Fatigue-resistant photochromic dithienylethenes by controlling the oxidation state

Yong-Chul Jeong,[a] Dae Gyu Park,[a] Eunkyoung Kim,*[b] Kwang-Hyun Ahn*[a] and Sung Ik Yang*[a]

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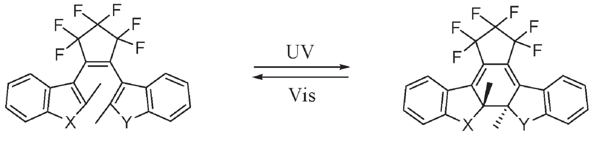
High fatigue-resistant photochromic dithienylethenes were synthesized by controlling the oxidation state of 1,2-bis(2-methyl-1-benzothiophene-3-yl)perfluorocyclopentene (BTF6) and 1,2-bis(2,5-dimethylthien-3-yl)perfluorocyclopentene (DMTF6).

Reversible photochromic reactions of diarylethenes are based on conrotatory cyclization of hexatriene and ring opening of cyclohexadiene derivatives.[1] Upon UV illumination, the open-ring isomer undergoes a photocyclization reaction which results in the closed-ring isomer, and the closed-ring isomer returns to the open-ring isomer upon visible light irradiation (Scheme 1). Currently, there is great interest in the diarylethene type of photochromic materials due to their potential application to photonic devices. In particular, the synthesis of photochromic materials with high fatigue resistance is important for the development of molecular optoelectronic devices such as optical memory and switches.[2]

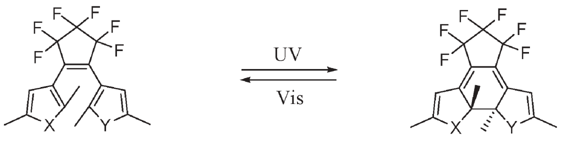
Among the photochromic materials, diarylethene derivatives have a good thermal stability and high fatigue resistance.[1] For example, BTF6 has been demonstrated to exhibit high thermal stability and fatigue resistance [read–erase >14 000 cycles in methylcyclohexane (1.2×10^{-4} M)].[3] These properties can be improved by varying the main body structure and substituent in the aryl ring or the hetero atoms. For example, diarylethenes with thiophene rings cease their photochromic effect in less than 200 cycles in the absence of a substituent at the 4- and 4′-positions of the thiophene rings, while the photochromic effect can be increased in the presence of a methyl group at these positions.[4] Thus, the development of new diarylethenes with a substituent ensures a significant impact on the practical application of these materials.

Our previous studies[5] have shown that oxidation of diarylethenes to di-sulfone leads to an enormous increase in the fluorescence quantum yield of the closed-ring isomer which may be useful for nondestructive readout memory and switch applications. Unfortunately, however, the fatigue property of the disulfone-diarylethene was found to be slightly inferior compared with unoxidized diarylethene.[5] To develop photochromic materials with high fatigue resistance, herein we report on the synthesis and characterization of the fatigue properties of a new series of oxidized diarylethene derivatives by controlling the oxidation states.

BTF6 and 1,2-bis(2-methyl-1-benzothiophene-1,1-dioxide-3-yl)perfluorocyclopentene (BTFO4)[5a] were prepared according to the procedures described in the literature. 1-(2-Methyl-1-benzothiophene-1,1-dioxide-3-yl)-2-(2-methyl-1-benzothiophene-3-yl)hexafluorocyclopentene (BTFO2) was prepared from the oxidation of BTF6 using 1.0 equivalent of 3-chloroperbenzoic acid (*m*-CPBA) in 30% yield.[6] We also synthesized DMTF6,[7] 1-(2,5-dimethylthien-1,1-dioxide-3-yl)-2-(2,5-dimethylthien-3-yl)-hexafluorocyclopentene (DMTFO2),[8] and 1,2-bis(2,5-dimethylthien-1,1-dioxide-3-yl)perfluorocyclopentene (DMTFO4),[5b] employing the methods used for BTFO2 and BTFO4 and characterized by ^{1}H NMR and HRMS.[6,8] To confirm the structure of BTFO2[9] and DMTFO2,[10] their crystal structures were determined using a single crystal obtained from a hexane–ethyl acetate solution. Fig. 1(A) and (B) show the



1. BTF6: X,Y = S,
2. BTFO2; X = S, Y = SO_2
3. BTFO4; X,Y = SO_2



4. DMTF6; X,Y = S
5. DMTFO2; X = S, Y = SO_2
6. DMTFO4; X,Y = SO_2

Scheme 1 Photochromism of diarylethenes.

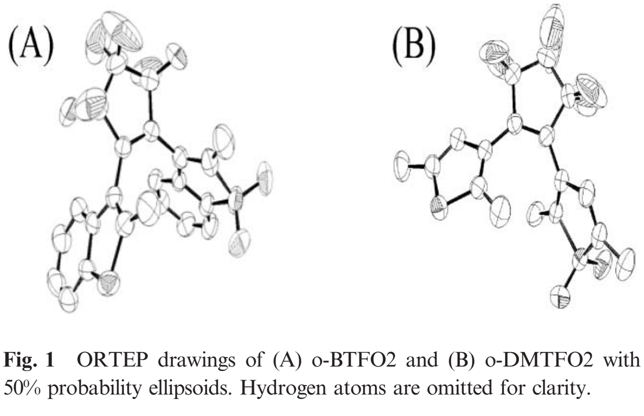


Fig. 1 ORTEP drawings of (A) o-BTFO2 and (B) o-DMTFO2 with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

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[a] *College of Environment and Applied Chemistry, and Institute of Natural Science, Kyung Hee University, Yongin, 449-701, Republic of Korea. E-mail: siyang@khu.ac.kr; khahn@khu.ac.kr; Fax: (+82) 31-202-7337; Tel: (+82) 31-201-3735*
[b] *Department of Chemical Engineering, Yonsei University, 134 Shinchon-dong, Seodaemun-gu, Seoul, 120-749, Republic of Korea. E-mail: eunkim@yonsei.ac.kr; Fax: (+82) 2-312-6401; Tel: (+82) 2-2123-5752*

ORTEP drawings of the molecular structures of the open-ring isomers of BTFO2 (o-BTFO2) and DMTFO2 (o-DMTFO2), respectively.

Fig. 2 shows the electronic ground-state absorption spectra of the open-ring isomer (dashed line) and at the photostationary state (solid line) of (A) BTF6, (B) BTFO2, and (C) BTFO4 in ethyl acetate solutions (1.0 × 10^{-5} M) at room temperature upon 312 nm irradiation. They undergo reversible photocyclization and ring opening reactions upon irradiation with UV and visible light, respectively.[11] Contrary to the closed-ring isomer of BTFO4 (c-BTFO4), which shows one absorption band at 398 nm, the closed-ring isomer of BTFO2 (c-BTFO2) shows two absorption bands at 530 and 450 nm in the visible region which were blue shifted compared with the closed-ring isomer of BTF6 (c-BTF6). Upon photo-excitation with visible light, c-BTF6, c-BTFO2 and c-BTFO4 were completely bleached back to the corresponding open-ring isomer. The photocyclization yields of c-BTFO2, c-BTFO4, c-DMTFO2, and c-DMTFO4 from the open-ring isomers were 83%, 80%, 99%, and 50%, respectively, according to ^{1}H NMR analysis, while the yields of c-BTF6 and c-DMTF6 were 40% and 68%, respectively.

It is known that an undesirable side reaction takes place to some extent during repeated cycles of the photocyclization–cycloreversion photochromic reaction, limiting the durability of the photochromic compounds.[5b,12] As a result of this irreversible photoreaction, the absorbance feature is changed, which is indicative of the fatigue properties of diarylethenes. To study the fatigue properties of those diarylethenes, we examined the change of absorption spectra as a function of UV illumination time. Fig. 3 represents the changes of the absorbance spectra of c-BTF6 (A), c-BTFO2 (B), and c-BTFO4 (C) as a function of UV illumination time for about 10 h. The figure shows that the absorbance of the closed-ring isomers of these diarylethenes slowly decreased under UV illumination implying that by-products were formed from the closed-ring isomers.[13] However, the absorbance changes of the closed-ring isomers of these diarylethenes, which are indicative of the relative fatigue properties of the diarylethenes, were quite different dependent upon the oxidation state of the diarylethenes. The absorbance change of the mono-sulfone, BTFO2 (B), by the photoreaction was much smaller than that of BTF6 (A), whereas that of di-sulfone, BTFO4 (C), was much more significant. Thus, BTFO2 showed an excellent fatigue resistance against the post UV excitation.

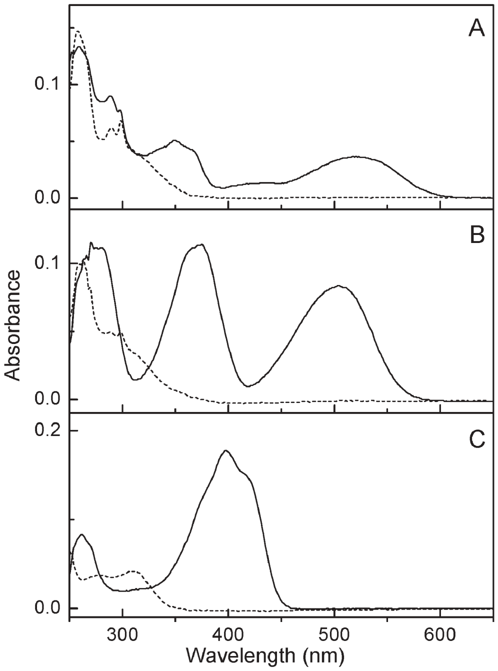

Fig. 2 The absorption spectra of the open-ring isomer (dashed line) and at the photostationary state (solid line) of (A) BTF6, (B) BTFO2, and (C) BTFO4 in ethyl acetate solutions (1 × 10^{-5} M) at room temperature.

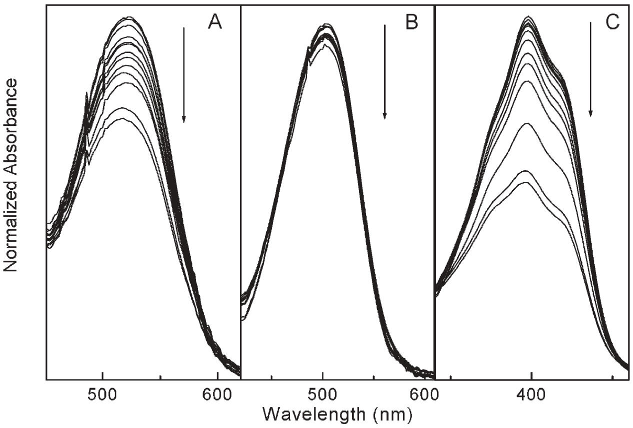

Fig. 3 The absorbance changes of BTF6 (A), BTFO2 (B), and BTFO4 (C) in ethyl acetate solutions as a function of UV illumination time for about 10 h (12, 20, 30, 40, 50, 60, 90, 120, 150, 210, 360, 570, 620 min).

To examine the effect of oxidation state on the fatigue properties of other diarylethenes, the fatigue properties were examined using a solution of diarylethenes in ethyl acetate (1.0 × 10^{-5} M) by UV irradiation at room temperature. Fig. 4 illustrates the absorbance changes of (A) BTF6 (open squares), BTFO2 (closed squares), and BTFO4 (closed circles), (B) DMTF6 (open squares) and DMTFO2 (closed squares) at $\lambda_{\max}$ of the closed-ring isomers as a function of UV illumination time. For DMTFO4 (closed circles),

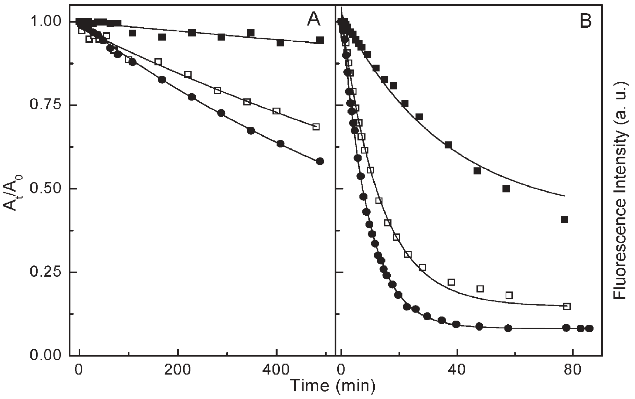

Fig. 4 The absorbance changes of (A) BTF6 (open squares), BTFO2 (closed squares), and BTFO4 (closed circles), (B) DMTF6 (open squares) and DMTFO2 (closed squares) at the absorption maximum of the closed-ring isomers and fluorescence intensity changes of DMTFO4 (closed circles) as a function of UV illumination time in ethyl acetate (1 × 10^{-5} M) at room temperature. The data are fitted with an exponential decay (line).

we monitored the changes of fluorescence intensity rather than the absorbance changes.[5b] As shown in Fig. 4, it is clear that the mono-sulfone diarylethenes (BTFO2 and DMTFO2) showed a significant improvement in the photostability compared with unoxidized diarylethenes (BTF6 and DMTF6) and di-sulfone diarylethenes (BTFO4 and DMTFO4). These findings are indicative that mono-sulfone derivatives are excellent candidates for applications requiring a good fatigue property in optical memory and switch applications based on photochromism.

In summary, we have demonstrated a simple approach for the synthesis of new high fatigue-resistant diarylethenes, BTFO2 and DMTFO2, by controlling the oxidation state of BTF6 and DMTF6, respectively. Photostability studies have shown that the photostability of diarylethenes with mono-sulfone was significantly improved compared with unoxidized diarylethenes. These results could lead to the development of molecular optoelectronic devices based on a reversible photochromic conversion with high fatigue resistance.

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6 (*a*) A mixture of BTF6 (1.0 g, 2.1 mmol) and 70% 3-chloroperbenzoic acid (0.6 g, 2.0 mmol) in dichloromethane (20 mL) was stirred for 8 h at room temperature. The solution was washed with a saturated Na_2SO_3 and $NaHCO_3$ solution. The organic layer was separated and dried over $MgSO_4$, and concentrated *in vacuo*. Flash chromatography (silica gel, hexane : ethyl acetate = 4 : 1) yields BTFO2 with 30% yield. o-BTFO2: mp 210 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.75–7.25 (m, 8H, aromatic H), 2.43 (s, 1.5H, CH_3 of p[6b] of sulfide), 2.30 (s, 1.5H, CH_3 of a–p[6b] of sulfide), 2.26 (s, 1.5H, CH_3 of p of sulfone), 1.92 (s, 1.5H, CH_3 of a–p of sulfone). HRMS (*m*/*z*); calcd. for $C_{23}H_{14}F_6O_2S_2$ 500.0339, found 500.0332. c-BTFO2: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.19 (d, 1H, J = 8.1 Hz), 8.05 (d, 1H, J = 8.1 Hz), 7.94 (d, 1H, J = 7.5 Hz), 7.81–7.72 (m, 2H), 7.41–7.20 (m, 3H), 1.91 (s, 3H), 1.62 (s, 3H); (*b*) p represents parallel conformation and a-p represents anti-parallel conformation.

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8 o-DMTO2: mp 91 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.75 (s, 1H), 6.27 (s, 1H), 2.45 (s, 3H), 2.15 (s, 3H), 2.09 (s, 3H), 1.78 (s, 3H). HRMS (*m*/*z*): calcd. for $C_{17}H_{14}F_6O_2S_2$ 428.0339, found 428.0332. c-DMTFO2: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.04 (s, 1H), 6.25 (s, 1H), 2.38 (s, 3H), 2.31 (s, 3H), 1.77 (s, 3H), 1.53 (s, 3H).

9 Crystal data for o-BTFO2: $C_{23}H_{14}F_6O_2S_2$, MW = 500.46, triclinic, space group $P\bar{1}$, a = 8.1239(14) Å, b = 10.7442(19) Å, c = 13.125(2) Å, α = 86.419(15)°, β = 76.057(13)°, γ = 74.297(13)°, V = 1070.3(3) Å^3, Z = 2, D_c = 1.553 g cm^{-3}, μ = 0.320 mm^{-1}, R_1 = 0.0709 for 3714 observed reflections with $I > 2\sigma(I)$ from 4004 unique reflection. CCDC 297166. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b600754f.

10 Crystal data for o-DMTFO2: $C_{17}H_{14}F_6O_2S_2$, MW = 428.40, monoclinic, space group $P2_1/c$, a = 13.078(3) Å, b = 6.433(2) Å, c = 22.410(6) Å, α = 90.00°, β = 105.828(17)°, γ = 90.00°, V = 1814.0(9) Å^3, Z = 4, D_c = 1.569 g cm^{-3}, μ = 0.320 mm^{-1}, R_1 = 0.0992 for 3419 observed reflections with $I > 2\sigma(I)$ from 4413 unique reflection. CCDC 297167. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b600754f.

11 Standard lamps used for visualizing TLC plate (VL-6M, 312 nm, 8 mW cm^{-2}) and a 100 W tungsten lamp that was passed through glass were used to carry out photochromic reactions in this study.

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13 Although we could not isolate the by-product, we believe the mechanism of by-product formation and the structures of the by-products are similar to those of ref. 5b and ref. 12.