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Synthesis, structure and fluorescence of a novel diarylethene

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Abstract—The photochromic diarylethene, 1,2-bis(2-methyl-5-(2-(1,3-dithiolpentane))-thien-3-yl)perfluorocyclopentene (BMDTP), has been synthesized in high yield and its structure was determined by X-ray crystallographic analysis. The compound undergoes a photochromic reaction both in solution and in the single crystalline phase. In addition, its fluorescence property in solution is discussed.

Generally, photochromism is defined as a light-induced reversible transformation between two isomers having a distinguishable absorption spectral change.[1] Photochromic compounds are classified into two categories, (1) thermally reversible compounds whose photogenerated colored isomers are thermally unstable and return to the initial colorless isomers in the dark and (2) thermally irreversible compounds whose photogenerated colored isomers are very stable and never return to the initial colorless isomers in the dark.[2] Recently, several thermally irreversible photochromic compounds, such as furylfulgides,[3] diarylethenes,[4] and phenoxynaphthacene-quinones,[5] have been developed. Among these compounds, diarylethenes with heterocyclic aryl rings are the most promising for the optoelectronic devices,[6–10] such as in optical memory, switching and display devices, and photodriven actuators, because of their good thermal stability of both isomers, high fatigue resistance, and rapid response time.[10]

Although many photochromic diarylethene compounds have been reported to date, compounds which show strong photochromic reactivity in the crystalline phase are quite rare.[10–12] However, they are very useful for rewritable holographic memory as well as nonlinear optical devices with switching properties.[13,14] Both in solution and crystal form, the diarylethenes undergo a 1,3,5-hexatriene ↔ cyclohexadiene type photochromic reaction by alternate irradiation with UV and visible light. According to the Woodward–Hoffmann rule, it is expected that photoinduced cyclization and cycloreversion reactions proceed in a conrotatory mode. In a previous paper, we reported the allomorphism of a diarylethene compound and discussed its photochromic properties both in solution and the single crystalline phase.[15] It is a good example of validating the rule exactly.

For practical applications it is required to further improve the performance of the photochromic diarylethenes by improving their properties such as thermal stability, sensitivity, response rate, and reactivity in the solid state. In addition, diarylethenes, which absorb at a short wavelength with high sensitivity, should be developed in order to improve the optical storage density. However, photochromic diarylethenes having these properties in their crystalline phase are quite rare.[16–18] In this letter, a novel dithienylethene compound, 1,2-bis(2-methyl-5-(2-(1,3-dithiolpentane))-thien-3-yl)perfluorocyclopentene (BMDTP) was synthesized from 1,2-bis(2-methyl-5-formyl-thien-3-yl)perfluorocyclopentene (BMFTP) in high yield. This compound has relatively short absorption wavelength, higher cyclization quantum yield (0.45), and efficient photoreactivity both in solution and the single crystalline phase. Using single crystal X-ray diffraction analysis method, we found that molecules of BMDTP-O and BMFTP-O were packed in an active *anti*-parallel conformation so that an efficient photocyclization reaction was able to occur in the crystalline phase.[10] The photochromism is shown in Scheme 1. In addition, fluorescence property of BMDTP was investigated.

The novel diarylethene BMDTP was prepared by the condensation reaction of BMFTP[19,20] with 1,2-Ethandithiol (Scheme 2). A solution of BMFTP (0.2121 g,

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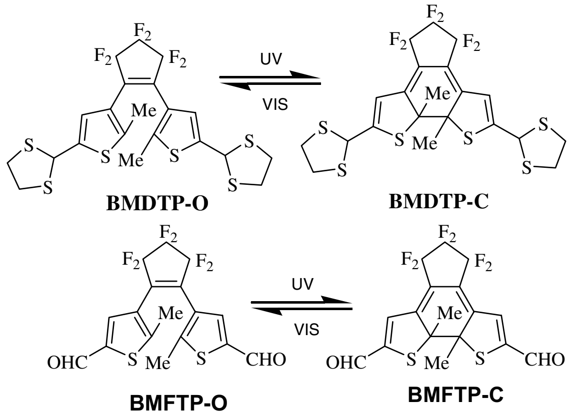
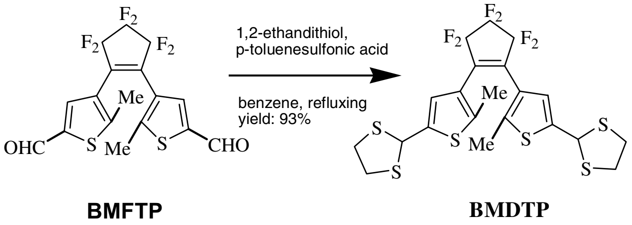


Scheme 1. Photochromism of BMDTP and BMFTP.



Scheme 2. Reagents and conditions.

0.5 mmol), 1,2-ethandithiol (0.9520 g, 10 mmol), and *p*-toluenesulfonic acid monohydrate (0.0210 g, 0.1 mmol) in benzene (200 mL) was refluxed for 6 h with a Dean–Stark condenser. After the reaction mixture was cooled to room temperature, the solvent was removed under vacuum. Column chromatography (silica gel, ethyl acetate–oil ether 1:5) afforded BMDTP (0.2678 g, 93%). Colorless crystals were obtained by slow vapor diffusion in chloroform. The structure of BMDTP was confirmed by melting point, NMR, and mass spectrometry.[21] Therefore, this synthetic method was very simple and effective.

The absorption spectral changes of BMDTP in hexane were shown in Figure 1. Upon irradiation with 254 nm UV light, the colorless solution of BMDTP-O turned to red and absorption maxima of BMDTP-C were observed at 200, 288, 358 and 522 nm. The cyclization–cycloreversion quantum yield[22,23] of the compound is 0.45/0.18 determined in hexane at room temperature. The photostationary spectrum is almost the same as that of the colored isomer, indicating a high conversion from the colorless to the colored isomer by irradiation with 254 nm light. The red colored solution of BMDTP-C returned to colorless upon irradiation with visible light ($\lambda > 450$ nm). This indicates that BMDTP-C returns to the initial open-ring isomer which the absorption maxima were observed at 198 and 248 nm. The coloration–decoloration cycle could be repeated more than 10 times and a clear isosbestic point was observed at 278 nm even after 10 cycles.

The X-ray experiment of the single-crystal of BMDTP-O was performed on a Bruker P4 diffractometer equipped with graphite monochromatized Mo Kα radiation at room temperature (293 ± 2 K). Raw intensities were corrected for Lorentz and polarization effects and for absorption by empirical method. Direct phase determination yielded the positions of all nonhydrogen atoms. Hydrogen atoms were generated geometrically and rode on their parent atoms in the final refinement. All nonhydrogen atoms were subjected to anisotropic refinement. For the crystal of BMDTP-O, the final full-matrix least-square refinement on F^2 converged with $R_1 = 0.0712$ and $wR_2 = 0.1720$ for 2976 observed reflections [$I \geqslant 2\sigma(I)$]. The final difference electron density map shows no features. The crystal structure is shown in Figure 2[24] and its packing diagram in Figure 3. The

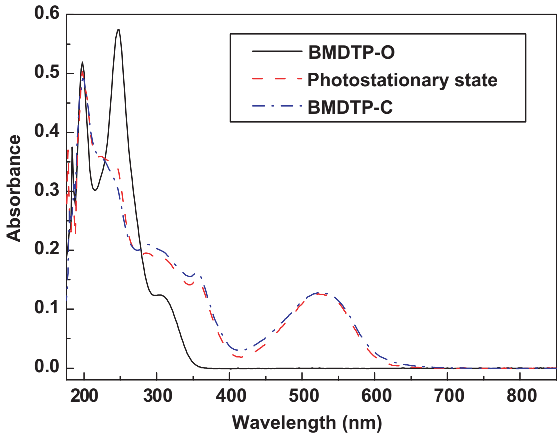


Figure 1. Absorption spectra of diarylethene BMDTP in ethanol solution (3.0×10^{-5} M): open-ring form (BMDTP-O, solid-line), closed-ring form (BMDTP-C, dash dotted-line), and in the photostationary state under irradiation with 254 nm UV light (dashed-line).

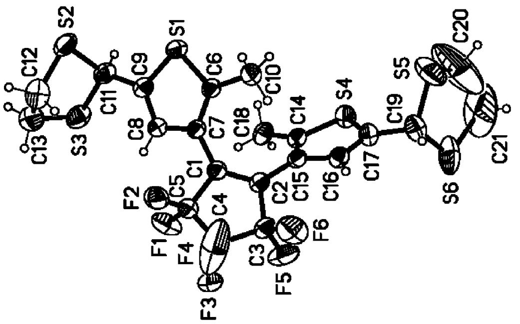


Figure 2. ORTEP drawings for BMDTP-O with 35% probability ellipsoids, showing the atomic numbering scheme. Selected bond distances (Å) and bond angles (°): S(1)–C(6) 1.725(5), S(1)–C(9) 1.734(5), S(2)–C(12) 1.798(8), S(2)–C(11) 1.811(6), S(3)–C(13) 1.801(8), S(3)–C(11) 1.818(6), F(1)–C(5) 1.342(6), F(3)–C(4) 1.245(9), C(1)–C(2) 1.351(6), C(1)–C(5) 1.504(7), C(4)–C(5) 1.501(8), C(3)–C(4) 1.491(8), C(2)–C(3) 1.496(6), C(1)–C(7) 1.459(6), C(6)–C(7) 1.372(7), C(6)–C(10) 1.494(7), C(9)–C(11), 1.506(7), C(6)–S(1)–C(9) 92.9(2), C(12)–S(2)–C(11) 93.0(3), C(13)–S(3)–C(11) 98.0(3), C(2)–C(1)–C(7) 131.1(4), C(2)–C(1)–C(5) 110.5(4), C(7)–C(1)–C(5) 118.4(4), F(6)–C(3)–F(5) 103.3(4), F(6)–C(3)–C(4) 111.0(5), F(5)–C(3)–C(4) 110.6(5), C(3)–C(4)–C(5) 107.2(4), C(4)–C(5)–C(1) 105.0(4), C(7)–C(6)–C(10) 129.9(4), C(7)–C(6)–S(1) 110.4(4), C(10)–C(6)–S(1) 119.6(4), C(6)–C(7)–C(1) 124.9(4), C(8)–C(9)–C(11) 130.0(5), S(2)–C(11)–S(3) 107.6(3), C(11)–C(9)–S(1) 119.7(4).

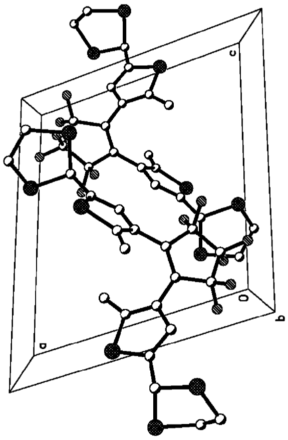


Figure 3. A packing views along the *b* direction.

ORTEP drawing of BMDTP-O indicates that BMDTP-O is packed in a photoactive *anti*-parallel conformation in the crystal, which can undergo a photocyclization reaction.[16]

In the perfluorocyclopentene ring of BMDTP-O, distances of C1–C2, C2–C3, C3–C4, C4–C5, and C1–C5 are 1.351(1) Å, 1.496(6) Å, 1.491(8) Å, 1.501(8) Å, and 1.504(7) 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. The distance of C6–C14 is 3.513 Å, which is short enough theoretically for the reaction to take place in the crystalline phase.[25] In addition, the molecule has five planer rings, including two 1,3-dithiolpentane rings, two thiophene rings, and one perfluorocyclopentene ring. So, they can form four dihedral angles between every two adjacent rings. The dihedral angle between perfluorocyclopentene ring and the left thiophene ring is 41.5°, and that of between the perfluorocyclopentene ring and the right thiophene ring is 42.4°. The dihedral angle between C19–S5–C20–C21–S6 plane and S4–C14–C15–C16–C17 plane is 84.5°, and that between C11–S2–C12–C13–S3 plane and S1–C6–C7–C8–C9 plane is 101.9°.

For comparison, the crystal structure of BMFTP-O was also determined as shown in reference.[20] BMFTP-O is packed in a photoactive *anti*-parallel conformation in the crystal, too. Therefore, both BMDTP-O and BMFTP-O can undergo a photocyclization reaction in the crystalline phase. In fact, crystals of BMDTP-O and BMFTP-O showed photochromic reactivity coincident with the theoretical analysis.

Table 1. The solvent effect on the fluorescence spectra of BMDTP-O at room temperature in various solutions at 5×10^{-5}

Solvent	λ_{max} (nm)[a]	λ_{max} (nm)[b]	λ_{max} (nm)[c]
Hexane	246 (528)	292	344
Chloroform	240 (528)	296	352
Ether	246 (532)	293	349
Acetic ether	246 (534)	294	351
Acetonitrile	246 (534)	296	352

[a] Absorption maxima (absorption of BMDTP-C).

[b] Excitation maxima, monitored at 350 nm.

[c] Fluorescence maxima, excited at 292 nm.

Upon irradiation with 254 nm UV light, the colorless crystal of BMDTP-O turned red immediately. When observed under polarized light, the red color intensity changed on rotation of the crystalline sample. This phenomenon suggested that the closed-ring isomers were regularly packed in the crystal. When the red crystal was dissolved in hexane, the solution turned to red, and the absorption maximum was observed at 528 nm, which was the same as that of the closed-ring form BMDTP-C shown in Table 1. Unfortunately, we could not give the single crystal diffraction pattern of BMDTP-C because it returns easily to BMDTP-O under the condition of experiment. Red color disappeared upon irradiation with 450 nm light and the absorption spectrum of the solution containing the colorless crystal was the same as that of the open-ring form BMDTP-O. Similarly, the colorless crystal of BMFTP-O turned blue on irradiation with 365 nm UV light, and its absorption maximum was observed at 614 nm after being dissolved in hexane. Their color changes upon UV light irradiation are shown in Figure 4. The original two photos collected using a Sony digital camera, showed the two kinds of crystals before and after UV light irradiation, respectively. The heterogeneous color distributions in Figure 4 resulted from the irregular surface of the crystals. According to the above description, Figure 4a should be colorless but it shows a pale yellow color due to the illuminating light source. However, by comparing the two photographs it is possible to demonstrate the photochromic process of the two kinds of diarylethenes (BMDTP and BMFTP).

Fluorescence spectral changes of BMDTP ($C = 5 \times 10^{-5}$ mol/L) in hexane were shown in Figure 5.

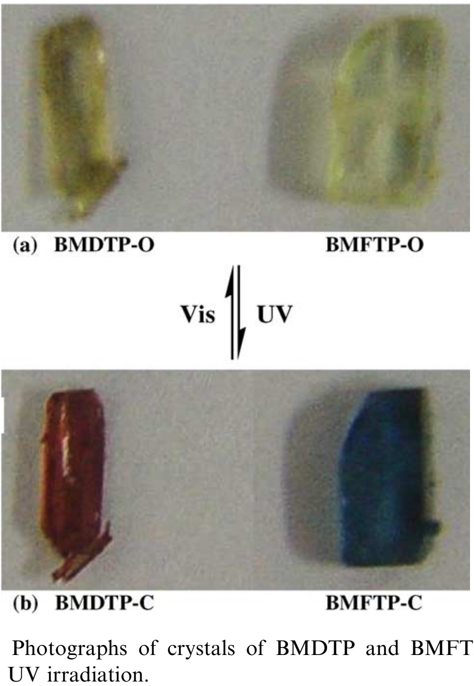


Figure 4. Photographs of crystals of BMDTP and BMFTP before and after UV irradiation.

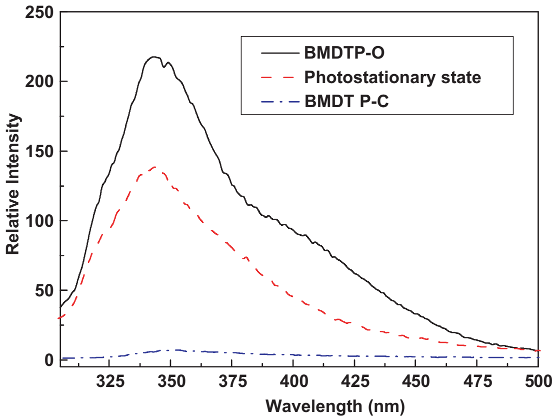


Figure 5. Fluorescence spectral changes of BMDTP in hexane ($C = 5 \times 10^{-5}$ mol/L) at room temperature, excited at 292 nm.

BMDTP-O exhibited fluorescence at 343 nm in hexane solution when excited at 292 nm. The fluorescence intensity decreased along with the photochromism from BMDTP-O to BMDTP-C upon irradiation with 254 nm light and the isolated BMDTP-C showed almost no fluorescence. The concentration dependence of fluorescence excitation spectra was measured in chloroform solution at room temperature, as shown in Figure 6. The fluorescence excitation spectra showed remarkable concentration dependence. It showed a systematic red shift and the fluorescence intensity decreased rapidly with the concentration increased. These results indicate that molecular aggregation and fluorescence quench take place due to concentration increasing.[26] The solvent effect on the fluorescence spectra was also investigated. The absorption, excitation, and fluorescence maxima of BMDTP-O in various solvents were summarized in Table 1. The fluorescence maximum was observed between 344 and 352 nm in all solvents, indicating that the solvent effect was not significant.

In conclusion, the compound described here has been first prepared in very high yield by a simple method and its structure was established by X-ray crystallographic analysis. The open-ring isomer of the compound exhibits relatively strong fluorescence at UV region and its closed-ring isomer has a short and narrow absorption wavelength and high cyclization quantum yield. Therefore, it is promising as a material possessing a rewritable optical memory for using with laser wavelengths, such as for holographic data storage and multi-wavelength and multi-step optical storage. Further work, especially in applying to super-high density optical storage, is currently in progress.

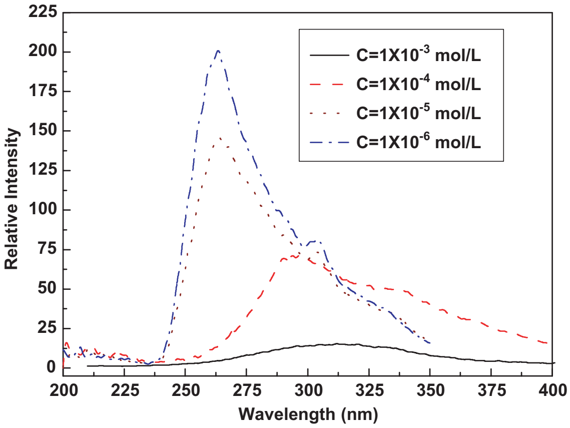


Figure 6. Fluorescence excitation spectra of BMDTP in chloroform at room temperature, monitored at 310, 370, 373, and 415 nm for 10^{-6}, 10^{-5}, 10^{-4}, and 10^{-3} mol/L, respectively. They are the best excitation wavelengths for the different concentrations of BMDTP.

Acknowledgments

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21. *Selected data for BMDTP-O*: colorless crystal; mp 102.8–103.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.87 (s, 6H), δ 3.31–3.47 (m, 8H), δ 5.78 (s, 2H), δ 6.95 (s, 2H); MS *m*/*z* (M^+) 575.
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24. *Crystal data of BMDTP-O*: $C_{21}H_{18}F_6S_6$, $M = 576.71$, triclinic, $a = 10.7626(15)$ Å, $b = 10.8709(16)$ Å, $c = 12.6181(15)$ Å, $\alpha = 112.750(11)°$, $\beta = 100.612(10)°$, $\gamma = 105.477(11)°$, $V = 1241.6(3)$ Å^3, $T = 293(2)$ K, space group $P\bar{1}$ (No. 2), $Z = 2$, $D_{calcd} = 1.543\ g \times cm^{-3}$, $F(000) = 588$, μ(Mo Kα) = 6.05 cm^{-1}, $R_1 = 0.0712$, $wR_2 = 0.1720$. Further details on the crystal structure investigation have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 247941. Copies of the data can be obtained, free of charge, on application to: CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk].
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