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# Synthesis, crystal structure and characterization of photochromic 1,2-bis{2-ethyl-5-[2-(1,3-dioxolane)]-3-thienyl}perfluorocyclopentene

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## Abstract

A novel photochromic diarylethene, 1,2-bis{2-ethyl-5-[2-(1,3-dioxolane)]-3-thienyl}perfluorocyclopentene (BEDTP), was synthesized and its structure was determined by single-crystal X-ray diffraction analysis. Its photochromic and fluorescent properties were also investigated. The results showed that this compound exhibited reversible photochromism, changing from colorless to magenta after irradiation with UV light both in solution and in the crystalline phase. In hexane solution, the open-ring isomer of BEDTP exhibited relatively strong fluorescence at 400 nm when excited at 282 nm. The fluorescence intensity decreased along with the photochromism upon irradiation with 254 nm light and its closed-ring isomer showed almost no fluorescence.

*Keywords:* Diarylethene; Crystal structure; Photochromism; Fluorescence

## 1. Introduction

Photochromism is referred to as a photoisomerization process between two isomers having different absorption spectra [1]. Generally, photochromic compounds are classified into two categories, i.e., thermally reversible compounds and thermally irreversible compounds [2,3]. Although various types of photochromic compounds have been reported to date [4–6], compounds that undergo thermally irreversible photochromic reactions are limited to diarylethenes [4,5,7], fulgides [8,9] and phenoxynaphthacenequinones, etc. [10,11]. Among these photochromic stable compounds, diarylethene derivatives bearing two thiophene-derived groups are the most promising because of their excellent thermal stability in both isomers, remarkable fatigue resistance, and rapid response and high reactivity in the solid state [4,12–14].

Upon photoirradiation, diarylethene derivatives can undergo cyclization/cycloreversion photochromic reactions either in solution or in the solid state. In solution, the open-ring isomer of diarylethene has two interconverting conformations, *anti*-parallel and parallel ones, in almost equal amounts. Only *anti*-parallel conformers can undergo effective photocyclization reaction by a conrotatory mechanism according to the Woodward–Hoffmann rule, while the parallel conformers are photochemically inactive [15,16]. The photogenerated closed-ring isomers of diarylethenes showed some colors with broad absorption bands in the visible region, and they could regenerate their open-ring isomers on irradiation with appropriate wavelength visible light. The absorption maxima of closed-ring isomers are known to depend on the π-conjugate length of the aryl groups. In fact, the longer π-conjugated systems were introduced into the molecule of diarylethene, the longer absorption wavelengths of the closed-ring isomers were observed.

Diarylethene crystals belong to a unique class of photochromic crystals, which exhibit thermally stable and fatigue resistant photochromic performance [17]. In the crystalline phase, there is no interconversion such as in solution between the two conformers of diarylethenes and the molecules are regularly oriented in a fixed conformation [18], except for one example where there are two independent molecules with different conformations in the asymmetric unit [19]. Diarylethene crystals in the *anti*-parallel conformation 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 ther-

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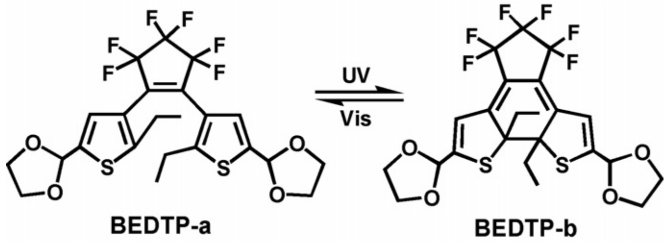


Scheme 1. Photochromism of diarylethene BEDTP.

mal stability and remarkable fatigue resistance [20]. Therefore, investigation of diarylethene crystals have attracted much attention today, and a larger number of diarylethene crystal structures and their properties have already been reported [17,20–22].

By far, many diarylethene compounds and their photochemical/photophysical properties have been reported [4,5,23]. Diarylethenes bearing dioxoane groups on the end are of special interest because the dioxoane group is an electron-donating substituent, which can be effective to increase the absorption coefficient and to decrease the ring-opening quantum yield [24]. The other merit of dioxoane substituent is that it can be easily hydrolyzed to formyl group, which can be changed further to many other functional groups by some simple reactions [25–27]. In this paper, on the basis of this idea, a novel photochromic diarylethene with dioxoane groups on the end, 1,2-bis{2-ethyl-5-[2-(1,3-dioxolane)]-3-thienyl}perfluorocyclopentene (BEDTP, shown in Scheme 1), was developed which exhibited good photochromism both in solution and in the crystalline phase. In addition, its X-ray crystal structure, photochromic and fluorescent properties were also presented here.

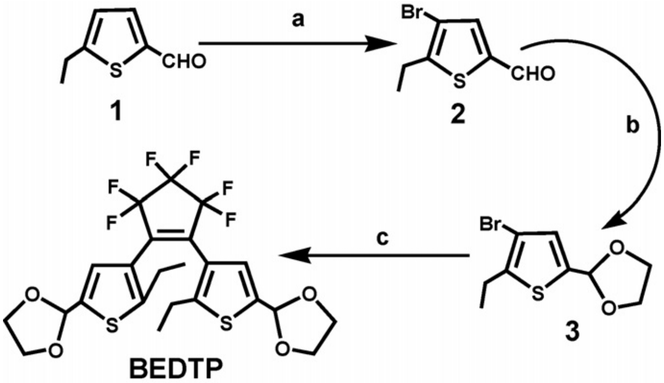
## 2. Experimental

### 2.1. General methods

$^1$H NMR and $^{19}$F NMR spectra were recorded on Bruker AV400 (400 MHz) spectrometer with $CDCl_3$ as the solvent and tetramethylsilane as an internal standard. Elemental analysis was performed on a Yanaco CHN C ORDER MT-3 apparatus. Fourier transform infrared (FT-IR) spectra were measured from KBr pellets using a Bruke (Vertex 70) system. The absorption spectra were measured using a PerkinElmer 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. The X-ray experiment of the single-crystal was performed on a Bruker P4 diffractometer equipped with graphite monochromatized Mo Kα radiation at room temperature (295 ± 2 K).

### 2.2. Synthesis of BEDTP

The synthesis method of diarylethene BEDTP was described in Scheme 2 and experimental details were carried out as following.



Scheme 2. Regents and conditions: (a) $Br_2$, $CH_3COOH$, r.t., 20 h, 73.3%; (b) glycol, *p*-toluene sulfolic acid, benzene, reflux, 16 h, 84.0%; (c) *n*-BuLi, THF, −78 °C, $C_5F_8$, 3 h, 57.7%.

#### 2.2.1. Synthesis of 3-bromo-2-ethyl-5-formylthiophene **2**

To a stirred solution of 5-ethylthiophene-2-carbaldehyde **1** (2.0 g, 14.3 mmol) in acetic acid was added dropwise an acetic acid solution of $Br_2$ at room temperature. Stirring was continued for 16 h at the temperature. Then the reaction was stopped by the addition of water. The reaction mixture was neutralized by $Na_2CO_3$ to neutrality. The product was extracted with ether, dried, filtrated, evaporated and obtained in 73.3% yield as yellow oil. $^1$H NMR (400 MHz, $CDCl_3$, TMS): $\delta$ 1.316–1.354 (t, 3H, $J = 7.6$ Hz, $-CH_3$), 2.839–2.895 (q, 2H, $J = 7.6$ Hz, $-CH_2$), 7.608 (s, 1H, thiophene-H), 9.789 (s, 1H, –CHO).

#### 2.2.2. Synthesis of 3-bromo-2-ethyl-5-(1,3-dioxolane) thiophene **3**

Compound **2** (2.28 g, 10.4 mmol), glycol (2 mL, 58.5 mmol), and *p*-toluenesulfonic acid (0.05 g) were dissolved in benzene (200 mL). Under the Dean-Stark condition, the reaction mixture was refluxed overnight, and then washed with $NaHCO_3$ (5% (w/v), 2 × 50 mL) aqueous. The combined benzene layers were dried, filtered and evaporated in vacuum to yield acetal **3** as a yellow oil (84.0%). $^1$H NMR (400 MHz, $CDCl_3$, TMS): $\delta$ 1.246–1.284 (t, 3H, $J = 7.6$ Hz, $-CH_3$), 2.7496–2.806 (q, 2H, $J = 7.6$ Hz, $-CH_2$), 3.968–4.022 (t, 2H, $J = 7.2$ Hz, $-CH_2$), 4.093–4.147 (t, 2H, $J = 7.2$ Hz, $-CH_2$), 6.006 (s, 1H, –CH), 6.976 (s, 1H, thiophene-H).

#### 2.2.3. Synthesis of 1,2-bis{2-ethyl-5-[2-(1,3-dioxolane)]-3-thienyl}perfluorocyclopentene BEDTP

To a stirred solution of **3** (2.296 g, 8.73 mmol) in THF was added dropwise a 2.5 mol/L *n*-BuLi (3.5 mL; 8.75 mmol) at −78 °C under nitrogen atmosphere. Stirring was continued for 30 min, perfluorocyclopentene (0.59 mL; 4.36 mmol) was slowly added to the reaction mixture, and the mixture was stirred for 2.5 h at −78 °C. The reaction was stopped by the addition of water. The product was extracted with ether. The organic layer was washed sequentially by 1.0 mol/L HCl aqueous solution and water. The organic layer was dried over $MgSO_4$, filtrated and evaporated. The crude product was purified by column chromatography on $SiO_2$ using $CHCl_3$ as the eluent and 1.2 g of BEDTP obtained in 57.7% yield. The compound crystallized from chloroform/hexane (v/v = 1/2) at room temperature and produced the crystals suitable for X-ray analysis. Mp: 127.6–127.4 °C; Anal. Calcd for $C_{23}H_{22}F_6O_4S_2$ (%); Found (calcd): C, 51.11; H, 4.10. Found: C, 51.23; H, 4.20. $^{19}$F NMR (400 MHz, $CDCl_3$, TMS): $\delta$ 110.48 (4F), 131.94 (2F). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 0.924–0.961 (t, 6H, $J = 7.8$ Hz, $-CH_3$), 2.192–2.248 (q, 4H, $J = 7.5$ Hz, $-CH_2$), 4.002–4.036 (t, 4H, $J = 6.8$ Hz, $-CH_2$), 4.101–4.136 (t, 4H, $J = 7.0$ Hz, $-CH_2$), 6.021 (s, 2H, –CH), 7.094 (s, 2H, thiophene-H). IR (KBr): $\nu$ 1081, 1131, 1274, 1566 and 2976 cm$^{-1}$.

### *2.3. Determination of the crystal structure of diarylethene BEDTP*

Crystal data were collected by a Bruker P4 diffractometer equipped with graphite monochromatized Mo Kα radiation at room temperature. Unit cell was obtained and refined by 24 well centered reflections with $4.8^\circ < \theta < 12.5^\circ$. Data collection was monitored by three standards every 100 reflection collected. No decay was observed except the statistic fluctuation in the range of ± 4.2%. Raw intensities were corrected for Lorentz and polarization effects. Direct phase determination yielded the positions of all non-hydrogen atoms. Hydrogen atoms were generated theoretically and ridden on their parent atoms in the final refinement. All non-hydrogen atoms were subjected to anisotropic refinement. The final full-matrix least-square refinement on $F^2$ converged with $R_1 = 0.0653$ and $wR_2 = 0.1201$ for 3377 observed reflections $[I \geq 2\sigma(I)]$. 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 274837 for this paper. These data can be obtained free of charge via http://www.ccdc.can.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Centre, 12 Union Road, Cambridge CB21EZ, UK [fax: (+44) 1223 336033; e-mail: deposit@ccdc.cam.ac.uk]).

## 3. Results and discussion

### *3.1. Photochromic properties of BEDTP in solution*

The photochromic behavior of BEDTP was investigated and its absorption spectra and color changes in hexane solution ($C = 5.0 \times 10^{-5}$ mol/L) were shown in Fig. 1. The absorption maximum of its colorless open-ring isomer (BEDTP-a) was observed at 238 nm. Upon irradiation with 254 nm UV light, the colorless solution turned to magenta with a new broad absorption band centered at 542 nm. This can be assigned to the formation of the closed-ring isomer (BEDTP-b), as shown in Fig. 1(a). The magenta colored solution of BEDTP-b returned to colorless upon irradiation with visible light ($\lambda > 510$ nm). This indicates that BEDTP-b returned to the initial open-ring form which the absorption maximum was observed at 238 nm. Their solution color changes upon UV light irradiation were

Table 1
Crystal data and structure refinement

| | |
|---|---|
| Empirical formula | $C_{23}H_{22}F_6O_4S_2$ |
| Formula weight | 540.53 |
| Temperature | 295(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Monoclinic |
| Space group | $P2_1/n$ (no. 14) |
| Unit cell dimensions | $a = 13.353(2)$ Å, $\alpha = 90.00^\circ$ |
| | $b = 13.370(2)$ Å, $\beta = 96.796(11)^\circ$ |
| | $c = 13.600(3)$ Å, $\gamma = 90.00^\circ$ |
| Volume | 2411.0(8) Å$^3$ |
| $Z$ | 4 |
| Density (calculated) | 1.489 g/cm$^3$ |
| Absorption coefficient | 0.296 mm$^{-1}$ |
| $F$ (0 0 0) | 1112 |
| Crystal size | 0.4 mm × 0.5 mm × 0.5 mm |
| $\theta$ range for data collection | 4.8–12.5° |
| Limiting indices | $-1 < h < 8$, $-9 < k < 9$, $-11 < l < 11$ |
| Reflections collected | 5323 |
| Unique reflections | 4231 [$R$(int) = 0.0255] |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data/restraints/parameters | 4231/14/323 |
| Goodness-of-fit on $F^2$ | 1.027 |
| Final $R$ indices $[I > 2\delta(I)]$ | $R_1 = 0.0653$, $wR_2 = 0.1201$ |
| $R$ indices (all data) | $R_1 = 0.0778$, $wR_2 = 0.1265$ |
| Largest diff. peak and hole | 1.033 and −0.742 e Å$^{-3}$ |

Table 2
Selected bond length (Å) and angles (°)

| | |
|---|---|
| S(1)–C(18) | 1.719(4) |
| S(1)–C(15) | 1.727(4) |
| F(3)–C(3) | 1.513(7) |
| F(3′)–C(3) | 1.533(8) |
| F(4)–C(3) | 1.252(6) |
| F(4′)–C(3) | 1.207(9) |
| O(1)–C(10) | 1.408(5) |
| O(2)–C(12) | 1.398(6) |
| C(1)–C(5) | 1.339(5) |
| C(1)–C(7) | 1.468(5) |
| C(1)–C(2) | 1.506(5) |
| C(2)–C(3) | 1.489(6) |
| C(3)–C(4) | 1.503(6) |
| C(4)–C(5) | 1.497(5) |
| C(6)–C(13) | 1.504(6) |
| C(13)–C(14) | 1.480(7) |
| C(18)–S(1)–C(15) | 92.58(15) |
| C(11)–O(1)–C(10) | 107.7(4) |
| C(5)–C(1)–C(2) | 110.6(3) |
| F(4′)–C(3)–C(2) | 128.8(8) |
| F(4)–C(3)–C(2) | 120.4(6) |
| F(4′)–C(3)–C(4) | 120.6(7) |
| F(4)–C(3)–C(4) | 125.3(6) |
| F(4)–C(3)–F(3) | 96.7(6) |
| C(2)–C(3)–F(3) | 99.0(5) |
| C(4)–C(3)–F(3) | 101.9(4) |
| F(4′)–C(3)–F(3′) | 97.8(7) |
| C(2)–C(3)–F(3′) | 96.4(5) |
| C(4)–C(3)–F(3′) | 94.9(5) |
| C(1)–C(5)–C(4) | 110.9(3) |
| O(1)–C(11)–C(12) | 107.4(4) |
| C(14)–C(13)–C(6) | 115.4(4) |

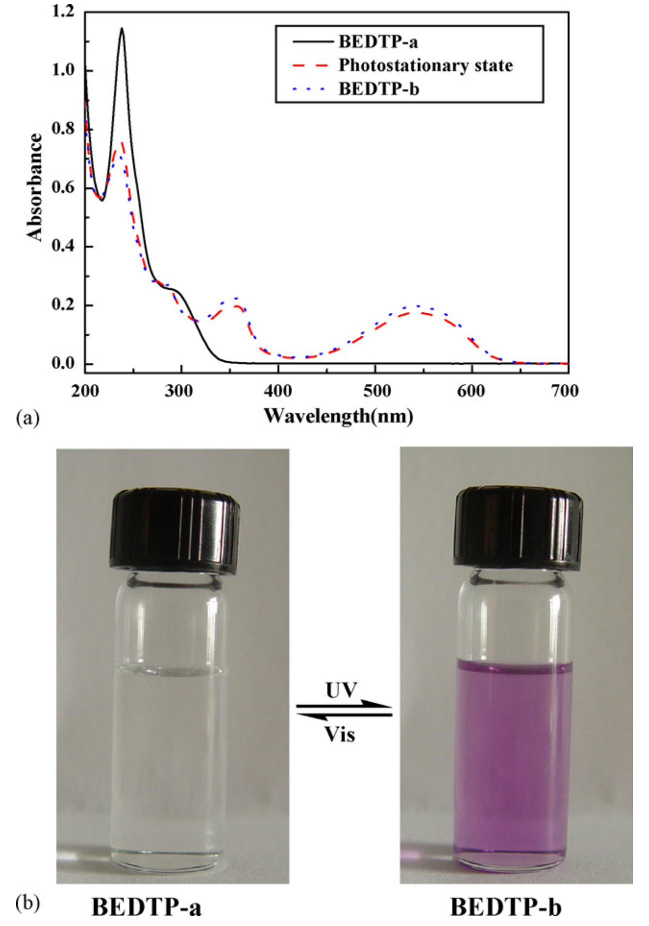


Fig. 1. Absorption spectra and color changes of diarylethene BEDTP in hexane solution ($5.0 \times 10^{-5}$ mol/L). (a) Absorption spectra: open-ring form (BEDTP-a, solid line), closed-ring form (BEDTP-b, dot line), and in the photostationary state (dash line) upon irradiation with 254 nm UV light; (b) color changes before and after UV irradiation.

shown in Fig. 1(b). The coloration–decoloration cycle could be repeated more than 20 times and a clear isosbestic point was observed at 314 nm even after 20 times. All these results described above indicated that it owned good photochromic properties. The quantum yields of cyclization and cycloreversion reactions of BEDTP were determined by comparing the reaction yields of the diarylethene in hexane against 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene in hexane at room temperature [28], and their values were 0.362 (254 nm) and 0.024 (510 nm), respectively.

### *3.2. Relationship between crystal structure and photochromic properties*

Final structural confirmation of diarylethene BEDTP was provided by X-ray crystallographic analysis. Its structure features were shown in Fig. 2 and a packing diagram was shown in Fig. 3 [18]. As shown in Fig. 2, the molecule occupied approximately in $C_2$ symmetry, and it was packed in a photoactive *anti*-parallel conformation in crystal, which can undergo photocyclization reaction [29]. It was found that the perfluorocyclopentene is planar which is the average of two envelope conformations so that two fluorine atoms of C(3) are split to two sets named as F(3), F(4) and F(3′), F(4′). The molecule has five planar ring, including one perfluorocyclopentene ring, two thiophene rings and two 1,3-dioxoane rings. So, they can form four dihedral angles between every two adjacent rings. The dihedral angle between perfluorocyclopentene ring and the left thiophene ring is 56.3(1)°, and that of between the perfluorocyclopentene ring and the right thiophene ring is 49.0(2)°. The dihedral angle between C10–O1–C11–C12–O2 and C6–C7–C8–C9–S2 plane is 79.9(2)°, and that between C19–O3–C20–C21–O4 and C15–C16–C17–C18–S1 plane is 84.0(2)°.

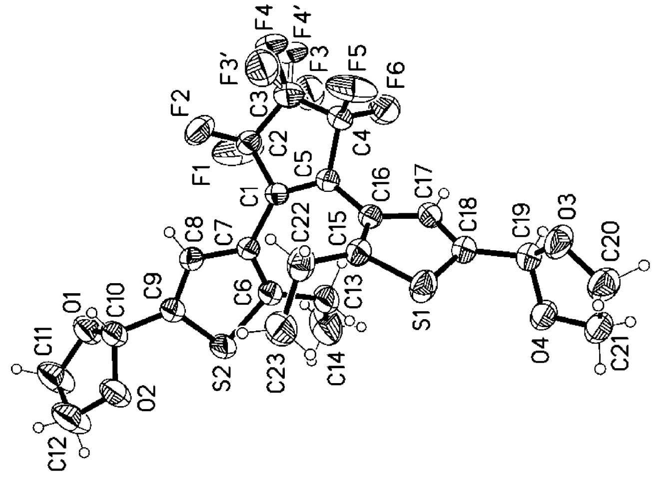


Fig. 2. ORTEP drawings of crystal BEDTP. The ellipsoids were drawn at 35% probability level.

In the perfluorocyclopentene ring of BEDTP-a, distances of C1–C2, C2–C3, C3–C4, C4–C5 and C1–C5 are 1.506(5), 1.489(6), 1.503(6), 1.497(5) and 1.339(5) Å, respectively. These data clearly indicate that the C1–C5 bond is a double bond, being

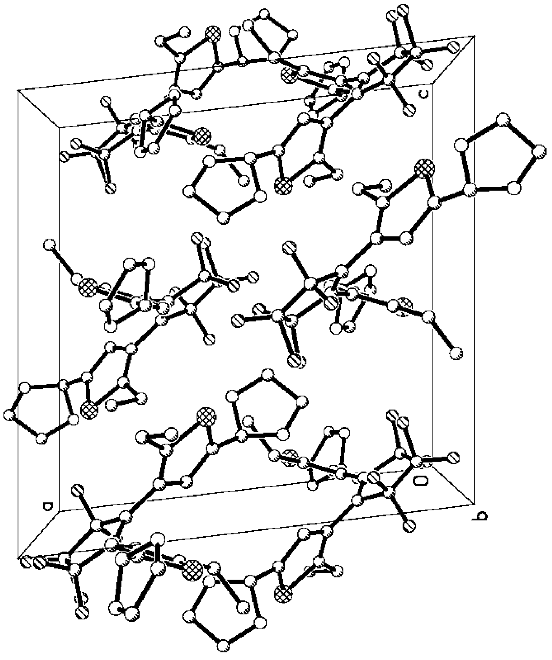


Fig. 3. A packing views along the *b* direction.

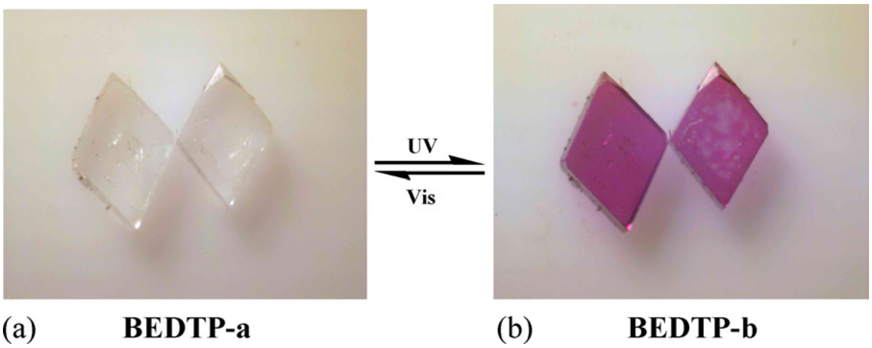


Fig. 4. Photographs of photochromic process of BEDTP in crystalline phase.

significantly shorter than the other carbon–carbon single bonds. Two justly symmetrical thiophene moieties were linked by a double bond C1–C5. The two-ethyl groups located on different sides of the double bond and *trans*-direction of the thiophene planes. This kind conformation was crucial to its photochromic and photoinduced properties [15]. The distance of C6–C15 is 3.828(6) Å, which is short enough theoretically for the reaction to take place in the crystalline phase [30]. 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 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.

As a mater of fact, crystal of BEDTP showed photochromic reaction coincident with the theoretical analysis. Their color changes upon photo-irradiation are shown in Fig. 4. Upon irradiation with 254 nm light, the colorless crystal of BEDTP-a turned to magenta quickly. When the magenta crystal was dissolved in hexane, the solution turned to magenta, and the absorption maximum was observed at 542 nm, which was the same as that of the closed-ring isomer BEDTP-b shown in Fig. 1. Unfortunately, the crystal structure of BEDTP-b could not be given because it returned easily to BEDTP-a under the condition of experiment. The magenta color disappeared upon irradiation with 510 nm light and the absorption spectrum of the solution containing the colorless crystal was the same as that of the open-ring isomer BEDTP-a. Comparing the two photographs shown in Fig. 4, it clearly showed that the photochromic process had taken place in BEDTP crystalline phase upon irradiation with UV and visible light. Furthermore, the diarylethene crystals exhibited many times of coloration/decoloration cycles by alternate irradiation with UV and visible light. So, the crystals of diarylethene BEDTP will be good candidates for optoelectronic applications [17].

### 3.3. Fluorescence properties of BEDTP

Fluorescent properties can be useful not only for tracking individual molecules within a microenvironment, but also in molecular-scale optoelectronics [31]. To date, many diarylethene derivatives and their fluorescent properties have been reported [32–36]. In this work, the fluorescence properties in the solution of the title compound were measured using a Hitachi F-4500 spectrophotometer, and the breadths of excitation and emission slit were selected 5.0 nm. The fluorescence excitation and emission spectra of BEDTP-a in hexane ($C = 1.0 \times 10^{-4}$ mol/L) at room temperature was illustrated in Fig. 5. From this figure, one can clearly see that the hexane of BEDTP exhibited relatively strong fluorescence at 400 nm when excited at 282 nm. The Stokes shift of the fluorescence was relatively large and the fluorescence spectral edge showed a red-shift in comparison with the absorption edge. This kind of large Stokes shift has already been discussed in detail by Sekiya and co-workers [6].

The concentration dependence of fluorescence emission spectra was measured in hexane solution at room temperature, and it was exhibited that the fluorescence intensity held the maximum value when the concentration of BEDTP was $1.0 \times 10^{-4}$ mol/L. So, we used this optimal concentration solution to investigate its fluorescence spectral changes upon irradiation with 254 nm UV light, and the results were shown in Fig. 6, and inset figure showed the relationships between −log(int) and the exposal time upon irradiation with 254 nm

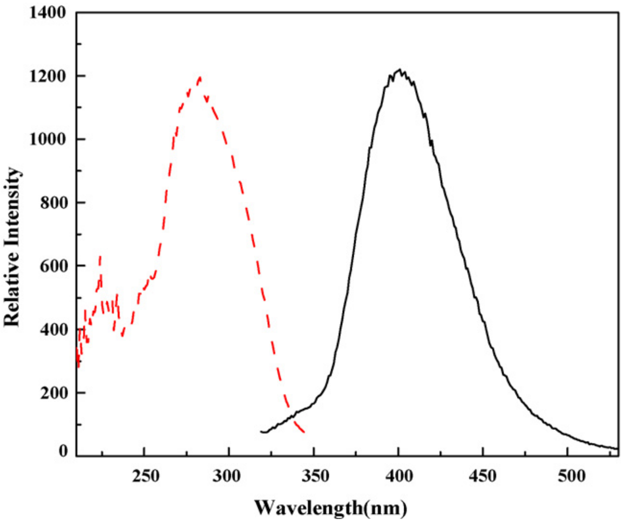


Fig. 5. Excitation spectra(dash line) and fluorescence spectra (solid line) of BEDTP-a in hexane ($1.0 \times 10^{-4}$ mol/L) at room temperature.

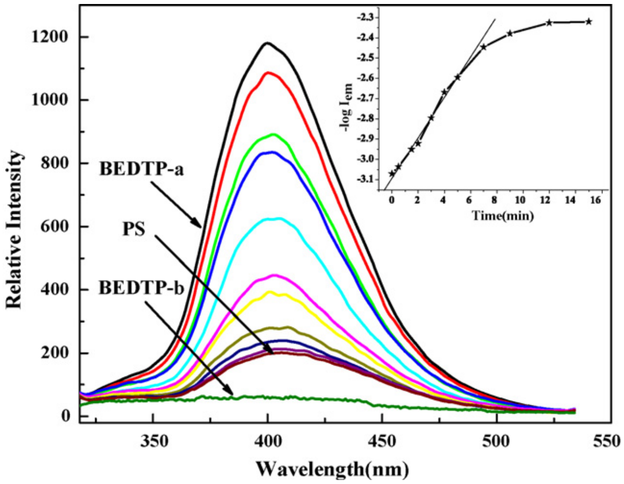


Fig. 6. Change in the intensity of the fluorescence spectra of BEDTP in hexane solution ($1.0 \times 10^{-4}$ mol/L) upon irradiation with 254 nm light at room temperature, excited at 282 nm. Inset figure shows the relationships between −log(int) and the exposal time upon irradiation with 254 nm UV light.

UV light. From this figure, it can be easily found that BEDTP-a exhibited relatively strong fluorescence at 400 nm. However, along with the photochromism from open-ring isomers BEDTP-a to closed-ring isomers BEDTP-b upon irradiation with 254 nm light, the fluorescence intensity decreased dramatically and −log(int) and the exposal time showed good linearity at the first 6 min, and the photostationary state (PS) showed weak fluorescence. The closed-ring isomers BEDTP-b showed almost no fluorescence. This fluorescent characteristics which use external photostimulation to switch the fluorescence on and off from open-ring isomers to closed-ring isomers is similar to those of some other diarylethene compounds reported [37,38]. 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 closed-ring isomer could be potentially applied to optical memory with fluorescence readout method and fluorescence modulation switches [4,14,38,39].

## 4. Conclusions

In summary, the diarylethene described here has been first synthesized and its structure was confirmed by X-ray crystallographic analysis. The compound took on good photochromic behavior both in solution and in crystalline phrase. The open-ring isomers of the diraylethene exhibited relatively strong fluorescence and the fluorescence intensity decreased upon irradiation with 254 nm light, and its closed-ring isomers showed on fluorescence. So, it can be potential to use as an optical recording material possessing fluorescence readout.

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## References

[1] H. Dürr, H. Bouas-Laurent, Photochromism: Molecules and Systems, Elsevier, Amsterdam, 1990.
[2] M. Irie, M. Mohri, J. Org. Chem. 53 (1988) 803.
[3] T. Kaieda, S. Kobatake, H. Miyasaka, M. Murakami, N. Iwai, Y.I. Nagata, A. Itaya, M. Irie, J. Am. Chem. Soc. 124 (2002) 2015.
[4] M. Irie, Chem. Rev. 100 (2000) 1685.
[5] T. He, S.-J. Yang, Chem. Soc. Rev. 33 (2004) 85.
[6] N. Tanaka, Ch. Okabe, K. Sakota, T. Fukaminato, T. Kawai, M. Irie, A. Goldberg, S. Nakamura, H. Sekiya, J. Mol. Struct. 616 (2002) 113.
[7] M. Irie, S. Kobatake, M. Horichi, Science 291 (2001) 1769.
[8] R. Matsushima, H. Sakaguchi, J. Photochem. Photobiol. A: Chem. 108 (1997) 239.
[9] Y. Yokoyama, Chem. Rev. 100 (2000) 1717.
[10] Z. Fang, S.-Z. Wang, Z.-F. Yang, B. Chen, F.-T. Li, J.-Q. Wang, S.-X. Xu, Z.-J. Jiang, T.-R. Fang, J. Photochem. Photobiol. A: Chem. 88 (1995) 23.
[11] A.J. Myles, N.R. Branda, J. Am. Chem. Soc. 123 (2001) 177.
[12] N. Tamai, T. Saika, T. Shimidzu, M. Irie, J. Phys. Chem. 100 (1996) 4689.
[13] S. Kobatake, K. Uchida, E. Tsuchida, M. Irie, Chem. Commun. (2002) 2804.
[14] K. Matsuda, M. Irie, J. Photochem. Photobiol. C: Photochem. Rev. 5 (2004) 169.
[15] R.B. Woodward, R. Hoffmann, The Conservation of Orbital Symmetry, Verlag Chemie, GmbH, Weinheim, Germany, 1970.
[16] S. Nakamura, M. Irie, J. Org. Chem. 53 (1988) 6136.
[17] M. Morimoto, S. Kobataka, M. Irie, Chem. Rec. 4 (2004) 23.
[18] S.-Z. Pu, T.-S. Yang, R.-J. Wang, J.-K. Xu, Acta Cryst. C61 (2005) o568.
[19] S. Kobatake, Y. Matsumoto, M. Irie, Angew. Chem. Int. Ed. 44 (2005) 2148.
[20] S. Kobatake, M. Irie, Bull. Chem. Soc. Jpn. 77 (2004) 195.
[21] K. Matsuda, M. Irie, J. Photochem. Photobiol. C 5 (2004) 169.
[22] M. Morimoto, M. Irie, Chem. Commun. (2005) 3895.
[23] S.-Z. Pu, T.-S. Yang, J.-K. Xu, L. Shen, G.-Z. Li, Q. Xiao, B. Chen, Tetrahedron 61 (2005) 6623.
[24] M. Irie, K. Sakemura, M. Okinaka, K. Uchida, J. Org. Chem. 60 (1995) 8305.
[25] S.-Z. Pu, F.-S. Zhang, F. Sun, R.-J. Wang, X.-H. Zhou, S.-K. Chan, Tetrahedron Lett. 44 (2003) 1011.
[26] S.-Z. Pu, F.-S. Zhang, R.-J. Wang, Q. Liang, Acta Crystallogr. C60 (2004) o305.
[27] S.-Z. Pu, L. Shen, J.-K. Xu, R.-J. Wang, Q. Xiao, G. Liu, Z. Kristallogr. NCS 219 (2004) 473.
[28] M. Irie, T. Lifka, S. Kobatake, N. Kato, J. Am. Chem. Soc. 122 (2000) 4871.
[29] T. Yamada, S. Kobatake, K. Muto, M. Irie, J. Am. Chem. Soc. 122 (2000) 1589.
[30] V. Ramamurthy, K. Venkatesan, Chem. Rev. 87 (1987) 433.
[31] M. Irie, T. Fukaminato, T. Sasaki, N. Tamai, T. Kawai, Nature 420 (2002) 759.
[32] T. Fukaminato, T. Sasaki, T. Kawai, N. Tamai, M. Irie, J. Am. Chem. Soc. 126 (2004) 14847.
[33] X.-C. Li, H. Tian, Macromol. Chem. Phys. 206 (2005) 1769.
[34] M. Frigoli, H. Mehl, Chem. Commun. (2004) 818.
[35] K. Yagi, C.-F. Soong, M. Irie, J. Org. Chem. 66 (2001) 5419.
[36] T. Fukaminato, T. Kawai, S. Kobatake, M. Irie, J. Phys. Chem. B 107 (2003) 8372.
[37] K. Yagi, M. Irie, Bull. Chem. Soc. Jpn. 76 (2003) 1625.
[38] A. Fernández-Acebes, J.-M. Lehn, Chem. Eur. J. 5 (1999) 3285.
[39] T.B. Norsten, N.R. Branda, J. Am. Chem. Soc. 123 (2001) 1784.