

Highly fluorescent photochromic diarylethene in the closed-ring form

Yong-Chul Jeong,^a Sung Ik Yang,^{*a} Kwang-Hyun Ahn^{*a} and Eunkyong Kim^{*b}

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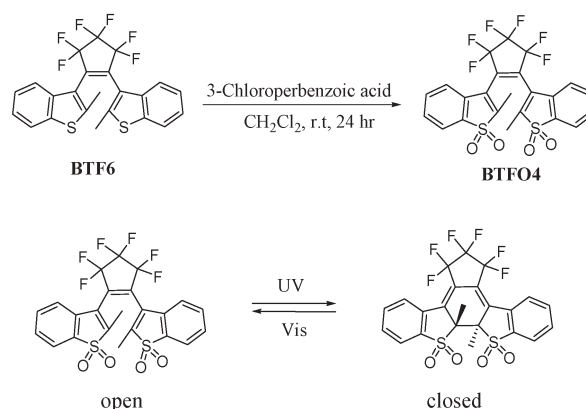
A highly fluorescent diarylethene in the closed-ring form was synthesized by the oxidation of 1,2-bis(2-methyl-1-benzothiophene-3-yl)perfluorocyclopentene (BTF6).

Recently, there has been great interest in photochromic materials, which reversibly change their optical properties upon photo-excitation. This has been mainly motivated by their potential applications in erasable memory and optical switches.^{1–3} In particular, diarylethenes with benzothiophene ring systems have been of considerable interest due to their thermal stability and fatigue resistancy.^{4,5} However, the diarylethene systems show rather small photochromic fluorescence changes, and thus the signals resulting from them were usually monitored by UV–Vis absorption spectroscopy. Since monitoring the absorption changes is not a viable method for reading-out the stored information owing to the signal interfering with photochromism, other methods were needed to achieve non-destructive read-out. These have included observing changes in optical rotation,⁶ refractive index,⁷ fluorescence,^{8–10} and IR.¹¹ In particular, fluorescence changes upon photochromic reaction are promising for non-destructive optical read-out systems due to the technique's single molecule sensitivity.

In the present study, we have synthesized and characterized the photochromic properties of 1,2-bis(2-methyl-1-benzothiophene-3-yl)perfluorocyclopentene (BTF6) and its sulfonyl derivative 1,2-bis(2-methyl-1-benzothiophene-1,1-dioxide-3-yl)perfluorocyclopentene (BTFO4) to develop an efficient, non-destructive, fluorescence based photochromic read-out system.

The synthesis of BTF6 was previously described by Irie *et al.*¹² BTFO4 was prepared in 90% yield by the oxidation of BTF6 using 3-chloroperbenzoic acid,^{13,14} as shown in Scheme 1.

The electronic ground state absorption spectra for the open ring isomers (o) (solid lines) and closed ring (c) at photostationary states (dashed lines, obtained after 10 min of UV irradiation) of BTF6 and BTFO4 in ethyl acetate are shown in Fig. 1A and 1B, respectively. Upon illumination at a wavelength of 254 nm, new absorption bands at 350 and 530 nm (for BTF6), and 400 nm (for BTFO4) appeared—originating from photo-cyclization and the formation of their c-isomers. Upon photo-excitation with visible light using a tungsten lamp, c-BTF6 and c-BTFO4 completely reverted to their o-isomers. The photo-cyclization yield of c-BTFO4 from o-BTFO4 after illumination for 10 min was 80% according to HPLC analysis, while the yield of c-BTF6 from o-BTF6 was 40%.¹⁵ The higher photo-cyclization yield of c-BTFO4 can be explained in terms of stability of its ground



Scheme 1

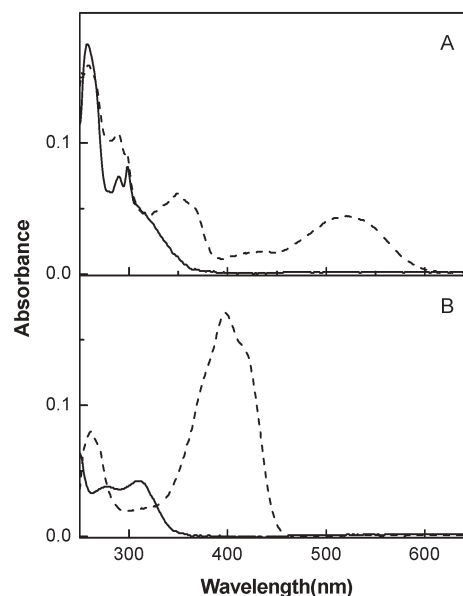


Fig. 1 The absorption spectra for the o- (solid lines) and c- (dashed lines) isomers of A: BTF6 and B: BTFO4 in ethyl acetate (1.0×10^{-5} M) at r.t.

state.¹⁴ A key finding is that the absorption spectrum of c-BTFO4 substantially deviates from that of c-BTF6 and its absorption extinction coefficient increases to $2.1 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$.

The emission spectra following photo-excitation at 315 nm for o-BTF6 and o-BTFO4 in ethyl acetate are shown in Fig. 2A and 2B (solid lines), respectively, and are very similar to each other. The steady-state fluorescence spectra of c-BTF6 and c-BTFO4 in ethyl acetate are also shown in Fig. 2A and 2B (dashed lines) respectively. Owing to the lack of fluorescence in c-BTF6, most of the fluorescence in the photostationary state comes from unreacted

*siyang@khu.ac.kr (Sung Ik Yang);
khahn@khu.ac.kr (Kwang-Hyun Ahn)
eunkim@yonsei.ac.kr (Eunkyong Kim)

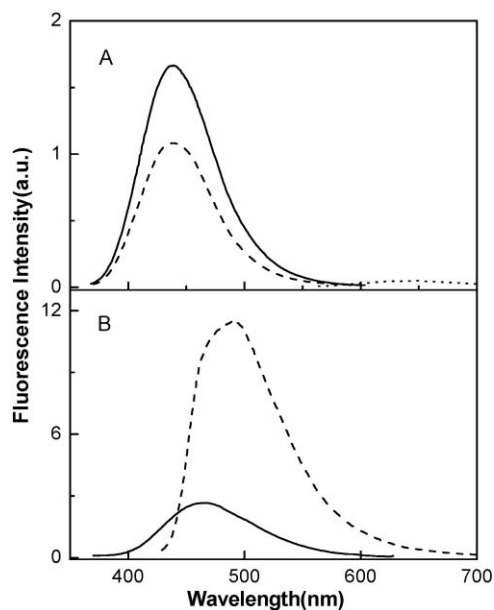


Fig. 2 The corrected fluorescence spectra upon photo-excitation at the absorption maxima for o- (solid lines) and c- (dashed lines) isomers of A: BTFO4 and B: BTF6 in ethyl acetate (1.0×10^{-5} M) at r.t. The dotted line in Fig. 2A shows the c-BTF6 emission spectrum observed at 625 nm upon 530 nm light excitation.

o-isomer, which results in decreased fluorescence intensity upon photo-cyclization (dashed line, Fig. 2A). Only a trace of c-BTF6 emission was observed at 625 nm upon 530 nm light excitation (dotted line, Fig. 2A). Surprisingly, upon photo-cyclization, the fluorescence intensity of c-BTFO4 increased enormously, whereas that of c-BTF6 decreased. Furthermore, following irradiation at a wavelength of 400 nm for 1 h, c-BTFO4 remained unaffected and was not converted to its o-isomer. This result demonstrates that the system can be utilized for non-destructive read-out applications. It is also important to note that the significant increase in fluorescence intensity of c-BTFO4 following 400 nm photo-excitation makes it an ideal material for fluorescence based read-out applications, because there are no absorption bands at this wavelength for its o-isomer. This in turn enhances its sensitivity.

Fig. 3A illustrates the modulation in fluorescence signal of BTFO4 in ethyl acetate at rt while alternating the illumination between UV 254 nm (unshaded regions) and visible 400 nm (shaded regions) wavelengths. The fluorescence signal was recorded as a function of time at 490 nm. For comparison, the fluorescence signal changes of the BTF6 system under the same conditions are shown in Fig. 3B. As can be seen in Fig. 3A and 3B, the fluorescence signal changes are much more pronounced in the BTFO4 system than they are in the BTF6 system. Illustrating this, the maximum : minimum ratio of the fluorescence signal change is 20 : 1 for BTFO4 compared to 1.6 : 1 for BTF6. The fact that the fluorescence intensity of the BTFO4 can be modulated in this way indicates that it can function as a reversible memory device using the high sensitivity fluorescence detection method.

In summary, we have synthesized a new fluorescent photochromic diarylethene system by the oxidation of BTF6. We found that the fluorescence quantum yield of BTFO4 increased following photo-cyclization, opposite to that found for BTF6. The oxidation

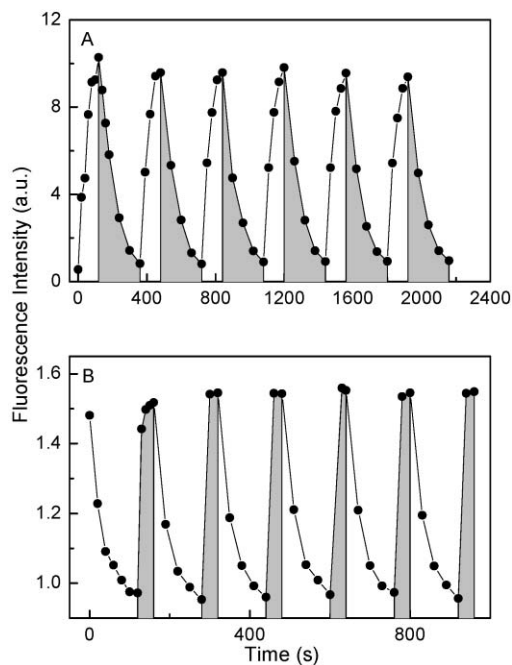


Fig. 3 The modulation of the fluorescence signal of A: BTFO4 and B: BTF6 in ethyl acetate (1.0×10^{-5} M) observed when alternating its illumination between UV (254 nm, unshaded regions) and visible (> 400 nm, shaded regions) wavelengths.

of the sulfide groups of the benzothiophene rings of BTF6 transformed the c-isomer from a very weak emitter to a highly fluorescent chromophore. Overall, the results of this study provide a new synthetic strategy for the design of highly fluorescent materials with potential applications in non-destructive photochromic read-out.

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Yong-Chul Jeong,^a Sung Ik Yang,^{*a} Kwang-Hyun Ahn^{*a} and Eunyoung Kim^{*b}

^aCollege of Environment and Applied Chemistry, Institute of Natural Science, Kyung Hee University, Yongin, 449-701, South Korea.

E-mail: siyang@khu.ac.kr; khahn@khu.ac.kr; Fax: 82-31-202-7337; Tel: 82-31-201-3735

^bDepartment of Chemical Engineering, Yonsei University, 134 Shinchondong, Seodaemun-gu, Seoul, 120-749, South Korea.

E-mail: eunkim@yonsei.ac.kr; Fax: 82-2-312-6401; Tel: 82-2-2123-5752

Notes and references

- 1 C. Joachim, J. K. Gimzewski and A. Aviram, *Nature*, 2000, **408**, 541.
- 2 F. M. Raymo, *Adv. Mater. (Weinheim, Ger.)*, 2002, **14**, 401.
- 3 V. Balzani, A. Credi and M. Venturi, *ChemPhysChem*, 2003, **4**, 49.
- 4 M. Irie and M. Mohri, *J. Org. Chem.*, 1988, **53**, 803.
- 5 M. Irie, *Chem. Rev.*, 2000, **100**, 1685–1716.
- 6 T. Yamaguchi, K. Uchida and M. Irie, *J. Am. Chem. Soc.*, 1997, **119**, 6066.
- 7 S. Y. Cho, M. Yoo, H.-W. Shin, K.-H. Ahn, Y.-R. Kim and E. Kim, *Opt. Mater. (Amsterdam)*, 2002, **21**, 279.
- 8 K. Yagi, C. F. Soong and M. Irie, *J. Org. Chem.*, 2001, **66**, 5419.
- 9 T. B. Norsten and N. R. Branda, *J. Am. Chem. Soc.*, 2001, **123**, 1784.
- 10 H. Cho and E. Kim, *Macromolecules*, 2002, **35**, 8684.
- 11 K. Uchida, M. Saito, A. Murakami, S. Nakamura and M. Irie, *Adv. Mater. (Weinheim, Ger.)*, 2003, **15**, 121.

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- 12 M. Hanazawa, R. Sumiya, Y. Horikawa and M. Irie, *J. Chem. Soc., Chem. Commun.*, 1992, 206.
- 13 A mixture of 1,2-bis(2-methyl-1-benzothiophene-3-yl)hexafluorocyclopentene (o-BTF6) (1.0 g, 2.1 mmol) and 70% 3-chloroperoxybenzoic acid (2.9 g, 11.8 mmol) in dichloromethane (50 mL) was stirred for 24 h at rt. The solution was washed with a saturated solution of Na₂SO₄. The organic layer was separated and dried over MgSO₄, and concentrated *in vacuo*. Flash chromatography (silica gel, hexane : ethylacetate = 4 : 1) yielded 1,2-bis(2-methyl-1-benzothiophene-1,1-dioxide-3-yl)perfluorocyclopentene (o-BTFO4) in 90% yield.
- Mp 294 °C (decomp). δ_{H} (CDCl₃, 300 MHz) 7.78 (1 H, d, $J = 7.2$ Hz), 7.72 (1 H, d, $J = 7.8$ Hz), 7.15 (2 H, d, $J = 7.2$ Hz), 2.20 (3 H, s), 2.06 (3 H, s). m/z (HRMS) 532.0244 (M⁺), C₂₃H₁₄F₆O₄S₂ requires 532.0237.
- 14 Y.-C. Jeong, S. I. Yang, K.-H. Ahn and E. Kim, manuscript in preparation.
- 15 δ_{H} for c-BTFO4 (CDCl₃, 300 MHz) 8.27–8.24 (2 H, m), 8.04–8.01 (2 H, m), 7.88–7.71 (4 H, m), 1.85 (6 H, s). For HPLC isolation and ¹H NMR for a c-BTF6 derivative, see M. Morimoto, S. Kobatake and M. Irie, *Cryst. Growth Des.*, 2003, **3**, 847.