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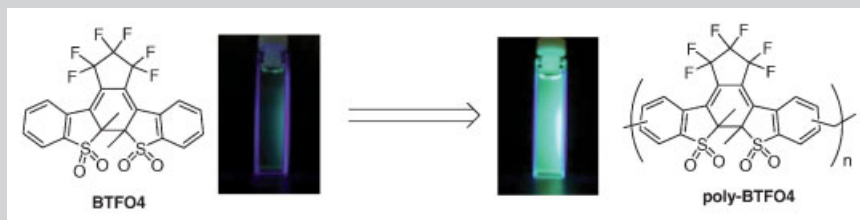
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**Summary:** A highly fluorescent photochromic polymer, poly-BTFO4, was prepared. The fluorescence quantum yield of the poly-BTFO4 was six times higher than that of BTFO4. Fatigue resistance of the polymer at its photostationary state was significantly enhanced compared with that of BTFO4.

Importantly, the poly-BTFO4 film also showed an efficient photochromism as well as strong fluorescence similar to the results in solution, which allow photoinduced fluorescence switching applicable to optical switches.



Improvement of fluorescence quantum yield and fatigue resistance.

## A High-Content Diarylethene Photochromic Polymer for an Efficient Fluorescence Modulation

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**Keywords:** diarylethene; fatigue analysis; fatigue resistance; fluorescence; photochromism; polymerization

### Introduction

Extensive research studies on photochromic materials in the last few years have been motivated by the potential applications of these molecules for photonics application such as optical memory and switch.<sup>[1,2]</sup> Photochromic materials based on diarylethene, efficiently undergo reversible photocyclization and ring-opening reaction upon irradiation with UV and visible light, respectively.<sup>[3–5]</sup> In order to apply the photochromic materials for information storage devices, the signal readout method for these photochromic materials should avoid the destruction of the recorded data.<sup>[6,7]</sup> Among the various non-destructive methods developed so far, measuring the fluorescence difference between the on and off states has been regarded as the promising readout method because of its single molecular detection sensitivity.<sup>[6]</sup> Our previous studies have shown that a diarylethene containing a sulfone group at the 1- and 1'-positions of benzothiophene subunit

such as 1,2-bis(2-methyl-1-benzothiophene-1,1-dioxide-3-yl)perfluorocyclopentene (BTFO4) is highly fluorescent only when it is in closed form.<sup>[8,9]</sup> This suggests that BTFO4 may be one of the best candidates for optical storage material using non-destructive fluorescence readout method. Since a polymeric material is preferred rather than the low molecular weight molecule for the practical application of the photochromic material,<sup>[10]</sup> we decided to prepare a polymer whose repeating monomeric unit contains BTFO4.

There are several examples of diarylethene polymers such as side-chain copolymers,<sup>[11–16]</sup> side-chain homopolymers,<sup>[17,18]</sup> main-chain copolymers,<sup>[19–23]</sup> and main-chain homopolymers.<sup>[24–27]</sup> However, for our purpose, to prepare a polymer capable of fluorescence readout, we decided to use poly-BTF6 that can be easily prepared from 1,2-bis(2-methyl-1-benzothiophene-3-yl)perfluorocyclopentene (BTF6) in the presence of TiCl<sub>4</sub> and chloromethyl methyl ether as we reported previously.<sup>[27]</sup> This paper

reports the synthesis and characterization of a high-content fluorescent photochromic polymer (poly-BTFO4), which showed a dramatic increase in fluorescence quantum yield and fatigue resistance compared with the corresponding monomeric BTFO4.

## Experimental Part

### Materials and Measurements

All reagents except octafluorocyclopentene (TCI) were purchased from Aldrich. The  $^1\text{H}$  NMR spectra were obtained using a JEOL JNM-AL300 spectrometer at 300 MHz, with tetramethylsilane as the internal reference. FT-IR measurements were performed using a JASCO FT/IR-430 instrument in KBr. GPC analyses (calibrated by polystyrene) were performed on THF solution of polymer using a Waters 515 HPLC pump and Waters TM 410 Differential Refractive Index Detector or Waters 996 Photodiode Array Detector at a flow rate of  $1.0\text{ mL} \cdot \text{min}^{-1}$  through a  $7.8 \times 300\text{ mm}$  column running at  $30^\circ\text{C}$ . DSC analysis was performed using a TA Instrument Q 100. A thermogravimetric analysis (TGA) was performed using a Perkin Elmer TGA 7 thermogravimetric analyzer and a TAC7/DX thermal analysis controller. A polymeric film was fabricated by spin-coating ( $1200\text{ rpm}$  for  $30\text{ s}$ ) onto a quartz plate using the polymer solution in  $\text{CHCl}_3$  ( $5\text{ mg} \cdot \text{mL}^{-1}$ ). The thickness was about  $100\text{ nm}$ , as measured using a surface profiler (Surfcorder ET 3000, Kosaka Laboratory Ltd.). The UV absorption spectra were recorded on a Shimadzu UV-3100 spectrophotometer in solution and film. The fluorescence emission spectra were measured in solution and film with a Fluoro Max-2 spectrophotometer. The standard UV lamps for visualizing the TLC plate (VL-6M,  $312\text{ nm}$ ,  $8\text{ mW} \cdot \text{cm}^{-2}$ ) and the  $100\text{-W}$  tungsten lamp in a glass

chamber were used to carry out the photochromic reaction in this study.

### Synthesis of Poly-BTFO4

A mixture of poly-BTF6<sup>[27]</sup> ( $1.0\text{ g}$ ,  $2.1\text{ mmol}$  based on the monomer unit) and  $70\%$  3-chloroperbenzoic acid ( $2.9\text{ g}$ ,  $11.9\text{ mmol}$ ) in dichloromethane ( $50\text{ mL}$ ) was stirred for  $72\text{ h}$  at room temperature. The solution was washed with a saturated  $\text{Na}_2\text{SO}_3$  and  $\text{NaHCO}_3$  solution. The organic layer was separated and dried over  $\text{MgSO}_4$ , and concentrated in vacuo to obtain the polymer ( $1.0\text{ g}$ ) in  $88\%$  yield.

$^1\text{H}$  NMR ( $300\text{ MHz}$ ,  $\text{CDCl}_3$ ):  $\delta = 7.58\text{--}7.26$  (m, 6H),  $4.13\text{--}3.66$  (m, 2H),  $2.18$  (br s, 3H,  $\text{p-CH}_3$ ), and  $2.06$  (br s, 3H,  $\text{ap-CH}_3$ ).

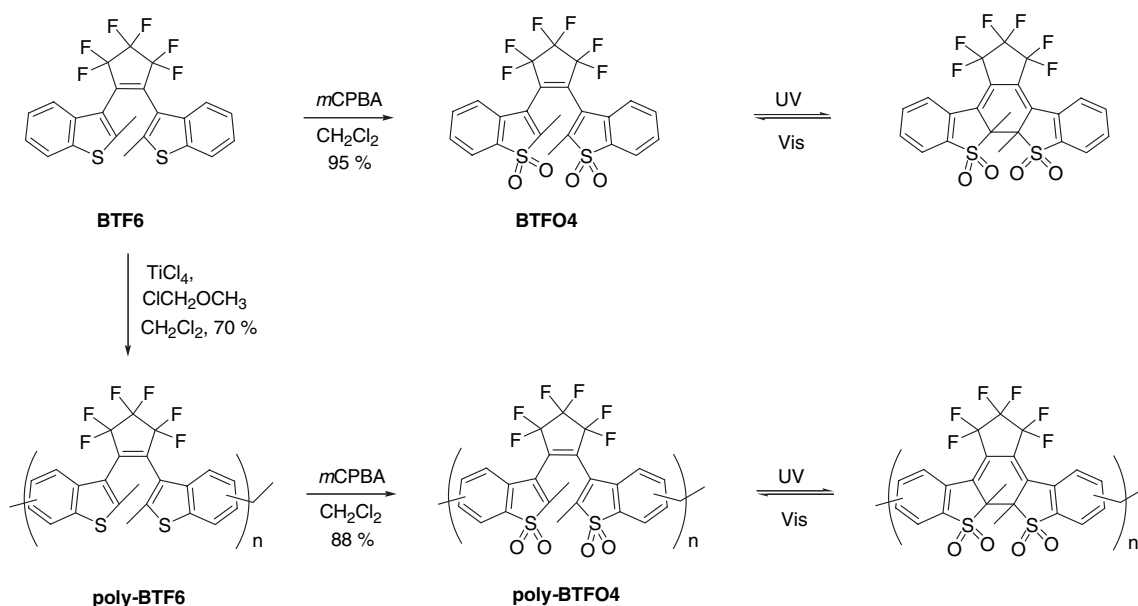
FT-IR (KBr):  $2921$ ,  $1712$ ,  $1635$ ,  $1481$ ,  $1436$ ,  $1316$  ( $\text{SO}_2$ ),  $1278$ ,  $1203$ ,  $1148$  ( $\text{SO}_2$ ),  $1043$ ,  $992$ ,  $955$ ,  $832$  ( $\text{SO}_2$ ),  $756$ ,  $680$ ,  $638$ ,  $559$ ,  $530$ ,  $474$ ,  $432$ ,  $422\text{ cm}^{-1}$ .

$\bar{M}_n = 5822$ , PDI =  $1.46$ .

$T_g = 115^\circ\text{C}$ .

## Results and Discussion

The fully oxidized poly-BTFO4 was prepared from the oxidation of poly-BTF6 using excess amount of 3-chloroperbenzoic acid ( $5.0\text{ equiv.}$ ) in  $88\%$  yield (Scheme 1). Although the poly-BTF6 was readily soluble in common organic solvents,<sup>[27]</sup> a high molecular weight poly-BTFO4 showed poor solubility in organic solvents. Thus the low molecular weight fraction of poly-BTF6 ( $\bar{M}_n\ 3078$ ,  $\bar{M}_w\ 7971$ ) was used to prepare poly-BTFO4. The TGA of the polymer indicated that it is stable upto  $300^\circ\text{C}$ . The



Scheme 1. Synthesis and photochromic reactions of BTFO4 and poly-BTFO4.

$^1\text{H}$  NMR spectrum of the polymer showed broadened peaks at 2.18 and 2.06 ppm similar to those of the monomer, and two additional broadened peaks at 4.13–3.66 ppm representing the bridged methylene proton. There are no signals at 4.66 and 2.94 corresponding to poly-BTF6 indicating that the content of unoxidized BTF6 monomer unit in poly-BTFO4 is negligible.

The ground-state absorption spectra of the open-ring isomer of BTFO4<sup>[8]</sup> and poly-BTFO4 in ethyl acetate at room temperature are illustrated by the solid lines in Figure 1(A) and 1(C), respectively. To compare their photophysical properties such as absorption extinction coefficient and photocyclization yield, the monomer unit concentration of the poly-BTFO4 solution was the same as the concentration of BTFO4 solution. Upon UV irradiation, both compounds underwent photocyclization accompanying their absorption spectral changes (Scheme 1). The dashed lines in Figure 1(A) and 1(C) represent the absorption spectra of BTFO4 and poly-BTFO4 at the photostationary states, respectively. The absorption band of the closed-ring isomer of poly-BTFO4 was slightly red-shifted from the  $\lambda_{\text{max}}$  of the BTFO4 (BTFO4, 398 nm and poly-BTFO4, 412 nm). The absorption intensity of the polymer was about 20% lower than that of the monomer at the photostationary state, implying the low conversion ratio to cyclization (ca. 65%) compared with BTFO4. This result might be related with the rigidity of the photochromic unit in the polymer, which hinders the photocyclization. Upon visible light illumination, the absorption band of the polymer at the visible region disappeared completely and returned to its open-ring isomer. Figure 1(B) and

1(D) show the steady-state fluorescence spectra of the open- and closed-ring isomers of BTFO4 and poly-BTFO4 with 398- and 412-nm photoexcitation, respectively, in ethyl acetate at room temperature. Upon photocyclization, the fluorescence intensities of both BTFO4 and poly-BTFO4 were significantly increased.<sup>[8,9]</sup> The fluorescence quantum yields ( $\phi_F$ ) of the closed-ring isomer of BTFO4 and poly-BTFO4 were determined to be 0.011 and 0.093, respectively, upon 400-nm photoexcitation using 3-aminofluoranthene ( $\phi_F = 0.53$  in cyclohexane) as the reference. This result suggests that the polymer form of BTFO4 leads to a significant increase in the fluorescence quantum yield. We believe that this result is related with the rigidity of light emitting chromophore backbone in the polymer, which diminishes the non-radiative decay process and enhances the fluorescence quantum yield. Figure 2 shows the pictures of solutions containing poly-BTFO4 and BTFO4 upon 400 nm photoexcitation ( $1.0 \times 10^{-4}\text{ M}$  in ethyl acetate). The colorless solutions of the open-ring isomer of BTFO4 and poly-BTFO4 [no emission, Figure 2(A) and 2(C)] were changed to the colored solutions of closed-ring isomer upon exposure to UV light, which emitted a strong green light upon 400-nm excitation as can be seen from the picture. The fluorescence of the closed-ring isomer of poly-BTFO4 is much stronger than that of BTFO4. The poly-BTFO4 film also exhibited good photochromic and fluorescence properties, as shown in Figure 1(E) and 1(F). Upon UV irradiation, a new absorption band appeared in the visible region and the fluorescence intensity was very strong. The color of the film was bleached back upon visible illumination.

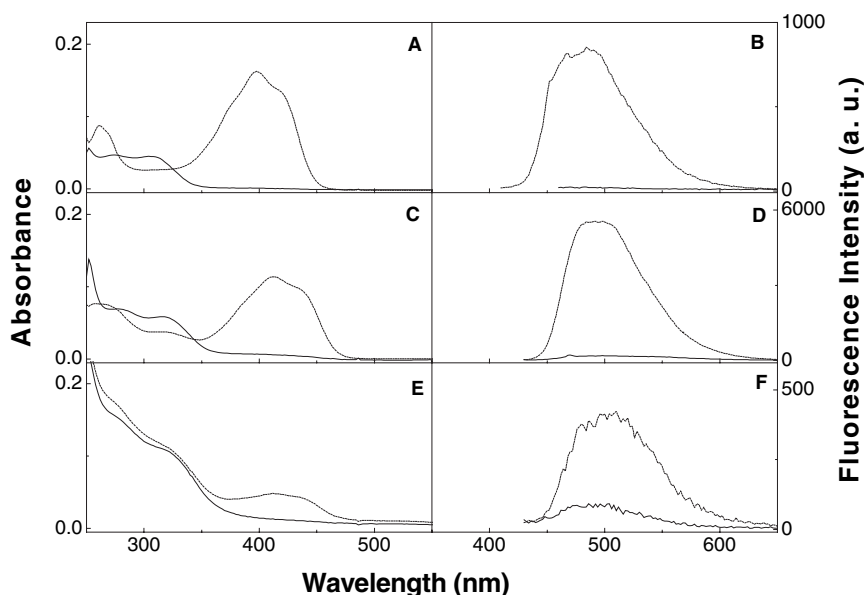


Figure 1. Absorption spectra of (A) BTFO4 ( $1.0 \times 10^{-5}\text{ M}$ ), (C) poly-BTFO4 in ethyl acetate ( $1.0 \times 10^{-5}\text{ M}$  based on the photochromic unit), and (E) poly-BTFO4 in the solid film. Fluorescence spectra of (B) BTFO4 ( $1.0 \times 10^{-5}\text{ M}$ , excitation 398 nm), (D) poly-BTFO4 in ethyl acetate ( $1.0 \times 10^{-5}\text{ M}$  based on the photochromic unit, excitation 412 nm), and (F) poly-BTFO4 in the solid film (excitation 412 nm) for the open-ring isomer (solid line) and the photostationary state (dashed line) at room temperature.

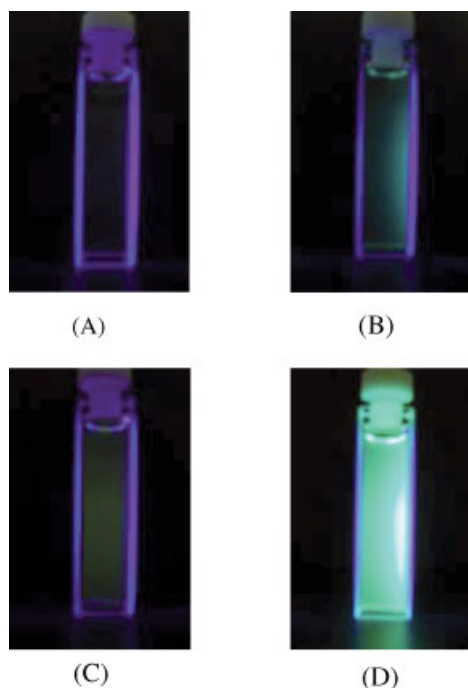


Figure 2. Photographs of the open-ring isomer (C) and a photostationary state (D) of the poly-BTFO4 solution in ethyl acetate ( $1.0 \times 10^{-4}$  M) under 400-nm light. For comparison, open-ring isomer (A) and in a photostationary state (B) of BTFO4 are also shown.

Since the fluorescence quantum yields of both opening isomers of BTFO4 and poly-BTFO4 were extremely low, the modulation of the fluorescence intensity through photochromic conversion can be performed. Thus, we investigated the fluorescence intensity changes of BTFO4 and poly-BTFO4 in ethyl acetate at room temperature using alternating UV and visible light illumination. Figure 3 illus-

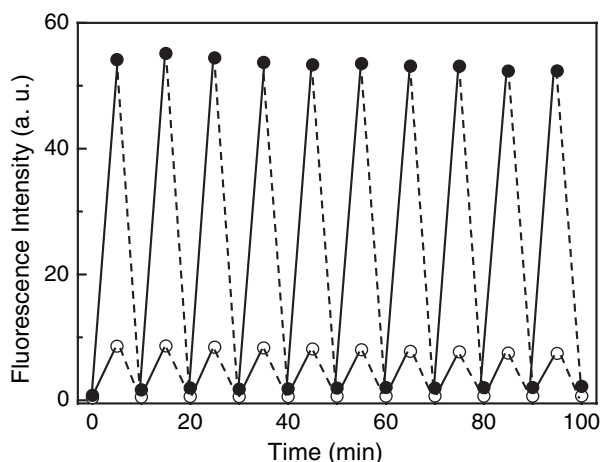


Figure 3. Modulation of the fluorescence signals of BTFO4 (open circles, excitation 398, emission 492 nm) and poly-BTFO4 (closed circles, excitation 412, emission 505 nm) in ethyl acetate ( $1.0 \times 10^{-5}$  M) upon alternative illumination with 312-nm (solid line) and visible (dashed line) light.

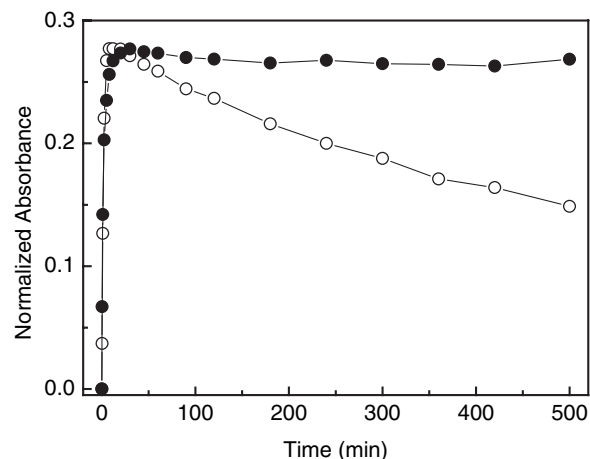


Figure 4. The absorbance changes of BTFO4 (open circles) and poly-BTFO4 (closed circles) at the maximum absorption of the closed-ring isomer as a function of the UV illumination time in ethyl acetate ( $1.0 \times 10^{-5}$  M).

trates the fluorescence signal recorded at 505 and 492 nm following 412- and 398-nm photoexcitation for poly-BTFO4 and BTFO4, respectively, as a function of time. Upon UV irradiation, the fluorescence intensity was increased, whereas it decreased upon visible light illumination. As expected from their fluorescence quantum yields, the fluorescence intensity of poly-BTFO4 through photochromic conversion was much stronger than that of BTFO4 (80 vs. 15 based on the max/min ratio), and persistent while the signal was recorded for more than 1 h, indicating that poly-BTFO4 might be an eligible active medium for a non-destructive optical readout system in an optical memory or all-optical switching device.

Finally, we have examined the photostability of the polymer to see the effect of polymerization on the fatigue property. Figure 4 shows the absorbance changes of BTFO4 (open circles) and poly-BTFO4 (closed circles) in ethyl acetate ( $1.0 \times 10^{-5}$  M) at room temperature at  $\lambda_{\text{max}}$  of the closed-ring isomer as a function of the UV illumination time. After initial increase in the absorbance, which is related to the photocyclization from the open- to the closed-ring isomer, the absorbance decreased. It is believed that prolonged illumination of the sample with UV light may transform the closed-ring isomer to side products as reported by Irie,<sup>[28,29]</sup> Branda,<sup>[30]</sup> and our group.<sup>[31,32]</sup> The most important finding from Figure 4 is that the polymer structure of BTFO4 such as poly-BTFO4 leads to a significant improvement in fatigue resistance compared with BTFO4.

## Conclusion

The highly fluorescent photochromic polymer poly-BTFO4 was prepared by oxidation of poly-BTF6. The fluorescence quantum yield of the poly-BTFO4 was six times higher than

that of BTFO4. Fatigue resistance of the polymer at its photostationary state was significantly enhanced compared with that of BTFO4. Importantly, the poly-BTFO4 film also showed an efficient photochromism as well as strong fluorescence similar to the results in solution, which allow photoinduced fluorescence switching applicable to optical switches.

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