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Photochromism of bis(2-alkyl-1-benzothiophen-3-yl) perfluorocyclopentene derivatives

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Abstract

Photochromism of bis(2-*n*-alkyl-1-benzothiophen-3-yl)perfluorocyclopentene derivatives has been studied in solution as well as in the single crystalline phase. Introduction of the long alkyl chains at 2-positions of bis(1-benzothiophen-3-yl)perfluorocyclopentene was found to increase the cyclization quantum yield and induce bathochromic shifts of the absorption spectra of the closed-ring isomers. The derivatives with ethyl, propyl, and butyl substituents at the 2-positions exhibit photochromism even in the single crystalline phase.

Keywords: Photochromism; Diarylethene; Single crystal

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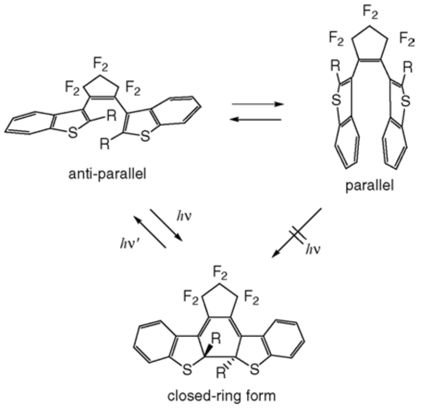
1. Introduction

Various types of photochromic compounds have been so far synthesized in an attempt to apply the compounds to optoelectronic devices [1–3]. Among the compounds diarylethene derivatives are the most promising candidates for the applications because of their fatigue resistant and thermally irreversible properties [4–7]. The diarylethene derivatives undergo the following cyclization/cycloreversion photochromic reactions upon photoirradiation. The open-ring form has two conformations, anti-parallel and parallel ones [8–11], and only the anti-parallel conformers undergo the photocyclization reaction.



Therefore, the population of the photoactive anti-parallel conformers controls the photocyclization quantum yield. Introduction of isopropyl substituents at 2-positions of the benzothiophene rings of bis(2-methyl-1-benzothiophen-3-yl)hexafluorocyclopentene is reported to increase the photocyclization quantum yield [12]. The increase is attributed to the increase in the population of the anti-parallel conformers, which was confirmed by ^{1}H NMR measurement.

Substituents also affect the photochromic reactivity in crystals. Although bis(2-methyl-1-benzothiophen-3-yl)perfluorocyclopentene is photochemically inactive in the single crystalline phase, bis(6-nitro-2-methyl-1-benzothiophen-3-yl)hexafluorocyclopentene having nitro substituents at 6-positions of the rings show single crystalline photochromism [13]. The photochromic reactivity in the single crystalline phase is dependent on the distance between central reactive carbons [13–15]. When the distance is shorter than 0.42 nm, the compound exhibits photochromic reactivity. Although bis(2-methyl-1-benzothiophen-3-yl)hexafluorocyclopentene (**1a**) has a distance (0.435 nm) longer than 0.42 nm, the distance of bis(6-nitro-2-methyl-1-benzothiophen-3-yl)hexafluorocyclopentene is as short as 0.384 nm. The nitro substituents decrease the distance and provide the photochromic reactivity to the crystal.

In this paper, we have introduced various long alkyl chains at 2-positions of the benzothiophene rings and examined the photochromic reactivity in solution as well as in the single crystalline phase.

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2. Experimental

2.1. General

The solvents used were spectrograde and were purified by distillation before use. Absorption spectra were measured with a spectrophotometer (Shimadzu, UV-2100). Absorption spectra in the single crystalline phases were measured using an OPTI-POL 2POL (Nikon) polarizing microscope connected with a Hamamatsu PMA-11 detector. A mercury lamp (Ushio, 500 W) was used as the light source. Light of appropriate wavelength was isolated by passing light through a monochromater (RITSU MC-10N) or through L-29, Y-42, Y-45 and UV-D36C filters. ^{1}H NMR was recorded on a Gemini 200 (200 MHz) and Brucker AVANCE 400 (400 MHz) spectrometer with $CDCl_3$ as solvent and tetramethylsilane as an internal standard. Mass spectrum was taken with a Shimadzu GCMS-QP5050A gas chromatography–mass spectrometer. X-ray crystallographic analysis was carried out using a Bruker SMART CCD X-ray diffractometer. HPLC was carried out on a Shimadzu LC-10AD liquid chromatography coupled with a Shimadzu SPD-10AV spectrophotomeric detector. A silicagel column (Wako Wakosil-5SIL) was used to analyze diarylethene isomers.

2.2. Synthesis

2.2.1. 2-Octadecyl-1-benzothiophene (*10*)

To a stirred THF solution (40 ml) containing benzo[*b*] thiophene (3.00 g, 22.6 mmol) was slowly added 15.8 ml of 1.6 M butyllithium hexane solution (25.3 mmol) at −78 °C, and the solution was stirred for 1 h at −78 °C. Then the octadecylbromide (5.40 ml, 25.0 mmol) was added slowly to the reaction mixture at −78 °C, and left to stand with stirring at −78 to 30 °C for 12 h. The reaction mixture was poured into concentrated sodium chloride solution and extracted with diethyl ether. The organic layer was dried over anhydrous magnesium sulfate and evaporated in vacuo. The crude product was purified by column chromatography on silica gel (hexane) to give 6.65 g of **10** in 97% yield.

10: Colorless liquid; ^{1}H NMR(200 MHz) δ 0.85–0.91(m, 3H), 1.22–1.43(m, 18H), 1.66–1.82(m, 2H), 2.89(t, J = 7.8 Hz, 2H), 7.29–7.46(m, 2H), 7.71–7.76(m, 2H). Ms (EI) *m/z* 302 (M^+). Anal. Calcd. for $C_{20}H_{30}S$: C 79.40, H 10.00%. Found: C 79.39, H 9.99%.

2.2.2. 3-Bromo-2-propyl-1-benzothiophene (*11*)

To a stirred THF solution (30 ml) containing 2-propyl-1-benzothiophene (3.0 g, 17.0 mmol) was slowly added 3.33 g of *N*-bromosuccinimide (18.7 mmol) at 5 °C. The reaction mixture was stirred for 15 h. The reaction mixture was poured into sodium thiosulfate solution, and extracted with diethyl ether. The organic layer was dried over anhydrous magnesium sulfate, and the solution was evaporated in vacuo. The crude product was purified by column chromatography on silica gel (hexane) to give 4.11 g of **11** in 95% yield.

11: Colorless liquid; ^{1}H NMR(200 MHz) δ 1.01(t, J = 7.2 Hz, 3H), 1.73(sex, J = 7.2 Hz, 2H), 2.92(t, J = 7.2 Hz, 2H), 7.28–7.45(m, 2H), 7.71–7.76(s, 2H). Ms (EI) *m/z* 256 (M^+). Anal. Calcd. for $C_{11}H_{11}BrS$: C 51.78, H 4.34%. Found: C 51.57, H 4.31%.

2.2.3. 3-Bromo-2-butyl-1-benzothiophene (*12*)

12 was prepared by a method similar to that used for **11** (94% yield).

12: Colorless liquid; ^{1}H NMR(400 MHz) δ 0.97(t, J = 7.2 Hz, 3H), 1.35–1.53(sex, J = 7.6 Hz, 2H), 1.65–1.80(qar, J = 7.6 Hz, 2H), 2.94(t, J = 7.6 Hz, 2H), 7.32–7.44(m, 2H), 7.71–7.76(m, 2H). Ms (EI) *m/z*: (M^+) 268. Anal. Calcd. for $C_{12}H_{13}BrS$: C 53.34, H 4.87%. Found: C 53.37, H 4.89%.

2.2.4. 3-Bromo-2-pentyl-1-benzothiophene (*13*)

13 was prepared by a method similar to that used for **11** (94% yield).

13: Colorless liquid; ^{1}H NMR(200 MHz) δ 0.87–0.94(m, 3H), 1.26–1.48(m, 4H), 1.66–1.81(m, 2H), 2.94(t, J = 7.8 Hz, 2H), 7.28–7.45(m, 2H), 7.71–7.76(m, 2H). Ms (EI) *m/z* 284 (M^+). Anal. Calcd. for $C_{13}H_{15}BrS$: C 55.13, H 5.34%. Found: C 55.00, H 5.30%.

2.2.5. 3-Bromo-2-hexyl-1-benzothiophene (*14*)

14 was prepared by a method similar to that used for **11** (90% yield).

14: Colorless liquid; ^{1}H NMR(200 MHz) δ 0.86–0.93(m, 3H), 1.28–1.49(m, 6H), 1.66–1.81(m, 2H), 2.94(t, J = 7.6 Hz, 2H), 7.28–7.45(m, 2H), 7.71–7.76(m, 2H). Ms (EI) *m/z* 298 (M^+). Anal. Calcd. for $C_{14}H_{17}BrS$: C 56.57, H 5.76%. Found: C 56.46, H 5.74%.

2.2.6. 3-Bromo-2-heptyl-1-benzothiophene (*15*)

15 was prepared by a method similar to that used for **11** (93% yield).

15: Colorless liquid; ^{1}H NMR(200 MHz) δ 0.85–0.92(m, 3H), 1.23–1.49(m, 8H), 1.66–1.80(m, 2H), 2.94(t, J = 8.0 Hz, 2H), 7.28–7.45(m, 2H), 7.71–7.76(m, 2H). Ms (EI) *m/z* 312 (M^+). Anal. Calcd. for $C_{15}H_{19}BrS$: C 57.88, H 6.15%. Found: C 57.73, H 6.16%.

2.2.7. 3-Bromo-2-dodecyl-1-benzothiophene (*16*)

16 was prepared by a method similar to that used for **11** (96% yield).

16: Colorless liquid; ^{1}H NMR(200 MHz) δ 0.85–0.92(m, 3H), 1.22–1.47(m, 18H), 1.66–1.80(m, 2H), 2.94(t, J = 7.8 Hz, 2H), 7.29–7.46(m, 2H), 7.71–7.76(m, 2H). Ms (EI) *m/z* 382 (M^+). Anal. Calcd. for $C_{20}H_{29}BrS$: C 62.98, H 7.66%. Found: C 62.95, H 7.64%.

2.2.8. 1,2-Bis(2-ethyl-1-benzothiophen-3-yl)-perfluorocyclopentene (*2a*)

To a stirred THF solution (40 ml) containing 3-bromo-2-ethyl-1-benzothiophene (2.00 g, 8.29 mmol) was slowly added 5.70 ml of 1.6 M butyllithium hexane solution (9.12 mmol) at −78 °C, and the solution was stirred for 15 min at −78 °C. Then the octafluorocyclopenthene (0.549 ml, 4.15 mmol) was added slowly to the reaction mixture at −78 °C, and left to stand with stirring at −78 to 30 °C for 12 h. The reaction mixture was poured into concentrated sodium chloride solution and extracted with diethyl ether. The organic layer was dried over anhydrous magnesium sulfate and evaporated in vacuo. The crude product was purified by column chromatography on silica gel (hexane) to give 0.943 g of **2a** in 46% yield.

2a: Colorless crystals; mp 133–134 °C; ^{1}H NMR(200 MHz) δ 0.78(t, J = 7.8 Hz, 4.2H), 1.29(t, J = 7.8 Hz, 1.8H), 2.38–2.91(m, 4H), 7.16–7.42(m, 4H), 7.60–7.74(m, 4H). Ms (EI) m/z 496 (M^+). Anal. Calcd. for $C_{25}H_{18}F_6S_2$: C 60.47, H 3.65%. Found: C 60.54, H 3.67%.

*2.2.9. 1,2-Bis(2-propyl-1-benzothiophen-3-yl)perfluorocyclopentene (**3a**)*

3a was prepared by a method similar to that used for **2a** (42% yield).

3a: Colorless crystals; mp 199–200 °C; ^{1}H NMR(200 MHz) δ 0.63(t, J = 7.0 Hz, 4.4H), 0.98–1.16(m, 5.6H), 1.34–1.78(m, 4H), 2.21–2.90(m, 4H), 7.15–7.20(m, 1H), 7.26–7.43(m, 3H), 7.54–7.63(m, 1H), 7.68–7.74(m, 3H). Ms (EI) m/z 524 (M^+). Anal. Calcd. for $C_{27}H_{22}F_6S_2$: C 61.82, H 4.23%. Found: C 61.79, H 4.24%.

*2.2.10. 1,2-Bis(2-butyl-1-benzothiophen-3-yl)perfluorocyclopentene (**4a**)*

4a was prepared by a method similar to that used for **2a** (37% yield).

4a: Colorless liquid; ^{1}H NMR(400 MHz) δ 0.70(t, J = 7.4 Hz, 4.6H), 0.97(t, J = 7.4 Hz, 1.3H), 1.00–1.14(m, 4H), 1.25–1.73(m, 4H), 2.24–2.32(m, 1.5H), 2.58–2.70(m, 2H), 2.83–2.92(m, 0.5H), 7.15–7.19(m, 0.9H), 7.26–7.38(m, 3.1H), 7.56–7.62(m, 0.9H), 7.69–7.72(m, 3.1H). Anal. Calcd for $C_{29}H_{26}F_6S_2$: C 63.03, H 4.74%. Found: C 63.10, H 4.62. Ms (FAB) m/z: (M^+) 552.

*2.2.11. 1,2-Bis(2-pentyl-1-benzothiophen-3-yl)perfluorocyclopentene (**5a**)*

5a was prepared by a method similar to that used for **2a** (40% yield).

5a: Colorless crystals; mp 117–118 °C; ^{1}H NMR(200 MHz) δ 0.73–1.13(m, 10H), 1.28–1.45(m, 4H), 2.18–2.33(m, 4H), 2.53–2.92(m, 4H), 7.15–7.20(m, 0.9H), 7.26–7.43(m, 3.1H), 7.54–7.63(m, 0.9H), 7.69–7.75(m, 3.1H). Ms (EI) m/z 580 (M^+). Anal. Calcd. for $C_{31}H_{30}F_6S_2$: C 64.12, H 5.21%. Found: C 64.16, H 5.20%.

*2.2.12. 1,2-Bis(2-hexyl-1-benzothiophen-3-yl)perfluorocyclopentene (**6a**)*

6a was prepared by a method similar to that used for **2a** (45% yield).

6a: Colorless crystals; mp 120–121 °C; ^{1}H NMR(200 MHz) δ 0.79–1.42(m, 18H), 2.18–2.33(m, 4H), 2.53–2.92(m, 4H), 7.15–7.19(m, 0.7H), 7.26–7.42(m, 3.3H), 7.54–7.63(m, 0.7H), 7.69–7.75(m, 3.3H). Ms (EI) m/z 608 (M^+). Anal. Calcd. for $C_{33}H_{34}F_6S_2$: C 65.11, H 5.63%. Found: C 65.13, H 5.63%.

*2.2.13. 1,2-Bis(2-heptyl-1-benzothiophen-3-yl)perfluorocyclopentene (**7a**)*

7a was prepared by a method similar to that used for **2a** (43% yield).

7a: Colorless crystals; mp 91–92 °C; ^{1}H NMR(200 MHz) δ 0.83–1.43(m, 22H), 2.18–2.33(m, 4H), 2.53–2.94(m, 4H), 7.12–7.20(m, 0.7H), 7.26–7.42(m, 3.3H), 7.54–7.62(m, 0.7H), 7.69–7.74(m, 3.3H). Ms (EI) m/z 636 (M^+). Anal. Calcd. for $C_{35}H_{38}F_6S_2$: C 66.01, H 6.01%. Found: C 65.99, H 6.01%.

*2.2.14. 1,2-Bis(2-octyl-1-benzothiophen-3-yl)perfluorocyclopentene (**8a**)*

8a was prepared by a method similar to that used for **2a** (36% yield).

8a: Colorless crystals; mp 60–62 °C; ^{1}H NMR(200 MHz) δ 0.85–1.42(m, 26H), 2.18–2.33(m, 4H), 2.53–2.94(m, 4H), 7.12–7.21(m, 0.7H), 7.26–7.43(m, 3.3H), 7.55–7.63(m, 0.7H), 7.70–7.74(m, 3.3H). Ms (EI) m/z 664 (M^+). Anal. Calcd. for $C_{37}H_{42}F_6S_2$: C 66.84, H 6.37%. Found: C 66.83, H 6.34%.

*2.2.15. 1,2-Bis(2-dodecyl-1-benzothiophen-3-yl)perfluorocyclopentene (**9a**)*

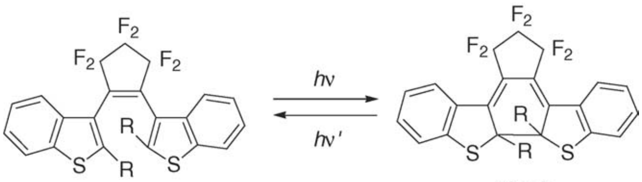
9a was prepared by a method similar to that used for **2a** (30% yield).

9a: Yellow liquid; ^{1}H NMR(200 MHz) δ 0.86–1.42(m, 34H), 2.18–2.33(m, 4H), 2.53–2.94(m, 4H), 7.12–7.21(m, 0.7H), 7.26–7.42(m, 3.3H), 7.54–7.62(m, 0.7H), 7.69–7.73(m, 3.3H). Ms (EI) m/z 776 (M^+). Anal. Calcd. for $C_{45}H_{58}F_6S_2$: C 69.55, H 7.52%. Found: C 69.43, H 7.47%.

3. Results and discussion

3.1. Synthesis of the diarylethene derivatives

Diarylethenes **1a**–**9a** were synthesized by coupling reactions of 3-bromo-2-(n-alkyl)-1-benzothiophene derivatives with perfluorocyclopentene according to the procedure described in ref. [5]. The structures of diarylethenes **1a**–**9a** were determined by ^{1}H NMR measurement, mass spectrum and elemental analysis. The structures of **1a**–**6a** were also determined by X-ray crystallographic analysis.



1a-9a **1b-9b**

1: R= CH_3
2: R= C_2H_5
3: R= C_3H_7
4: R= C_4H_9
5: R= C_5H_{11}
6: R= C_6H_{13}
7: R= C_7H_{15}
8: R= C_8H_{17}
9: R= $C_{12}H_{25}$

First, population of the anti-parallel conformers was determined with a ^{1}H NMR spectrometer. The methyl protons attached to the benzothiophene rings of the anti-parallel and parallel conformers of **1a** were observed at 2.49 and 2.69 ppm, respectively. Based on the intensity ratio of the two signals the relative population of the anti-parallel and the parallel conformers was estimated to be 62:38 for **1a** at room temperature.

^{1}H NMR spectrum of **2a** also showed the presence of two conformers. The methyl signals of the anti-parallel and the parallel conformers were observed at 0.78 and 1.29 ppm, respectively. The intensity rate of the two signals (69:31) indicates that the relative population of the anti-parallel conformers increases. The relative population of the anti-parallel conformers further increases to 77% for **4a**. In addition, the methyl protons of the butyl substituents of the anti-parallel conformer of **4a** were observed at 0.70 ppm, which suggests the interaction between the butyl chain and the benzothiophene ring. The proton signals locate at a higher field shift in comparison with the methyl protons for 2-butyl-1-benzothiophene (0.95 ppm) or 3-bromo-2-butyl-1-benzothiophene (0.97 ppm). The proton signal of the parallel conformer of **4a** was observed at 0.97 ppm, which is similar to the above non-interactive signals. In the parallel conformation, there is no interaction between the benzothiophene ring and butyl units. The relative populations of the anti-parallel and parallel conformers are summarized in Table 1. Introduction of long alkyl chains at 2-positions of the benzothiophene rings increases the population of the anti-parallel conformers.

Table 1
Ratio of parallel and anti-parallel conformation obtained by ^{1}H NMR analysis ($CDCl_3$)

	Anti-parallel conformation	Parallel conformation
1a	0.65	0.35
2a	0.69	0.31
3a	0.74	0.26
4a	0.77	0.23
5a	0.78	0.21
6a	0.82	0.18
7a	0.82	0.18
8a	0.82	0.18
9a	0.82	0.18

3.2. *Photochromic reactions in hexane solution*

1a shows a photochromic reaction in hexane [5]. The conversion from **1a** to **1b** in the photostationary state under irradiation with 313 nm light is 47.0%. Fig. 1(a) shows the absorption spectral change of **2a** in hexane by photoirradiation. Upon irradiation with 313 nm light, the colorless solution of **2a** turned violet, in which a visible absorption band was observed at 536 nm. The violet color is due to the closed-ring isomer. The conversion from **2a** to **2b** in the photostationary state under irradiation with 313 nm light is 51.9%. The color disappeared by irradiation with visible light (λ > 480 nm).

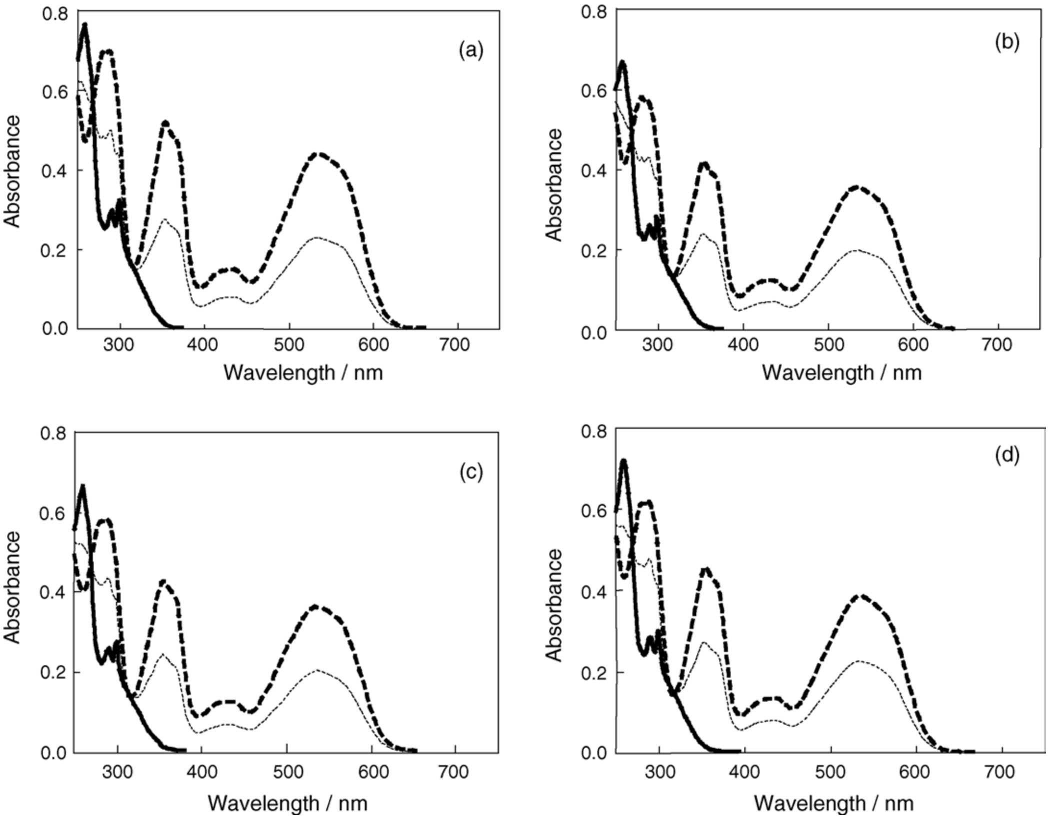


Fig. 1. Absorption spectra of (a) **2** (4.7×10^{-5} mol/l), (b) **3** (3.8×10^{-5} mol/l), (c) **4** (3.9×10^{-5} mol/l) and (d) **5** (4.1×10^{-5} mol/l) in hexane solution. Solid, dashed, and dotted lines represent **a** (open form), **b** (closed-ring form), and in the photostationary state under the irradiation with 313 nm light, respectively.

Table 2
Absorption maxima and their coefficients of the open- and closed-ring forms of **1**–**9**, quantum yields of cyclization and cycloreversion reactions, and conversion upon irradiation with 313 nm light in hexane

	Absorption spectra		Quantum yield		Conversion (313 nm)	
	Open form (ε, $M^{-1}cm^{-1}$) (λ_{max}, nm)	Closed-ring form (ε, $M^{-1}cm^{-1}$) (λ_{max}, nm)	Cyclization (313 nm)	Cycloreversion (517 nm)	Observed (%)	Calculated (%)[a]
1	1.40×10^4 (258)[b]	9.10×10^3 (517)[b]	0.35[b]	0.35[b]	47.0	47
2	1.65×10^4 (258)	9.62×10^3 (536)	0.39	0.35	51.9	53
3	1.76×10^4 (258)	9.31×10^3 (533)	0.41	0.35	55.5	55
4	1.71×10^4 (259)	9.32×10^3 (536)	0.44	0.35	55.5	57
5	1.71×10^4 (259)	9.15×10^3 (536)	0.49	0.35	58.1	59
6	1.72×10^4 (259)	9.00×10^3 (536)	0.49	0.34	58.2	60
7	1.72×10^4 (259)	9.09×10^3 (536)	0.49	0.35	58.0	59
8	1.72×10^4 (259)	9.05×10^3 (536)	0.48	0.35	58.8	59
9	1.72×10^4 (259)	8.98×10^3 (536)	0.47	0.34	58.0	59

[a] The values are calculated from the Eq. (1).
[b] Reference [12] data.

Just as **2a**, **3a** shows photochromism in hexane solution (Fig. 1(b)). The conversion from **3a** to **3b** in the photostationary state under irradiation with 313 nm light increased to 55.5%. The conversions from **4a** to **4b** and **5a** to **5b** under irradiation with 313 nm light were observed to be 55.5% (Fig. 1(c and d)).

The absorption characteristics of **6a**–**9a** and **6b**–**9b** were similar to **5a** and **5b**. Table 2 summarizes the absorption maxima and the absorption coefficients of the open- and closed-ring isomers in hexane. The cyclization and cycloreversion quantum yields were also measured and included in Table 2. Although the absorption spectrum of **1b** was observed at 517 nm, the maximum shifted to 536 nm in **2b** upon replacing the methyl groups with ethyl ones. Even if the alkyl chain becomes longer, further shift of the absorption maximum was not observed (536–537 nm).

The cyclization quantum yields of **1**–**9** increase with increasing the alkyl chain length. As described before, the relative population of the anti-parallel conformers increases with increasing the alkyl chain length. The increase in the population is responsible to the increase in the cyclization quantum yields. The cycloreversion quantum yields of **1**–**9** are constant (0.35). The alkyl chain does not affect the cycloreversion reaction.

The conversion at the photostationary state is expressed as follows:

$$(\text{Conversion})_{O\rightarrow C} = \frac{\varepsilon_O \Phi_{O\rightarrow C}}{\varepsilon_O \Phi_{O\rightarrow C} + \varepsilon_C \Phi_{C\rightarrow O}} \quad (1)$$

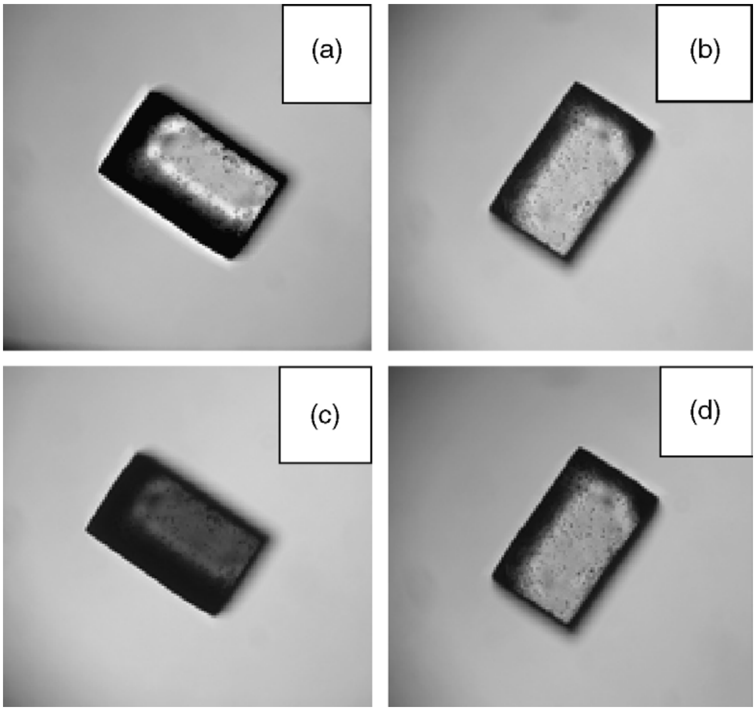


Fig. 2. Photographs of single crystal **4** under polarized light before (a, $\theta = 0°$; b, $\theta = 90°$) and after (c, $\theta = 0°$; d, $\theta = 90°$) irradiation with 365 nm light. θ is a rotation angle of the crystal.

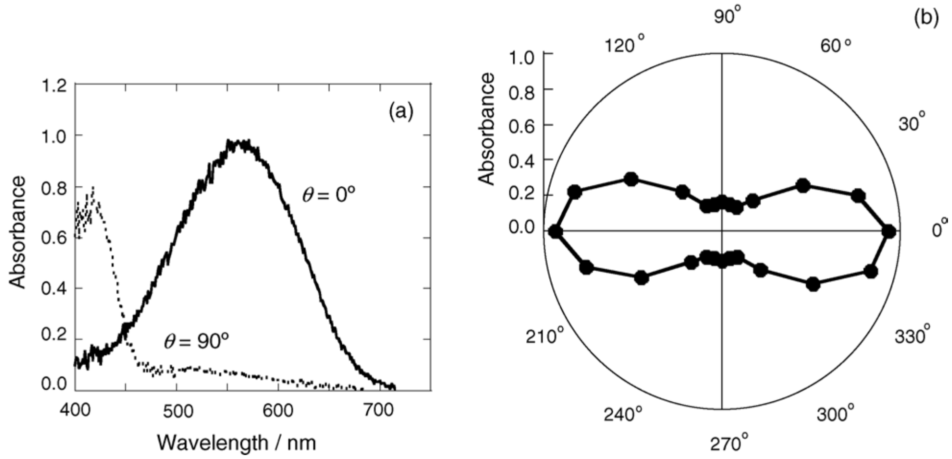


Fig. 3. Polarized absorption spectra of the colored crystal **4** polarized absorption spectra (a) and the polar plots (b).

where ε_O and ε_C are extinction coefficients of the open- and closed-ring isomers at the irradiation wavelength. $\Phi_{O \rightarrow C}$ and $\Phi_{C \rightarrow O}$ are quantum yields of cyclization and cycloreversion reactions, respectively. The calculated ratios and the experimental ones are also shown in the Table 2. These two values show relatively good agreement.

3.3. Photochromic reactions in the crystalline phase

Single crystals of **1a**–**6a** were obtained by recrystallization from the mixture of diethyl ether and hexane. Although **1a** did not show any photochromic reactivity in the single crystalline phase, **4a** underwent photochromism in the crystalline phase. The color of the crystal was observed under polarized light as shown in Fig. 2. Before photoirradiation the crystal is colorless (Fig. 2(a and b)). Upon irradiation with 365 nm light, the crystal turns violet (Fig. 2(c)). When the crystal is rotated as much as 90°, the color of the crystal changes to pale yellow (Fig. 2(d)). The colors disappeared by irradiation with visible light (λ > 480 nm).

Fig. 3(a) shows the polarized absorption spectra of the colored crystal **4**. By rotating the crystal sample under polarized light, the absorption intensity ratio at 560 and 420 nm changed. Fig. 3(b) shows the polar plots at 560 nm. The change of the color from violet to yellow by rotating the crystal sample indicates that the colored closed-ring isomers are regularity orientated in the crystal. The color of the crystal disappeared upon irradiation of the crystal with visible light (λ > 450 nm).

Table 3
Crystal data for **2a**–**6a**

	2a	**3a**	**4a**	**5a**	**6a**
Formula	$C_{25}H_{18}F_6S_2$	$C_{27}H_{22}F_6S_2$	$C_{29}H_{26}F_6S_2$	$C_{31}H_{30}F_6S_2$	$C_{33}H_{34}F_6S_2$
Formula weight	496.51	524.57	552.64	580.67	608.72
Temperature (K)	123(2)	93(2)	123(2)	123(2)	123(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	*P*2(1)/*c*	*Cc*	*P*2(1)/*c*	*P*-1	*P*-1
Unit cell dimensions					
a (Å)	8.627(4)	19.377(10)	12.498(5)	10.968(10)	10.925(3)
b (Å)	15.122(7)	12.411(7)	12.515(5)	11.728(10)	11.474(3)
c (Å)	17.199(8)	11.689(6)	16.361(6)	13.160(12)	14.346(4)
α (°)	90	90	90	98.499(13)	101.574(4)
β (°)	100.656(7)	122.427(7)	95.133(6)	105.337(13)	105.719(4)
γ (°)	90	90	90	113.857(13)	111.885(4)
Volume (Å^3)	2205.0(18)	2373(2)	2548.8(17)	1429(2)	1512.0(7)
Z	4	4	4	2	2
Density(calcd.) (g/cm^3)	1.496	1.468	1.440	1.349	1.337
Goodness-of-fit on F^2	1.055	1.044	1.048	1.045	1.085
Final *R* indices[$I/2\sigma(I)$]					
*R*1	0.0450	0.0579	0.0496	0.0627	0.0498
*wR*2	0.1158	0.1425	0.1251	0.1675	0.1361
R indices (all data)					
*R*1	0.0607	0.0605	0.0660	0.0702	0.0603
*wR*2	0.1274	0.1406	0.1379	0.1785	0.1464

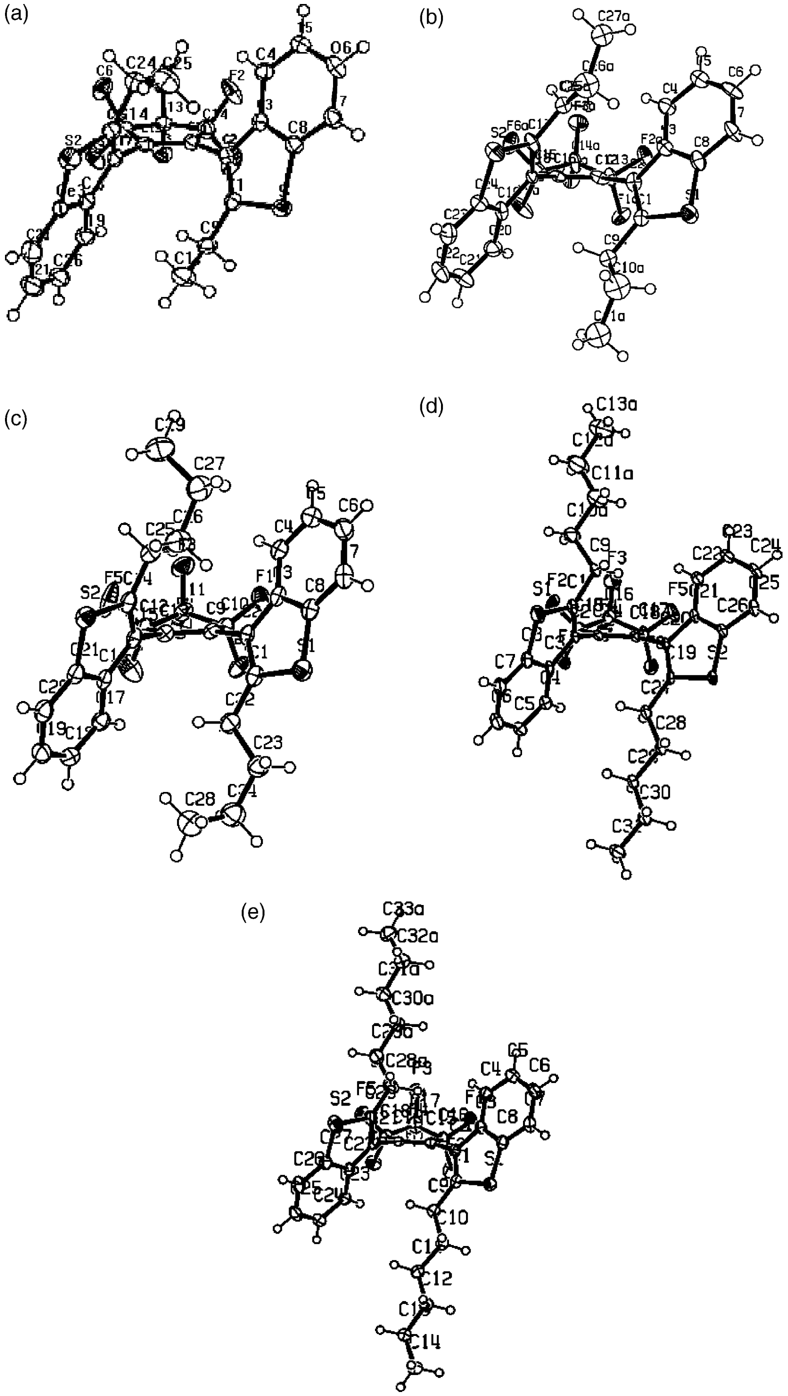


Fig. 4. ORTEP drawings of (a) **2a**, (b) **3a**, (c) **4a**, (d) **5a** and (e) **6a** showing 50% probability displacement ellipsoids.

2a and **3a** also showed photochromic reactivity in the single crystalline phase. The absorption characteristics of **2a** and **3a** were similar to **4a**. Upon irradiation with 365 nm light, the single crystals **2a** and **3a** turned purple, in which the absorption maxima are observed at 560 nm. By rotating the crystal sample under polarized light, the absorption intensity ratio at 560 nm changed. The purple color disappeared upon irradiation with visible light ($\lambda > 450$ nm).

Compounds **5a** and **6a** did not show any photochromism in the single crystalline phase. The reactivity is strongly dependent on the molecular conformation in the single crystal. To know the relation between the conformation and the reactivity X-ray crystallographic analyses of single crystals of **1a**–**6a** were carried out.

Table 3 shows the X-ray crystallographic analysis data of the single crystals **2a**–**6a** [16] and Fig. 4 shows the ORTEP drawings. Fig. 4(c) shows that **4a** is packed in a photoactive anti-parallel conformation in the crystal. The distance between the reactive carbon atoms is 0.408 nm, which is short enough for the reaction to take place in the crystalline phase.

Fig. 4(a and b) shows the ORTEP drawings of **2a** and **3a**. The drawings indicate that **2a** and **3a** are also packed in an anti-parallel conformation in the crystal. The distances between the reacting carbon atoms are 0.391 and 0.407 nm, respectively, which are close enough for the reaction to take place. All these crystals **2a**, **3a** and **4a** showed single crystalline photochromism.

Fig. 4(d and e) show the ORTEP drawings of **5a** and **6a**. Both molecules are also packed in a photoactive anti-parallel conformation. However, the distances between the reactive carbon atoms are 0.429 and 0.428 nm, respectively. The distances are too far to undergo photochromism in the crystalline phase. The lack of photochromic reactivity in **1a**, **5a** and **6a** can be explained by the long distance between the reactive carbons.

The anti-parallel conformer of **4a** showed an interaction between the benzothiophene ring and butyl unit by ^{1}H NMR spectrum, as described before. The ORTEP drawing for **4a** shows the distance between the benzothiophene ring and butyl unit is fairly close (0.37–0.49 nm). The compact molecular conformation leads to be the short distance between the reactive carbon atoms and favors the photocyclization reaction.

4. Conclusions

Bis(2-*n*-alkyl-1-benzothiophen-3-yl)perfluorocyclopentene having different long alkyl chains at 2-positions of the benzothiophene rings were synthesized and their photochromic reactivity was examined in solution as well as in the single crystalline phase. Introduction of the long alkyl chains at 2-positions of the benzothiophene rings increased the population of the anti-parallel conformers. The increase in the population is responsible to the increase in the cyclization quantum yields. The alkyl chain did not affect the cycloreversion reaction. The distance between reactive carbon atoms is influenced by the alkyl chain in crystals. When the derivatives have ethyl, propyl, and butyl chains, the distance between the reactive carbons become shorter than 0.420 nm, and the photocyclization reactions can take place in the single crystalline phase.

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[16] CCDC285109-285113 (Compounds 2a–6a) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.