Photochromism

Reductive Electrochemical Cyclization of a Photochromic 1,2-Dithienylcyclopentene Dication[**]

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The construction of functional molecular devices requires access to molecular components with physical properties that can be reversibly modified by applying one or more external stimuli. Molecular isomerization reactions triggered by a physical stimulus such as heat, light, electricity, or through the

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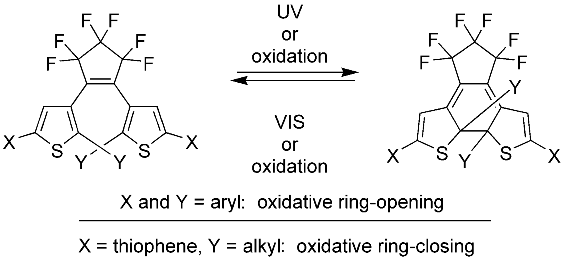
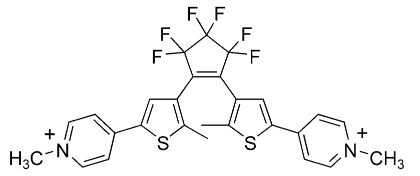
remote complexation of ions or molecules have all been instrumental in the development of molecular systems that display active switching functions.[1] Photochromic[2] compounds containing the dithienylethene (DTE) backbone[3] undergo thermally irreversible cyclization reactions between colorless and colored forms when stimulated with UV and visible light (Scheme 1). Because of the notable differences in the nature of π conjugation between the two DTE isomers, these photoresponsive systems offer several choices of changes in properties such as absorbance, luminescence, refractive index, and redox potential, all of which are useful in photo-optical and photoelectronic device applications.



Scheme 1. The photo- and electrochemical (oxidation) ring-closing and ring-opening reactions of 1,2-dithienylethenes.

Developing examples of more sophisticated switching components that take advantage of more than one stimulus is an important goal. We have recently demonstrated that when several DTE derivatives are chemically or electrochemically oxidized, they undergo the same ring-closing and ring-opening reactions that are induced by light.[4] Although the precise structural requirements and mechanism of these important electrochromic reactions are still to be fully defined, the tendency for ring closure or ring opening to dominate appears to be dictated by where aryl groups are located on the photochromic skeleton: the presence of aryl rings on the two carbon atoms involved in forming the new C–C single bond induces oxidative ring opening while their absence results in electrochemical cyclization of easily oxidized bis(dithiophene) derivatives (Scheme 1). This exciting new discovery prompted us to examine the electrochemical properties of other photochromic dithienylethene derivatives.

One such example is dicationic bispyridinium **1**, a versatile compound designed by Lehn and co-workers[5] to demonstrate how the redox properties of DTE derivatives can be optically modulated due to the enhanced electronic communication between the two easily reduced pyridinium groups through the linearly π-conjugated DTE backbone in the ring-closed form. More recently, the groups of Irie[6], Tian,[7] and our group[8] have used the unalkylated neutral dipyridine precursor of **1** as a binary Lewis base to construct supramolecular coordination complexes. Herein we show that the electrochemical reduction of the ring-open isomer of dication **1** results in cyclization to generate the same ring-closed isomer as is produced photochemically as well as an additional ring-closed isomer that has never been observed.



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Cyclic voltammetry was used to study the reduction of the ring-open isomer of dication **1**.[9] Representative cyclic voltammograms (CVs) are shown in Figure 1. The CV exhibits an irreversible cathodic reduction at -0.95 V versus a standard calomel electrode (SCE) at $0.2\ \mathrm{V\,s^{-1}}$, and a smaller anodic peak on the return scan. This latter anodic peak is part of a reversible couple formed in the initial reduction and it has a standard potential of -0.18 V versus SCE. This redox couple is illustrated in Figure 1 a, which shows the result of repetitively cycling through the potential range. The standard potential of this couple is the same as that measured for the reduction of the ring-closed isomer of **1**. This is illustrated in

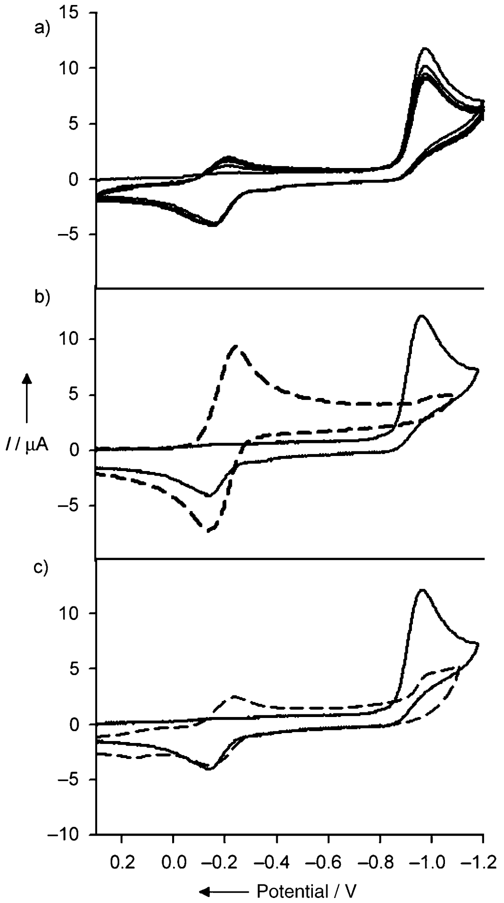


Figure 1. Cyclic voltammograms of DMF solutions (1.6×10^{-3} M) of ring-open isomer **1** containing tetrabutylammonium (0.1 M) perchlorate at $0.2\ \mathrm{V\,s^{-1}}$ a) showing repetitive cycling through the irreversible reduction, b) before (solid line) and after (dashed line) irradiation with 365 nm light, and c) before (solid line) and after (dashed line) electrolysis at -0.9 V vs SCE.

Figure 1 b, which shows CVs measured by using solutions of ring-open isomer of dication **1** before (solid line) and after irradiation with 365 nm light (dashed line). The photochemical ring closure of ring-open **1** is essentially quantitative and yields an equivalent of the ring-closed dication **1** (see Figures 2 a and d), thus the CVs before and after photolysis are indicative of equimolar solutions of the ring-open and ring-closed isomers of **1**, respectively.

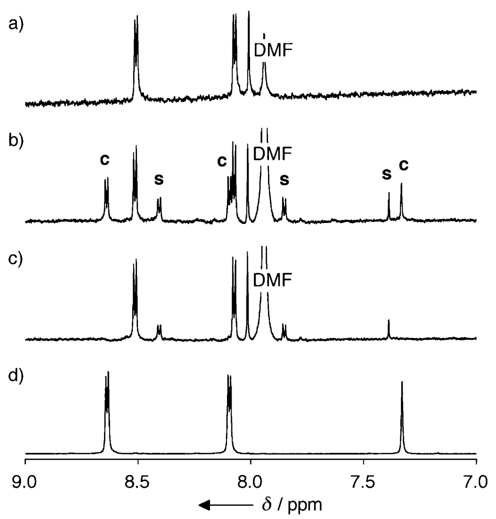
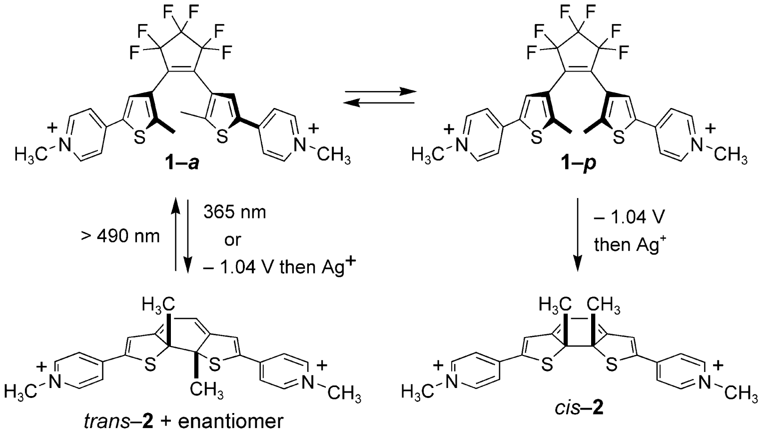


Figure 2. Partial ^{1}H NMR spectra of CD_3CN solutions of the ring-open isomer **1**, a) before electrolysis, b) after 10 min of electrolysis (−1.2 V) followed by quenching with $AgPF_6$, c) after the electrolysis experiment followed by 10 min of irradiation (> 490 nm) and d) the PSS of **1** obtained by irradiating a solution of **1** with 365 nm light until no spectral changes were observed. Signals corresponding to the ring-closed isomer ('c') and the side product ('s') are highlighted in plot (b).

Electrolysis of the solution of ring-open **1** at the position of the irreversible reduction wave (ca. −0.9 V) consumes 1 F mol^{-1}, or one electron equivalent. Cyclic voltammograms recorded before and after 95 % electrolysis are shown in Figure 1 c and illustrate the formation of the ring-closed isomer of **1** as the main electroactive (and soluble) product. This result was confirmed by a ^{1}H NMR spectroscopy study of the electrolysis mixture (discussed below). By comparing the relative peak currents of the ring-closed isomer of **1** formed after electrolysis (Figure 1 c) with that formed photochemically (Figure 1 b), the yield of electrochemically induced ring-closure can be estimated to be about 22 %. These electrolysis experiments suggest that the ring-open isomer of dication **1** undergoes an electrochemically induced cyclization to its ring-closed counterpart via its radical cation. Although this process has never been reported in DTE systems, a reductive ring-closing reaction was reported for a fulgide derivative as early as 1984.[11]



Scheme 2. Photoexcitation ring closure of conformers **1-*a*** and **1-*p*** only produces the *trans*-stereoismer, while electrochemical ring-closure can produce both *cis* and *trans* products.

A UV/Vis absorption spectrum measured after electrolysis of **1** exhibits intense absorptions with maxima at 766 and 689 nm. These absorptions, presumably due to the radical cation of the ring-closed form of **1**, disappear on addition of silver ions and generate a deep-blue solution and a UV/Vis spectrum characteristic of the ring-closed form of the dication of **1**. The electrochemically induced cyclization is not quantitative and the majority (75 %) of the radical cation of the ring-open form of **1** must be consumed in other reactions, such as radical cation dimerization or coupling reactions with the dication. During the electrolysis, there is a significant amount of a dark precipitate that forms and settles out of the solution, and this precipitate is likely to be made up of products formed by the reaction of the radical cation of the ring-open form of **1**.

The progress of the electrochemical ring closure can also be monitored by using ^{1}H NMR spectroscopy by treating the electrolysis reaction with an excess (10 equiv) of $AgPF_6$ to oxidize the paramagnetic products back to their dications.[10] The results of these experiments are shown in Figure 2. After 10 minutes of electrolysis, signals arising from a substantial amount of the ring-closed isomer of **1** are observed in the ^{1}H NMR spectrum along with signals corresponding to an additional minor product that have similar chemical shifts (Figure 2 b). Irradiation of the postelectrolysis samples with light greater than 490 nm results in the regeneration of the ring-open form of **1** at the expense of its ring-closed counterpart, however, the side product is unaffected by this irradiation (Figure 2 c).

We are suggesting that this side product is the previously unobserved ring-closed compound *cis*-**2** (Scheme 2) although it has yet to be isolated. This ring-closed diastereomer has its two methyl groups in the *cis*-orientation and is not formed under photochemical conditions, as it can only result from the disrotatory pericyclic reaction of the parallel conformer, **1-*p***, which has the two thiophene rings in mirror symmetry. Despite the fact that this conformer coexists in almost equal proportion to the antiparallel conformer, **1-*a***, which has the two thiophene rings in a C_2 orientation, and the interconversion rate is estimated to be much slower than the lifetimes of the photoexcited states, only photoexcited **1-*a*** can be converted to its ring-closed form *trans*-**2**.[12] Irie and co-workers have shown that locking the dithienylethene skeleton into its parallel conformation completely prevents ring closure,[13] while increasing the population of the antiparallel conformation enhances the extent of ring closure.[14] Because the electrochemical ring-closing reaction proceeds via radical intermediates, it is not prone to the same limitations as the photochemical reaction and the formation of *cis*-**2** should be expected. It is, however, generated to a smaller extent than its *trans*-counterpart as it is less stable.[15]

We offer the following evidence to support our claim. The side product is not a result of the electrolytic reaction pathways typically observed for viologen derivatives, including polymerization, demethylation to generate the pyridines, or α oxidation to form the corresponding pyridinones.[16] All of these possibilities can be ruled out based on the fact that the ^{1}H NMR spectrum of the side-product does not resemble those of the mono-*N*-methyl and bis(pyridine) derivatives in either their ring-open and ring-closed forms, and the symmetry of the spectrum does not correspond to a pyridinone. The similarity of the ^{1}H NMR spectrum of the side product to that of the ring-closed isomer is one support for assigning the side product as *cis*-**2**. Another support is the fact that only one redox couple is observed in the CV experiment. As *cis*-**2** and *trans*-**2** would be expected to have similar (or identical) reduction potentials, they would appear as a single redox couple. Electrochemically formed polymers may be produced after extended periods of electrolysis and could be responsible for the precipitate observed in the electrolysis experiments.

Irie and co-workers[17] as well as our group[18] have reported that the ring-closed forms of some DTE derivatives undergo photochemical rearrangements to a non-photochromic isomer. Although the mechanism of this reaction is not fully understood, we rule out this rearrangement as a possibility in the case discussed here based on the thermal instability of both the side-product and the ring-closed isomer *trans*-**2**. When samples of the electrochemically generated products are heated to 80 °C for 3 h or left at room temperature for one week, the signals in the ^{1}H NMR spectrum corresponding to both ring-closed products disappear and only those corresponding to the ring-open isomer are observed. This thermal reaction would be highly unlikely for the known rearranged product and was not witnessed in either our or Irie's case. Another observation that supports this claim is that the ^{1}H NMR spectrum for the electrochemically generated side product does not display similarities with the rearranged photoproducts reported by Irie and co-workers as well as us. Current efforts are focused on isolating this side product and elucidating the precise mechanism for its formation. Both will be reported in due course.

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[10] After each electrolysis period, the reaction was treated with 10 equivalents of $AgPF_6$, stirred at room temperature for 3 h, and filtered through Celite to remove solid silver metal before the solvent was evaporated in vacuo and the sample analyzed by ^{1}H NMR spectroscopy.

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