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Development of highly fluorescent photochromic material with high fatigue resistance

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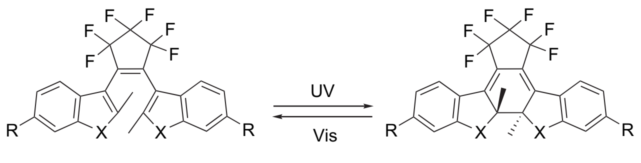
Abstract—Efficient and reversible fluorescence modulation with excellent photo-stability was achieved from a sulfone form of diacetyl diarylethene, 1,2-bis(6-acetyl-2-methyl-1-benzothiophene-1,1-dioxide-3-yl)perfluorocyclopentene (DABTFO4). The DABTFO4 emits strong fluorescence in the closed-ring isomer even in the absence of extra fluorophores. The fluorescence quantum yield, fatigue resistance, and photo-cyclization yield of DABTFO4 were significantly improved compared with the unsubstituted 1,2-bis(2-methyl-1-benzothiophene-1,1-dioxide-3-yl)perfluorocyclopentene (BTFO4) and the sulfide analogue, 1,2-bis(6-acetyl-2-methyl-1-benzothiophene-3-yl)perfluorocyclopentene (DABTF6).

1. Introduction

Photochromic materials have attracted extensive attention due to their potential applications in photonics such as photo-switching and optical memory systems.[1] Thermal stability and fatigue resistance are important considerations in the design of photochromic systems and in this consideration, diarylethenes (Scheme 1) are one of the most promising candidate for the systems.[2] According to Irie et al.,[3] 1,2-bis(2-methyl-1-benzothiophene-3-yl)perfluorocyclopentene (BTF6) is highly fatigue resistant and can carry out write/erase cycles more than 10,000 times without significant loss of performance. Nondestructive readout is another consideration to avoid interference with the photochromism. Among nondestructive readout methods, measuring fluorescence changes upon photochromic reaction is the promising method due to its single molecular detection sensitivity.[4] Previous works on the fluorescence based photochromic readout system adopted PPV,[5] porphyrin,[6] Lucifer yellow,[7] and metal complexes[8] as a fluorescence chromophore, rather than photochromic diarylethenes themselves. Those systems have the fluorescence changes upon photo-reaction based on energy transfer.[9] To utilize the photochromic diarylethene as the fluorophore, it is important to develop the system, which emits light in the closed-ring isomer and ideally enables the infinite signal change. However, in the diarylethene system, the fluorescence was observed when the molecule exists in the form of open-ring isomer, in general. Therefore, the sensitivity obtained in the system depends on the photo-cyclization yield because the unreacted open-ring isomer still emits fluorescence. There have been reports on the fluorescence of the closed-ring isomer by Lehn and Fernández-Acebes[10a] and Irie et al.[10b] However, Lehn and Fernández-Acebes adapted a tungsten metal complex as an emitter, which resulted in only fivefold signal change upon photo-cyclization due to same spectral features in open- and closed-ring isomer. Irie et al. reported a diarylethene derivative, which emits fluorescence upon photo-cyclization, but the fluorescence intensity of the closed-ring isomer is still weaker than that of the open-ring isomer.



o-BTF6 X = S, R = H
o-DABTF6 X = S, R = acetyl
o-BTFO4 X = SO_2, R = H
o-DABTFO4 X = SO_2, R = acetyl

c-BTF6 X = S, R = H
c-DABTF6 X = S, R = acetyl
c-BTFO4 X = SO_2, R = H
c-DABTFO4 X = SO_2, R = acetyl

Scheme 1. Photochromic reaction of diarylethene derivatives.

Keywords: Photochromic reaction; Diarylethene; Fluorescence modulation; Fatigue resistance.

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In our previous study, we found that 1,2-bis(2-methyl-1-benzothiophene-1,1-dioxide-3-yl)perfluorocyclopentene (BTFO4) is very suitable for the nondestructive fluorescence readout application because of the high fluorescence intensity of the closed-ring isomer.[11] However, the photo-stability of BTFO4 is rather worse compare with unoxidized diarylethene, BTF6. As part of a program for the design of an efficient and highly fluorescent photochromic material with high photo-stability, we report herein a new diarylethene molecule, 1,2-bis(6-acetyl-2-methyl-1-benzothiophene-3-yl)-perfluorocyclopentene (DABTFO4), a modified structure of the BTFO4, which demonstrates good fluorescence and photochromic properties with excellent photo-stability eligible for the nondestructive readout.

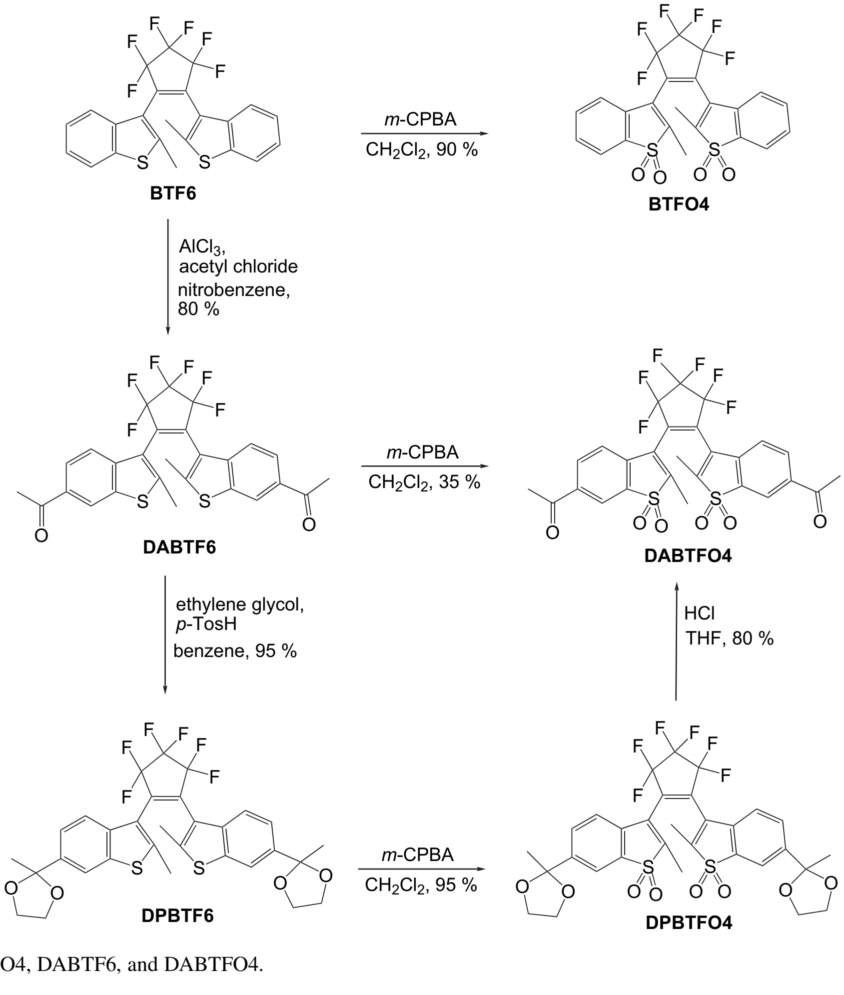
2. Results and discussion

2.1. Synthesis

Diarylethenes were prepared according to Scheme 2. The syntheses of 1,2-bis(2-methyl-1-benzothiophene-3-yl)perfluorocyclopentene (BTF6) and 1,2-bis(6-acetyl-2-methyl-1-benzothiophene-3-yl)perfluorocyclopentene (DABTF6) were previously described in the literature.[12] The direct oxidation of BTF6 and DABTF6 using 3-chloroperbenzoic acid gave BTFO4 (90%)[11] and DABTFO4 (35%), respectively. It was thought that the low yield obtained in the DABTF6 oxidation might be due to the Baeyer–Villiger oxidation type side reaction. Thus, to increase the yield of DABTFO4 formation, the carbonyl group of DABTF6 was converted to 1,3-dioxolane group[13] (DPBTF6) before the oxidation. The subsequent oxidation of DPBTF6 using *m*-CPBA followed by deprotection of the dioxolane group gave DABTFO4 in high yield (72% in three steps).

^{1}H NMR of the open-ring isomer of DABTFO4 (o-DABTFO4) showed two methyl peaks at 2.26 and 2.11 ppm corresponding to parallel (p-) and anti-parallel (ap-) form of o-DABTFO4, respectively. The relative population between the p- and ap-conformer calculated from the integration of the two peaks was determined to be 50:50, which is similar to that of o-BTFO4, however, quite different from that of o-BTF6 and o-DABTF6 (35:65).[14]

The photo-cyclization process of DABTFO4 under UV light (312 nm) was followed using ^{1}H NMR in $CDCl_3$ (5×10^{-3} M). Interestingly, a new singlet peak at 1.87 ppm, which may correspond to the closed-ring isomer of DABTFO4 (c-DABTFO4) was appeared along with decreasing intensities of o-DABTFO4 signals. At the photostationary state, the signals of o-DABTFO4 were almost disappeared indicating that the photo-cyclization yield of the reaction is higher than 99%, which is far better than that of other diarylethenes such as BTFO4 (80%), DABTF6 (73%), and BTF6 (43%).



Scheme 2. Synthesis of BTFO4, DABTF6, and DABTFO4.

2.2. Photophysical properties

2.2.1. Absorption spectra. Ground-state absorption spectra of (A) o-BTF6, (B) o-BTFO4, (C) o-DABTF6, and (D) o-DABTFO4 in ethyl acetate (1.0×10^{-5} M) at room temperature are shown in Figure 1 (solid line). The dashed line in Figure 1 represents the absorption spectra of the photostationary state of (A) BTF6, (B) BTFO4, (C) DABTF6, and (D) DABTFO4 in ethyl acetate at room temperature following UV illumination for 10 min. Photo-cyclization upon UV exposure, yielding the closed-ring isomer leads to spectral change toward longer wavelength compared to the corresponding open-ring isomer. A key finding is that the absorption maximum (λ_{max}) of the closed-ring isomer of the oxidized BTF6 derivatives (c-BTFO4 and c-DABTFO4) substantially deviate from that of the corresponding BTF6 derivatives (c-BTF6 and c-DABTF6). The c-DABTF6 showed two absorption bands at 370 and 552 nm, whereas the c-DABTFO4 showed only one absorption band at 412 nm. The spectral feature of the c-DABTFO4 is similar to that of previously reported c-BTFO4 molecule, except the slight red-shift of the absorption maximum from 398 to 412 nm and increase in molar absorption extinction coefficient from 21,000 to 27,900 $M^{-1}\,cm^{-1}$ in c-DABTFO4. Table 1 summarizes the photophysical properties of diarylethene derivatives.

2.2.2. Fluorescence spectra. Steady-state fluorescence spectra of o-DABTF6 and o-DABTFO4 with 315 nm photo-excitation in ethyl acetate (1.0×10^{-5} M) are shown in Figure 2A and B (solid line), respectively. Upon photo-cyclization, the fluorescence intensity of c-DABTF6 (λ_{ex} 552 nm) was decreased, whereas that of c-DABTFO4 (λ_{ex} 412 nm) was significantly increased as shown in Figure 2A and B (dashed line), respectively. The inset of Figure 2B shows the fluorescence spectra of c-DABTFO4 and c-BTFO4 (λ_{ex} 398 nm), indicating that the fluorescence intensity of c-DABTFO4 is five times stronger than that of

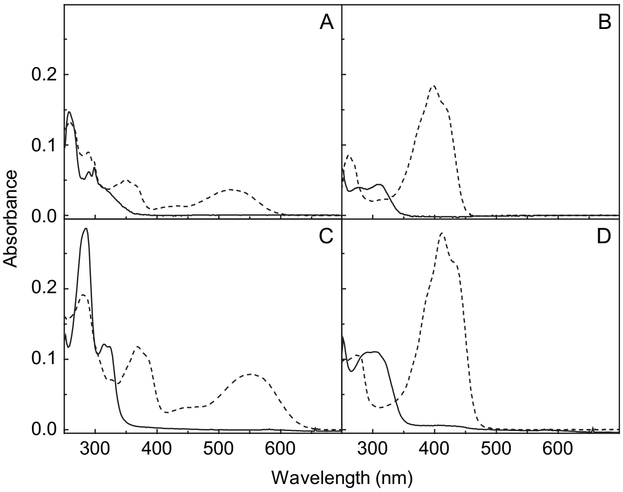


Figure 1. Absorption spectra of (A) BTF6, (B) BTFO4, (C) DABTF6, and (D) DABTFO4 in ethyl acetate (1.0×10^{-5} M) at room temperature; open-ring isomer (solid line), photostationary state (dashed line).

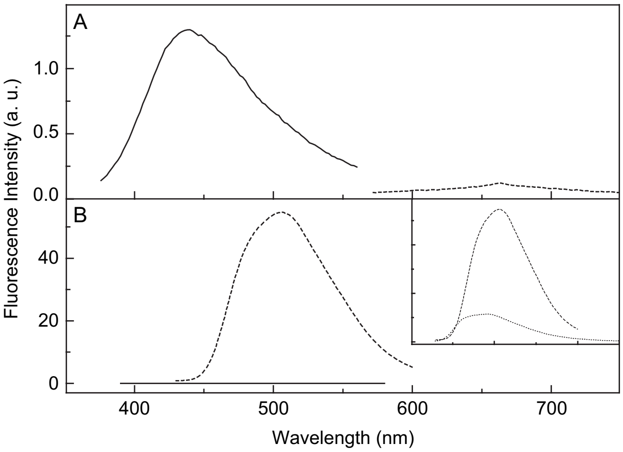


Figure 2. Steady-state fluorescence spectra upon photo-excitation at absorption maximum for (A) o-DABTF6 (solid line) and c-DABTF6 (dashed line), (B) o-DABTFO4 (solid line) and c-DABTFO4 (dashed line) in ethyl acetate (1×10^{-5} M) at room temperature. The inset shows the fluorescence spectra of c-DABTFO4 (dashed) and c-BTFO4 (dotted line).

Table 1. Photophysical properties of diarylethene derivatives

	Absorption λ_{max} (nm)/ ε ($10^3\,M^{-1}\,cm^{-1}$)		Emission λ_{max} (nm)/ fluorescence quantum yield (Φ_{em})		Fluorescence intensity ratio (Δ_{fl}) between open-ring and closed-ring isomer[a]	
	Open-ring isomer	Closed-ring isomer[b]	Open-ring isomer[c]	Closed-ring isomer[d]	Δ_{fl} (315 nm excitation)	Δ_{fl} (excitation at λ_{max} of closed-ring isomer)
BTF6	258/16.0 290/6.2 299/6.8	276/14.0 352/12.0 523/10.0	436/0.012	—[e]	1.4	—[e]
DABTF6	286/28.6 316/12.0 324/12.8	276/16.2 368/16.0 552/10.8	430/0.0055	—[e]	2.9	—[e]
BTFO4	276/3.7 308/4.1	262/9.1 398/21.0	464/0.025	492/0.011	2.7	12
DABTFO4	302/11.1	274/10.6 412/27.9	484/0.0027	506/0.036	0.34	58

[a] Determined at photostationary state.

[b] Calculated from UV spectra by using Eq. $[A]_{PSS}=[A]_{open}\times(1-\text{conversion})+[A]_{closed}\times(\text{conversion})$. Ignored the shoulder peak.[18]

[c] Determined using fluoranthene as the reference (0.30:312 nm photo-excitation in cyclohexane).

[d] Determined using 3-aminofluoranthene as the reference (0.53:400 nm photo-excitation in cyclohexane).

[e] Not determined due to weak signal.

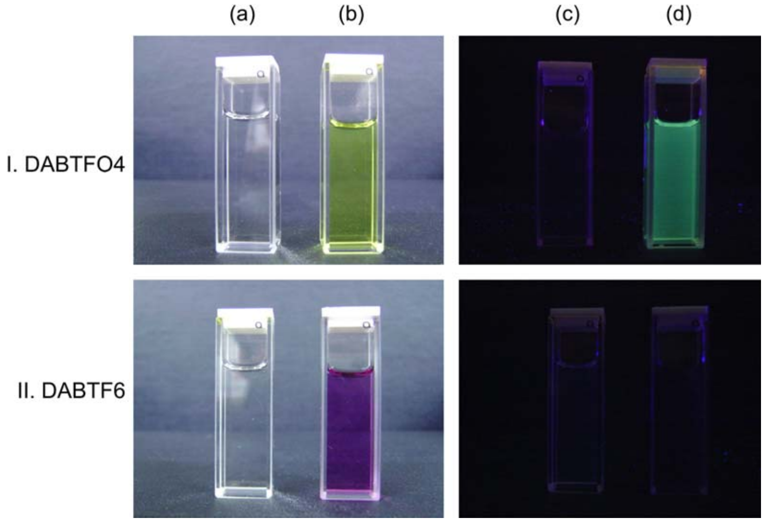


Figure 3. Photographs of solutions containing DABTFO4 (1.0×10^{-4} M in ethyl acetate) (I): color of (a) o-DABTFO4 (before UV irradiation under room light) and (b) c-DABTFO4 (under photostationary state after UV irradiation); fluorescence (photo-excitation with 365 nm UV lamp) of (c) o-DABTFO4 (no emission), and (d) c-DABTFO4 (green emission), as compared to those of o-DABTF6 and c-DABTF6 (no emission) in II, respectively.

c-BTFO4. The fluorescence quantum yield of c-BTFO4 and c-DABTFO4 is determined to be 0.011 and 0.036, respectively, using 3-aminofluoranthene (0.53 in cyclohexane) as the reference upon 400 nm photo-excitation (Table 1). Thus, it is clear that the introduction of acetyl group at 6 and 6′ positions as well as sulfonyl group at 1 and 1′ positions of the benzothiophene ring in diarylethene unit significantly enhances the fluorescence quantum yield of the closed-ring isomer and leads spectral shift to red (14 nm). Such a high fluorescence quantum yield of the c-isomer is unique to the oxidized diarylethenes. Diarylethenes have been known to exhibit fluorescence only in open-ring isomer. Upon oxidation of sulfide to sulfone, however, they show high fluorescence in the closed-ring isomer even though they do not contain extra fluorophore, as we reported before for BTFO4.[11] As a result of increasing fluorescence quantum yield, the photochromism and photo-induced fluorescence modulation of DABTFO4 could be easily observable with naked eyes. Figure 3 shows photographs exhibiting color change and emission of the solution containing DABTFO4 and DABTF6 (1.0×10^{-4} M in ethyl acetate). The colorless solution containing o-DABTFO4 (no emission) changed to yellow upon exposure to a UV light to form c-DABTFO4, which emits strong green light upon 365 nm photo-excitation. On the other hands, DABTF6 shows color change to a reddish purple upon photo-cyclization, which doesn't have any emission under the same condition.

2.3. Photochromic properties

2.3.1. Ring closing and ring opening quantum yield. Figure 4 represents the photochromic change of BTF6 (open square), DABTF6 (open circle), BTFO4 (closed square), and DABTFO4 (closed circle) by alternating UV and visible illumination as a function of time. The absorption change was monitored at absorption maximum of the closed-ring isomer (542 nm for DABTF6, 412 nm for DABTFO4, 524 nm for BTF6, and 398 nm for BTFO4). Upon 312 nm irradiation, the absorbance at $\lambda_{\max}$ of the samples was increased, while it was decreased upon visible light illumination using Xenon lamp. The cyclization and ring opening quantum yield of DABTF6, DABTFO4, and BTFO4 were determined using Eqs. 1 and 2, respectively.[15] BTF6 was used as a reference.[16]

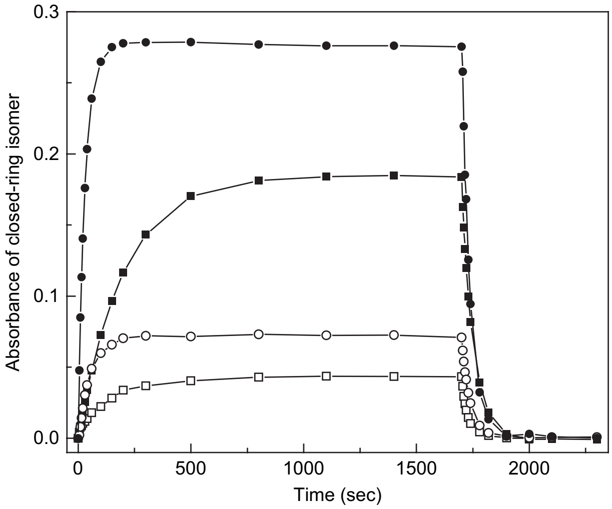


Figure 4. Photochromic behavior of BTF6 (open square), DABTF6 (open circle), BTFO4 (closed square), and DABTFO4 (closed circle) in ethyl acetate solution (1×10^{-5} M) at room temperature upon alternating 312 nm and visible illumination (BTF6: 523 nm, DABTF6: 552 nm, BTFO4: 398 nm, DABTFO4: 412 nm) using Xenon lamp as a function of time.

$$\ln\frac{\mathrm{Abs}(\infty)-\mathrm{Abs}(0)}{\mathrm{Abs}(\infty)-\mathrm{Abs}(t)}=2.303\times10^{3}\times I_0\times\varepsilon_0\times\Phi_{\mathrm{o-c}}\frac{C_0}{C_\mathrm{c}(\infty)}t \tag{1}$$

$$\ln\frac{\mathrm{Abs}(0)}{\mathrm{Abs}(t)}=2.303\times10^{3}\times I_0\times\varepsilon_0\times\Phi_{\mathrm{c-o}}t \tag{2}$$

Where Abs(∞) is the photostationary state, Abs(t) is the absorbance at $\lambda_{\max}$ of closed-ring isomer at time t. I_0 is the irradiation light intensity, and ε_o and ε_c are molar extinction coefficients of open and closed-ring isomer at the irradiation

Table 2. Photochromic properties of diarylethene derivatives in ethyl acetate

	Quantum yield		By-product formation time constant (min)[c]
	Cyclization[a]	Ring opening[b]	
BTF6	0.31[d]	0.28[d]	1300±100
DABTF6	0.46	0.15	11,000±1000
BTFO4	0.22	0.061	900±50
DABTFO4	0.40	0.055	3300±200

[a] Measured at 312 nm.
[b] Measured at λ_{max}.
[c] Fitted with exponential decay.
[d] Taken from Ref. 16.

wavelength, respectively. Φ_{o-c} and Φ_{c-o} are cyclization and ring opening quantum yield and C_0 and C_c are the total concentration and the concentration of closed-ring isomer at the photostationary state, respectively. The cyclization and ring opening quantum yield are summarized in Table 2.

2.3.2. Fluorescence modulation. We also investigated the photochromic properties of DABTFO4 in ethyl acetate (1.0×10^{-5} M) at room temperature by modulating the fluorescence intensity using alternating UV and visible light irradiation. Figure 5 illustrates the photochromically driven fluorescence modulation recorded at 505 nm with 412 nm photo-excitation as a function of time. Upon UV irradiation, the fluorescence intensity was increased (unshaded regions), whereas upon visible light illumination, it was decreased to the original intensity (shaded regions). For comparison, the photochromically driven fluorescence modulation of BTFO4 are also shown in Figure 5.

We have found two important features for DABTFO4 compared with the unsubstituted BTFO4 system. First, the photo-induced fluorescence change (Δ_{fl}) is much significant in DABTFO4 (Δ_{fl}=58) than in BTFO4 system (Δ_{fl}=12), as determined from the ratio of the maximum (closed-ring isomer) and minimum (open-ring isomer) fluorescence intensity (Table 1). It is desirable to have high fluorescence contrast (Δ_{fl}) for signal readout, which is essential for nondestructive photochromic readout application. Second, as mentioned before in Figure 4, the photo-cyclization rate is much improved in DABTFO4 and the ring opening rate is slightly improved compared with BTFO4, which is related to the writing (recording) and erasing speed in the erasable optical memory application. In addition, we have not observed significant fluorescence intensity decay while reading the signal with 412 nm light for longer than 1 h, indicating that DABTFO4 can be applied as an active media for a nondestructive optical readout system in the optical memory or all-optical switching device.

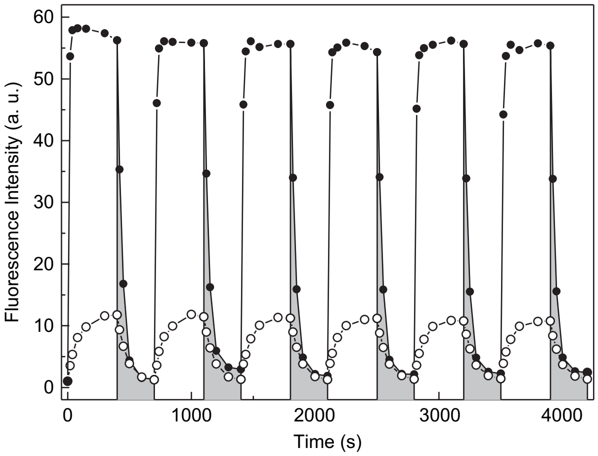


Figure 5. Modulation of fluorescence intensity of BTFO4 (open circle, λ_{ex}=398 nm, λ_{em}=492 nm) and DABTFO4 (closed circle, λ_{ex}=412 nm, λ_{em}=505 nm) in ethyl acetate (1×10^{-5} M) upon alternating 312 nm UV lamp (unshaded areas) and visible light (shaded areas) illumination.

2.3.3. Fatigue properties. Finally, we investigated the fatigue properties of various types of diarylethenes in ethyl acetate (1.0×10^{-5} M) at room temperature by UV light irradiation for 500 min. Figure 6 illustrates the absorbance changes of diarylethenes (BTF6, open square; DABTF6, open circle; BTFO4, closed square; and DABTFO4, closed circle) at λ_{max} of closed-ring isomer as a function of UV illumination time. Initially, the absorbance was increased to A_t (t=0) as a result of photo-cyclization from open-ring isomer to closed-ring isomer and then decreased probably due to an irreversible photo-reaction (Scheme 3), which is strongly related with fatigue property.[17] Interestingly, as shown in Figure 6, the substitution of acetyl group at 6-position of benzothiophene subunit leads to a significant improvement in the photo-stability of the oxidized diarylethene (DABTFO4) as compared with BTFO4 (3300 vs 900 min). Similar effect was observed for DABTF6 and BTF6 (DABTF6: 11,000 min vs BTF6: 1300 min). Table 2 summarizes the by-product formation rate constant of diarylethene derivatives. Considering the photo-cyclization rate (DABTFO4: 0.5 min and BTFO4: 3.5 min) and the photo-induced fluorescence change (DABTFO4: Δ_{fl}=58 and BTFO4: Δ_{fl}=12) of the oxidized diarylethenes, the overall fatigue property of DABTFO4 have improved more than 140 times compared with BTFO4. This result suggests that DABTFO4 is an ideal material for photo-induced fluorescence modulation and other applications based on photochromism with high fatigue resistance.

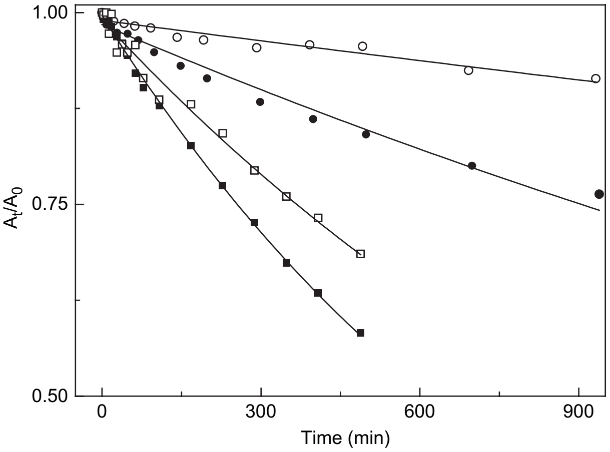
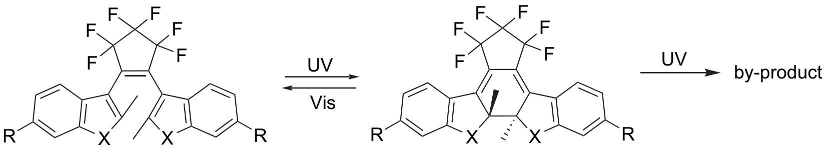


Figure 6. The absorbance changes of BTF6 (open square), DABTF6 (open circle), BTFO4 (closed square), and DABTFO4 (closed circle) at absorption maximum of closed-ring isomer as a function of UV illumination time in ethyl acetate (1×10^{-5} M). The data are fitted with exponential decay (line) and the fitting data (photo-reaction time) represent the time to reach 37% of its initial absorbance following UV illumination.



Scheme 3. Photochromic reaction and the by-products formation of diarylethene derivatives.

3. Conclusion

In summary, by diacetylation and oxidation of BTF6, we have synthesized highly fluorescent photochromic material with high fatigue resistance. The fluorescence quantum yield of c-DABTFO4 was enhanced significantly, and the photochromic properties such as cyclization yield and the photostability of DABTFO4 were greatly improved compared with unsubstituted BTFO4. Overall, the results suggest that DABTFO4 is a challenging material to realize a photo-induced fluorescence modulation applicable for nondestructive fluorescence readout memory and switch applications based on a reversible photochromic conversion.

4. Experimental

4.1. General

Octafluorocyclopentene was purchased from TCI. All other reagents and spectrograde solvents were purchased from Aldrich. Melting points were determined with Laboratory Devices Mel-Temp 3.0 melting point apparatus. The ^{1}H and ^{13}C NMR spectra were obtained using JEOL JNM-AL300 spectrometer at 300 and 75 MHz in $CDCl_3$, respectively, with tetramethylsilane as the internal reference. HRMS spectra were obtained with JEOL JMS-700 spectrometer. FTIR measurements were performed using a JASCO FTIR-430 instrument. UV absorption spectra were recorded on a Shimadzu UV-3100 spectrophotometer in spectroscopy grade ethyl acetate. Fluorescence spectra were collected in spectroscopy grade ethyl acetate on Fluoro Max-2 spectrophotometer equipped with a 150 W ozone-free xenon lamp. UV and visible irradiations were performed with standard lamps used for visualizing TLC plates (VL6L; 312 nm, 8 mW cm^{-2}) and a 100 W tungsten lamp and the samples were placed in a glass chamber maintained at room temperature. The photochromic changes as a function of time were carried out using 500 W Xe lamp (Newport 74000) equipped with a monochromator (Newport 66921) (312 nm–408–410 μW, 398 nm–1.3 mW, 412 nm–1.5 mW, 406 nm–1.4 mW, 524 and 528 nm–2.6 mW, and 550 nm–2.8 mW). Then, photochromic reaction quantum yields were determined according to the method described in Ref. 15. Flash column chromatography was performed with Merck silica gel 60 (70–230 mesh). BTF6 and DABTF6 were synthesized according to the literature procedure.[12] ^{1}H NMR (5×10^{-3} M, $CDCl_3$) of closed-ring isomer and conversion were determined after irradiation at 312 nm using UV lamp until reached photostationary state.

4.1.1. 1,2-Bis(2-methyl-1-benzothiophene-1,1-dioxide-3-yl)perfluorocyclopentene (BTFO4). A mixture of o-BTF6 (1.0 g, 2.1 mmol), and 70% 3-chloroperbenzoic acid (2.9 g, 11.8 mmol) in dichloromethane (50 mL) was stirred for 24 h at room temperature. The solution was washed with a saturated solution of Na_2SO_4. The organic layer was separated and dried over $MgSO_4$ and concentrated in vacuo. Flash chromatography (silica gel) yielded o-BTFO4 in 90% yield. Mp 294 °C (decomp.); ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.78 (d, J=7.2 Hz, ap-2H), 7.72 (d, J=7.2 Hz, p-2H), 7.66–7.55 (m, ap-4H), 7.50–7.41 (m, p-4H), 7.15 (d, J=7.2 Hz, ap-2H and p-2H), 2.20 (s, p-6H), 2.06 (s, ap-6H), ap:p=50:50; FTIR (KBr-cast): 2995, 2952, 2927, 2851, 1459, 1451, 1433, 1312, 1278, 1248, 1225, 1205, 1172, 1144, 1114, 1081, 1060, 1040, 991, 963, 946, 849, 836, 825, 770, 762, 744, 736, 690, 558, 541, 525 cm^{-1}; HRMS (70 eV, EI) m/z calcd for $C_{23}H_{14}F_6O_4S_2$: 532.0244; found: 532.0237; ^{1}H NMR (300 MHz, $CDCl_3$) of the closed-ring isomer (c-BTFO4): δ=8.26 (d, J=7.5 Hz, 2H), 8.04 (d, J=7.5 Hz, 2H), 7.88–7.71 (m, 4H), 1.85 (s, 6H).

4.1.2. 1,2-Bis[6-{1′-(1″,3″-dioxolanyl)ethyl}-2-methyl-1-benzothiophene-3-yl]perfluorocyclopentene (DPBTF6). A mixture of o-DABTF6 (0.88 g, 1.6 mmol), ethylene glycol (2 mL, 32 mmol), and *p*-toluenesulfonic acid monohydrate (61 mg, 0.32 mmol) in benzene (300 mL) was refluxed for two day with a Dean–Stack condenser. The solution was washed with a saturated solution of $NaHCO_3$. The organic layer was separated and dried over $MgSO_4$ and concentrated in vacuo. Flash chromatography (silica gel) yielded o-DPBTF6 in 95% yield. Mp 87–89 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.81 (s, ap-2H), 7.71 (s, p-2H), 7.59 (d, J=8.4 Hz, ap-2H), 7.49–7.44 (m, ap-2H and p-2H), 7.27 (d, J=8.4 Hz, p-2H), 4.05–3.99 (m, ap-4H and p-4H), 3.80–3.75 (m, ap-4H and p-4H), 2.47 (s, p-6H), 2.20 (s, ap-6H), 1.67 (s, ap-6H), 1.54 (s, p-6H), ap:p=70:30; HRMS (70 eV, EI) m/z calcd for $C_{31}H_{26}F_6O_4S_2$: 640.1177; found: 640.1171; ^{1}H NMR (300 MHz, $CDCl_3$) of the closed-ring isomer (c-DPBTF6): δ=7.82 (d, J=8.1 Hz, 2H), 7.36 (d, J=1.5 Hz, 2H), 7.25 (dd, J_1=8.1 Hz, J_2=1.5 Hz, 2H), 4.06–3.99 (m, 4H), 3.81–3.77 (m, 4H), 1.99 (s, 6H), 1.63 (s, 6H).

4.1.3. 1,2-Bis[6-{1′-(1″,3″-dioxolanyl)ethyl}-2-methyl-1-benzothiophene-1,1-dioxide-3-yl]perfluorocyclopentene (DPBTFO4). The o-DPBTFO4 was prepared in 95% yield using the method to prepare o-BTFO4. Mp 117–119 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.89 (s, ap-2H), 7.83 (s, p-2H), 7.70 (d, J=7.8 Hz, ap-2H), 7.50 (d, J=6.9 Hz, p-2H), 7.10–7.04 (m, ap-2H and p-2H), 4.06–3.81 (m, ap-4H and p-4H), 3.77–3.61 (m, ap-4H and p-4H), 2.17 (s, p-6H), 2.04 (s, ap-6H), 1.63 (s, ap-6H), 1.56 (s, p-6H), ap:p=60:40; HRMS (70 eV, EI) m/z calcd for $C_{31}H_{26}F_6O_8S_2$: 704.0973; found: 704.0978; ^{1}H NMR (300 MHz, $CDCl_3$) of the closed-ring isomer (c-DPBTFO4): δ=8.19 (d, J=8.5 Hz, 2H), 8.12 (s, 2H), 7.92 (d, J=8.5 Hz, 2H), 4.09

(t, J=7.0 Hz, 4H), 3.80 (t, J=7.0 Hz, 4H), 1.82 (s, 6H), 1.67 (s, 6H).

4.1.4. 1,2-Bis(6-acetyl-2-methyl-1-benzothiophene-1,1-dioxide-3-yl)perfluorocyclopentene (DABTFO4). A solution of o-DPBTFO4 (0.46 g, 0.65 mmol) in THF (25 mL) was added 37% HCl (1 mL). The solution was stirred for 3 h at room temperature. After completion of reaction, H_2O (50 mL) was added, extracted with CH_2Cl_2 (2×50 mL), and washed with aqueous Na_2CO_3 (2×50 mL). The organic layer were dried $MgSO_4$, filtered, and the solvent was removed. The residue was purified by chromatography on silica gel to give o-DABTFO4 (0.32 g) with 80% yield. Mp 128–130 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=8.31 (s, ap-2H), 8.25 (s, p-2H), 8.22 (d, J=8.5 Hz, ap-2H), 8.06 (d, J=8.5 Hz, p-2H), 7.27–7.23 (m, ap-2H and p-2H), 2.67 (s, ap-6H), 2.62 (s, p-6H), 2.26 (s, p-6H), 2.11 (s, ap-6H); FTIR (KBr-cast): 3098, 9067, 3049, 3004, 2923, 1695, 1600, 1569, 1436, 1413, 1318, 1276, 1246, 1202, 1151, 1077, 1043, 994, 956, 913, 844, 805, 734, 682, 667, 643, 612, 601, 570, 537 cm^{-1}; HRMS (70 eV, EI) m/z calcd for $C_{27}H_{18}F_6O_6S_2$: 616.0449; found: 616.0452; ^{1}H NMR (300 MHz, $CDCl_3$) of the closed-ring isomer (c-DABTFO4): δ=8.52 (d, J=1.3 Hz, 2H), 8.41 (dd, J_1=8.5 Hz, J_2=1.3 Hz, 2H), 8.35 (d, J=8.5 Hz, 2H), 2.75 (s, 6H), 1.87 (s, 6H).

4.1.5. Synthesis of DABTFO4 from DABTF6. A mixture of o-DABTF6 (1.0 g, 1.8 mmol) and 70% 3-chloroperbenzoic acid (2.5 g, 10 mmol) in dichloromethane (50 mL) was stirred for 24 h at room temperature. The solution was washed with a saturated solution of Na_2SO_4. The organic layer was separated and dried over $MgSO_4$ and concentrated in vacuo. Flash chromatography (silica gel) yielded o-DABTFO4 in 35% yield.

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