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Tetrahedron Letters 49 (2008) 1582–1585

Tetrahedron Letters

Novel photochromic macrocycles composed of thiophene and ethylene building blocks: synthesis, structure, and photochromic property

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Received 6 October 2007; revised 8 January 2008; accepted 11 January 2008
Available online 15 January 2008

Abstract

Two novel photochromic macrocycles composed of thiophene and ethylene building blocks have been synthesized, and their crystal structure and photochromic properties are described. Macrocycle **2** shows good photochromic properties.

Keywords: Macrocycle; Thiophene; Synthesis; Structure; Photochromic property

Over the past 30 years, macrocyclic chemistry has been developed into a field of major scientific and technological importance due to their guest inclusion, the widespread and possibilities of functionalization.[1] So a wealth of applications have been discovered for the vast range of macrocyclic structures thus far prepared. They have also played a pivotal role in the synthesis and study of challenging molecular architecture.[2]

Among many macrocyclic systems, thiophene-containing macrocycles represent an important class of compounds in the field of materials science,[3] and have been extensively investigated as potential molecular devices, machines, switches, and molecular electronics due to their excellent photoelectric properties. Hence tremendous effort has been devoted toward the design and preparation of thiophene-containing macrocycles, especially cyclic oligothiophenes, which have attracted much attention. In the previous studies, there were two linked mode between thiophenes: (1) thiophenes were linked directly;[4] (2) thiophenes were linked by some groups or bridged atoms (such as boron-bridged,[5] sulfur-bridged,[6] and ethynylene[4,7]). To the best of our knowledge, ethene-bridged oligothiophenes are rare. In the present study, two novel photochromic macrocycles composed of thiophene and ethylene building blocks are synthesized, and their structure and property are described.

Our synthetic work is summarized in Scheme 1. 1,2-Bis-(5-chloro-2-methylthien-3-yl)perfluorocyclopentene[8] was lithiated with *n*-butyllithium and then reacted with perfluorocyclopentene to give macrocycles **1** and **2**, which were purified by chromatography.[10] 3,5-Dibromo-2-methylthiophene[9] as the starting material reacted with *n*-butyllithium and perfluorocyclopentene was also tried, and but macrocycles **1** and **2** were obtained in lower yields.

Macrocycles **1** and **2** were characterized by NMR, MS,[10] and X-ray.[11] In the ^{1}H NMR spectrum of macrocycle **1**, the methyl-H, and thienyl-H resonance were observed at δ 2.06 and δ 7.52 ppm, respectively. Similar signals were observed at δ 2.02 and δ 7.51 ppm for macrocycle **2**. Mass spectrum of macrocycles **1** and **2** showed the *m*/*z* ratio at 1082 and 1620, respectively, which were in good agreement with the theoretic result. Furthermore, single crystal suitable for X-ray diffraction was obtained by slow diffusion of hexane into a solution of macrocycles **1** and **2** in dichloro-

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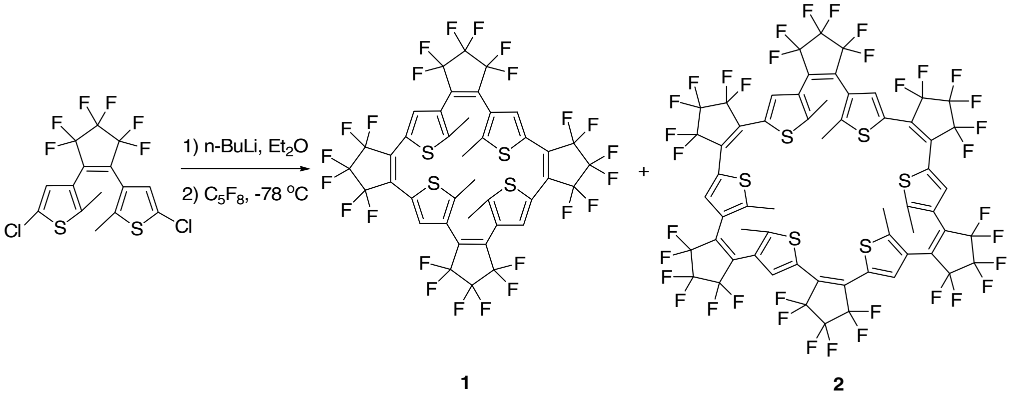
doi:10.1016/j.tetlet.2008.01.052



Scheme 1. Synthesis of macrocycles **1** and **2**.

methane. The X-ray diffraction study gave unambiguous assignment of the macrocyclic structures of **1** and **2** although the disorder of some of the fluorine made the refinement very difficult. The crystal structures of **1** and **2** (including atomic labeling) are given in Figure 1.

Figure 1 confirms that macrocycle **1** comprises 20 chain members. There is distortion between every two adjacent thiophene rings because the distortion could be advantageous to decrease the strain energies of the cycles. The nonbonding distances of macrocycle **1** between two diagonal sulfur atoms are 3.823 and 9.824 Å, respectively. For crystal structure of macrocycle **1**, there are intermolecular hydrogen bonds for C–H···F hydrogen bond and C–H···Cl hydrogen bond because of two dichloromethane molecules.

While macrocycle **2** comprises 30 chain members. The nonbonding distances of S1···S2b, S2···S1a and S2a···S1b were 0.8213(3) nm that reflected the size of the interior cavity. Because the molecule has 12 planner rings, including six thiophene rings and six perfluorocyclopentene ring, there are twelve dihedral angles between every two adjacent rings. The dihedral angles between the perfluorocyclopentene ring (C2–C3–C4–C5–C6) and the thiophene ring (C7–C8–S1–C11–C10) are 45.4(1), suggesting the presence of some π-conjugation between the thiophene ring and the ethene unit.[12] The thiophene ring (C7–C8–S1–C11–C10) and perfluorocyclopentene ring (C12–C13–C14–C15–C16) are nearly vertical. Every two adjacent perfluorocyclopentene rings do not lie in a same plane, and the dihedral angles are 53.4°. There are intermolecular hydrogen bonds for C–H···F hydrogen bond in the molecular packing.

Photochromic materials have received a much attention because of their potential applications including optoelectronics such as optical memory, switching, and display devices. Dithienylethene is one of the most well-known and extensively investigated classes of photochromic molecules because of its excellent thermal stability and fatigue resistant properties required for optoelectronic applications. The photochromic reaction of dithienylethenes is based on the reversible ring-closing and ring-opening reactions as shown in Scheme 2. Upon irradiation with UV light, the open-ring isomer is converted into the closed-ring isomer, which has a new absorption band in the visible wavelength region. The closed-ring isomer

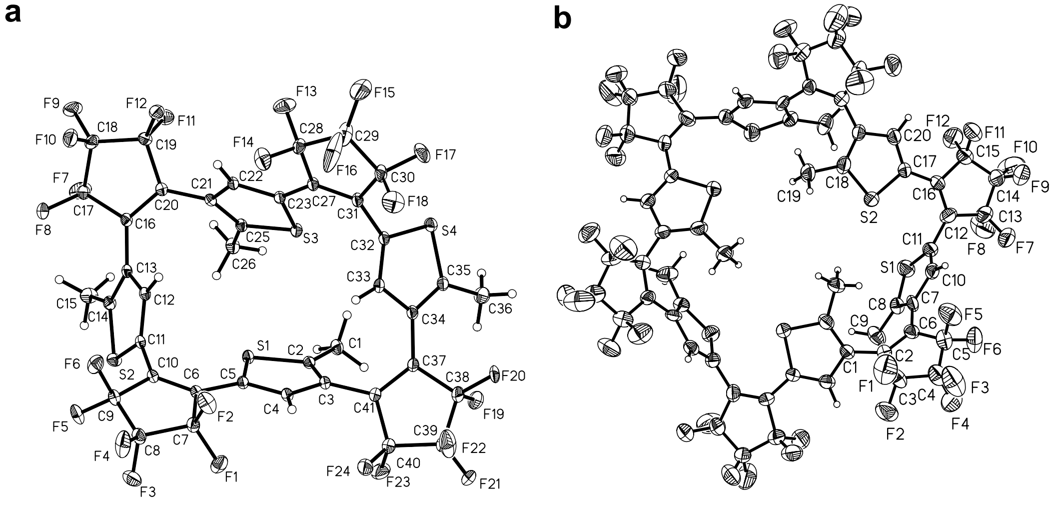
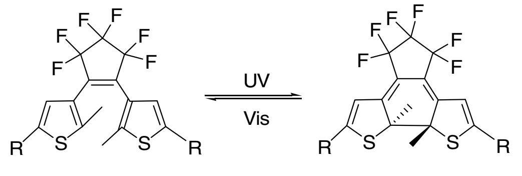


Fig. 1. (a) The molecular structure of macrocycle **1** and (b) the molecular structure of macrocycle **2**.



Scheme 2. The reversible photocyclization reactions of dithienylethene.

reverts to the open-ring isomer upon irradiation with visible light.

Macrocycles **1** and **2** contain two and three dithienylethene units, respectively. Upon irradiation with UV light, the colorless dichloromethane solution of macrocycle **2** turned into yellow-green, then to green, at the same time a new absorption band was observed at 604 nm as shown in Figure 2. The change indicated that the open-ring form of dithienylethene unit in macrocycle **2** was converted into the close-ring form. Upon irradiation with visible light, the green solution of macrocycle **2** turned into colorless as shown in Figure 3, which indicated that the open-ring form reverted to the close-ring form. Based on these results, macrocycle **2** has good photochromic properties.[13,14] However, no new absorption band was observed upon irradiation with UV light in the dichloromethane solution of macrocycle **1**, which indicated that the open-ring form of dithienylethene unit in macrocycle **1** was not converted into the close-ring form, due to the ring strain.

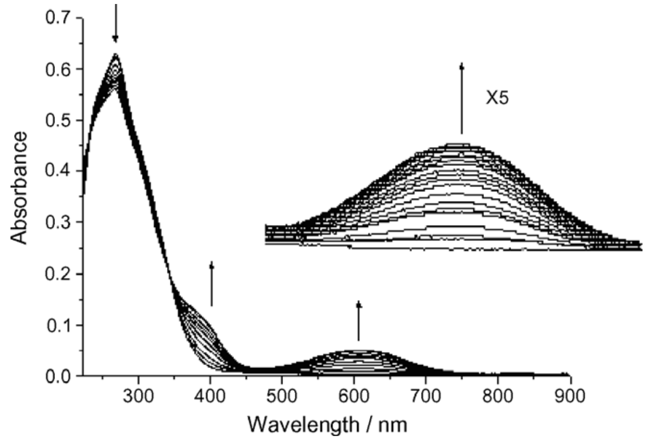


Fig. 2. UV/vis absorption spectral changes of **2** (2.0×10^{-5} M) in CH_2Cl_2 upon the UV light irradiation at 0, 5, 10, 15, 20, 25, 30, 35, 40…(s).

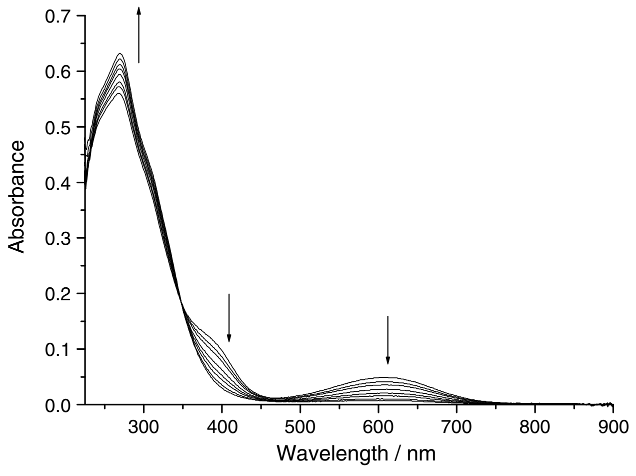


Fig. 3. UV/vis absorption spectral changes of the ring-closed isomer **2** (2.0×10^{-5} M) in CH_2Cl_2 upon the visible light irradiation at 0, 10, 20, 30, 40, 50, 60…(s).

In conclusion, we have successfully prepared two novel macrocycles composed of thiophene and ethylene building blocks, and described their design, synthesis, and structural characterization. The study of photoisomerization shows that macrocycle **2** has good photochromic properties. Further research efforts will focus on increasing their yields and exploring the possibilities of functionalization. These results will be reported in due course.

Acknowledgments

The authors acknowledge financial support from National Natural Science Foundation of China (Nos. 20572029, 20772039), New Century Excellent Talents in University (NCET-04-0743), the Cultivation Fund of the Key Scientific, and Technical Innovation Project, Ministry of Education of China (No. 705039).

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10. Synthetic procedure and data of macrocycle **1** and macrocycle **2**: *n*-butyllithium (1.6 mL, 4 mmol, 2.5 M in hexane) was added slowly to a stirred solution of 1,2-bis-(5-chloro-2-methylthien-3-yl)perfluorocyclopentene (0.88 g, 2 mmol) in anhydrous diethyl ether (30 mL) under a nitrogen atmosphere at −78 °C. After 1.5 h of stirring at that temperature, a solution of perfluorocyclopentene (0.43 g, 2 mmol) in anhydrous diethyl ether (5 mL) was added slowly to the mixture in about 10 min. The reaction mixture was stirred for 2 h at −78 °C, after which time the reaction was allowed, then warmed to ambient temperature. After an additional 2 h, the reaction solution was diluted with diethyl ether containing little water and washed by water. The aqueous layer was then extracted with diethyl ether (3 × 30 mL). The combined diethyl ether phase layers were dried (anhydrous sodium sulfate) and evaporated in vacuo to yield a yellow-brown solid. The solid was purified by column chromatography (silica gel, CH_2Cl_2/hexane = 1:10–1:2) to give macrocycle **1** (yield: 8.4%) and **2** (2.6%). Macrocycle **1**: Anal. Calcd for $C_{40}H_{16}F_{24}S_4\cdot 2CH_2Cl_2$: C, 40.34; H, 1.61; S, 10.25. Found: C, 40.60; H, 1.47; S, 10.12. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.06 (s, 12H, CH_3), 5.32 (s, 4H, CH_2Cl_2), 7.52 (s, 4H, thiophene-H). ^{19}F NMR (376 MHz, $CDCl_3$, internal standard $CFCl_3$): δ −111.72(m), −133.25(m). MALDI-TOF mass: 1082 [M+2H]. Macrocycle **2**: Anal. Calcd for $C_{60}H_{24}F_{36}S_6$: C, 44.45; H, 1.49; S, 11.87. Found: C, 44.68; H, 1.28; S, 12.13. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.02 (s, 18H, CH_3), 7.51 (s, 6H, thiophene-H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 14.09 (CH_3), 125.05, 125.87 (CF_2), 127.46, 129.89, 132.67, 135.21 (thiophene-C), 147.64 (C=C). ^{19}F NMR (376 MHz, $CDCl_3$, internal standard $CFCl_3$): δ −111.65(m), −133.06(m). MALDI-TOF mass: 1620 [M^+].
11. Crystallographic data (excluding structure factors) for **1** and **2** have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication Numbers CCDC 621191 and 621192, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif, or by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.
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