Photoelectrochromic Dithienylperfluorocyclopentene Derivatives

Xin-Hong Zhou, Fu-Shi Zhang,* Peng Yuan, Fan Sun, Shou-Zhi Pu, Fu-Qun Zhao, and Chen-Ho Tung*
Key Lab of Organic Optoelectronics & Molecular Engineering of Ministry of Education,
Department of Chemistry, Tsinghua University, Beijing 100084, P. R. China

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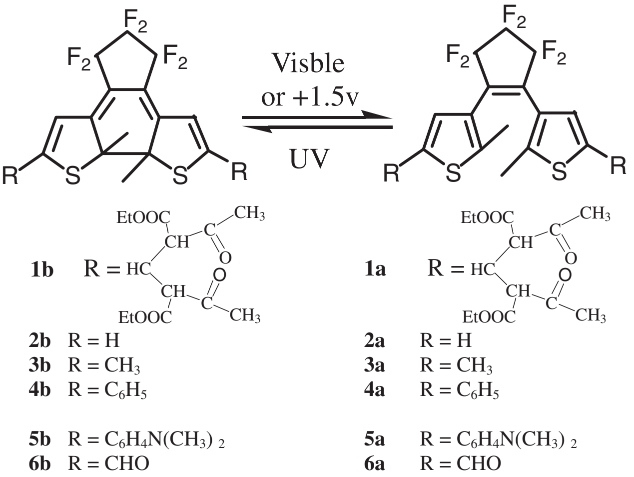
Dithienylperfluorocyclopentene derivatives that bear alkyl substituents connected onto the two carbon atoms of the thiophene heterocycles where, in their ring-closed form, the new C–C single bond is formed (the 2-positions of the thiophene), can exhibit photochromic ring-closing, and both photochromic and electrochromic ring-opening.

Photochromic and electrochromic materials have been investigated for potential applications in displays, imaging devices, and molecular electronics.[1] Considerable interest has been focused on photochromic dithienylperfluorocyclopentene compounds because of their high conversion efficiency in reversible photochromic reactions, the excellent thermal stability of both isomers, and good fatigue resistance. The compounds have shown great promise as new materials for opto-electronic devices and molecular swiches.[2] However, there have been few investigations of the electrochromism of dithienylethene. To the best of our knowledge, the only two published reports by Branda and co-worker demonstrated that photochromic 1,2-dithienylcyclopentenes that bear aromatic rings connected onto the two carbon atoms of thiophene heterocycles where, in their ring-closed form, the new C–C single bond is formed (the 2-positions of the thiophene), can convert to their ring-open forms from the ring-closed when electrochemically oxidized, while the analogues with alkyl substituents undergo electrochemical ring-closing.[3,4] Here we wish to report that dithienylcyclopentene derivatives that bear alkyl substituents, in their ring-closed forms also can undergo ring-opening upon electrochemical oxidation.

Compound **1a** was prepared from **6a**. First, dithienylethene **6a** was synthesized from 5-methyl-2-thiophenecarboxaldehyde according to literature.[5] Then condensation between **6a** and ethyl acetoacetate yielded **1a**. The identity of this compound was confirmed by ^{1}H NMR spectroscopy, MS spectrometry and elemental analysis.[6] Compounds **2a**, **3a**, **4a**, and **5a** were synthesized according to procedures in the literature.[7]

Figure 1 gives the cyclic voltammogramm of **1b** and **2b** (photostationary state) in acetonitrile solution.[8] Compound **1b** shows an irreversible peak at 1.09 V and **2b** at 1.02 V. With reference to previous work on thiophenes we assigned the peak to the oxidation of the ring-closed isomer.



Scheme 1.

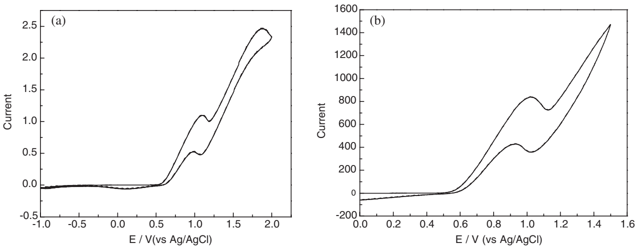


Figure 1. Cyclic voltammgrams of dithienylethene **1b** (a) and **2b**(b) (photostationary state) in CH_3CN solutions (1×10^{-3} M).

Photoelectrochromic dithienylperfluorocyclopentene derivatives such as **1**, **2**, **3**, and **4**, which bear alkyl substituents connected onto the two carbon atoms of the thiophene heterocycles where, in their ring-closed forms the new C–C single bond is formed (the 2-positions of the thiophene), can rapidly convert to their ring-open forms from the ring-closed upon electrochemical oxidation (Scheme 1). Moreover, the substituent attached to the 5-position of the thiophene heterocycle has a decisive influence on the electrochemical ring-opening reaction. When the substituents have no hetero-atom (as in compounds **2b**, **3b**, and **4b**), or even when they have hetero-atoms but the hetero-atoms are not conjugated with the main structure of the dithienylcyclopentene (**1b**), the derivatives could undergo a ring-opening reaction when electrochemically oxidized. However, when the substituents have hetero-atoms conjugated to the main structure, the hetero-atoms of the substituents participate in the electrochemical reaction and the derivatives could not be converted to the ring-open state, as is the case for compounds **5b** and **6b** (Scheme 1). This is ascribed to the relatively higher electronegativity of the conjugated hetero-atoms which decreases the energy of the corresponding orbital.[9] Thus the electrochemical reaction first takes place on the substituents, and the derivatives cannot be converted to the ring-open state.

The electrochemically driven ring-opening reaction of **1b** was performed with its solution in acetonitrile containing tetrabutylammonium hexafluorophosphate as the electrolyte in a quartz cell. Platinum slice electrodes were used as the working and counter electrodes, and Ag/AgCl as the reference electrode.[10] Progress of the reaction was monitored by UV–vis absorption spectroscopy in situ. When the red solution of **1b** was

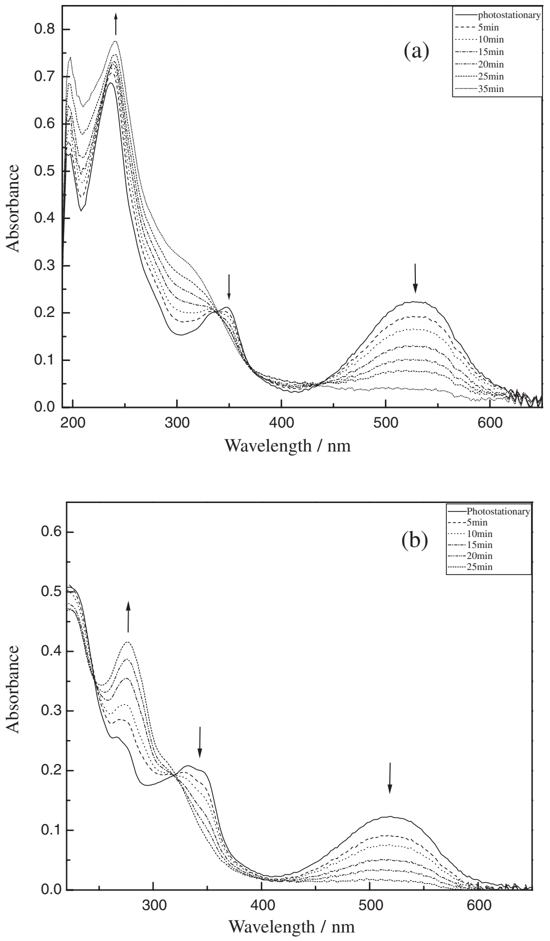


Figure 2. UV–vis absorption spectra of diarylethene **1b** (a) and **2b** (b) (photostationary state) in CH_3CN ($c = 2 \times 10^{-5}$ M) upon electrolysis at 1.5 V (vs Ag / AgCl) with a Pt electrode.

electrolyzed at 1.5 V (vs Ag/AgCl), it turned pale and generated the same spectrum as was observed of the photochemical ring-opening process. Figure 2a shows the absorption spectra of **1b** as a function of electrolysis time in the case of platinum slice electrodes as the working and counter electrodes. Evidently, after 35 minutes' electrolysis, the absorption at 520 nm almost completely disappears, and the resulting absorption spectrum is the same as that recorded when **1b** is photochemically ring-opened. Subsequently, we irradiated the resulting colorless solution with light of 365 nm and found that it turned to red, and the absorption profiles were the same as shown in Figure 2a. By alternately irradiating the solution of the ring-open isomer **1a** with 365 nm light and electrolyzing the generated solution of the ring-closed isomer **1b** at 1.5 V (vs Ag/AgCl), we could cycle the dithienylcyclopentene between its two states, **1a** and **1b**. After 30 cycles, no significant degradation of the compound was observed, as indicated by the existing of the isosbestic points in Figure 2a. Diarylethene **2**, **3**, and **4** can also cycle the photochemical ring-closing and both photochemical and electrochemical ring-opening reactions. Upon irradiation with 365-nm light, the colorless solution of the ring-open isomer **2a** and **3a** turned red and **4a** turned blue along with the formation of the ring-closed isomer. Subsequent electrolysis resulted in the bleaching of each solution due to the cycloreversion of **2b**, **3b**, and **4b** to **2a**, **3a**, and **4a**. Figure 2b shows the absorption spectra change of **2b** as the electrolysis progressed. ^{1}H NMR spectroscopy has demonstrated that the resulting compound of the electrochemical ring-opening reaction is the ring-open isomer.

To summarize, we have demonstrated that the dithienylcyclopentene derivatives with alkyl groups attached to the carbons involved in forming the new single bond, may undergo a photochemical ring-closing reaction and both photochemical and electrochemical ring-opening reactions. Moreover, the substituent attached to the 5-position of the thiophene heterocycle has a decisive influence on the electrochemical ring-opening reaction. The derivatives show good fatigue resistance in the dual-mode photochemical-ring-closing/electrochemical-ring-opening process.

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References and Notes

1 P. M. S. Monk, R. J. Mortimer, and D. R. Rosseinsky, "Electrochromism: Fundamentals and Applications," VCH, Weinheim (1995); C. Bechinger, S. Ferrere, A. Zaban, J. Sprague, and B. A. Gregg, *Nature*, **383**, 608 (1996); X. F. Guo, D. Q. Zhang, T. X. Wang, and D. B. Zhu, *Chem. Commun.*, **2003**, 914.

2 M. Irie, S. Kobatake, and M. Horichi, *Science*, **291**, 1769 (2001); M. Irie, *Chem. Rev.*, **100**, 1685 (2000); T. Yamada, S. Kobatake, K. Muto, and M. Irie, *J. Am. Chem. Soc.*, **122**, 1589 (2000); H. Tian, B. Qin, R. X. Yao, X. L. Zhao, and S. J. Yang, *Adv. Mater.*, **15**, 24, 2104 (2003); K. Uchida, A. Takata, S. Nakamura, and M. Irie, *Chem. Lett.*, **2002**, 476; K. Higashiguchi, K. Matsuda, T. Yamada, T. Kawai, and M. Irie, *Chem. Lett.*, **2000**, 1358.

3 A. Peters and N. R. Branda, *J. Am. Chem. Soc.*, **125**, 3404 (2003).

4 A. Peters and N. R. Branda, *Chem. Commun.*, **2003**, 954.

5 S. L. Gilat, S. H. Kawai, J.-M. Lehn, *J. Chem. Soc., Chem. Commun.*, **1993**, 1439.

6 Preparation of **1a**: To a solution of compound **6a**, diethylamine was added slowly at room temperature. The mixture was stirred and ethyl acetoacetate was subsequently added. After 8 h, the resultant mixture was then extracted with ether. Column chromatography through silica (hexane:ether = 1:3) afforded dithienylcyclopentene **1a**. Purification by column chromatography gave **1a** as light yellow grain in 73% yield. Selected data for **1a**: MS m/z (M^+): $M = 908$. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm: 1.27 (t, 12H), 1.98 (s, 6H), 2.34 (s, 12H), 3.60 (m, 2H), 4.08 (q, 8H), 4.21 (m, 4H), 6.78 (s, 2H), 12.32 (s, the enol form of **1a**). Elemental Analysis: Calcd for $C_{41}H_{46}O_{12}S_2F_6$: C, 54.18; H, 5.10; S, 7.06%. Found: C, 54.08; H, 5.08; S, 7.03%.

7 M. Irie, K. Sakemura, M. Okinaka, and K. Uchida, *J. Org. Chem.*, **60**, 8305 (1995); T. Saika, M. Irie, and T. Shimidzu, *J. Chem. Soc., Chem. Commun.*, **1994**, 2123; M. Irie, T. Lifka, S. Kobatake, and N. Kato, *J. Am. Chem. Soc.*, **122**, 4871 (2000); M. Irie and K. Uchida, *Bull. Chem. Soc. Jpn.*, **71**, 985 (1998).

8 Electrochemical cyclic voltammetric experiments were undertaken with an EG&G PARC Model 283 potentiostat / Galvanostat system in a conventional three-electrode electrochemical cell. The working and counter electrode was a platinum wire, and the reference electrode was Ag/AgCl (in a saturated NaCl solution).

9 F. P. Schäfer, B. B. Snavely, H. Gerhardt, C. V. Shank, E. P. Ippen, K. H. Drexhage, J. J. Snyder, and T. W. Hänsch, "Topics in Applied Physics, Vol. 1: Dye Lasers," Springer-Verlag (1990).

10 Electrolysis experiments were performed in a quartz cell. Platinum slice electrodes were used as the working and counter electrodes, and Ag/AgCl as the reference electrode. At the same time, UV–vis spectra were measured *in situ* to monitor the electrolysis. CH_3CN solutions of the dithienylcyclopentene derivatives **1**–**6** containing 0.1 M NBu_4PF_6 were analyzed.

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