Bistable Photoswitching in the Film of Fluorescent Photochromic Polymer: Enhanced Fluorescence Emission and Its High Contrast Switching

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Photochromism refers to the photoinduced reversible transformation of chemical species between two electronic states characterized by different absorption spectra.[1] Among various photochromic compounds, 1,2-bis(thienyl)ethene (BTE) derivatives are gaining ever-increasing attention in the fields of erasable optical memory and fast optical switch, owing to their high thermal stability, excellent photofatigue resistance, high sensitivity, and characteristic bistability.[2] However, the practical employment of BTEs to the ultrahigh-density erasable optical memory further demands the capabilities of nondestructive readout as well as high-density inclusion of active molecular units into solid media. As for the former issue, reversible photochromic recording which brings about the photoluminescence (PL) modulation has been one of the several viable methods investigated so far.[3] This is attributed to the minimized photoirradiation for PL excitation as well as the weak and narrow PL emission inducing negligible photochromic reaction, i.e., erasure of memory, during the readout cycles. Many recent papers demonstrate that the principle of fluorescence readout modulated by the photochromic reaction works efficiently in the fluorescent BTE-based molecules dissolved in solutions or dilutely embedded in polymer matrices.[3] Multifunctional molecules consisting of integrated fluorescence and BTE units in a single molecule are normally exploited to ensure efficient energy transfer between them. Considering the latter issue of high-density media, on the other hand, only a limited number of papers have dealt with the neat amorphous films of fluorescent BTE-based molecules but with rather unclear and qualitative discussions.[4] One difficult challenge for the practical high-density medium of fluorescent BTE system is the “concentration quenching problem” of fluorescence emission which has long been considered to be inherent as far as the fluorescent molecules are concerned.[5] For the device realization, therefore, innovative classes of fluorescent BTE molecules free from this problem are critically needed, which must provide reversible and bistable photochromism and good film processability at the same time.

Recently, unconventional fluorescent molecules which show gradually enhanced fluorescence emission with increasing concentration, so-called “aggregation-induced enhanced emission (AIEE)”, were originally developed by several groups including us.[6] AIEE molecules are virtually nonfluorescent in the isolated molecular state but strongly fluorescent (typical fluorescence quantum yield >0.6) in the bulk phase due to the specific intermolecular interactions. Therefore, the AIEE fluorophores, if employed, were expected to clear up the above-mentioned two issues of fluorescent BTE system at once. In fact, in our previous work, we have synthesized a cyanostilbene-based AIEE fluorophore with covalently bonded BTE switch, which formed strongly fluorescent nanoparticles as well as the molecular aggregates in poly(methyl methacrylate) (PMMA) film showing reversible and bistable photochromism.[7] High contrast (>10) on/off fluorescence switching and erasable optical recording was successfully demonstrated in these relatively high-loaded solid media.[7]

To further increase the number density of fluorescent BTE molecules in the polymer film and to impart self-processability as well, we aimed at the synthesis of fluorescent photochromic polymer consisting solely of AIEE and BTE units in this work. This plan of fluorescent photochromic polymer synthesis was also encouraged by the significant “polymer effects” in enhancing the photochromic and fluorescent quantum yields as reported by Stellacci et al.[8] and Cho et al.,[9] respectively. Inspired by the molecular structures of our previous AIEE molecules,[6a,b] we have designed poly(DCS−BTE) (see Figure 1 for its chemical structure) as the fluorescent photochromic polymer in this work.

Before proceeding to the polymer synthesis, we tried to identify the AIEE properties of the 1,4-bis(β-cyano-4′-methylstyryl)benzene (DCS) unit in comparison to the structurally related conventional fluorophore, 1,4-bis(4′-methylstyryl)benzene (DS). Syntheses of DCS and DS were carried out according to the reaction routes shown in Scheme 1, and their structures were fully characterized by ^{1}H NMR, FT-IR, mass spectroscopy, and elemental analysis (see Supporting Information for the synthesis and identification data). Polymeric films consisting of DCS (0.2−7.0 wt %) or DS (0.2−5.0 wt %) in PMMA matrix were fabricated by spin-coating, and their UV−vis absorption and PL emission spectra were measured. As a measure of PL efficiency, integrated fluorescence emission in the PL spectra divided by the absorbance in the UV−vis spectra were calculated and subsequently normalized as shown in parts a and b of Figure 2 for DCS and DS, respectively. It is shown in strong contrast that the normalized PL efficiency of DCS increases while that of DS decreases with their concentration in PMMA. Evidently, DCS shows a unique AIEE phenomenon with ultimate fluorescence quantum efficiency of 0.56 (this value was evaluated with the nanoparticle suspension of DCS according to the method reported earlier[7]), but DS shows significant concentration quenching with initial fluorescence quantum efficiency of 0.66 in dilute solution. It is very surprising and worth noting that these structurally identical molecules except for the added CN groups in DCS behave this much differently. Despite these substantial differences in fluorescence intensity change, the bathochromic shift of PL emission as a function of the emitter concentration is commonly observed as seen in Figure 2a,b. This is attributed to the molecular planarization and J-type aggregation in the DCS molecules gated by the specific intermolecular interactions in the solid state,[6,7,10,11] which is clearly supported by the red-shifting absorption band of DCS with increasing con-

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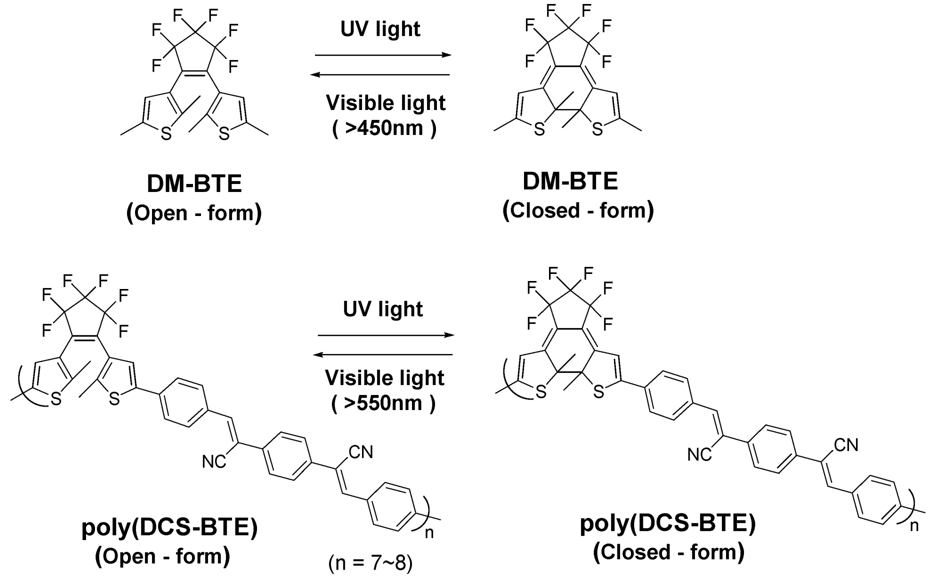
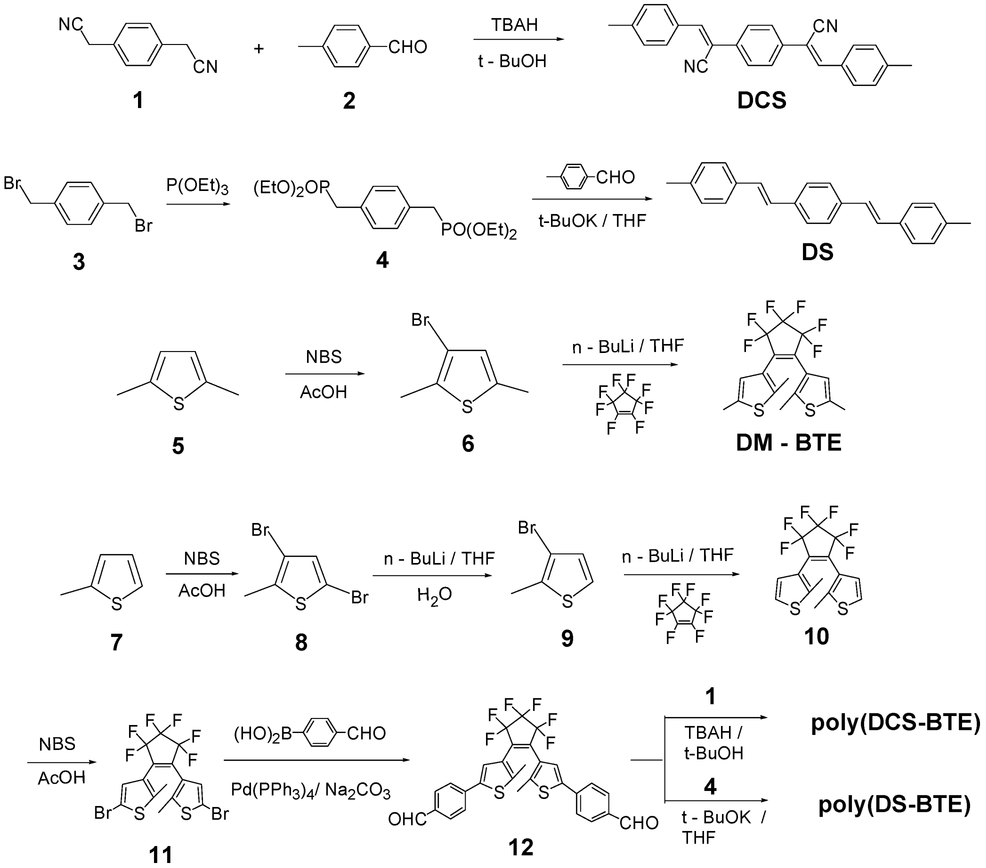


Figure 1. Photochromic reactions of DM−BTE and poly(DCS−BTE).

Scheme 1. Synthetic Routes to the Model Compounds and Fluorescent Photochromic Polymers



centration as shown in the inset of Figure 2a. On the other hand, invariant absorption spectra of DS suggest the excimer emission as the main mechanism of red-shifted PL. Ever increasing PL efficiency of DCS but only at the cost of serious light scattering was observed at the >7 wt % of DCS/PMMA, which again justifies our plan of synthesizing fluorescent photochromic polymer. Because the emission band of DCS in solid state ($\lambda^{\text{film}}_{\text{max em}}$ = 474−536 nm) suitably overlaps with the absorption band of the closed form of 1,2-bis(2′,5′-dimethylthien-3′-yl)perfluorocyclopentene (DM−BTE)[12] photochrome in the solid state ($\lambda^{\text{film}}_{\text{max abs}}$ = 518 nm; see the inset in Figure 2c and see Scheme 1 and Figure 1 for its structure), it is expected that the intramolecular and/or intermolecular energy transfer between them may be very effective in their fluorescent photochromic polymer films.[7]

Encouraged by these model compound studies, an AIEE-based fluorescent photochromic polymer poly(DCS−BTE) was synthesized by the Knoevenagel condensation of 1,4-phenylenediacetonitrile (**1**) and 1,2-bis(2′-methyl-5′-(4″-formylphenyl)thien-3′-yl)perfluorocyclopentene (**12**) according to the reaction sequences illustrated in Scheme 1 (see Supporting Information for

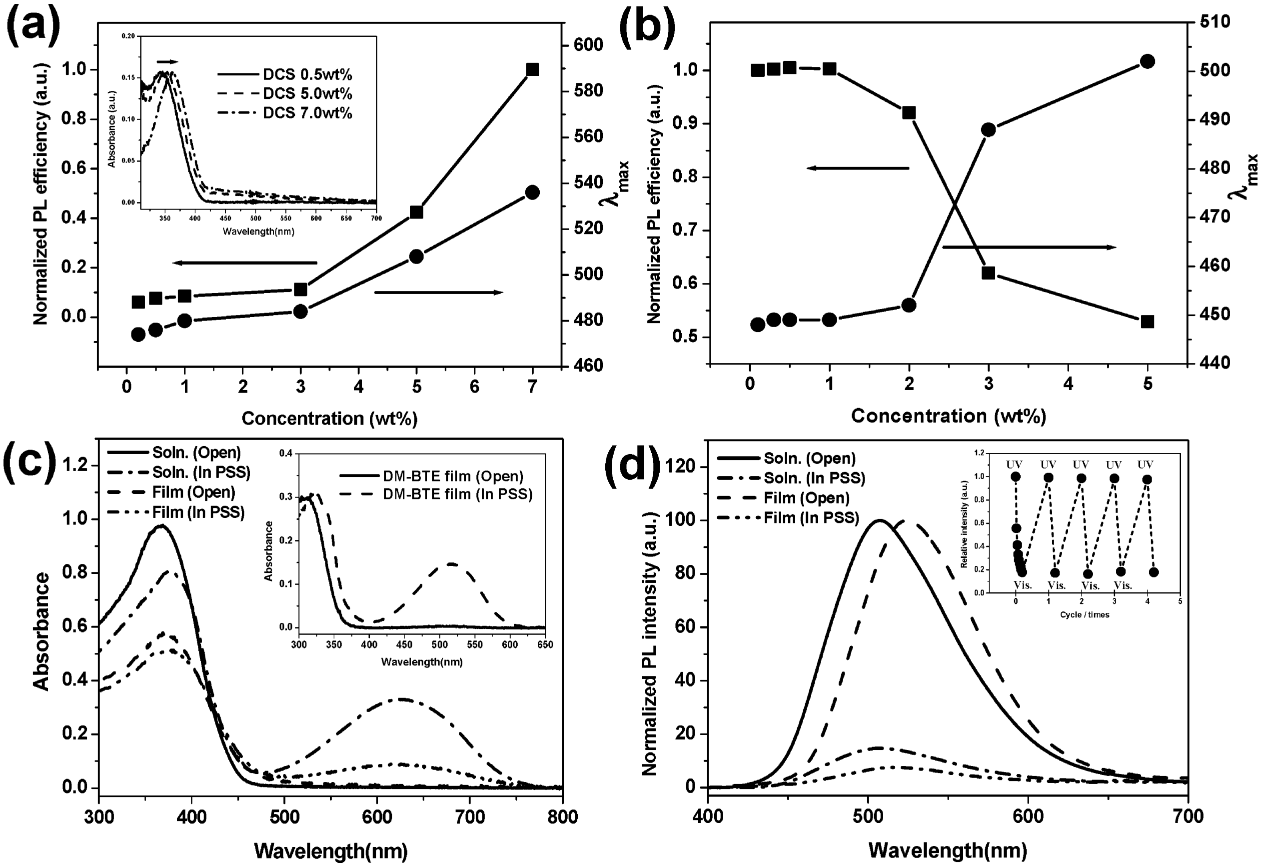


Figure 2. Normalized PL efficiency (■) and the wavelength of PL emission (●) in the spin-coated DCS/PMMA film (a) and DS/PMMA film (b) as a function of their concentration in PMMA matrix. Inset in (a) shows the bathochromic shift of UV–vis absorption in DCS/PMMA films with increasing concentration. UV–vis absorption (c) and PL spectra (d) of the poly(DCS–BTE) in the open form and at the 290 nm photostationary state (PSS). Inset in (c) shows the UV–vis absorption spectra of 6 wt % DM–BTE-loaded PMMA film, and inset in (d) shows the photochromic modulation of PL intensity in the poly(DCS–BTE) film.

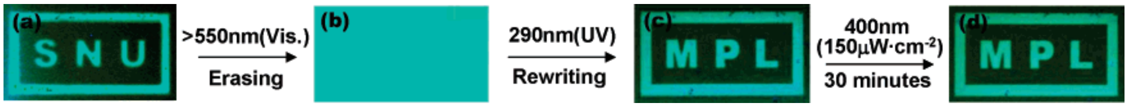


Figure 3. Erasable fluorescence imaging on the spin-coated poly(DCS–BTE) film and its nondestructive readout capability. Writing (a), erasing (b), rewriting (c), and a continuous reading under irradiation with 400 nm light (150 μW cm^{-2}) for 30 min (d). The dark region represents the irradiated area with 290 nm UV light, and the real size of the photomasks is about 1 cm × 2 cm.

the synthesis and identification data for the intermediates, monomers, and polymers). The weight-average molecular weight (M_w) of the poly(DCS–BTE) was ~ 13 000 (M_w/M_n = 2.47), indicating that 7–8-mers of BTE–cyanostilbene repeating units were linked together. Poly(DCS–BTE) showed glass transition temperature at 188 °C and possessed good solubility in common organic solvents, such as chloroform, tetrahydrofuran, and 1,2-dichloroethane, from which optically transparent and highly fluorescent polymer films could be spin-coated easily. On the other hand, poly(DS–BTE) was much less soluble in organic solvents seriously limiting its characterization and film fabrication. Only the low molecular weight oligomer fraction (n = 2–3, M_w = 3705, M_w/M_n = 1.99) of poly(DS–BTE) was marginally soluble in chloroform; thus, it had to be dispersed in PMMA matrix in <5 wt % concentration to afford a transparent polymeric film. Importantly, strongly fluorescent poly(DCS–BTE) film showed high-contrast bistable photochromic switching (vide infra), while weakly fluorescent polymer film containing poly(DS–BTE) was not bistable enough because its photostationary state (PSS) consisted mostly of closed BTE ring under ambient lighting.[2,13,14]

Parts c and d of Figure 2 show the UV–vis absorption and PL spectra, respectively, of the poly(DCS–BTE) in the open form as well as in the 290 nm PSS. When the 290 nm UV light isolated from xenon arc lamp (Driel Instruments, 300 W) through a monochromator was irradiated to the solution or the film of poly(DCS–BTE), the open-form BTE began to photoisomerize into the closed form, which was easily monitored by the appearance of new absorption band at the visible regions (λ_{max} = 626 nm, $\Phi_{pc}^{o\to c}$ = 0.36).[15] Modulated by this photochromic ring closure, PL emission intensity from poly(DCS–BTE) has significantly diminished as shown in Figure 2d. In the PSS, integrated PL intensities were reduced down to the 17% and 10% levels of open-form isomers in solution and film states, respectively. It is most likely that such an outstanding fluorescence quenching in solution at PSS originates from the highly efficient intramolecular energy transfer within a single polymer chain, where the fluorescent DCS unit and the closed-form of BTE photochrome are closely coupled with each other. In the film state, additional intermolecular energy transfer must contribute to the further enhanced fluorescence quenching resulting in the higher contrast ratio of about 10. When the poly(DCS−BTE) sample stabilized in the 290 nm PSS were irradiated with visible light (>550 nm, hand-held lamp, 30 W), the absorption spectra as well as the PL spectra were reversibly and completely restored to the initial open-form states ($\Phi_{pc}^{c\to o} = 0.75 \times 10^{-2}$, $\lambda_{ex} = 575$ nm).[15] The inset graph in Figure 2d shows the photochromic modulation of the fluorescence intensity in the poly(DCS−BTE) film.

Such a strongly enhanced fluorescence emission coupled with high-contrast photochromic switching in poly(DCS−BTE) film suggests their viable application to the erasable optical memory. By employing the patterned illumination through the photomasks, it was successfully demonstrated that the different images could be successfully recorded and erased on the poly(DCS−BTE) film as shown in Figure 3. As indicated by Murase et al. in the literature,[3h] furthermore, all the recorded images in Figure 3 could be nondestructively and repeatedly monitored with the different wavelength, i.e. 400 nm, from the writing and erasing wavelengths inducing photochromic reactions of poly(DCS−BTE), i.e. 290 and >550 nm, respectively, as well as with the minimized photoirradiation for the fluorescence excitation.

In conclusion, we have designed and synthesized a novel class of AIEE-based fluorescent photochromic polymer, poly(DCS−BTE), whose strong fluorescence in the neat polymer film could be photoswitched through the highly efficient bistable photochromism (fluorescence switching ratio >10). Erasable fluorescence photoimaging on the spin-coated poly(DCS−BTE) film was successfully demonstrated.

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Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Crano, J. C.; Guglielmetti, R. J. *Organic Photochromic and Thermochromic Compounds*; Plenum Press: New York, 1999.

(2) (a) Nakamura, S.; Irie, M. *J. Org. Chem.* **1988**, *53*, 6136. (b) Nakayama, Y.; Hayashi, K.; Irie, M. *J. Org. Chem.* **1990**, *55*, 2592. (c) Hanazawa, M.; Sumiya, R.; Horikawa, Y.; Irie, M. *J. Chem. Soc., Chem. Commun.* **1992**, 206. (d) Irie, M. *Chem. Rev.* **2000**, *100*, 1685.

(3) (a) Fernandez, A.; Lehn, J.-M. *Adv. Mater.* **1998**, *10*, 1519. (b) Kawai, T.; Sasaki, T.; Irie, M. *Chem. Commun.* **2001**, 711. (c) Osuka, A.; Fujikane, D.; Shinmori, H.; Kobatake, S.; Irie, M. *J. Org. Chem.* **2001**, *66*, 3913. (d) Yagi, K.; Soong, C. F.; Irie, M. *J. Org. Chem.* **2001**, *66*, 5419. (e) Norsten, T. B.; Branda, N. R. *J. Am. Chem. Soc.* **2001**, *123*, 1784. (f) Chen, B.; Wang, M.; Wu, Y.; Tian, H. *Chem. Commun.* **2002**, 1060. (g) Irie, M.; Fukaminato, T.; Sasaki, T.; Tamai, N.; Kawai, T. *Nature (London)* **2002**, *420*, 759. (h) Murase, S.; Teramoto, M.; Furukawa, H.; Miyashita, Y.; Horie, K. *Macromolecules* **2003**, *36*, 964.

(4) (a) Kim, M.-S.; Kawai, T.; Irie, M. *Opt. Mater.* **2002**, *21*, 271. (b) Kawai, T.; Kim, M.-S.; Sasaki, T.; Irie, M. *Opt. Mater.* **2002**, *21*, 275.

(5) Birks, J. B. In *Photophysics of Aromatic Molecules*; Wiley: London, 1970.

(6) (a) An, B. K.; Kwon, S. K.; Jung, S. D.; Park, S. Y. *J. Am. Chem. Soc.* **2002**, *124*, 14410. (b) An, B. K.; Lee, D.-S.; Lee, J.-S.; Park, Y.-S.; Song, H.-S.; Park, S. Y. *J. Am. Chem. Soc.* **2004**, *126*, 10232. (c) Luo, J.; Xie, Z.; Lam, J. W. Y.; Cheng, L.; Chen, H.; Qiu, C.; Kwok, H. S.; Zhan, X.; Liu, Y.; Zhu, D.; Tang, B. Z. *Chem. Commun.* **2001**, 1740. (d) Murata, H.; Kafafi, Z. H.; Uchida, M. *Appl. Phys. Lett.* **2002**, *80*, 189. (e) Ren, Y.; Lam, J. W. Y.; Dong, Y. Q.; Tang, B. Z.; Wong, K. S. *J. Phys. Chem. B* **2005**, *109*, 1135.

(7) Lim, S.-J.; An, B.-K.; Jung, S. D.; Chung, M.-A.; Park, S. Y. *Angew. Chem., Int. Ed.* **2004**, *43*, 6346.

(8) Stellacci, F.; Bertarelli, C.; Toscano, F.; Gallazzi, M. C.; Zotti, G.; Zerbi, G. *Adv. Mater.* **1999**, *11*, 292.

(9) Cho, H.; Kim, E. *Macromolecules* **2002**, *35*, 8684.

(10) Oelkrug, D.; Tompert, A.; Gierschner, J.; Egelhaaf, H. -J.; Hanack, M.; Hohloch, M.; Steinhuber, E. *J. Phys. Chem. B* **1998**, *102*, 1902.

(11) Crenshaw, B. R.; Weder, C. *Chem. Mater.* **2003**, *15*, 4717.

(12) Kobatake, S.; Yamada, T.; Uchida, K.; Kato, N.; Irie, M. *J. Am. Chem. Soc.* **1999**, *121*, 2380.

(13) According to the literature,[14] it has been reported that the cycloreversion quantum yield ($\Phi_{pc}^{c\to o}$) of BTEs is reduced when their aryl groups have long π-conjugated chains. It is considered that such a drastic incline toward the closed-form poly(DS−BTE) under ambient lighting is attributed to the great difference between the cyclization quantum yield ($\Phi_{pc}^{o\to c}$) and the $\Phi_{pc}^{c\to o}$ of poly(DS−BTE), whose aryl groups comprise fully π-conjugated rigid DS (or stilbene) fluorophores, under ambient visible lighting: The relative $\Phi_{pc}^{o\to c}$ and $\Phi_{pc}^{c\to o}$ of poly(DS−BTE) are determined to 0.42 (λ_{ex} = 290 nm) and 1.04×10^{-3} (λ_{ex} = 575 nm) in THF, respectively.[15] This is the reason why a high-intensity visible light illumination (>550 nm, 300 W, 30 min) is inevitably needed to generate the open-form poly(DS−BTE), which immediately and completely returns to the closed form once it is exposed to the weak room light. However, the $\Phi_{pc}^{c\to o}$ of poly(DCS−BTE) is 7 times higher than that of poly(DS−BTE) showing a highly efficient bistable photochromism.

(14) (a) Gilat, S. L.; Kawai, S. H.; Lehn, J.-M. *Chem.—Eur. J.* **1995**, *1*, 275. (b) Irie, M.; Eriguchi, T.; Takada, T.; Uchida, K. *Tetrahedron* **1997**, *53*, 12263. (c) Kaieda, T.; Kobatake, S.; Miyasaka, H.; Murakami M.; Iwai, N.; Nagata Y.; Itaya, A.; Irie, M. *J. Am. Chem. Soc.* **2002**, *124*, 2015.

(15) The $\Phi_{pc}^{o\to c}$ and $\Phi_{pc}^{c\to o}$ of THF solutions of poly(DCS−BTE) and poly(DS−BTE) were relatively calculated using 1,2-bis-(2′-methyl-5′-phenyl-3′-thienyl)perfluorocyclopentene as a reference according to the equations and the methods in the literatures: (a) Irie, M.; Lifka, T.; Kobatake, S.; Kato, N. *J. Am. Chem. Soc.* **2000**, *122*, 4871. (b) Mejiritski, A.; Polykarpov, A. Y.; Sarker, A. M.; Neckers, D. C. *J. Photochem. Photobiol. A: Chem.* **1997**, *108*, 289. (c) Kasatania, K.; Kambea, S.; Irie, M. *J. Photochem. Photobiol. A: Chem.* **1999**, *122*, 11.

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