i>E</i> ^o = 0.80 V)	61	1	531(6.8)
Perfluorocyclopentene Ring				
1	1o 1.99	48	2	242(24.9)
-Cl	1c 1.21	65	1	501(3.9)
7	7o 1.78	68	2	242(14.7)
-I	7c 1.20	80	1	514(1.8)
3	3o 1.49	63	1.6	241(12.0)
-Si(CH ₃) ₃	3c 1.05	90	1	554(3.8)
5	5o 1.42	44	2	247(35.8)
-SPh	5c <i>E</i> ^o = 0.76 ^g	56	2	553(17.1)
10	10o 2.29	60	2	255(14.2)
-CHO	10c 1.42	75	1	606(3.2)

^a Open isomers are denoted using o after the compound number; while in closed isomers are denoted using c after the compound number.

^b Cyclic voltammetry data of **1–11** solutions ca. 1 × 10⁻³ M in ACN + 0.1 M *n*-Bu₄NPF₆ at room temperature using brown glassware. For irreversible waves, *E*_{pa} is given. For reversible waves, *E*^o is given. Δ*E*_p (mV) is the peak width value *E*_p - *E*_{p/2} at 0.1 V·s⁻¹. ^c All the samples contain 0.1 M *n*-Bu₄NPF₆. ^d Previously reported in the literature with other solvents.¹⁷ ^e Under our experimental conditions, no protonation effects were observed during the course of the electrochemical experiments. ^f A second consecutive one-electron reversible oxidation wave at 0.674 V vs SCE was also found. ^g The *E*^o value corresponds to a two-electron reversible oxidation wave.

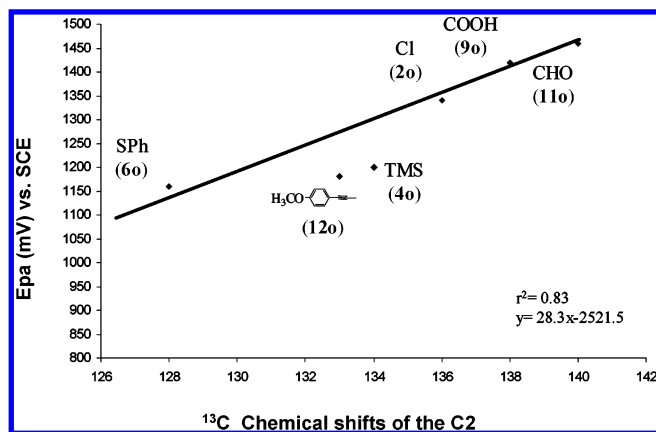


Figure 2. Correlation between the E_{pa} (anodic peak potential) value of several dithienylcyclopentene derivatives and their correspondent ^{13}C chemical shifts at the C-2 position of thiophene.

oxidation waves in the entire range of available scan rates (from 0.1 to 50 $\text{V}\cdot\text{s}^{-1}$). The number of electrons involved in the oxidation process was determined by a comparison with the very well known one-electron oxidation of ferrocene and tris-(4-bromophenyl)amine, in the same medium, using cyclic voltammetry. The number of electrons involved was also confirmed by controlled-potential electrolysis.

It is noteworthy that for the complete set of substituents, closed isomers oxidize at lower potentials than their open counterparts. This is in agreement with the fact that the highest occupied molecular orbital (HOMO) increases in energy from open to closed; thus, the ionization potential of the closed compounds is expected to be smaller than the open compounds (see the DFT calculations below). It is also important to point out the following:

(A) The strong acceptor effect of the saturated tris(difluoromethylene) chain is evidenced by the 500 mV anodic shift from the hydrogen-substituted series to the fluorine series observed for all compounds.

(B) In the same photochromic family (perhydro or perfluoro), the first oxidation potential value was strongly substituent dependent, and as expected, the more electron-withdrawing, the more positive it became. The accumulation of electron-withdrawing substituents brought the oxidation potential of the open photochromes up to 2.2 V vs SCE. The easiest compound to oxidize was the phenylthioether closed isomer **6o** at ca. 0.40 V vs SCE.

(C) Three tendencies in the number of electrons were observed:

(1) For all the open compounds two-electron oxidation waves were observed.

(2) For the closed perhydrocyclopentene isomers family, reversible oxidation waves were obtained for most of the compounds at the first oxidation level.

(3) With regard to the closed form of perfluorocyclopentene series, a one-electron irreversible wave was observed in most of the compounds, except for **5o**.

The presence of a substituent on the α position affects not only the redox potential but also the local electronic density in the thiophenes rings, as it can be measured on the ^{13}C NMR spectra. The impact is very clear for the “inner” carbon (C2), involved in the pericyclic reactivity and roughly in the position para to the substituent. Indeed, a rather good correlation was found by plotting the anodic peak potential against the carbon chemical shift for the open isomer of the hydrogen family (Figure 2).

TABLE 2: Kinetic Behavior of Dithienylcyclopentene Derivatives under Pure Kinetic Conditions¹⁶

compound	E_{pa} vs. $\log \nu$ slope (mV. decade ⁻¹)	E_{pa} vs. $\log c$ slope (mV. decade ⁻¹)	n ($\text{F}\cdot\text{mol}^{-1}$)	predicted mechanism ^{16,b}
Open Isomer				
2o^a	20	18	2	EC2CnE or DISP2
5o	30		2	ECE/DISP1
6o	34		2	ECE/DISP1
8o	19	19	2	EC2CE or DISP2
12o	30		2	ECE/DISP1
Closed Isomer				
1c	30		1	EC
9c	30		1	EC
11c	31		1	EC

^a For a detailed analysis see the Supporting Information. ^b Although we cannot distinguish, at this point, the nature of the consecutive chemical reaction linked to the first electron transfer, it is possible to say that the second electron transfer will, at least, happen in a second chemical reaction.

Study of the Irreversibility. Cyclic voltammograms can be analyzed in terms of kinetics in order to get more insight on the chemical process of the decay of the cation-radical generated at the electrode. We first noticed that over the range of scan rates studied, the chemical process following the first heterogeneous electron transfer is rate limiting;¹⁶ in other words, all irreversible processes are in the “pure kinetic area” of the kinetic zone diagram for any of the possible proposed mechanisms. The anodic process remains irreversible for most of the studied compounds and the peak width value is always about 48 mV (Table 1, column 3). The second step in the study was to determine the partial order for the chemical process involving the generated cation-radical. This can be done by studying how E_{pa} depends upon the logarithm of the scan rate ν and the concentration (c) of the starting material. If linear dependences are obtained, one can label the main decay route according to the number of electrons previously determined.

When the chemical reaction linked to the electron transfer is first-order, it leads to an E_{pa} variation of 29 mV per decade of scan rate (EC or ECE or DISP1).¹⁶ Conversely, if it is second-order, a 19 mV per decade of scan rate variation is predicted. In this case, if the E_{pa} value is concentration dependent, then the global order is also the partial order for the electrogenerated species. Thus, an EC₂CE (where the subscript indicates the order of the first chemical reaction) or a DISP2 mechanism should take place.

This general procedure to determine the decay mechanism of the transient cation-radical from the kinetic analysis of an irreversible wave was applied to the family of compounds we prepared. The most representative compounds depicted in Table 1 were studied in detail in order to elucidate their electrochemical oxidation mechanism. Although it is possible to work up to 2.2 V vs SCE in dry acetonitrile, we selected compounds with an oxidation potential lower than about 1.50 V vs SCE in MeCN, since reliable data are easier to collect. The experimental results obtained for some of them are presented in Table 2.

When we performed this analysis, a very good fit between the theoretical prediction and the experimental data was observed. See the results for compound **6o** (Figure 3) as an example. The inset shows the linear dependence observed for the E_{pa} value with $\log \nu$. The experimental slope of 34 mV, very close to the theoretical value of 29 mV, suggests an ECE or DISP1 mechanism since it is a two-electron irreversible wave.

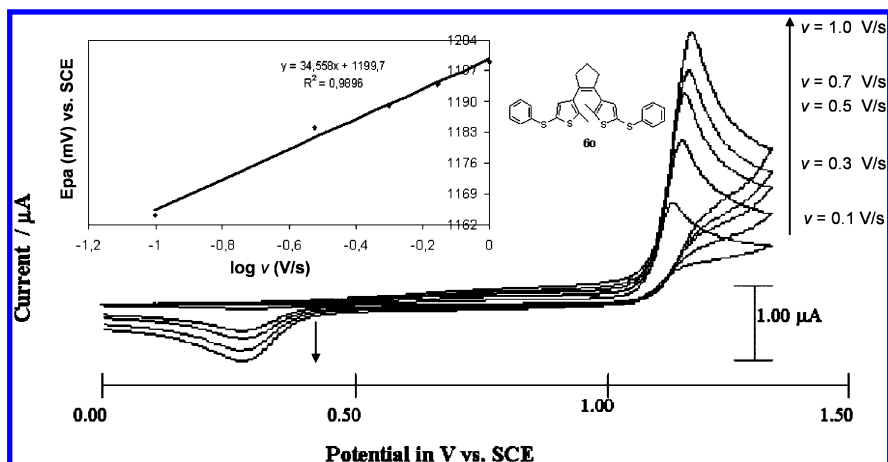


Figure 3. Cyclic voltammograms of **60** (1.35 mM) in ACN + 0.1 M *n*-Bu₄NPF₆ at different scan rates: 0.1, 0.3, 0.5, 0.7, and 1 V·s⁻¹. Working electrode: glassy carbon electrode (0.5 mm diameter).

As can be seen in Table 2, the experimental data obtained for the analysis of the mechanism fits very well with the prediction by the above electrochemical theory.

Thus, at this point, it is possible to distinguish at least three types of reactions linked to the electron transfer:

(1) A second-order reaction in the case of Cl and I open substituted photochromes, but it is not possible to distinguish between a EC₂CE or DISP2 mechanism.^{17,12,23}

(2) A first-order reaction involving the oxidized species of the ring-open isomers (the phenylthiofluorinated and non-fluorinated photochrome and for the anisylacetylene) that could be part of an ECE or DISP1 mechanism.

(3) A first-order reaction in an EC mechanism involving ring-closed compounds.

Taking in account the possibility of no chemical reaction linked to the electron transfer for some ring-closed compounds (i.e. a reversible wave), at least four possibilities of evolution have been identified for the photochrome's cation-radical. Note that no bimolecular processes involving ring-closed oxidized species have been found.

Identification of the Chemical Process. Taken together, cyclic voltammetry and controlled-potential electrolysis after the first oxidation wave allow us to determine the nature of the chemical reaction. This was performed for all compounds, but for this paper, we only describe the behavior of some representatives of the two kinetic classes previously determined: a second-order coupled reaction (**20**) and a first-order coupled reaction for ring-opened (**60**) or -closed compounds (**11c**).

The analysis of the resulting mixture of compound **20** after the passage of 2F at 1.50 V (controlled-potential electrolysis) by thin-layer chromatography revealed the presence of several more polar photochromic compounds. The most abundant one could be isolated by preparative TLC. The only structure consistent with the analytical data (mass spectrometry, UV-vis, and ¹H NMR) corresponds to a dimer containing two photochromic units coupled by the β positions²⁴ but not dehydrogenated; thus, we calculated a yield of 30%.²⁵ The isolation of this compound allowed us to rule out the hypothesis of having a DISP2 mechanism because rarely, if ever, would it lead to such compounds. Moreover, the proposed mechanism, EC₂CE, is widely accepted to describe the early steps of the anodic polymerization of thiophenes. Analogously, upon the oxidation of **20**, the corresponding cation-radical dimerizes leading to a doubly charged dihydro dimer.²⁴ The latter either can be twice oxidized again at this potential or can eliminate the two protons forming the neutral dimer that will also be

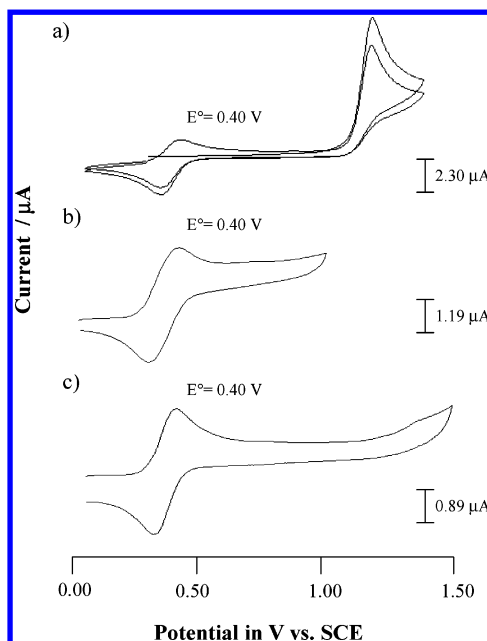


Figure 4. (a) Cyclic voltammogram (CV) of **60** (1.35 mM) in ACN + 0.1 M *n*-Bu₄NPF₆. Scan range: 1.00/1.50/0.00 V (two cycles). (b) CV of **5c** (0.45 mM) (c) CV of a solution of **60** (1.35 mM) in ACN + 0.1 M *n*-Bu₄NPF₆ electrolyzed at 1.20 V (2F), and ensuing electrolyzed at 0.00 V (2F). Scan range: 0.10/1.50/0.10 V. Working electrode: glassy carbon electrode (0.5 mm diameter). Scan rate $\nu = 1 \text{ V} \cdot \text{s}^{-1}$.

oxidized at this potential.^{12,23} This type of mechanism is operating in the case of thiophene cation-radical derivatives, where the dimerization takes place preferentially in the α-position.^{12,23} In some cases when the α-position is blocked, the electro-oxidative dimerization can occur in the β position.²⁴ A similar mechanism should apply for the other photochromic compounds that contain a halogen as a substituted group (**1**, **2**, **7**, and **8**).

Belonging to the “first-order coupled reaction” class, compound **60** was expected to show an entirely different behavior. Its voltammogram, recorded at 1.00 V·s⁻¹ in ACN, is shown in Figure 4a. The irreversible two-electron oxidation wave (ca. 1.20 V vs SCE) on the first anodic scan is followed by a reduction wave on the cathodic scan. The expected anodic counterpart was obtained on the second cycle, giving a reversible wave centered on a redox potential value of 0.40 V vs SCE. This E° value corresponds to the standard oxidation potential of **6c**²⁶ (Table 1).

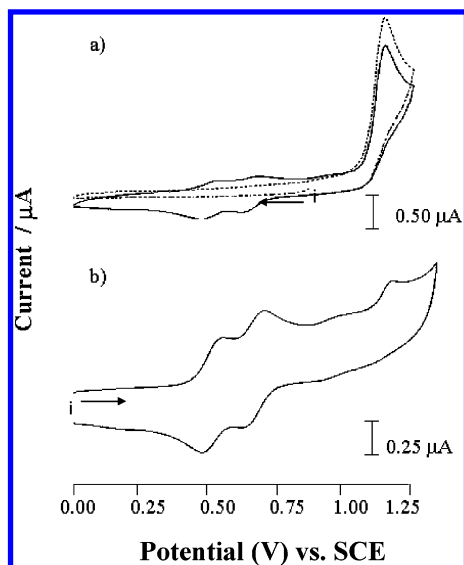
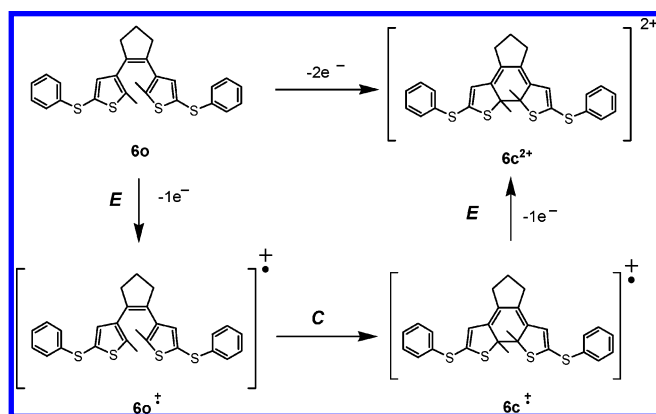


Figure 5. (a) Cyclic voltammogram of **12o** (1.53 mM) in ACN + 0.1 M *n*-Bu₄NPF₆ at 1.00 V·s⁻¹ (two cycles). (b) Cyclic voltammogram of **12c** obtained by irradiation of the **12o** sample (0.76 mM) at 1.00 V·s⁻¹.

SCHEME 5



The nature of the chemical reaction linked to the electron transfer is thus the ring closure, a first-order reaction. Once cyclized, the **6c**^{•+} cation-radical is oxidized again at this potential, yielding the final stable dication **6c**²⁺ (Scheme 5). Thus, two electron transfers separated by a chemical reaction are taking place, leading to the aforementioned global ECE or DISP1 mechanistic scheme for the entire process^{16,27} (Table 2).

A similar behavior is obtained for the fluorinated analogue **5o**. Interestingly, since such structures are often used as molecular wires, the long **12o** follows the same mechanistic path (Figure 5). Indeed, the voltammogram of the ring-opened compound shows, on the second scan, the corresponding ring-closed isomer. However, the latter presents two successive oxidation waves ($E_1^\circ = 0.520$ V, $E_2^\circ = 0.674$ V).

The last category of compounds belonging to the “first-order coupled reaction class” is the ring-closed compound that undergoes an irreversible oxidation, the prototype of which is **11c**. Controlled potential electrolysis at 1.2 V resulted in the bleaching of the original characteristic blue-purple color. Under these conditions, the ring-open compound **11o** is the only one obtained, as shown by the analysis of the mixture by TLC, cyclic voltammetry, and UV-vis absorption spectroscopy. The one-electron, irreversible wave at ca. 0.98 V obtained at the low scan rates (0.1–0.4 V·s⁻¹) typical of an EC mechanism tends to become quasi-reversible at a higher scan rate. A fully

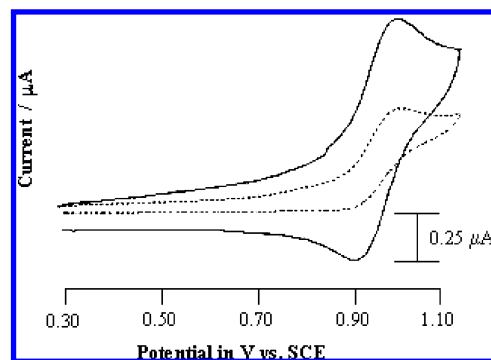
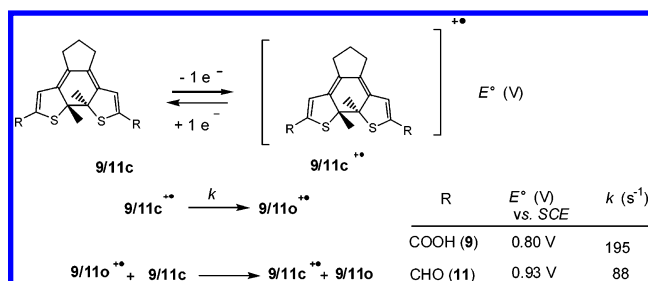


Figure 6. Cyclic voltammograms of **11c** 0.50 mM in ACN + 0.1 M *n*-Bu₄NPF₆. Dotted line, 0.4 V·s⁻¹; solid line, 2 V·s⁻¹.

SCHEME 6



reversible wave was obtained at 2 V·s⁻¹, enabling us to determine both the redox potential of the closed compound (0.93 V vs SCE) (Figure 6, Scheme 6) and the rate constant of the ring-opening reaction (88 s⁻¹).^{16,28}

Since the ring-open cation-radical **11c**^{•+} is more oxidizing than the reactant **11c**, the process was expected to be catalytic in electrons. To test this hypothesis, a chemical oxidation was performed using tris(4-bromophenyl)aminium hexachloroantimonate as a chemical oxidant ($E^\circ = 1.10$ V vs SCE in ACN). In this test, 0.4 equiv of chemical oxidant was required to fully convert the sample and no satisfactory explanation has been found to date.

In the family of ring-closed compounds belonging to the same kinetic class, only two were found to present this quasi-reversibility in the range of the explored scan rate, the other one being the diacid, **9c**. Thermodynamic and kinetic results are gathered in Scheme 6.^{16,28}

More commonly, the wave remains irreversible for all scan rates. A question that arises for these cases is whether or not the electron transfer and the C–C bond breaking are concerted or stepwise, as has been reported²⁹ for the reductive cleavage of some σ bonds. This problem is usually addressed by determining of the value of the apparent coefficient transfer α_{app} , deriving directly from the peak width value (eq 1), when the electron transfer is kinetically determinant.

$$\alpha_{app} = 47.5/(E_p - E_{p/2}) \quad (1)$$

It is well-known that if the apparent transfer coefficient is greater than 0.5, then the two reactions are stepwise. In the case of compound **1c**, its cyclic voltammogram presents an irreversible wave up to a scan rate of 50 V·s⁻¹. However, in the case of compound **1c**, it is clear that the kinetic control is a mixture between the electron transfer and the chemical reaction (peak width ($E_p - E_{p/2}$) = 65 mV). Thus, a stepwise mechanism is the only possibility.²⁹ At this point it is possible to conclude that **1c**, like **9c** and **11c**, follows an EC overall process. The ring-opening is confirmed by controlled potential electrolysis at 1.4 V (Figure 7) (the original red-pink color is discharged

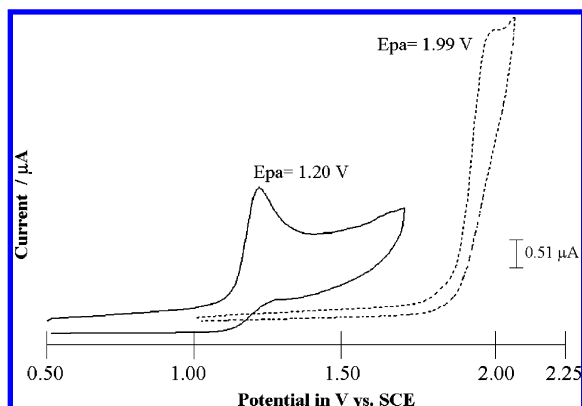


Figure 7. Cyclic voltammograms of **1c** 1.10 mM in ACN + 0.1 M *n*-Bu₄NPF₆ at 1 V·s⁻¹. Solid line, before electrolysis; dashed line, after controlled potential electrolysis at 1.40 V, 1F.

within a few minutes) or by chemical oxidation (similar bleaching is observed upon addition of 1 equiv of tris(4-bromophenyl)amininium hexachloroantimonate). The same result was obtained for compound **10c**.³⁰

To summarize, in the case of open isomers, the initial cation-radical can evolve following either an *intermolecular* or *intramolecular* reaction pathway. While the former one, rather rare since it is limited to halogen-substituted compounds, is strongly reminiscent of what is typically found in the mechanistic studies of thiophene cation-radical chemistry, the intramolecular reaction seems to involve mainly the hexatriene system. Note that at the high-potential value where the oxidative cyclization takes place, the corresponding closed-isomer cation-radical will be quickly oxidized at least to the dication level. In the cases studied, these dications were stable enough in the cyclic voltammetry time scale to give rise to their characteristic reduction waves. Where the ring-closed isomers are concerned, two cases can also be distinguished. First, the corresponding cation-radical of the closed form (even the dication in some cases) is stable enough for the compound to present reversible oxidation wave(s). The high stability of this species can be explained by the delocalization of the positive charge(s) along the octatetraene system. The long lifetime of the charged species will be favored by electron-donor substituents. In the second case, an intramolecular reaction can take place in the ring-opening that could be interpreted as the thermal cycloreversion of the oxidized photochrome's cyclohexadiene core. The presence of electron-withdrawing substituents as well as the replacement of the hydrogen for fluorine in the cyclopentene ring will favor this second case. When the ring-closed cation-radical follows the ring-opening reaction, a highly oxidizing species is generated in solution, so it will quickly react and lead to the neutral ring-opened isomer.

From these electrochemical considerations, it can be envisioned to develop combined electrochromic/photochromic systems with three states of different colors. Classically, electrochromic dyes present, once oxidized (or reduced), a color different from the neutral form. This reversible color change is due to the new electronic configuration and involves very weak structural changes. From our electrochemical data, only ring-closed compounds with an oxidation potential below 0.8 V belong to this category. However, the dication/monocation redox couple is usually very close; thus, overoxidation to a dicationic species is unavoidable at the potential required for the ring closure of their open isomer. Eventually, to observe the *dication's* color, a photochromic compound with an ECE oxidation mechanism, in which the last electrochemical reaction

(*E*) is reversible must be used. According to the results presented above, the best candidate to achieve such a three-state system is the bis(phenylthioether), **6**. Indeed, due to its great stability, solutions of the dication **6c**²⁺ are readily prepared by an exhaustive, oxidative, controlled-potential electrolysis of a solution of **6o** at +1.25 V (2F). The two closed compounds, **6c** (bright orange) and **6c**²⁺ (dark orange), have very similar absorption spectra; both present an intense absorption band centered around 480 nm. However, the closed compound **6c**²⁺ shows an intense band around 385 nm and a less intense band around 710 nm which is not present in the compound **6c** (Figure 8).

Thus, a possible way to use this three-state system is to perform an exhaustive, oxidative, controlled-potential electrolysis of a solution of **6o** at +1.30 V (2F) to generate, quantitatively, **6c**²⁺. Ring-closed compound **6c** can then be obtained by simply switching the potential down to 0.00 V for an exhaustive reduction to proceed. Eventually, the photochemical cycloreversion is used to revert back **6c** to the colorless open isomer **6o** by simply exposing the electrochemical cell's content to dimmed daylight (Figure 9).

Ring-opening can also be used in the design of electrophotochromic dyes. Since the ring-open cation-radical is a highly oxidizing species, it will quickly be reduced back to a, usually, colorless ring-opened compound. Hence, the electrochemical reaction will then be used to discharge the color of the closed compound while the photochemistry is required to restore it. This alternative "bleaching reaction" could be particularly useful for compounds having a particularly low cycloreversion quantum yield. Following our data, it is then necessary to raise the ring-closed isomers' redox potential above 0.8 V; thus, electron-withdrawing substituents are required. Combination of electro- and photochromic properties in a single molecular unit may lead to electrical—optical switching applications; thus, such a system may be recognized as a dual-mode chemical signal transducer with distinctive color changes.³¹ In this sense, we would like to design as well as explore related systems presenting a more dramatic change of color between redox states. For such a purpose, electrochemistry proved to be an efficient tool to screen potential candidates.

As the final rationalization of electrochemical results, the structures of compounds **2**, **6**, and **11** in the neutral forms and cation-radical forms for open and closed isomers were computed using the DFT/B3LYP method, which is particularly suitable to cation-radicals when introducing spin-polarization effects.³²

DFT Calculations on Neutral and Cation-Radical Forms. Compounds **11**, **2**, and **6** represent typical cases of compounds substituted respectively by an acceptor (aldehyde), a "neutral" substituent (Cl, for which the σ acceptor character is compensated by a π donor character), and a strong donor (phenylthio). Results of the DFT calculations are summarized in Figure 10 and Table 3 (also see Supporting Information).

For the neutral open forms, the most important internal degree of freedom is the rotation around the thiophene—cyclopentene single CC bond. In a first calculation using the dichloro **2** compound, the methyl groups were disposed either syn or anti before allowing the geometries to relax (Figure 11). The very small energy difference between the two conformers (0.7 kcal/mol) seems to indicate that both should be present in solution, the equilibrium being slightly shifted, favoring the anti group (Table 3). The ring closure induced an important change (11.7 kcal/mol) since a similar calculation performed on the ring-closed **2c** showed that the trans diastereoisomer is much more stable than the cis one. According to the stability order observed

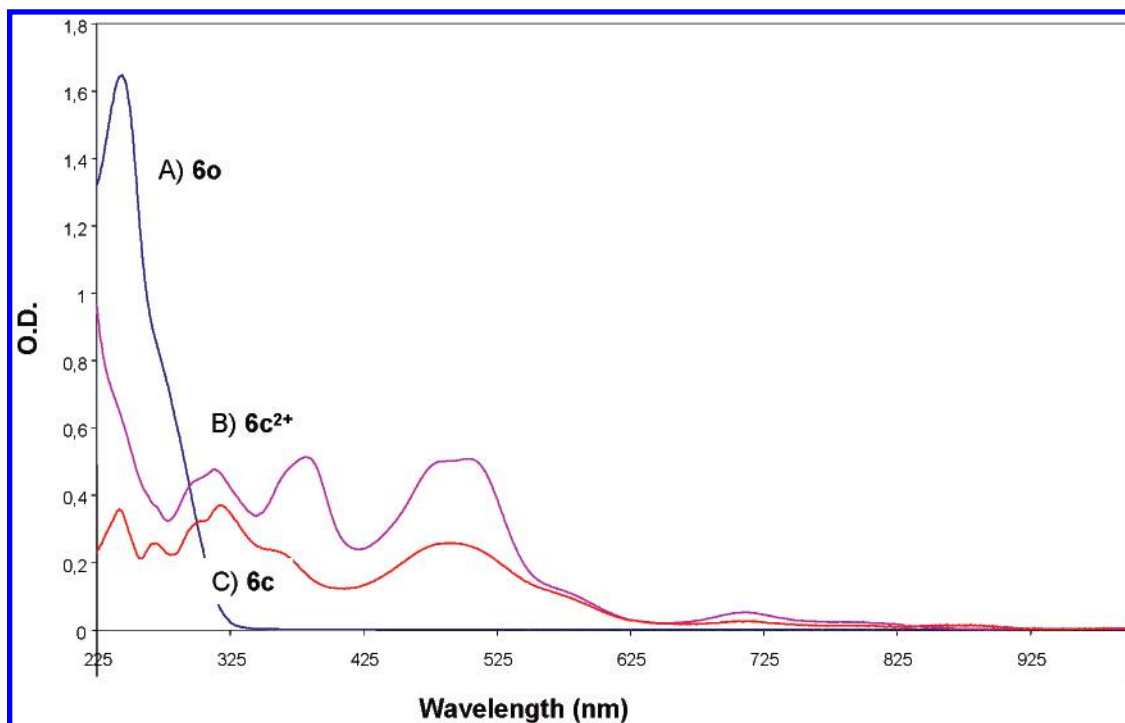


Figure 8. In situ UV/vis spectra in ACN + 0.1 M *n*-Bu₄NPF₆ of **6o**: (a) before electrolysis (b) after electrolysis at 1.25 V vs SCE (1.8F) (compound **6c**²⁺), and (c) ensuing electrolysis at 0.00 V vs SCE (2F) (compound **6c**).

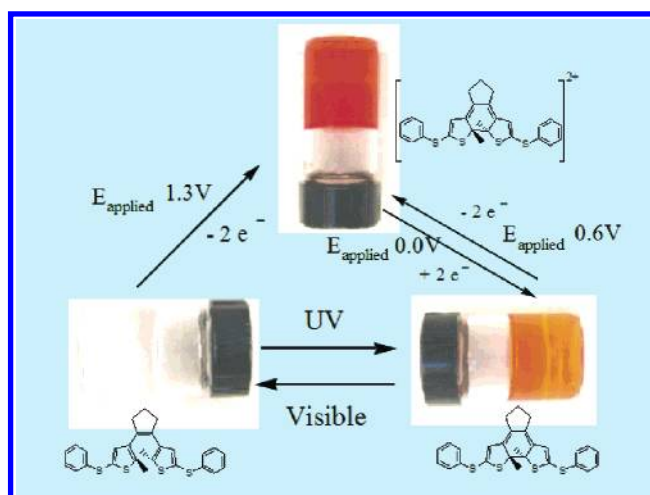


Figure 9. Scheme for photoelectrochemical operation.

for the possible **2** geometries and since only trans ring-closed compounds were detected during the electrolysis experiments, the chromophore's geometries were chosen as anti for ring-open and trans for the ring-closed isomers for the further calculations. Moreover, this reduces the computational cost since in the case of **11** and **6**, additional degrees of freedom corresponding to the possible rotations of the terminal groups must be considered.

A preliminary study on **11** showed that the most stable conformation was the one in which the aldehyde groups were in the thiophene plane, with the oxygen atom on the same side as sulfur for both the ring-closed (**11c-form 1**, 1.4 kcal/mol) and ring-opened isomers (**11o-form 1**, 1.2 kcal/mol) (Table 3, Figure 10). This was chosen as the initial geometry for all optimizations, and this disposition was kept in the final structures. In the case of compound **6o**, the situation is more complex since there are two possible torsions around the essentially single bonds of each phenylthio unit. Several conformations were tested and the situations with a planar

TABLE 3: Calculated Absolute Equilibrium Energies in Arbitrary Units and the Relative Energies in kcal/mol (in Parentheses) for the Ground States of Derivatives **2**, **6**, and **11**

compound	neutral	cation-radical
2o-anti	−142.606 603 (0.00)	−142.346 137 (163.0)
2o-syn	−142.605 536 (0.7)	−142.349 574 (160.7)
2c-trans	−142.604 786 (1.2)	−142.369 783 (148.1)
2c-cis	−142.586 149 (12.9)	−142.347 852 (161.9)
6o-form2	−206.454 363 (0.00)	−206.223 895 (144.2)
6c-form2	−206.466 322 (−7.5)	−206.250 295 (127.7)
6o-form1	−206.451 274 (1.9)	−206.213 591 (150.7)
6c-form1	−206.450 921 (2.1)	−206.226 731 (142.6)
11o-form1	−157.141 606 (0.00)	−156.867 032 (171.8)
11c-form1	−157.131 713 (6.2)	−156.881 620 (162.6)
11o-form2	−157.139 746 (1.2)	−156.864 940 (173.2)
11c-form2	−157.129 406	−156.881 405

thiophene–sulfur–phenyl moiety in the disposition (Figure 10) (**6o-form 1** or **form 2**) were found to be the most stable and were chosen as initial geometries for optimizations. **Form 2** was found to be slightly more stable than **form 1**.

This geometrical choice was further confirmed by the comparison between the experimental spectroscopic data and the calculated energies of the first $\pi \rightarrow \pi^*$ transitions since the DFT calculation at the B3LYP level provided good quality molecular orbitals obtained by a SCF procedure (although this is not the purpose of the standard DFT method). Thus the highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO–LUMO) gap can give a reasonable estimation of the

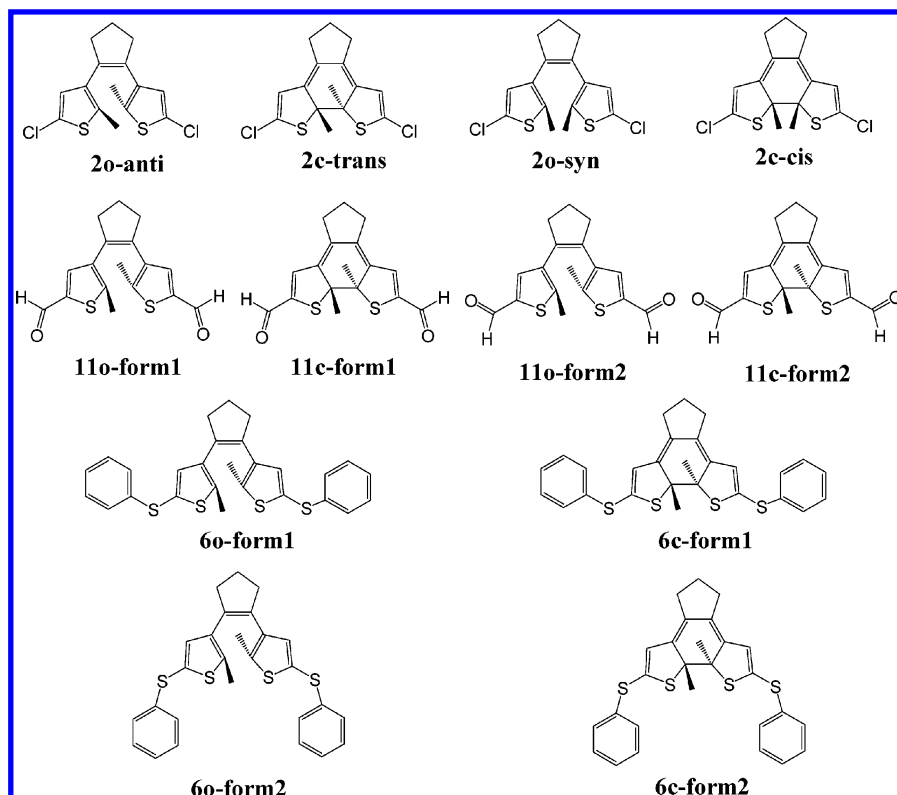


Figure 10. Designation and conformational orientation for **2**, **6**, and **11** studied by the DFT/B3LYP method.

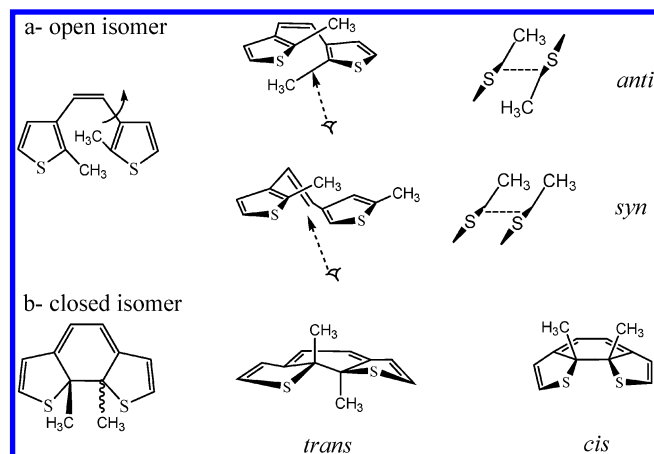


Figure 11. (a) Schematic view of the two possible syn and anti conformations resulting from a 180° rotation around the CC single bond for the "open" photochromic core; (b) the cis–trans nomenclature for the ring-closed pair of diastereoisomers.

first transition energy.³³ This is probably due to a similarity of correlation effects in the ground and the excited states.

Table 4 shows, in comparison to the observed values, the calculated wavelengths $\lambda_{\pi \rightarrow \pi^*}$ associated with the first $\pi \rightarrow \pi^*$ transition for the neutral forms of dithienylcyclopentene derivatives **2**, **6**, and **11**. For the **2o** and **2c** compounds, the calculated $\lambda_{\pi \rightarrow \pi^*}$ values corresponding to the conformers with the methyl groups in the antiparallel orientation are in good agreement with the experimental data. Thus, this confirms our initial choice of the anti conformation as the only relevant one. For the **6** and **11** compounds, the experimental λ_{\max} values are closer to the calculated $\lambda_{\pi \rightarrow \pi^*}$ values of the isomers in their most stable conformation (**form 2** for **6**, and **form 1** for **11**). The two frontier molecular orbitals (FMOs) are usually used to explain the chemical reactivity. For instance, the HOMO gives some information on the behavior upon oxidation (ease of oxidation

TABLE 4: Calculated $\lambda_{\pi \rightarrow \pi^*}$ Wavelengths (nm) Associated with the $\pi \rightarrow \pi^*$ Transition for the Neutral **2**, **6**, and **11**, in Comparison with the UV–Vis Experimental λ_{\max} ^a

compound	anti/trans ^b	syn/cis ^b	experimental
2o	256	263	240
2c	423	379	444
	form1 ^b	form2 ^b	experimental
6o	292	282	246
6c	437	454	490
11o	314	423	280
11c	588	614	580

^a The theoretical values giving the best match with experiment are in *italics*. ^b anti and syn correspond to compound **2o**, trans and cis to **6**, and **form 1** and **form 2** are associated to compounds **6** and **11**.

and expected geometrical changes). Thus, an analysis that takes the influence of the substituent into account was carried out.

Starting from the chlorinated derivative **2** (in which the chlorine p-type valence orbitals are too low in energy to interact with the dithienylcyclopentene fragment), the replacement of the two Cl atoms by electron-withdrawing CHO groups has affected the LUMO stabilization by 1.27 eV for the open form and by 1.19 eV for the closed form. This stabilization is due to a bonding overlap between the thienyl carbon at the α position of the sulfur (C_α) atom and the carbon of the aldehyde group (see Supporting Information). The HOMO is also stabilized, but only by 0.38 eV; this is due to the disappearance of the C_α –Cl antibonding overlap which is present in the chlorinated compound **2**. However, in the case of electron-donor substituents (here the phenylthio group on the derivative **6**), both HOMO and LUMO are destabilized, but in contrast with the electron acceptor case (derivative **11**), the change bears mainly on the HOMO rather than on the LUMO (see energies in the Supporting Information and Figure 12). To summarize, for an acceptor it is mainly the LUMO which is stabilized and for a donor it is mainly the HOMO which is destabilized. As a result, the

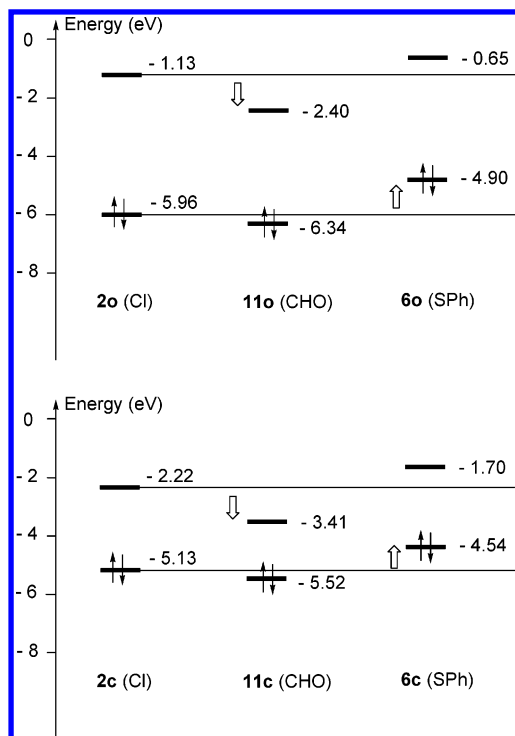


Figure 12. Energy variation representation for the ground states (open and closed neutral forms). The tendency is indicated by the direction of the white arrows.

HOMO–LUMO gap decreases in both cases with respect to **2**, in agreement with the optical UV–vis results reported in Table 4. Finally, the HOMO-relative positions are in qualitative agreement with the relative oxidation potentials in the sequence **11** > **2** > **6**.

Another trend resulting from the molecular orbital analysis is that going from compound **2** to compound **11**, the FMOs mainly keep their electronic structure and describe the same electron cloud distribution around the dithienylcyclopentene molecular fragment, while for the derivative **6**, the HOMO has the same structure as the HOMO-2 of the chlorinated compound, which is destabilized by a repulsive interaction with a p-type valence orbital of the sulfur of the phenylthio group (Supporting Information). The electron-donor phenylthio group seems to induce an electron cloud reorganization around the dithienylcyclopentene so that the LUMO of **11** has no equivalent in the energy range of the valence molecular orbitals of the **2** and **6** compounds.

Once the neutral forms' geometries were optimized, calculation of the energies corresponding to each cation-radical was performed with reoptimization of the geometry. This resulted, for each compound and each conformation, in four minima corresponding to (i) the open neutral form, (ii) the closed neutral form, (iii) the open cation-radical form, and (iv) the closed cation-radical form. From this optimization, only the most stable conformers, i.e., **form 1** for **11** and **form 2** for **6** (see Figure 10), will be considered in the following discussion. Starting from **11** and going to **2** and then to **6**, i.e., following the sequence acceptor group, neutral group, and donor group, we found the following trends:

(i) The adiabatic ionization energy (i.e. the difference between relaxed neutral and cation-radical forms) decreases as a consequence of better stabilization of the cation-radical forms by donor groups. This is in agreement with the experimental results that show easier oxidation of the compounds in the series.

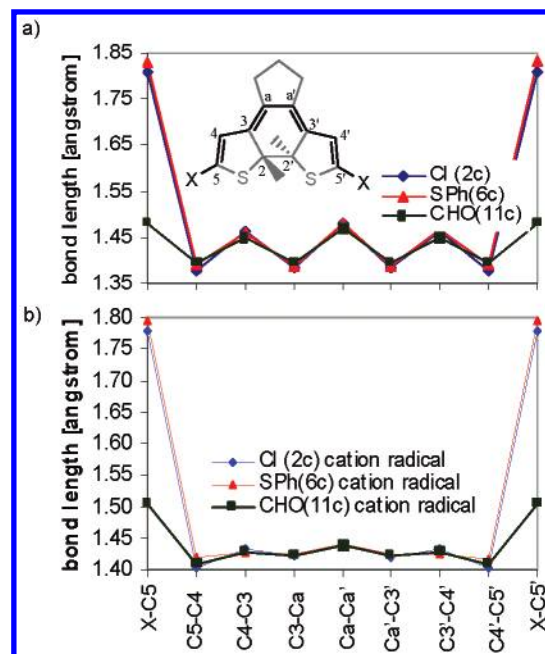


Figure 13. (a) Bond lengths of neutral closed-isomers. (b) Bond lengths of closed-isomer cation-radicals.

(ii) The relative stability of the closed form with respect to the open one increases in the series, for the neutral as well as the cation-radical form. In the case of **6**, the closed form is predicted to be the stable isomer. Thus, donor groups stabilize the closed form with respect to the open form, while the converse is true with acceptors. This effect is in agreement with the general observation made on the series of compounds described in this paper, and also with observations reported in the literature.¹¹ Note that our earlier experiment with ruthenium groups grafted on the photochromic core is in line with this general behavior since we observed that when ruthenium(II) is oxidized to ruthenium(III), hence becoming an acceptor, a reopening occurred.⁹

(iii) For each compound the stability of the closed form vs the open form was greater in the cation-radical state than in the neutral state.

A tool widely used to analyze the extension of conjugation is the bond length alternation (BLA) parameter. In our case this is easily applied to ring-closed compounds, resulting in the octatetraene unit. Figure 13a presents the results obtained for neutral and for cation-radical species. One can define a BLA parameter by computing the difference between the average length of the single and double bonds (see Supporting Information). As expected, a marked alternation is found for all neutral compounds. Heteroatom-substituted compounds **2c** and **6c** have almost the same BLA value (0.087 and 0.079 Å, respectively) while the bis-aldehyde **11c** has a lower value of 0.064 Å, in agreement with the “push–pull” effect of the two carbonyl groups.

The electron removal induces a dramatic geometric change since the bond length alternation is strongly diminished for all compounds. The most spectacular variation is observed for the bis-thioether **6c**⁺ since the calculated BLA value is closed to 0 (0.009 Å), indicating a full delocalization of the charge. This may explain the high stability of oxidized forms of **6c**. For the other two compounds (**2c**⁺ and **11c**⁺) an “edge effect” is found by a local analysis (Figure 13b) since the alternation persists toward the ends of the π system, as previously noticed for the carotenoids' cation-radicals.³⁴ Thus, one can conclude that the effect of the charge is concentrated at the center of the molecule.

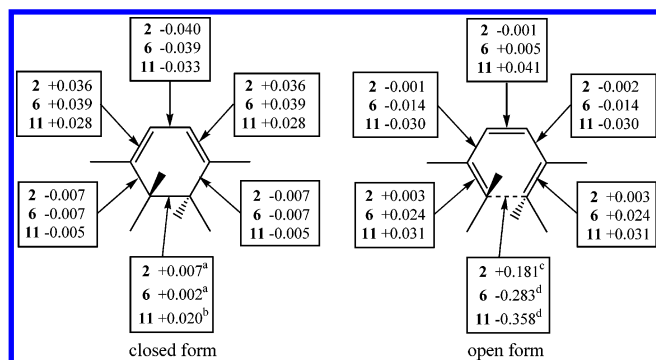


Figure 14. Variation of the calculated R_{CC} distances (Å) between the carbon atoms of the hexatriene/cyclohexadiene system implied in the closure/opening process for the derivatives **2**, **6**, and **11**, upon oxidation to the corresponding cation-radical (for more details, see Supporting Information). For closed isomers: ^aNo significant variation upon oxidation (generation of stable charged species). ^bVariation toward ring-opening. For open isomers: ^cNo tendency to ring closure (experimentally: dimerization). ^dMarked variation toward ring closure.

TABLE 5: Calculated R_{cc} Distances (Å) between the Two Carbon Atoms Implied in the Closure/Opening Process for the Dithienylcyclopentene Derivatives, Compounds **2, **6**, and **11****

compound	neutral	cation-radical
2o-syn	4.19	4.22
2c-cis	1.58	1.56
2o-anti	3.61	3.79
2c-trans	1.56	1.56
6o-form1	3.62	3.33
6c-form1	1.56	1.55
6o-form2	3.56	3.34
6c-form2	1.58	1.58
11o-form1	3.67	3.31
11c-form1	1.56	1.56
11c-form2	3.69	3.56
11o-form2	1.56	1.58

Bond-length variation during oxidation also concerns the entire “cyclohexadiene” core of ring-closed compounds. The most spectacular effect is observed for the central CC σ bond of closed compounds. Indeed, with the notable exception of **6c**⁺, the CC bond of the closed compounds is stretched from the neutral to the cation-radical forms and the maximum value is for the bis aldehyde **11c**⁺.

Geometrical variations are also noticed for ring-opened compounds, especially for their “reactive center”, namely the

hexatriene moiety. Except for the dichloro compound **2o**, variation of the bond lengths upon oxidation follows the same trend as for the polyenic part (see Table 5 and Figure 14). During the cyclization, a bond between the C2 and C2' of the thiophene groups is created; hence, the distance between these two carbons is also of crucial importance. For compounds **6o**⁺ and **11o**⁺ it gets shorter, while **2o**⁺ behaves in the reverse way.

Inspection of Figure 14 reveals that the bond lengths in the open cation-radical have evolved toward the value corresponding to a closed form and vice versa. Thus, there is a “geometrical convergence” in the cation-radical state for the **11** and **6** compounds (Figures 14 and 15) that tends to explain their reactivity, particularly ring-opening and ring-closure. This can be easily explained at a qualitative level by just looking at the shape of the HOMO (see Supporting Information). The depopulation of the HOMO by oxidation leads to bond length changes in agreement with the bonding/antibonding character for a given atom pair. The anomalous geometrical behavior of **2o**⁺ may explain its tendency to undergo oxidation following a bimolecular reaction. Indeed, oxidation of **2o** neither brings the two thiophene moieties closer nor prepares the necessary bond alternation accompanying the cyclization.

Figure 15 represents a summary of the energetic and geometric features: the energy difference between open and closed isomers and between relaxed neutral and cation-radical forms (note that this is not vertical ionization energy). This latter difference is the adiabatic ionization energy (or “well-to-well” ionization energy) and determines, in part, the electrochemical oxidation potential of the neutral species. The abscissa in Figure 15 corresponds to a reaction coordinate, and the relative horizontal positions of the different minima were qualitatively adjusted from the computed equilibrium geometries. We have not calculated the saddle points connecting the minima, since such calculations would involve too many uncertainties, but the results on stable species already carry a lot of useful information.

First of all, results are consistent with the experimental observations: the tendency of **11** to re-open upon oxidation, of **6** to cyclize, and **2** to do something else. Furthermore, similar geometries between isomeric cation-radicals should have an impact on the kinetics of the interconversion reaction. One can assume that the activation energy has been lowered upon oxidation. This is in agreement with the fast (thermal) isomerizations we observed.

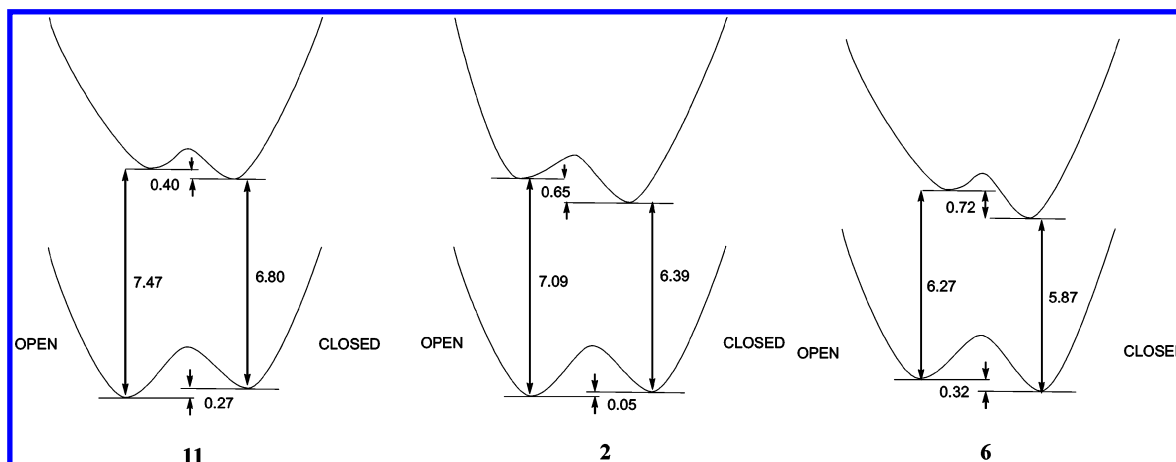


Figure 15. Representation of the energy differences (eV) for the most stable conformers, the energy difference between open and closed isomers, and the energy difference between the equilibrium geometries of neutral and cation-radical forms for compounds **11**, **2**, and **6** after geometry optimization using B3LYP/DZVP approximation. The abscissa and the shape of the curves are only qualitative (see text).

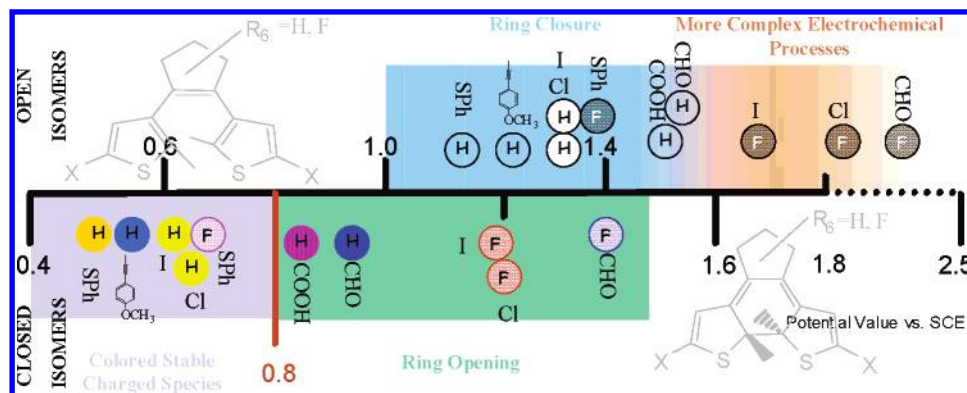


Figure 16. Graphical representation of the electrochemical and optical data given in Table 1.

Conclusion

We have unveiled the very rich electrochemical behavior of the dithienylethene photochromic unit by using classic kinetic analyses of electrochemical data.

While some open compounds present a thiophene-like behavior, undergoing intermolecular reactions, and some closed compounds undergo reversible successive oxidations typical of a polyene, the oxidation triggers, for some of the studied compounds, an isomerization mimicking the photochemical reactivity of the hexatriene/cyclohexadiene core. Since this phenomenon occurs on very simple molecules, it can be considered an intrinsic property of the chromophore, thus, generalizing the previously published data. Strikingly, a variety of electrochemical reaction paths were encountered, despite the fact that all compounds presented a similar σ bond environment with no heavy geometric constraints. Thus, only electronic factors seem to lead to either a ring-closure or a ring-opening reaction.

The possibility of having a low activation barrier for the cyclization via cation-radical intermediate can be grasped by considering that depleting the HOMO of its electrons reduces the secondary antibonding interactions between the reactive carbons. This is, in fact, analogous to the photochemical path. On the other hand, electron removal from the closed isomers should destabilize the carbon-carbon σ bond. This hypothesis was partly verified by DFT calculations showing the tendencies between the equilibrium geometries of the intermediate cation-radicals to converge. Still, this approach lacks a more “qualitative” explanation to decipher the subtle balance between all the electronics influences and the role of each, rather remote, substituent.

At the very least, we can say that the course of the reaction is driven by the relative energies of the intermediates and also by the energy differences between neutral and cationic species. Since the latter parameter is included in the redox potential, this justifies a possible classification of the possible behavior according to the compound’s electrochemical data (see Figure 16). For instance, ring-closed compounds fall into two electrochemical domains. Below 0.8 V, oxidations are electrochemically reversible and the generated charged species is usually stable. This necessitates the presence of electron-donating groups such as a hydrogenated side chain and, for instance, thioether substituents. Above 0.8 V, the oxidation is quasi-reversible to irreversible and leads to the ring-opening via a stepwise mechanism. The resulting “open” cation-radical is a better oxidizer than the starting material and it is quickly reduced to the neutral ring-open compound. This, thus, requires electron-withdrawing substituents such as a perfluorinated side chain.

On the other hand, with the notable exception of the halogenated perhydro compounds, ring-closure is observed for all opened isomers that could be studied. Since this represents only the “easiest to oxidize”, compounds were characterized by at least two electron donor substituents.

According to our results, the basic parameters determining the fate of the generated cation-radical are, thus, the inductive effect of the saturated branch (cyclopentene vs perfluorocyclopentene) and the nature (donor or acceptor) of the substituent on the methyl-2-thiophene rings. Such a rule of thumb can help in the design of dyes for electrochromic purpose. While only ring-closed, electron-rich ($E^\circ < 0.8$ V) photoisomers give rise to “true electrochromism” for which no structural changes are observed, most of the other compounds, closed or opened and for which the oxidation lies between 0.8 and 1.5 V vs SCE, undergo a permanent modification of the color after an oxidation–reduction cycle. This could be qualified as “electrochromism with memory” since the system does not return to its initial state after the cycle. It is even possible to make a “three-state–two commands” system by carefully choosing the substituents in order to bring the ring-closed isomer’s redox couple below the 0.8 V limit, and using a well suited sequence of oxidation–reduction–photolysis. Beyond the simple design of multicolored systems is the possibility to replace low quantum yield photochemical transformation by its electrochemical twin. This is particularly true for the cycloreversion reaction since the oxidative conditions give the neutral, ring-open compound. Eventually it is of interest to look at antagonist substituent effect, having in mind the goal to parallel all photochemical reactions by an electrochemical one. Work in this direction is in progress.

Finally, let us note that the design of molecular switches aimed to control an electrical current will have to cope with the problem that an unwanted redox process on the switch itself might be able to change its state.

Experimental Section

All synthetic grade commercial reagents were used as received. Tetrahydrofuran (THF) was dried with Na/benzophenone ketyl. All reactions were carried out under argon using the Schlenk tube technique, and the handling of the compounds sensitive to UV light was carried out in the dark. Preparative TLC plates were purchased from Merck. ^1H and ^{13}C NMR spectra were recorded on a Bruker 250 MHz instrument. Chemical shifts are reported in parts per million (δ) downfield from TMS. Mass spectra were recorded by the “Service de Spectrométrie de Masse” of the University of Toulouse-Paul Sabatier. For electrochemistry, solvent (extra-dry acetonitrile (ACN), stored under argon on 4 Å molecular sieves, ACROS)

and supporting electrolyte (tetrabutylammonium hexafluorophosphate, TBAHP) were used as received (Fluka, purity > 98%).

1,2-Bis(5'-chloro-2'-methylthien-3'-yl)-perfluorocyclopentene 1o. Following ref 17, **1o** was obtained. ^1H NMR (250 MHz, CDCl_3) δ : 6.87 (s, 2H), 1.87 (s, 6H). MS (CI, NH_3): m/z (%) 436(100) [$\text{M}^+ - 1$], 437(23) [M^+].

1,2-Bis(5'-chloro-2'-methylthien-3'-yl)-cyclopentene 2o. Following ref 17, **2o** was obtained. ^1H NMR (250 MHz, CDCl_3) δ : 6.56 (s, 2H), 2.70 (t, $J = 7.50$ Hz, 4H), 2.02 (m, 2H), 1.87 (s, 6H). ^{13}C NMR (63 MHz, CDCl_3) δ : 14.2, 22.8, 38.3, 125.1, 126.7, 133.3, 134.4, 134.8. MS (CI, NH_3): m/z (%) 329(100) [M^+], 346(10) [$\text{M}^+ + \text{NH}_3$].

1,2-Bis(5'-iodo-2'-methylthien-3'-yl)-cyclopentene 8o. To a solution of 1,2-bis(5'-chloro-2'-methylthien-3'-yl)-cyclopentene (190 mg, 0.576 mmol) in THF (20 mL) cooled to -78°C was added *tert*-butyllithium (0.9 mL of a 1.5 M solution in pentane) slowly under argon, followed, after 85 min, by iodine (0.333 g, 1.316 mmol). The reaction mixture was stirred at -78°C for 60 min, warmed slowly to room temperature, and quenched with H_2O . The resulting mixture was extracted with diethyl ether (3×25 mL). Organic phases were combined and washed, first by aqueous ascorbic acid to destroy excess iodine, and then with water, before being dried (MgSO_4) and filtered. The solvent was evaporated under reduced pressure and the resulting crude product was purified using column chromatography through silica (pentane) in the dark to afford 0.203 g (66%) of the pure product as white solid. ^1H NMR (250 MHz, CD_2Cl_2) δ : 6.91 (s, 2H), 2.73 (t, $J = 7.50$ Hz, 4H), 2.00 (m, 2H), 1.98 (s, 6H). ^{13}C NMR (63 MHz, CDCl_3) δ : 14.2, 22.8, 38.3, 125.1, 126.7, 133.3, 134.4, 134.8. MS (CI, NH_3): m/z (%) 386(100) [$\text{M}^+ - \text{I}$], 513(23) [MH^+], 530(46) [$\text{M} + \text{NH}_4^+$], 547(6) [$\text{M} + \text{N}_2\text{H}_7^+$].

1,2-Bis(5'-trimethylsilyl-2'-methylthien-3'-yl)-cyclopentene 4o. To a solution of 1,2-bis(5'-chloro-2'-methylthien-3'-yl)-cyclopentene (145 mg, 0.440 mmol) in THF (10 mL) cooled to -78°C was added *tert*-butyllithium (0.7 mL of a 1.5 M solution in pentane) slowly under argon, followed, after 85 min, by trimethylsilyl chloride (0.2 mL). The reaction was stirred at -78°C for 60 min, warmed slowly to room temperature, and quenched with H_2O . The resulting mixture was extracted with diethyl ether (3×25 mL). Organic phases were combined, washed with water, dried (MgSO_4), and filtered. The solvent was evaporated under reduced pressure and the resulting crude product was purified using column chromatography through silica (pentane) afford 0.157 g (88%) of the pure product as a colorless, viscous oil. ^1H NMR (250 MHz, CDCl_3) δ : 6.78 (s, 2H), 2.79 (t, $J = 7.25$ Hz, 4H), 2.03 (m, 2H), 1.94 (s, 6H), 0.20 (s, 18H). ^{13}C NMR (63 MHz, CDCl_3) δ : -0.19, 14.1, 23.2, 38.1, 134.5, 134.6, 135.5, 137.2, 134.0. MS (CI, NH_3): m/z (%) 405(100) [M^+], 422(10) [$\text{M}^+ + \text{NH}_3$].

1,2-Bis(5'-phenylsulfide-2'-methylthien-3'-yl)-cyclopentene 6o. To a solution of 1,2-bis(5'-chloro-2'-methylthien-3'-yl)-cyclopentene (190 mg, 0.576 mmol) in THF (20 mL) cooled to -78°C was added *tert*-butyllithium (0.9 mL of a 1.5 M solution in pentane) slowly under argon, followed, after 85 min, by diphenyl disulfide (Ph-S-S-Ph) (0.328 g, 1.5 mmol). The reaction was stirred at -78°C for 1 h, warmed slowly to room temperature, and quenched with H_2O . The resulting mixture was extracted with diethyl ether. Organic phases were combined, washed with water, dried (MgSO_4), and filtered. The solvent was evaporated under reduced pressure and the resulting crude product was purified using column chromatography through silica (pentane) in the dark to afford 0.200 g (73%) of the pure product as a pale yellow waxy solid. ^1H NMR (250 MHz,

CD_2Cl_2) δ : 7.15 (m, 10H), 6.91 (s, 2H), 2.79 (t, $J = 7.50$ Hz, 4H), 2.05 (m, 2H), 2.04 (s, 6H). ^{13}C NMR (63 MHz, CDCl_3) δ : 15.1, 23.7, 38.9, 126.6, 126.7, 127.4, 129.7, 135.6, 137.6, 138.7, 139.7, 141.9. MS (CI, NH_3): m/z (%) 477(100) [M^+], 494(62) [$\text{M}^+ + \text{NH}_3$], 369(10) [$\text{MH}^+ - \text{PhS}$].

1,2-Bis(5'-carboxy-2'-methylthien-3'-yl)-cyclopentene 9o. To a solution of 1,2-bis(5'-chloro-2'-methylthien-3'-yl)-cyclopentene (200 mg, 0.607 mmol) in THF (10 mL) cooled to -78°C was added *tert*-butyllithium (1 mL of a 1.5 M solution in pentane) slowly under argon. After 85 min the reaction mixture was transferred under argon using a cannula to 100 mL of a CO_2 -THF saturated solution. The reaction was allowed to warm to room temperature and stirred for a further 30 min. The THF was removed under vacuum, and the residue was partitioned in 100 mL of CH_2Cl_2 and washed twice with 125 mL of 5% NaOH solution. The combined aqueous layers were acidified by dropwise addition of concentrated HCl until $\text{pH} = 1$. The resulting white precipitate was collected by vacuum filtration, triturated with cold CH_2Cl_2 (3×5 mL) to remove the monoacid, then dried in vacuo affording the pure di-acid as a white solid, 0.204 g (96%). ^1H NMR (250 MHz, CD_3OD) δ : 7.57 (s, 2H), 2.92 (t, $J = 7.50$ Hz, 4H), 2.19 (m, 2H), 2.05 (s, 6H). MS (CI, NH_3): m/z (%) 477(100) [M^+], 494(62) [$\text{M}^+ + \text{NH}_3$], 369(10).

1,2-Bis(5'-formyl-2'-methylthien-3'-yl)-cyclopentene 11o. Following ref 17, we performed this operation. To a solution of 1,2-bis(5'-chloro-2'-methylthien-3'-yl)-cyclopentene (197 mg, 0.598 mmol) in THF (10 mL) cooled to -78°C was added *tert*-butyllithium (1 mL of a 1.5 M solution in pentane) slowly under argon. After 85 min, the reaction mixture was quenched with anhydrous dimethylformamide (0.3 mL). The mixture was stirred at -78°C for 60 min, warmed slowly to room temperature, and poured into 50 mL of 2 M HCl. The resulting mixture was extracted with diethyl ether (3×25 mL). Organic phases were combined, washed with a saturated NaHCO_3 solution (2×25 mL) and water (1×25 mL), dried (MgSO_4), and filtered. The solvent was evaporated under reduced pressure, affording the pure product as a white solid, 0.182 g (98%). ^1H NMR (250 MHz, CDCl_3) δ : 9.73 (s, 2H), 7.42 (s, 2H), 2.85 (t, $J = 7.50$ Hz, 4H), 2.11 (m, 2H), 2.04 (s, 6H). MS (CI, NH_3): m/z (%) 344(46) [$\text{M} + \text{NH}_4^+$].

1,2-Bis(5'-(*p*-anisylethynyl)-2'-methylthien-3'-yl)-cyclopentene 12o. 1-Ethynyl-4-methoxybenzene (0.253 g, 1.92 mmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (7 mg, 0.0078 mmol), CuI (10.5 mg, 0.05 mmol), and finally 3.5 mL of diisopropylethylamine were added to 3 mL of a THF solution containing 0.209 g of 1,2-bis(5'-iodo-2'-methylthien-3'-yl)-cyclopentene (0.407 mmol). The reaction was stirred at room temperature under argon for 36 h. The solvent was evaporated under reduced pressure and the resulting crude product was triturated with diethyl ether. The solvent was removed and the crude product redissolved in pentane and directly applied on top on a silica-packed chromatography column for purification (pentane/ CH_2Cl_2 (increasing the percentage of CH_2Cl_2 until 50%)) in the dark. Pure product was isolated as a pale yellow solid, 0.204 g (93%). ^1H NMR (250 MHz, CD_2Cl_2) δ : 7.41 (d, $J = 8.75$ Hz, 4H), 6.95 (s, 2H), 6.86 (d, $J = 8.75$ Hz, 4H), 3.81 (s, 6H), 2.79 (t, $J = 7.50$ Hz, 4H), 2.04 (m, 2H), 2.16 (s, 6H). ^{13}C NMR (63 MHz, CDCl_3) δ : 14.3, 38.6, 55.3, 81.2, 92.4, 114.1, 115.1, 119.1, 132.5, 132.8, 134.0, 134.7, 135.7, 159.6, 160.2. MS (CI, NH_3): m/z (%) 521(63) [M^+], 538(20) [$\text{M} + \text{NH}_4^+$].

General Procedure for the Preparation of 4o, 6o, 8o, and 11o. To a solution of **1o** (100 mg, 0.23 mmol) in THF (20 mL) cooled to -78°C was added *tert*-butyllithium (0.4 mL of a 1.5 M solution in pentane, 0.6 mmol) slowly under argon, followed,

after 85 min, by 2.2 equiv of the desired electrophile in each case. The compounds were purified, characterized by standard organic chemistry techniques, and compared with the reported data in the literature.^{9,17–19}

1,2-Bis(5'-phenylsulfide-2'-methylthien-3'-yl)-perfluorocyclopentene 6o. ¹H NMR (250 MHz, CD₂Cl₂) δ : 7.14 (m, 10H), 6.96 (s, 2H), 2.09 (s, 6H). ¹³C NMR (63 MHz, CDCl₃) δ : 16.5, 127.3, 128.6, 129.5, 131.0, 132.4, 137.4, 139.4, 149.6; for perfluorocyclopentene (multiplets): 112.9, 117.9, 121.9. MS (CI, NH₃): *m/z* (%) 585(100) [M⁺], 602(62) [M⁺ + NH₃].

Photochemical Isomerizations. Photochromic open compounds (ca. 3 mg) were dissolved in dichloromethane (3 mL) or 5 mL of acetonitrile (or dichloromethane) containing 0.1 M supporting electrolyte. Irradiations, were performed in 1 cm quartz cells or in large vials placed in front of a standard TLC-visualization UV-lamp. The solutions were irradiated at 254 nm until no starting material was detected or photostationary states were achieved. Cyclic voltammetry was used as analytical technique to monitor the isomerization process.

Cyclic Voltammetry. Electrochemical techniques were performed with an AUTOLAB PC-controlled potentiostat. Cyclic voltammetry experiments were carried out using a glassy carbon 0.5 mm diameter disk as working electrode, a platinum wire as counter electrode, a saturated calomel electrode (SCE), separated from the solution by a double frit system, and tetrabutylammonium hexafluorophosphate (0.1 M) as a supporting electrolyte. A 5 mL electrochemical cell made of brown glassware was used to protect the solutions from ambient light throughout all experiments.

Controlled potential electrolysis experiments were performed using a platinum grid as a working electrode. The applied potential was ca. 100 mV more positive than the anodic peak potential value. The oxidation process was monitored by UV–vis absorption spectroscopy.

For analytical investigations, photochemical irradiations were performed in 1 cm quartz cells placed in front of a standard TLC-visualization UV-lamp. They were used to carry out the ring-closing reactions. The compositions of all photostationary states were measured using cyclic voltammetry.

Computational Details. DFT calculations were performed with the GAMESS (General Atomic and Molecular Electronic Structure System) software³⁵ using the conventional Becke-3–Lee–Yang–Parr (B3LYP) exchange–correlation functional,³⁶ the Stevens–Basch–Krauss–Jasien–Cundari effective core potential (SBKJEC-PCP), and the corresponding double- ζ valence + polarization basis set (DZVP).³⁷ After some preliminary calculations, this level of approximation was found to be an accurate and computationally affordable combination on platform within four Intel-Xeon processors at 2.8 GHz with 2MB-iL3 cache. Initial geometries of the molecules were prepared by a molecular mechanics calculation using the universal force field 1.02 of Goddard and Rappe,³⁸ in a Cerius² environment.³⁹ A full geometry optimization was performed starting from planar molecules (without any symmetry constraint) to get the C₂-symmetry equilibrium geometries corresponding to either the neutral or the cation-radical forms. The electron open-shell cation-radicals were computed at the spin-unrestricted-B3LYP level.

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Supporting Information Available: Detailed mechanistic electrochemical studies carried out for compounds **2o** and **11o**, bond length alternation (BLA) determination, and HOMO (π) and LUMO (π^*) FMOs plots for the neutral ground state of dithienylcyclopentene derivatives **2**, **6**, and **11**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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