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Synthesis, crystal structure and its optical and electrochemical properties of a new unsymmetrical diarylethene

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Abstract

A new unsymmetrical photochromic diarylethene, 1-(2-methyl-5-phenyl-3-thienyl),2-(2-methyl-5-(3-methylphenyl)-3-thienyl)-3,3,4,4,5,5-hexafluorocyclopent-1-ene (**MPMTH**), was synthesized and its structure was determined by single-crystal X-ray diffraction analysis. Its optical and electrochemical properties, including photochromic reactivity both in solution and in the crystalline phase, fluorescence and electrochemical property were investigated. The diarylethene underwent reversible photochromism, changing from colorless to blue after irradiation with UV light or visible light. The maximum absorption of the closed-ring isomer of **MPMTH** was observed at 577 nm in hexane. In hexane, the open-ring isomer of **MPMTH** exhibited relatively strong fluorescence at 310 nm when excited at 280 nm. The irreversible anodic oxidation of **MPMTH** was observed by performing linear sweep experiment. © 2006 Elsevier B.V. All rights reserved.

Keywords: Photochromism; Diarylethene; Crystal structure; Optical and electrochemical properties

1. Introduction

The development of photochromic compounds is an ever-growing field due to some new potential applications of this class of materials [1,2]. Generally, the reversible photochemical isomerization of photochromic molecules can lead to global changes of the bulk materials characteristics such as UV-vis absorption spectra, fluorescence spectra, oxidation/reduction potentials and refractive indices, etc. [3,4], or trigger a mechanical deformation, from reorientation to a matter transfer that could be used for various purposes from data technology (data storage) to astronomy (active filters) [5–7]. To date, some thermally irreversible photochromic compounds, such as diarylethenes, furylfulgides and phenoxynaphthacene-quinones [8-10], have been developed. Of all these compounds, diarylethene derivatives are the most promising materials for applications to high-density

optical recording, photo-switches, and full-color displays and photodriven actuators, because of the good thermally irreversible properties of the two isomers and their high sensitivity, fast response and remarkable fatigue resistance [3,11-16].

Although many photochromic diarylethene derivatives with two thiophene-derived groups have been reported to date, compounds which show strong photochromic reactivity in the crystalline phase are very rare [17-20]. However, they are very useful for practical applications, such as rewritable three-dimentional (3D) optical storage as well as nonlinear optical devices with switching properties [21,22]. Diarylethene crystals belong to a unique class of photochromic crystals, which exhibit thermally stable and fatigue resistant photochromic performance, and they are very promising for practical applications because they can not only reversibly turn various colors (yellow, red, blue or green) from colorless, depending on their molecular structure, upon irradiation with UV and appropriate wavelength visible light, but also exhibit good thermal stability and remarkable fatigue resistance [19,23]. Therefore,

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Scheme 1. Photochromism of diarylethene MPMTH.

investigation of diarylethene crystals have attracted much attention today, and a larger number of diarylethene crystal structures and their properties have already been reported [17,19,23,24].

Among these diarylethene compounds reported, many of them are symmetrical diarylethenes; reports on unsymmetrical derivatives are very rare [25]. In a previous publication, Irie et al., reported photochromism of a diarylethene compound [1,2-bis(2,4-dimethyl-5-phenyl-3thienyl)perfluorocyclopentene (1a) [26], and they found that the single crystal of this compound could reversibly shrink and expand by alternate irradiation with UV and visible light. The results showed that the shrinkage of the surface was digital, and each step corresponded to the thickness of one molecular layer as short as 1 nm. The reversible surface morphological changes could be applied to photodriven, nanoscale actuators that reversibly change thickness stepwise by alternate irradiation with UV and visible light [16]. In 2000, Irie et al., revealed the photochromic properties of 1,2-bis(2-metheyl-5phenyl-3-thienyl)perfluorocyclopentene (2a) both in solution and in a single-crystalline phase [11]. In that paper, they carried out kinetic study of photochromism of this compound and its derivatives in the single-crystalline phase and examined the reactivities in crystals at various temperatures. In addition, they had also reported their remarkably different fatigue resistance of compounds 1a and 2a [27]. Compared with these publications, we found that the methyl groups at 4 and 4'-positions of thiophene rings can affect significantly not only on their crystal structures but also on their various photochemical properties, such as absorption maxima, ease of cyclization quantum yield and fatigue resistant properties. These results are very interesting and important, and they also give us some good suggestions. We supposed that diarylethene had some new properties when the methyl groups at 4 and 4'-positions of thiophene rings were transferred to the benzene rings. In this study, in order to investigate one methyl group at the *meta*-position of the benzene of diarylethene effect on crystal structure and photochemical properties, we have now synthesized a new unsymmetrical diarylethene, 1-(2-methyl-5-phenyl-3-thienyl),2-(2-methyl-5-(3-methylphenyl)-3-thienyl)-3,3,4,4,5,5-hexafluorocyclopent-1-ene (MPMTH, shown in Scheme 1). We also investigated systematically its X-ray crystal structure, photochromism, and optical and electrochemical properties.

2. Experimental

2.1. General methods

¹H NMR and ¹⁹F NMR spectra were recorded on Bruker AV400 (400 MHz) spectrometer with CDCl₃ as the solvent and tetramethylsilane as an internal standard. Fourier transform infrared (FT-IR) spectra were measured from KBr pellets using a Bruke (Vertex 70) system. The absorption spectra were measured using a Perkin-Elmer Lambda-900 UV/VIS/NIR spectrometer. Photo-irradiation was carried out using SHG-200 UV lamp, CX-21 ultraviolet fluorescence analysis cabinet, and BMH-250 Visible lamp. Light of appropriate wavelengths was isolated by different light filters. Fluorescence spectra were measured using a Hitachi F-4500 spectrophotometer. Elemental analysis was performed on a Yanaco CHN C ORDER MT-3 apparatus. The X-ray experiment of the single-crystal was performed on a Bruker P4 diffractometer equipped with graphite monochromatized Mo Ka radiation at room temperature $(295 \pm 2 \text{ K}).$

2.2. Synthesis of MPMTH

The new diarylethene **MPMTH** was derived originally from 2-methylthiophene. The synthesis method of diarylethene **MPMTH** was described in Scheme 2 and experimental details were carried out as following.

2.2.1. Synthesis of 3,5-dibromo-2-methylthiophene 2

To a stirred solution of 2-methylthiophene (24.0 g, 244.8 mmol) in acetic acid (100 mL) at 0 °C was slowly added Br₂/acetic acid (v/v = 29/40) solution. The reaction mixture was stirred overnight at this temperature. The reaction was stopped by the addition of water. The mixture was neutralized by Na₂CO₃ and extracted with ether. The ether extract was dried, filtrated, and concentrated. The residue was purified by distillation *in vacuo*. Compound **2** was obtained as colorless oil of 50.7 g in 81.2% yield. ¹H NMR (400 MHz, CDCl₃, TMS): δ 2.94 (s, 3H), 7.61 (s, 1H); IR (v, cm⁻¹): 780, 810, 950, 1010, 1139, 1302, 1451, 1536, 2786, and 3081.

2.2.2. Synthesis of 3-bromo-2-methyl-5-thienylboronic acid 3

To a stirred solution of 2 (16.3 g, 63.7 mmol) in dry ether (150 mL) was added a 1.6 mol/L *n*-BuLi/hexane solution (40.6 mL, 65.0 mmol) at -78 °C under nitrogen atmosphere. Stirring was continued for 30 min, boric acid tri-butyl ester (18.8 mL) was quickly added to the reaction mixture. After increasing to room temperature, the reaction was stopped by the addition of 4% HCl (10 mL). The mixture was extracted with 4% NaOH (100 mL), and the aqueous NaOH solution was neutralized by 10% HCl. The residue was washed, filtrated, and dried. The product **3** was obtained as yellowish solid of 12.0 g in 85.5% yield. ¹H NMR (400 MHz, CDCl₃, TMS): δ 2.51 (s, 3H), 4.59 (s, 2H), 7.33 (s,1H); IR (ν , cm⁻¹): 690, 790, 832, 1010, 1132, 1340, 1474, 1528, 1291, and 3202.



MPMTH

Scheme 2. Synthetic route for diarylethene MPMTH.

2.2.3. Synthesis of 3-bromo-2-methyl-5-(3-methylphenyl)thiophene **4**

Compound 4 was prepared by reacting compound 3 (2.4 g, 10.7 mmol) with 1-bromo-3-methylbenzene (1.8 g, 10.7 mmol) in the presence of Pd(PPh₃)₄ (0.3 g) and Na₂CO₃ (4.2 g, 40 mmol) in THF (100 mL containing 10% water), for 16 h at 70 °C. The mixture was cooled at room temperature and then extracted with ether. The ether extract was dried over MgSO₄, filtered and concentrated. The residue was purified by silica gel column chromatography using petroleum ether as the eluent. Compound 4 was obtained as yellowish solid powder of 1.9 g in 65.0% yield. ¹H NMR (400 MHz, CDCl₃, TMS): δ 2.41(s, 3H, -CH₃), 2.38 (s, 3H, phenyl-H), 6.92 (s, 1H, thiophene-H), 7.09–7.37 (m, 4H, J = 8.4 Hz, phenyl-H).

2.2.4. Synthesis 1-(2-methyl-5-phenyl-3-thienyl), 2-(2-methyl-5-(3-methylphenyl)-3-thienyl)-3,3,4,4,5, 5-hexafluorocyclopent-1-ene **MPMTH**

To a stirred THF solution (100 mL) of compound 4 (1.8 g, 6.6 mmol) was slowly added a 1.6 mol/L n-BuLi/hexane solution (4.2 mL, 6.7 mmol) at -78 °C under a nitrogen atmosphere. After 30 min, 2-methyl-5-phenyl-3-thienyl-perfluorocyclopentene 5 [26] (2.4 g, 6.6 mmol) was added and the mixture was stirred for 2h at this temperature. The reaction mixture was extracted with diethyl ether and evaporated *in vacuo*, then purified by column chromatography (petroleum ether) to give MPMTH (2.1 g, 3.9 mmol), in 59.5% yield. The compound was recrystallized from chloroform/ hexane (v/v = 1/5) at room temperature and produced the crystals suitable for X-ray analysis. The structure of **MPMTH** was also confirmed by the melting point, elemental analysis, and NMR spectroscopy and IR. Mp: 114.6–115.7 °C. Anal. Calcd. for C₂₈H₂₀F₆S₂ (%): C, 62.91; H, 3.77; found: C, 63.03; H, 3.91. ¹⁹F NMR (376 MHz, CDCl₃, TMS): δ 109.97 (4F), 131.80 (2F). ¹H NMR (400 MHz, CDCl₃, TMS): δ 1.96 (s, 6H, -CH₃), 2.39 (s, 3H, -CH₃), 7.13

(s, 1H, thiophene-H), 7.29 (s, 1H, thiophene-H), 7.26–7.27 (m, 4H, J = 7.6 Hz, phenyl-H), 7.34–7.56 (m, 5H, J = 7.8 Hz, phenyl-H). ¹³C NMR (100 MHz, CDCl₃, TMS): δ 14.56, 21.43, 29.72, 122.20, 122.70, 125.60, 125.80, 127.90, 128.70, 129.00, 133.20, 138.70, and 142.20. IR (ν , cm⁻¹): 536, 692, 740, 757, 779, 837, 899, 986, 1054, 1110, 1137, 1192, 1265, 1336, 1440, 1605, and 2915.

2.3. Determination of the crystal structure of diarylethene *MPMTH*

Crystal data were collected by a Bruker P4 diffractometer equipped with graphite monochromatized Mo Ka radiation at room temperature. Unit cell was obtained and refined by 53 well centered reflections with $1.8^{\circ} < \theta < 17.4^{\circ}$. Data collection was monitored by three standards every 100 reflection collected. No decay was observed except the statistic fluctuation in the range of $\pm 4.8\%$. Raw intensities were corrected for Lorentz and polarization effect. Direct phase determination yielded the positions of all non-hydrogen atoms. All non-hydrogen atoms were subjected to anisotropic refinement. All hydrogen atoms were generated geometrically with C-H bond distances of 0.93-0.96 Å according to criteria described in the SHELXTL manual. They were included in the refinement with $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}(methyl)$ C). The final full-matrix least-square refinement on F^2 converged with $R_1 = 0.0645$ and $wR_2 = 0.1225$ for 2079 observed reflections $[I \ge 2\sigma(I)]$. The final difference electron density map shows no features. The crystallographic data obtained and experimental details employed were summarized in Table 1. Selected bond lengths (Å) and angles (°) were listed in Table 2. Further details on the crystal structure investigation have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 608148 for this paper. These data can be obtained free of charge via www.ccdc.can.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Centre, 12 Union

Table 1

Crystal data and structure refinen	nent
Empirical formula	C28H2

Empirical formula	$C_{28} \Pi_{20} \Gamma_6 S_2$	
Formula weight	534.56	
Temperature	295(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	<i>P</i> 2 ₁ / <i>n</i> (No. 14)	
Unit cell dimensions	$a = 11.956(2) \text{ Å} \alpha = 90.00^{\circ}$	
	$b = 9.2230(19) \text{ Å } \beta = 92.04(22)^{\circ}$	
	$c = 22.630(9) \text{ Å } \gamma = 90.00^{\circ}$	
Volume	2493.9(12) Å ³	
Ζ	4	
Density (calculated)	$1.424 \mathrm{g/cm^3}$	
Absorption coefficient	$0.274 \mathrm{mm^{-1}}$	
F(000)	1096	
Crystal size	$0.2 \times 0.3 \times 0.4 \text{ mm}$	
θ range for data collection	1.8–17.4°	
Limiting indices	-1 < h < 14, -10 < k < 4, -26 < l < 26	
Reflections collected	5573	
Unique reflections	4256 [R(int) = 0.0405]	
Refinement method	Full-matric least-squares on F^2	
Data/restraints/parameters	4256/10/366	
Goodness-of-fit on F^2	1.028	
Final <i>R</i> indices $[I > 2\delta(I)]$	$R_1 = 0.0645, \omega R_2 = 0.1225$	
R indices (all data)	$R_1 = 0.1430, \omega R_2 = 0.1693$	
Largest diff. peak and hole	0.461 and $-0.280 e \text{ Å}^{-3}$	

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Table 2

Selected bond length (Å) and angles (°)

S(1)-C(6)	1.717(2)	C(6)-S(1)-C(9)	93.25(10)
S(1)–C(9)	1.725(2)	F(4A)-C(4A)-F(3A)	107.8(2)
S(2)–C(18)	1.710(2)	C(5)-C(4A)-C(3)	103.52(18)
S(2)–C(21)	1.731(2)	C(3)-C(4B)-C(5)	104.2(2)
C(4A)-C(5)	1.526(3)	C(2)-C(1)-C(7)	128.99(19)
C (4A)–C(3)	1.527(3)	C(2)–C(1)–C(5)	111.15(17)
C(4B)–C(3)	1.517(4)	C(1)–C(2)–C(19)	131.17(18)
C(4B)–C(5)	1.522(4)	C(1)–C(2)–C(3)	109.52(17)
C(1)–C(2)	1.353(3)	C(2)-C(3)-C(4B)	107.21(19)
C(1)–C(5)	1.494(3)	C(2)-C(3)-C(4A)	105.79(16)
C(2)–C(3)	1.495(3)	C(1)-C(5)-C(4B)	105.67(19)
C(6)–C(7)	1.371(3)	C(1)-C(5)-C(4A)	105.72(16)
C(6)–C(16)	1.500(3)	C(6)-C(7)-C(1)	124.67(18)
C(9)–C(10)	1.477(3)	C(7)–C(6)–C(16)	130.61(18)
C(12)–C(17)	1.496(4)	C(8)–C(9)–C(10)	128.66(19)
C(18)–C(28)	1.501(3)	C(11)-C(12)-C(17)	120.1(3)

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3. Results and discussion

3.1. Photochromic properties of MPMTH in solution

Photochromic **MPMTH** underwent photochromism in solution. The absorption spectral change of **MPMTH** in hexane (C = 2.0×10^{-5} mol/L) by irradiation with 313 nm light was shown in Fig. 1. The absorption maximum of its colorless open-ring isomer (**MPMTH-o**) was observed at 278 nm (ε , 3.9×10^4 L mol⁻¹ cm⁻¹). Upon irradiation with 313 nm UV light, the colorless solution turned to blue with a new broad absorption band centered at 577 nm. The blue color is due to the formation of the closed-ring isomer



Fig. 1. Absorption spectral change of diarylethene **MPMTH** in hexane solution $(2.0 \times 10^{-5} \text{ mol/L})$ upon irradiation with 313 nm UV light.

(MPMTH-c). The conversion from MPMTH-o to **MPMTH-c** in the photostationary state under irradiation with 313nm light was 89%. The absorption coefficient of **MPMTH-c** at 577 nm was $1.9 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$. The blue color disappeared by irradiation with visible light $(\lambda > 450 \text{ nm})$. The coloration–decoloration cycle could be repeated more than 100 times and a clear isosbestic point was observed at 306 nm even after 100 times. All these results described above indicated that it owned good photochromic properties. The quantum yields of cyclization and cycloreversion reactions of MPMTH were determined by comparing the reaction yields of the diarylethene in hexane against diarylethene 1a in hexane at room temperature [11], and their values were 0.51 (278 nm) and 0.032 (577 nm), respectively. Compared with those of diarylethenes 1a and 2a, the cyclization quantum of MPMTH was appreciably larger than that of 1a ($\Phi = 0.46$) and less than that of 2a $(\Phi = 0.59)$, while the cycloreversion quantum yield of the diarylethene was remarkably larger than those of diarylethenes 1a and 2a ($\Phi = 0.015$ and 0.013, respectively) [11]. The molar absorption coefficients, both open-ring and closedring forms, of diarylethene MPMTH were much higher than those of diarylethenes 1a and 2a [11,26]. The methyl group at meta-position of the benzene of diarylethene increased significantly the cycloreversion quantum yield and the molar absorption coefficient.

3.2. Relationship between crystal structure and photochromic properties

Final structural confirmation of diarylethene **MPMTH** was provided by X-ray crystallographic analysis. Its structure features was shown in Fig. 2 and a packing diagram was shown in Fig. 3. As shown in Fig. 2, the molecule occupied approximately in C_2 symmetry, and it was packed in a photoactive *anti*-parallel conformation in the crystal-line phase, which can undergo photocryclization reaction [28]. It was found that the methyl group substitutes randomly to the benzene rings of both wings of each molecule. They were named as C17 and C29 and their occupancies



Fig. 2. ORTEP drawings of crystal MPMTH. The ellipsoids were drawn at 35% probability level.



Fig. 3. A packing views along the b direction.

were assigned to be 0.5 in the final refinement according to the refinement of occupancy before [29]. The conformation of perfluorocyclopentene ring is an envelope and the C4 atom is disordered which was named as C4A and C4B. Therefore, the two fluorine atoms of C4 are split to two sets named as F3A, F3B and F4A, F4B. The occupancies for the different conformations were refined to be 0.720(2): 0.280(2). The dihedral angles between the least-squares plane of the central perfluorocyclopentene ring and the two thiophene rings, S1/C6–C9 and S2/C18–C21, are 44.5(1)° and 42.0(1)°, respectively. The dihedral angle between the thiophene ring and adjacent benzene ring is 3.6(3)° for the C10–C15 benzene ring and 26.0(3)° for the C22–C27 benzene ring.

In the perfluorocyclopentene ring of **MPMTH**, distances of C1–C2, C2–C3, C3–C4A, C4A–C5 and C1–C5 are 1.353(3)Å, 1.495(3)Å, 1.527(3)Å, 1.526(3)Å and 1.494(3)Å, respectively. These data clearly indicate that the C1–C2 bond is a double bond, being significantly shorter than the other carbon-carbon single bonds. Two justly symmetrical thio-

phene moieties were linked by the C1=C2 double bond, with both of them attached to the ethylene group via the 3-position. The two methyl groups located on different sides of the double bond, reflected in the torsion angles C1-C2-C19-C18 [42.0(3)°] and C2-C1-C7-C6 [43.5(3)°], and thus trans with respect to the double bond. Such a conformation is crucial to the photochromic and photo-induced properties of such materials [30]. The intramolecular distance between the two reactive C atoms (C6…C18) is 3.537(3)Å. The value is in between those of diarylethenes 1a and 2a (they are 3.96 Å for 1a and 3.51 Å for 2a) [16,31]. The crystal can be expected to undergo photochromism to generate the closed isomer of diarylethene MPMTH (MPMTH-c) (see Scheme 1), because photochromic reactivity usually appears when the distance between the reactive C atoms is less than 4.2 Å and the molecule is fixed in an anti-parallel mode [32-34]. It is well known that the absorption spectrum and color are dependent on the substituent effects and the π -conjugation length in molecule. The arrangement described above was very beneficial to form the extended π -conjugation. After irradiation with UV light, the π -conjugation extended throughout the whole molecule, and the UV-vis absorption spectra displayed drastic changes resulting in displaying remarkable different color.

In fact, crystal of **MPTHP** showed photochromic reaction coincident with the theoretical analysis. Upon irradiation with 313 nm light, the colorless crystal of **MPMTH-o** turned to blue quickly. When the blue crystal was dissolved in hexane, the solution turned to blue, and the absorption maximum was observed at 577 nm, which was the same as that of the closed-ring isomer **MPMTH-c**. The blue color disappeared upon irradiation with appropriate wavelength visible light and the absorption spectrum of the solution containing the colorless crystal was the same as that of the open-ring isomer **MPMTH-o**.

3.3. Fluorescence properties of **MPMTH**

The fluorescence properties in the solution of the compound were measured using a Hitachi F-4500 spectrophotometer, and the breadths of excitation and emission slit were selected 5.0 nm. Fig. 4 shows the fluorescence spectral



Fig. 4. Fluorescence spectra changes of **MPMTH** in hexane at $c = 1.0 \times 10^{-5}$ mol/L and room temperature, excited at 280 nm.

changes of **MPMTH-o** in hexane $(c = 1.0 \times 10^{-5} \text{ mol/L})$ at room temperature upon irradiation with 313 nm light. As shown in this figure, it can be clearly seen that the hexane of MPMTH-o exhibits relatively strong fluorescence at 310 nm when excited at 280nm. Solution fluorescence spectroscopy at different irradiation times shows that the fluorescence intensity in the range of 295-400 nm decreases with increasing the exposal time upon irradiation with 313 nm UV light (Fig. 4). This phenomenon verified that MPMTH has good photochromic properties in solution. Along with the photochromism from open-ring isomers MPMTH-o to closedring isomers MPMTH-c upon irradiation with 313 nm light, the fluorescence intensity decreased dramatically, and the photostationary state showed relatively weak fluorescence. The closed-ring isomers MPMTH-c showed almost no fluorescence. It had been reported that this kind of diarylethenes which showed fluorescence in the open-ring isomer and showed no fluorescence or weak fluorescence in the closedring isomer could be potentially applied to optical memory with fluorescence readout method [35].

The concentration dependence of fluorescence emission spectra was measured in hexane solution at room temperature, as shown in Fig. 5. When the concentration of diarylethene **MPMTH** in hexane increased from 5.0×10^{-6} to 1.0×10^{-4} mol/L, the maximum emission arose from 329 to 360 nm when excited at 290 nm, and the relative fluorescence intensity decreased dramatically. The hexane solution showed no fluorescence when the concentration increased to 1.0×10^{-3} mol/L. Therefore, the fluorescence spectra of **MPMTH-o** showed remarkable concentration dependence. It showed a systematic red shift and the fluorescence intensity decreased that molecular aggregation and fluorescence quench take place due to concentration increasing [36].

3.4. Electrochemical properties of MPMTH

The electrochemical properties of diarylethene are being used for molecular switching and also can be potentially



Fig. 5. Fluorescence emission spectra of **MPMTH** in various concentrations in hexane solution at room temperature, monitored at 290 nm.



Fig. 6. The anodic polarization curves of diarylethene MPMTH.

applied to molecular-scale electronic switches [37]. The oxidative cyclization and cycloreversion of diarylethenes have been reported [38–40]. In order to investigate the electrochemical properties of diarylethene MPMTH, we performed electrochemical examinations by linear sweep method. Experimental method and condition were described in Ref. [37]. The typical electrolyte was acetonitrile (5 ml)containing 0.10 mol/L LiClO₄ and 4.0×10^{-3} mol/L diarylethene **MPMTH**. The solution was deaerated by a dry argon stream and maintained at a slight argon overpressure during electrochemical experiments. Fig. 6 showed the anodic polarization curves of MPMTH-o and MPMTH-c on Platinum electrode. It can be clearly seen from Fig. 6 that the oxidation of MPMTH-o and **MPMTH-c** was initiated at 0.52 and 0.38 V, respectively. The oxidation potential onset of closed-ring from (MPMTH-c) is lower than that of open-ring form (MPMTH-o), and the oxidation potential difference between **MPMTH-o** and **MPMTH-c** was 0.14 V. This is in accordance with the theory that longer conjugation length generally leads to less positive potentials, with the addition of each heterocycle [41]. During the cyclization reaction, the π -conjugation length of **MPMTH-c** was much longer than that of **MPMTH-o**. Thus the oxidation onset of **MPMTHc** was much lowered than that of **MPMTH-o**. In addition, three oxidation processes can be easily seen during anodic oxidation of **MPMTH-o** and **MPMTH-c**, indicating that the anodic oxidation processes may involve the oxidation of thiophene ring, benzene ring, together with the methylbenzene ring of this compound.

4. Conclusions

In conclusion, a new diarylethene presented here were synthesized and its structure was established by X-ray crystallographic analysis. The compound exhibited reversible photochromism both in solution and in the crystalline phase and exhibited relatively strong fluorescence at 310 nm when excited at 280 nm. The molecules of **MPMTH** adopt a photoactive anti-parallel in the single crystalline phase, and the distance between the two reactive C atoms is 3.537(3) Å. The irreversible anodic oxidation of **MPMTH** in acetonitrile containing LiClO₄ as the supporting electrocyte was initialed at 0.52 V.

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