

Electrochromism in Photochromic Dithienylcyclopentenes

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Molecules that toggle between two distinct forms when exposed to specific external stimuli, where each form exhibits unique physical properties, are promising candidates for fabricating controllable nanodevices.¹ Photochromic compounds exhibit reversible variations in color when stimulated by light. Few photochromic compounds possess the favorable properties displayed by the 1,2-dithienylcyclopentene skeleton, which interconverts between its colorless ring-open and colored ring-closed isomers with a high level of fatigue resistance and bistability.² We have previously reported how the photochromic 1,2-bis(5',2'-di(thiophen-2-yl)thien-3'-yl)perfluorocyclopentene can be toggled between its pale yellow ring-open form (**1o**) and its deep blue ring-closed form (**1c**) by alternating its exposure to ultraviolet and visible light (Scheme 1).³ Here we report the significant discovery that the ring-closed form of this photochromic compound is also electrochromic: it rapidly returns to its ring-open form when electrochemically oxidized. This is, to the best of our knowledge, the first example of a 1,2-dithienylalkene derivative that exhibits both photochromic and electrochromic ring-opening.⁴

The electrochemical oxidation of poly- and oligothiophene derivatives has been extensively studied,⁵ and it is well documented that the oligomers generally tend to possess less positive oxidation potentials with the addition of each heterocycle. Cyclic voltammetry would, therefore, provide a useful means to compare the extent of π -conjugation in both isomers of photochromic compounds **1** and **2**. Cyclic voltammetry experiments clearly reveal the difference in the oxidation potentials of **1o** and bis(dithiophene) **2o** (Figure 1a).⁶ As expected, **2o** requires a more positive potential (1.41 V) to be oxidized than does bis(terthiophene) **1o** (1.27 V), highlighting the communication extending throughout each terthiophene arm in compound **1o**. In their ring-closed states (**1c** and **2c**),⁷ the π -conjugated pathways trace out polyene backbones that are essentially identical for both photochromic compounds. This is the reasoning we originally used to justify the similarity of the electronic absorption properties of **1c** and **2c**,³ and the same argument can be used to propose that the oxidation properties of both ring-closed forms should also be virtually identical. This is clearly not the case as illustrated in Figure 1b. The reversible anodic wave that appears at 0.85 V for bis(dithiophene) **2c** is almost too small to be measured in the cyclic voltammogram of **1c**, which appears to be identical to that of the ring-open form **1o**.⁸

We assign the small peak at 0.85 V to the oxidation of bis(terthiophene) **1c** on the basis of its appearing at the same potential as that for the bis(dithiophene) **2c**, and we offer the following to explain its low intensity and irreversibility. During the cyclic voltammetry experiments, the ring-closed form of the bis(terthiophene) **1c** loses an electron to the anode and forms its radical cation at the same potential as for bis(dithiophene) **2c** (0.85 V). Before a significant change in current can be recorded under the experimental conditions, the radical cation undergoes a rapid ring-opening reaction to produce the radical cation of isomer **1o**. Because the neutral form of isomer **1o** requires a substantially more positive

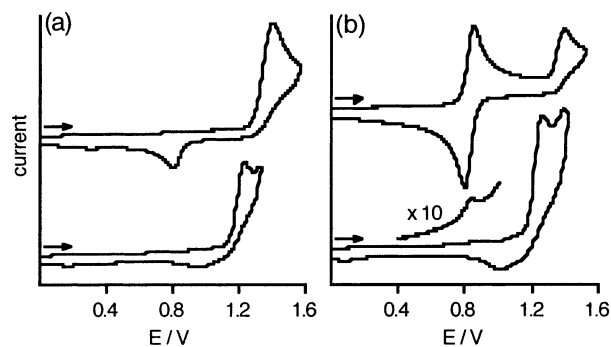
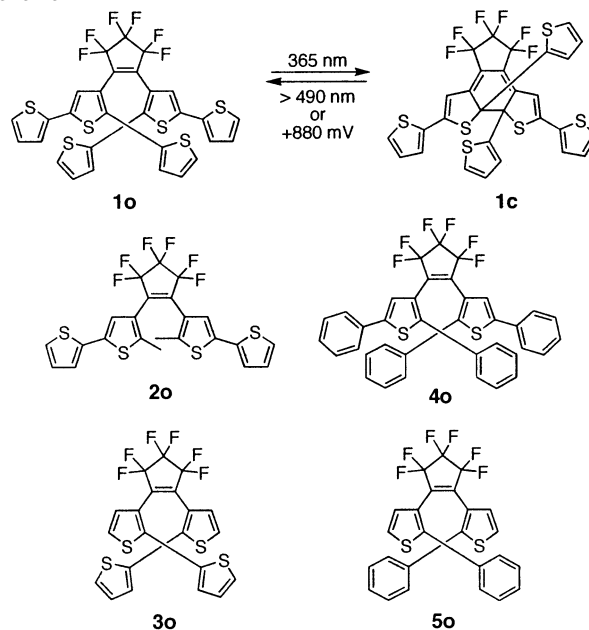


Figure 1. Cyclic voltammograms of CH_3CN solutions (1×10^{-3} M) of (a) **2o** (top) and **1o** (bottom) and (b) **2c** (top) and **1c** (bottom) at a scan rate of 200 mV/s.

Scheme 1



potential to undergo oxidation (1.27 V), its radical cation immediately oxidizes a neighboring molecule of **1c** and is effectively neutralized.

The electrochemical ring-opening process is easily monitored by ^1H NMR spectroscopy.⁹ A CD_3CN solution of bis(terthiophene) **1o** containing tetrabutylammonium hexafluorophosphate was irradiated at 365 nm until the photostationary state of the photochromic compound was attained. This solution was transferred in the dark into the electrochemical cell where it was subjected to electrolysis at 0.88 V. After 10 min at this potential, the color of the solution returned to the original pale yellow, signifying the complete reversion to the ring-open isomer **1o**. The ^1H NMR spectrum recorded immediately after the electrolysis shows the complete disappearance of the peaks corresponding to the ring-

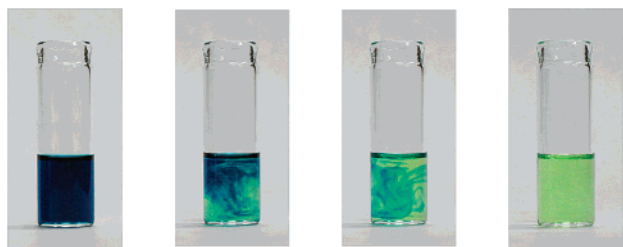


Figure 2. Gradual color change of a CH_2Cl_2 solution of compound **1** containing 75% of the ring-closed isomer **1c** when treated with a catalytic amount of $[(4\text{-BrC}_6\text{H}_4)_3\text{N}][\text{SbCl}_6]$.

closed form **1c** and the concomitant regeneration of the peaks representing the ring-open form **1o**. The photochromic bis(dithiophene) **2c** displayed no electrochemical ring-opening.

The implications of this redox ring-opening process are significant: it is catalytic. Only a small fraction of the ring-closed form **1c** present in solution is required to undergo the redox reaction to completely drive the ring-opening reaction. As soon as the radical cation of **1c** is produced, it will ring-open to **1o**, which will subsequently remove an electron from another molecule of **1c** and regenerate the original radical cation. The continuation of this oxidize/ring-open/reduce cycle will eventually result in the complete conversion of **1c** to **1o**. We offer the following to support the existence of this process. When an aliquot of a CH_2Cl_2 solution (2×10^{-5} M) of the one-electron-accepting radical cation $[(4\text{-BrC}_6\text{H}_4)_3\text{N}][\text{SbCl}_6]$ ($E_{\text{ox}} = 1.15$ V), corresponding to merely 1 mol %, was added to a deep blue CH_2Cl_2 solution (2×10^{-5} M) of irradiated **1**, which contained 75% of the ring-closed isomer **1c**, the solution immediately returned to the color corresponding to the ring-open isomer (Figure 2).

The fatigue resistance of this dual-mode photochemical-ring-closing/electrochemical-ring-opening process was examined by cycling the bis(terthiophene) between its two states (**1o** and **1c**) by alternately irradiating solutions of the ring-open isomer **1o** with 365 nm light and electrolyzing the generated solutions of the ring-closed isomer **1c** at a voltage of 0.88 V. The cycling experiment was monitored using ^1H NMR spectroscopy, which showed no significant degradation of the compound after 10 cycles.

Although the photochromic bis(dithiophene) **2c** does not exhibit any electrochromic behavior, the electrochromic phenomenon is not unique to the bis(terthiophene) **1c**. The ring-closed forms of compounds **3**, **4**, and **5** all undergo electrochromic ring-opening reactions under conditions similar to those described for **1c**. CH_3CN solutions of the ring-open forms **3o**, **4o**, and **5o** can be converted to their purple (38% **3c**), blue (42% **4c**), and purple (27% **5c**) photostationary states by irradiating them with either 313 or 365 nm light.⁷ Subsequent electrolysis at the potential at which the closed form becomes oxidized (1.16 V for **3c**, 0.89 V for **4c**, and 1.05 V for **5c**) resulted in the decolorization of each solution due to the rapid electrochemical ring-opening reaction. The ring-

closed isomer of the photochromic tetraphenyl derivative **4c** also undergoes rapid chemical ring-opening when a small amount of $[(4\text{-BrC}_6\text{H}_4)_3\text{N}][\text{SbCl}_6]$ is added to the solution. The chemically promoted ring-opening reactions of compounds **3c** and **5c** are sluggish due to the mismatch of their oxidation potentials with that of the radical cation initiator, but they still occur.

It appears that the presence of aromatic rings connected onto the two carbon atoms of the thiophene heterocycles where the new C–C single bond is formed (the 2-positions of the thiophene) is the critical structural requirement for electrochromism. The exact structure/property relationships, their limitations, and the requirements for electrochromism are currently under investigation and will be reported in due course.

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Supporting Information Available: ^1H NMR spectral changes for the photochemical ring-closing of **1o** and electrochemical ring-opening of **1c** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) *Molecular Switches*; Feringa, B. L., Ed.; Wiley-VHC: New York, 2001.
- (2) (a) Irie, M. *Molecular Switches*; Feringa, B. L., Ed.; Wiley-VHC: New York, 2001; p 37. (b) Irie, M. *Chem. Rev.* **2000**, *100*, 1685.
- (3) Peters, A.; McDonald, R.; Branda, N. R. *Chem. Commun.* **2002**, 2274.
- (4) For an overview of electrochromism, see: *Electrochromism: Fundamentals and Applications*; Monk, P. M. S., Mortimer, R. J., Rosseinsky, D. R., Eds.; VHC: New York, 1995. For examples of electrochemically gated photochromic systems, see: (a) Miki, S.; Noda, R.; Fukunishi, K. *Chem. Commun.* **1997**, 925. (b) Zhi, J.-F.; Baba, R.; Hashimoto, K.; Fujishima, A. *J. Photochem. Photobiol., A* **1995**, *92*, 91. (c) Zhi, J.-F.; Baba, R.; Hashimoto, K.; Fujishima, A. *Ber. Bunsen-Ges. Phys. Chem.* **1995**, *99*, 32. (d) Kawai, S. H.; Gilat, S. L.; Ponsinet, R.; Lehn, J.-M. *Chem.-Eur. J.* **1995**, *1*, 285. (e) Saika, T.; Iyoda, T.; Honda, K.; Shimidzu, T. *J. Chem. Soc., Perkin Trans. 2* **1993**, 1181. (f) Newell, A. K.; Utley, J. H. P. *J. Chem. Soc., Chem. Commun.* **1992**, 800. (g) Iyoda, T.; Saika, T.; Honda, K.; Shimidzu, T. *Tetrahedron Lett.* **1989**, *30*, 5429.
- (5) *Handbook of Oligo- and Polythiophenes*; Fichou, D., Ed.; Wiley-VHC: New York, 1999. (b) *Electronic Materials: The Oligomer Approach*; Mullen, K., Wegner, G., Eds.; Wiley-VHC: New York, 1998.
- (6) Electrochemical cyclic voltammetry experiments were performed using a platinum disk working electrode, a platinum wire counter electrode, a Ag/AgCl (in a saturated NaCl solution) reference electrode, and tetrabutylammonium hexafluorophosphate (0.1 M) as the electrolyte. All results were referenced against ferrocene (0.40 V vs SCE). Electrolysis experiments were performed under similar conditions, except the platinum working electrode was replaced by a platinum coil.
- (7) Standard lamps used for visualizing TLC plates (Spectroline E-series, 470 mW/cm^2) were used to carry out the ring-closing reactions (365 nm for **1o**, **2o**, and **4o**; 313 nm for **3o** and **5o**). The compositions of all photostationary states were detected using ^1H NMR spectroscopy. The ring-opening reactions were carried out using the light of a 150 W tungsten source that was passed through a 490 nm (for **1c**, **2c**, and **4c**) or a 434 nm (for **3c** and **5c**) cutoff filter to eliminate higher energy light.
- (8) Identical results were obtained when the photostationary state (~80% **1c**) or purified samples (recrystallized from hexane) of **1c** were used.
- (9) See Supporting Information for details.

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