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Photochromism of Diarylethene Derivatives Having *n*-Alkylbenzothiophene and *n*-Alkylbenzofuran Units

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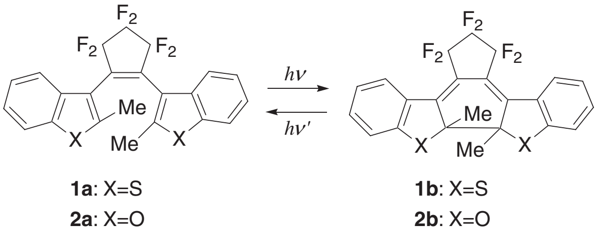
Photochromic diarylethenes having benzofuran and benzothiophene rings have been synthesized and their photochromic performance in a single-crystalline phase has been examined. Although 1,2-bis(2-methyl-1-benzothiophen-3-yl)perfluorocyclopentene (**1a**) is photochemically inactive in the single-crystalline phase, diarylethene derivatives having a benzofuran ring (**2a** and **3a**) undergo photochromism in the single-crystalline phase. 1-(1-Benzofuran-3-yl)-2-(1-benzothiophen-3-yl)hexafluorocyclopentene having ethyl, propyl, and butyl chains at the 2-position (**4a**–**6a**) were also synthesized. The derivative having propyl chains (**5a**) underwent photochromism in a single-crystalline phase. Upon UV irradiation, the crystal showed a brilliant red color in the single-crystalline phase.

Photochromism has attracted considerable attention because of its potential application to molecular devices, such as optical memories and switches.[1,2] Among various thermally irreversible photochromic compounds diarylethene derivatives are the most promising candidates for the application because of their fatigue resistant and thermally irreversible properties.[3–9] Diarylethene derivatives so far synthesized have heteroaryl moieties such as thiophene,[10] benzothiophene,[11] benzofuran,[12] thiazole,[13] chrysothiophene,[14] and indole rings.[15]

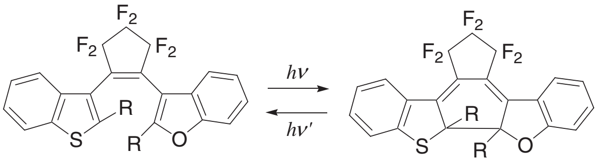
We have reported on 1,2-bis(2-*n*-alkyl-1-benzothiophen-3-yl)ethene derivatives,[16] which undergo photochromism in the single-crystalline phase. Their photochromic performance is strongly dependent on the distance between the reactive carbons. When the distance is within 0.42 nm, they undergo photochromism in the crystalline phase,[17] but compounds that have a distance larger than 0.42 nm did not show any photochromism in the single-crystalline phase. 1,2-Bis(2-methyl-1-benzothiophen-3-yl)perfluorocyclopentene (**1a**), which has the distance of 0.435 nm, was photochemically inactive.[12] However, 1,2-bis(2-methyl-1-benzofuran-3-yl)perfluorocyclopentene (**2a**) showed photochromism in the single-crystalline phase. The reaction distance is as short as 0.356 nm. Diarylethene derivatives having benzothiophene and benzofuran rings may undergo a photochromic reaction in the single-crystalline phase. In this work, various diarylethene derivatives having benzofuran and benzothiophene rings with *n*-alkyl substituent at the 2-position of the rings were synthesized and the photochromic performance was examined in solution as well as in the single-crystalline phase.



(1)

1a: X=S
2a: X=O

1b: X=S
2b: X=O



(2)

3a: R=CH_3
4a: R=C_2H_5
5a: R=n-C_3H_7
6a: R=n-C_4H_9

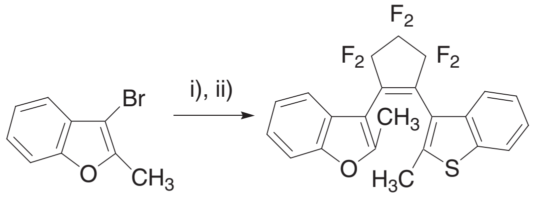
3b: R=CH_3
4b: R=C_2H_5
5b: R=n-C_3H_7
6b: R=n-C_4H_9

Results and Discussion

1-(2-Methyl-1-benzofuran-3-yl)-2-(2-methyl-1-benzothiophen-3-yl)hexafluorocyclopentene (**3a**) was synthesized as shown in Scheme 1. The coupling reaction between 1-(2-methyl-1-benzothiophen-3-yl)heptafluorocyclopentene and 3-bromo-2-methyl-1-benzofuran (**7**) gave **3a** in 42% yield.

The diarylethenes **4a**, **5a**, and **6a** having ethyl, propyl, and butyl units were synthesized following the procedures used for the synthesis of **3a**.

Photochromic Reactions in Hexane. Figure 1a shows the absorption spectral change of **3** in hexane. In the photostationary state, upon irradiation with 313 nm light, the open-ring isomers **3a**, which has the maximum at 299 nm (ε: 0.69×10^4



3a

Scheme 1. Synthesis of the diarylethene **3a**. i) *n*-Butyllithium (1.1 equiv), THF at $-78\,^{\circ}C$. ii) 1-(2-Methyl-1-benzothiophen-3-yl)heptafluorocyclopentene (42%).

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$M^{-1}\,cm^{-1}$), was transformed into **3b**, which has the maximum at 493 nm (ε: $1.53 \times 10^4\,M^{-1}\,cm^{-1}$). Upon irradiation with visible light ($\lambda > 480$ nm) the closed-ring isomer returned to the original **3a**.

Just as **3**, **4–6** underwent photochromism upon irradiation with UV and visible light in hexane. Figure 1b shows the photochromism of **5** in hexane. In the photostationary state under irradiation with 313 nm light, 47% of the open-ring isomers, converted to the closed-ring isomers **5b**, having the maximum at 507 nm. The colorless solution changed to red. By changing alkyl units from methyl to propyl, the absorption maximum of the closed-ring isomer shifted to longer wavelengths by as much as 14 nm. Upon irradiation with visible light ($\lambda > 440$ nm), the closed-ring isomer returned to the original **5a**.

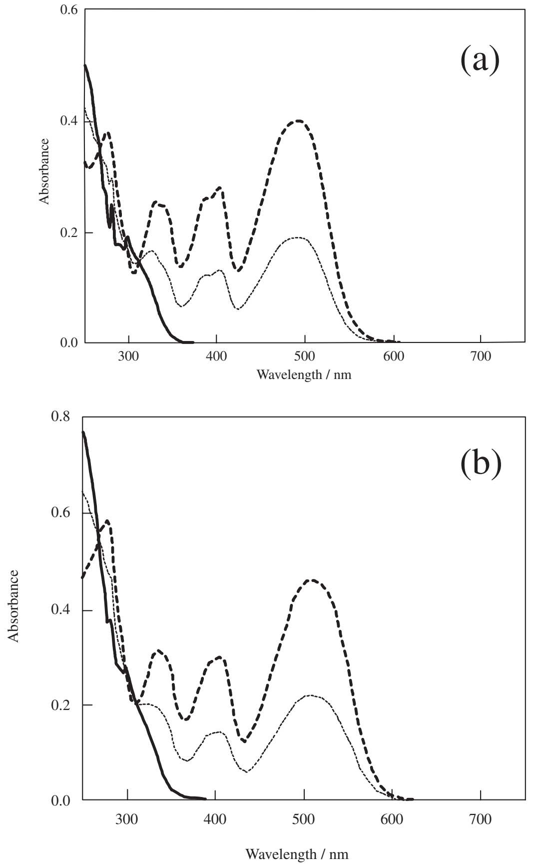

Fig. 1. (a) Absorption spectra of **3a** (solid line), **3b** (dashed line), and in the photostationary state (dotted line) under irradiation with 313 nm light in hexane (2.6×10^{-5} mol L^{-1}). (b) Absorption spectra of **5a** (solid line), **5b** (dashed line), and in the photostationary state (dotted line) under irradiation with 313 nm light in hexane (4.6×10^{-5} mol L^{-1}).

The cyclization and cycloreversion quantum yields were measured for compounds **3–6**. Table 1 summarizes the quantum yields along with the absorption characteristics. The properties of bisbenzothiophene and bisbenzofuran derivatives **1** and **2** are also included in the Table. The cyclization quantum yield of **2** is slightly larger than those of **1** and **3**. The cyclization quantum yield increases with increasing the chain length. As observed for the benzothiophene and benzofuran derivatives, the increase in the relative population of the anti-parallel conformers enhances the quantum yield of the cyclization reaction.[12,16] Compounds **4**, **5**, and **6** gave similar cycloreversion quantum yield. The value is slightly larger than the value of **3**. The molar absorption coefficient for **3b** is the largest among **3b–6b**.

X-ray Crystallographic Analysis for 3a and 5a. A single crystal was obtained by recrystallization from hexane and X-ray crystallographic analysis of the crystal was carried out. Suitable crystals for X-ray crystallographic analysis were obtained for **3a** and **5a**.

Figure 2 shows an ORTEP drawing of **3a**. The drawing indicates that **3a** is packed in an anti-parallel conformation in the single-crystalline phase. The distance between the reac-

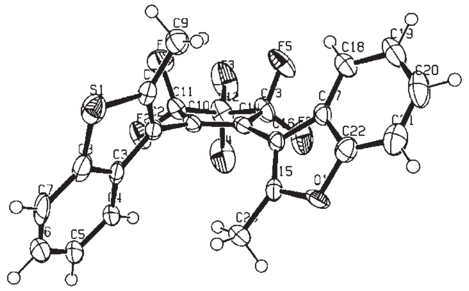

Fig. 2. An ORTEP drawing of **3a**. The ellipsoid represents 50% displacement of atoms.

Table 1. Absorption Characteristics and Photoreactivity of the Diarylethene Derivatives **1–6** in Hexane

Compound	$\varepsilon/10^4\,dm^3\,mol^{-1}\,cm^{-1}$		Quantum yield		Conversion (313 nm)
	a	**b**	Cyclization	Cycloreversion	
1	1.41 (254 nm)	0.91 (517 nm)	0.35 (313 nm)	0.35 (517 nm)	47%
2	1.00 (274 nm)	1.44 (469 nm)	0.38 (313 nm)	0.35 (469 nm)	48%
3	0.69 (299 nm)	1.53 (493 nm)	0.32 (313 nm)	0.25 (493 nm)	47%
4	0.64 (299 nm)	1.15 (507 nm)	0.40 (313 nm)	0.30 (507 nm)	55%
5	0.60 (299 nm)	1.00 (507 nm)	0.44 (313 nm)	0.31 (507 nm)	47%
6	0.58 (299 nm)	1.09 (508 nm)	0.50 (313 nm)	0.30 (508 nm)	58%

tive carbons is 0.402 nm, which is between that of **1a** and **2a**. The distance is short enough for the reaction to take place in the crystalline phase.

Figure 3 shows an ORTEP drawing of **5a**. The aryl moieties are in an anti-parallel conformation, and the distance between the reactive carbons is 0.398 nm. The distance is also short enough for the reaction to take place in the crystalline phase.

Photochromism in the Single-Crystalline Phase. Both **3a** and **5a** undergo photochromism even in the single-crystalline phase. Figures 4a–4d show photographs of a single crystal of **3** observed using a polarizing microscope (Nikon, OPTIPOL-2POL). The surface corresponds to (021) face. Upon irradiation with 365 nm light, compound **3** showed an orange color (Figs. 4c and 4d). Upon irradiation with visible light (>440 nm), the orange color disappeared immediately. The color change was observed deep in the crystal bulk when the crystal was irradiated with 390 nm light. The light could penetrate the crystal as deep as several hundred µm.

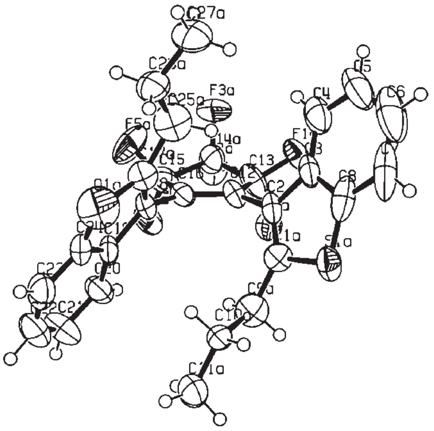

Fig. 3. An ORTEP drawing of **5a**. The ellipsoid represents 50% displacement of atoms.

Figure 5a shows the polarized absorption spectra upon irradiation with 365 nm light. The clear dichroism was observed by rotating the single crystal. Figure 5b shows a polar plot of the absorption at 510 nm. The clear dichroism confirms that the photochromism of **3** occurs in the single-crystalline phase.

In the case of **5a**, the crystal was colorless before irradiation (Fig. 6a). Upon irradiation with 365 nm light, the crystal turned brilliant red (Fig. 6b). When the crystal was rotated by as much as 90°, the color of the crystal changed to pale yellow. The colors disappeared by irradiation with visible light ($\lambda > 440$ nm).

Figure 7a shows the polarized absorption spectra of the colored crystal. The observed crystal face is (001). The absorption maximum of the closed-ring is 540 nm at 0°. By rotating the crystal sample under polarized light, the absorption intensity was changed as shown in Fig. 7b. The coloration/decoloration cycles of the crystals of **3** and **5** could be repeated more than 10000 times without destruction of the crystal shape. The brilliant red color of **5** after UV irradiation may be used for a kind of display.

In the case of **4a** and **6a**, crystals large enough to study the single-crystalline photochromism were not obtained. Although the crystals showed color changes upon UV irradiation, detailed analysis could not be carried out.

In conclusion, new types of photochromic compounds having benzofuran and benzothiophene units were synthesized and their photochromic reactivity has been examined in hexane as well as in the single-crystalline phase. Single crystals of **3** and **5** showed photochromism upon irradiation with UV and visible light. A single crystal of **5** showed a color change from colorless to a brilliant red color. The benzofuran derivatives showed fatigue resistant photochromism in the single-crystalline phase.

Experimental

General. The solvents used were spectrograde and were

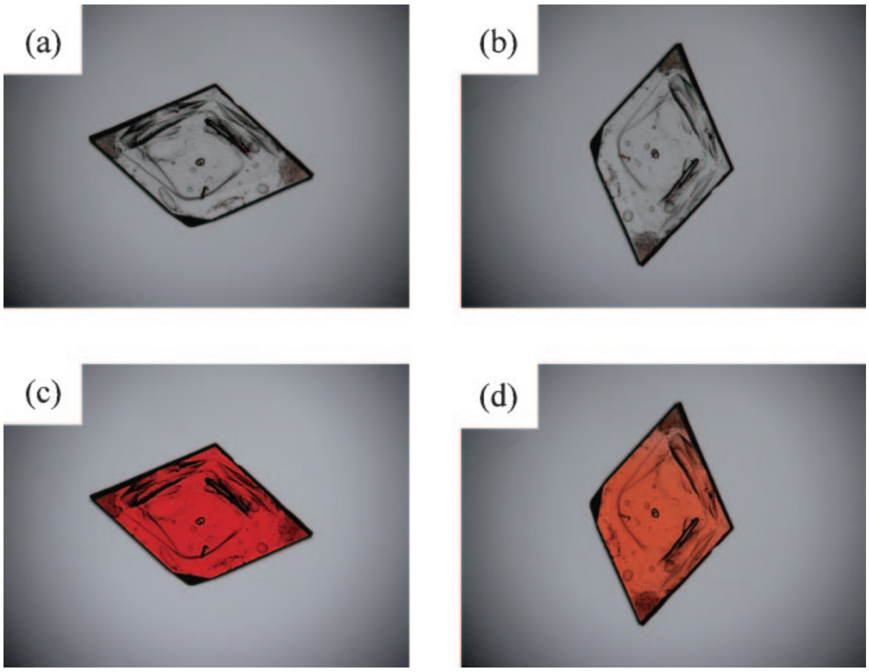

Fig. 4. Photographs of a single crystal of **3** ((a) $\theta = 0°$ and (b) 90°) and after irradiation with 365 nm light ((c) $\theta = 0°$ and (d) 90°).

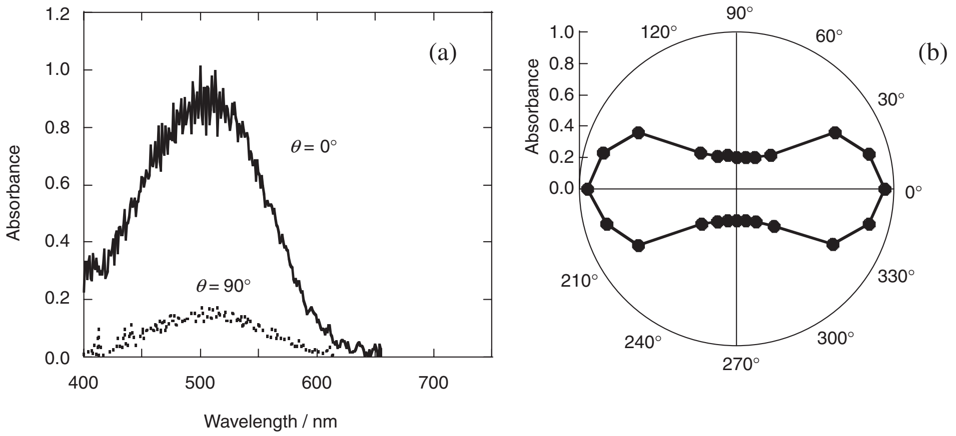

Fig. 5. (a) Absorption spectra of a single crystal of **3** after irradiation with 365 nm light. (b) Polar absorption plot of a single crystal of **3** after irradiation with 365 nm light at 510 nm.

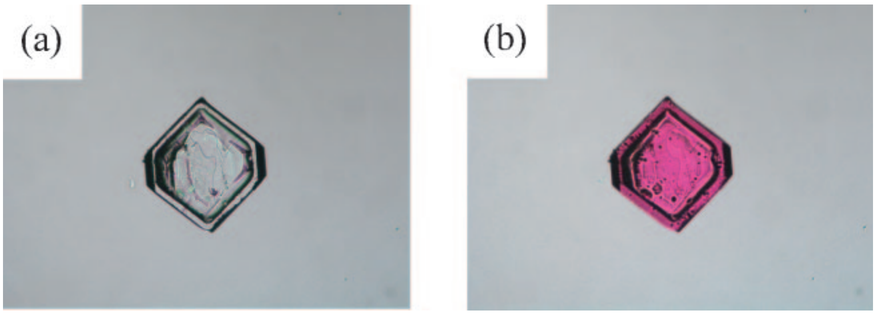

Fig. 6. Photographs of **5** (a) before and (b) after irradiation with 365 nm light.

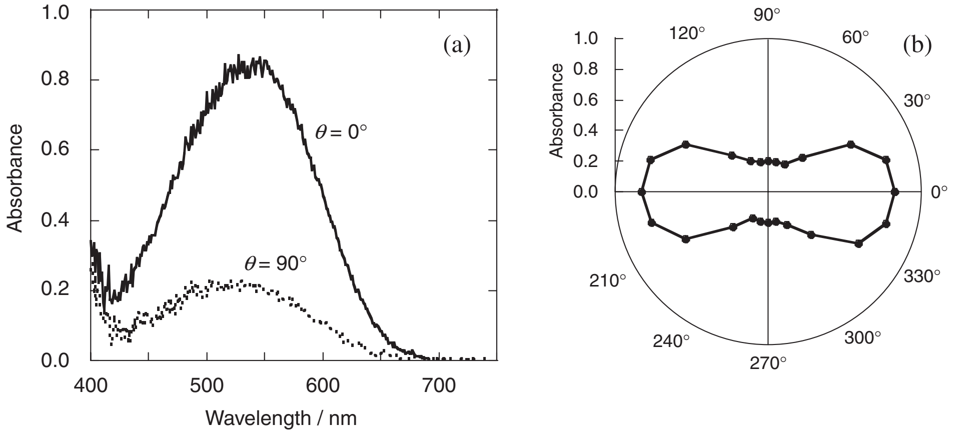

Fig. 7. (a) Absorption spectra of a single crystal of **5** after irradiation with 365 nm light. (b) Polar absorption plot of a single crystal of **5** after irradiation with 365 nm light at 540 nm.

purified by distillation before use. Absorption spectra were measured with a spectrophotometer (Hitachi, U-3310). The quantum yields were determined by comparing the reaction rates of the diarylethene derivatives in hexane against that of furylfulgide in toluene. The samples were not degassed. Absorption spectra in the single-crystalline phases were measured using an OPTI-POL 2POL polarizing microscope connected to a Hamamatsu PMA-11 detector. Photoirradiation for single-crystal measurements was carried out using a 100 W mercury lamp (Nikon, C-SHG1 and LH-M100CB-1) as the light source. For solution measurements, a mercury lamp (Ushio, 500 W) was used as the light source. Light of appropriate wavelength was isolated by passing light through a monochromator (RITSU MC-10N) or through Y-44 and UV-D33S filters. ^{1}H NMR was recorded on a Gemini 200 spectrometer (200 MHz) with $CDCl_3$ as the solvent and tetramethylsilane as an internal standard at room temperature. At low temperature (−90 °C), ^{1}H NMR was recorded on a 400 MHz spectrometer (JEOL, JNM-ECP400) at the Center of Advanced Instrumental Analysis (Kyushu University) in CD_3OD as the solvent and tetramethylsilane as an internal standard. Good quality crystals (**3a**: $0.2 \times 0.1 \times 0.1\,\mathrm{mm}^3$ and **5a**: $0.15 \times 0.1 \times 0.1\,\mathrm{mm}^3$) were selected for the X-ray diffraction study. The data collection was performed on a Bruker SMART 1000 CCD-based diffractometer (55 kV, 35 mA) with Mo Kα irradiation. Fatigue resistance measurements of the single crystals were carried out using the apparatus described in Ref. 18.

Synthesis. 1-(2-Ethyl-1-benzothiophen-3-yl)heptafluorocyclopentene (7): To a stirred THF solution (20 mL) containing 3-bromo-2-ethyl-1-benzothiophene (0.548 g, 2.27 mmol) was slowly added 1.56 mL of a 1.6 M butyllithium hexane solution (2.50 mmol) at −78 °C, and the solution was stirred for 15 min at −78 °C. Then, the solution was slowly added dropwise to a mixture of octafluorocyclopentene (0.530 mL, 4 mmol) and THF (20 mL) at −78 °C, and left to stand with stirring at −78 to 30 °C for 12 h. The reaction mixture was poured into a concentrated sodium chloride solution and extracted with diethyl ether. The organic phase was dried over anhydrous magnesium sulfate and evaporated in vacuo. The crude product was purified by column chromatography on silica gel (hexane) to give 0.487 g of **7** in 61% yield. **7**: colorless liquid; ^{1}H NMR (200 MHz, $CDCl_3$, rt) δ 1.36 (t, $J = 3.6$ Hz, 3H), 2.85 (q, $J = 3.6$ Hz, 2H), 7.34–7.51 (m, 3H), 7.81–7.83 (m, 1H). HRMS(FAB) m/z 354.0314 ([M$^+$]), calcd for $C_{15}H_9F_7S$ 354.0316.

1-(2-Propyl-1-benzothiophen-3-yl)heptafluorocyclopentene (8): The reaction of 3-bromo-2-propyl-1-benzothiophene (1.00 g, 3.9 mmol), a 1.6 M butyllithium hexane solution (2.69 mL, 4.3 mmol), and octafluorocyclopentene (1.06 mL, 8.0 mmol) was performed as described for compound **7**. The crude product was purified by column chromatography on silica gel (hexane) to give 0.918 g of **8** in 64% yield. **8**: colorless liquid; ^{1}H NMR (200 MHz, $CDCl_3$, rt) δ 1.00 (t, $J = 3.6$ Hz, 3H), 1.74–1.80 (m, 2H), 2.79 (t, $J = 3.6$ Hz, 2H), 7.35–7.46 (m, 3H), 7.79–7.82 (m, 1H). HRMS(FAB) m/z 368.0474 ([M$^+$]), calcd for $C_{16}H_{11}F_7S$ 368.0478.

1-(2-Butyl-1-benzothiophen-3-yl)heptafluorocyclopentene (9): The reaction of 3-bromo-2-butyl-1-benzothiophene (1.23 g, 4.57 mmol), a 1.6 M butyllithium hexane solution (3.14 mL, 5.0 mmol), and octafluorocyclopentene (1.19 mL, 9.0 mmol) was performed as described for compound **7**. The crude product was purified by column chromatography on silica gel (hexane) to give 1.05 g of **9** in 60% yield. **9**: colorless liquid; ^{1}H NMR (200 MHz, $CDCl_3$, rt) δ 0.94 (t, $J = 3.8$ Hz, 3H), 1.38–1.48 (m, 2H), 1.68–1.77 (m, 2H), 2.81 (t, $J = 3.8$ Hz, 2H), 7.35–7.48 (m, 3H), 7.80–7.82 (m, 1H). HRMS(FAB) m/z 382.0617 ([M$^+$]), calcd for $C_{17}H_{13}F_7S$ 382.0626.

1-(2-Methyl-1-benzofuran-3-yl)-2-(2-methyl-1-benzothiophen-3-yl)perfluorocyclopentene (3a): To a stirred THF solution (30 mL) containing 3-bromo-2-methyl-1-benzofuran (0.632 g, 2.99 mmol) was slowly added 2.06 mL of a 1.6 M butyllithium hexane solution (3.29 mmol) at −78 °C, and the solution was stirred for 15 min at −78 °C. Then, the 1-(2-methyl-1-benzothiophen-3-yl)heptafluorocyclopentene (1.02 g, 2.99 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 a concentrated sodium chloride solution and extracted with diethyl ether. The organic phase was dried over anhydrous magnesium sulfate and evaporated in vacuo. The crude product was purified by column chromatography on silica gel (hexane) to give 0.569 g of **3a** in 42% yield. **3a**: colorless crystals; mp 102.5–103.2 °C; ^{1}H NMR (200 MHz, $CDCl_3$, rt) δ 2.01 (s, 3H), 2.29 (s, 3H), 7.17–7.36 (m, 5H), 7.52–7.72 (m, 3H). MS (EI) m/z 452 (M$^+$); Anal. Calcd for $C_{23}H_{14}F_6OS$: C, 61.06; H, 3.12%. Found: C, 60.94; H, 3.21%. Crystal data for **3a**: $C_{23}H_{14}F_6OS$, MW = 452.41, monoclinic, space group $P2_1/n$, $a = 11.539(4)$ Å, $b = 14.539(5)$ Å, $c = 13.147(4)$ Å, $\alpha = 90°$, $\beta = 114.700(4)°$, $\gamma = 90°$, $V = 2003.9(11)$ Å^3, $Z = 4$, $D_{calcd} = 1.500$ g cm^{-3}, $R_1 = 0.0477$ for 2199 observed reflections with $I > 2\sigma(I)$ from 2891 unique reflections. CCDC deposition number: 289583.

1-(2-Ethyl-1-benzofuran-3-yl)-2-(2-ethyl-1-benzothiophen-3-yl)perfluorocyclopentene (4a): The coupling of 3-bromo-2-ethyl-1-benzofuran (0.668 g, 2.97 mmol), **7** (1.05 g, 2.97 mmol), and a 1.6 M butyllithium hexane solution (2.04 mL, 3.27 mmol) was performed as described for compound **3a**. The crude product was purified by column chromatography on silica gel (hexane) to give 0.401 g of **4a** in 28% yield. **4a**: colorless crystals; mp 85.9–87.2 °C; ^{1}H NMR (200 MHz, $CDCl_3$, rt) δ 0.68 (t, $J = 7.6$ Hz, 3H), 1.02 (t, $J = 7.6$ Hz, 3H), 2.17–2.84 (m, 4H), 7.19–7.39 (m, 5H), 7.54–7.63 (m, 2H), 7.69–7.73 (m, 1H). ^{1}H NMR (400 MHz, CD_3OD, −90 °C) δ 0.05 (brs, 2.1H), 0.68 (brs, 2.1H), 0.82 (brs, 0.9H), 1.37 (brs, 0.9H), 2.15 (brs, 0.7H), 2.31–2.46 (m, 1.9H), 2.64–2.79 (m, 0.9H), 2.96–3.02 (m, 0.5H), 7.08–7.13 (m, 0.7H), 7.25–7.54 (m, 4.3H), 7.65–7.95 (m, 3H). MS (EI) m/z 480 (M$^+$); Anal. Calcd for $C_{25}H_{18}F_6OS$: C, 62.50; H, 3.78%. Found: C, 62.50; H, 3.79%.

1-(2-Propyl-1-benzofuran-3-yl)-2-(2-propyl-1-benzothiophen-3-yl)perfluorocyclopentene (5a): The coupling of 3-bromo-2-propyl-1-benzofuran (0.591 g, 2.47 mmol), **8** (0.910 g, 2.47 mmol), and a 1.6 M butyllithium hexane solution (1.70 mL, 2.71 mmol) was performed as described for compound **3a**. The crude product was purified by column chromatography on silica gel (hexane) to give 0.493 g of **5a** in 39% yield. **5a**: colorless crystals; mp 133.6–134.4 °C; ^{1}H NMR (200 MHz, $CDCl_3$, rt) δ 0.49 (t, $J = 7.2$ Hz, 3H), 0.69 (t, $J = 7.2$ Hz, 3H), 0.77–1.51 (m, 4H), 2.11–2.82 (m, 4H), 7.22–7.40 (m, 5H), 7.57–7.67 (m, 2H), 7.72–7.76 (m, 1H). ^{1}H NMR (400 MHz, CD_3OD, −90 °C) δ −0.28 (brs, 0.9H), −0.08 (brs, 2.7H), 0.29 (brs, 2.7H), 0.55 (brs, 0.9H), 0.90 (brs, 0.3H), 1.08 (brs, 0.3H), 1.25–1.34 (m, 1.8H), 1.70–1.80 (brs, 0.4H), 2.05 (brs, 0.9H), 2.21–2.43 (m, 1.9H), 2.49–2.58 (m, 1.0H), 2.85 (brs, 0.2H), 7.14–7.27 (m, 0.2H), 7.36–7.52 (m, 5.0H), 7.76–7.81 (m, 1.9H), 7.94–7.96 (m, 0.9H). MS (EI) m/z 508 (M$^+$); Anal. Calcd for $C_{27}H_{22}F_6OS$: C, 63.77; H, 4.36%. Found: C, 63.80; H, 4.36%. Crystal data for **5a**: $C_{27}H_{22}F_6OS$, MW = 508.51, monoclinic, space group Cc, $a = 19.1296(9)$ Å, $b = 12.8476(6)$ Å, $c = 11.5394(6)$ Å, $\alpha = 90°$, $\beta = 123.047(3)°$, $\gamma = 90°$, $V = 2377.2(2)$ Å^3, $Z = 4$, $D_{calcd} = 1.421$ g cm^{-3}, $R_1 = 0.0538$ for 3158 observed reflections with $I > 2\sigma(I)$ from 4193 unique reflections. CCDC deposition number: 294195.

1-(2-Butyl-1-benzofuran-3-yl)-2-(2-butyl-1-benzothiophen-3-yl)perfluorocyclopentene (6a): The coupling of 3-bromo-2-butyl-1-benzofuran (0.663 g, 2.62 mmol), **9** (1.00 g, 2.62 mmol), and a 1.6 M butyllithium hexane solution (1.80 mL, 2.87 mmol) was performed as described for compound **3a**. The crude product was purified by column chromatography on silica gel (hexane) to give 0.351 g of **6a** in 25% yield. **6a**: colorless crystals; mp 82.1–83.6 °C; ^{1}H NMR (200 MHz, $CDCl_3$, rt) δ 0.62–0.72 (m, 6H), 0.85–1.48 (m, 8H), 2.08–2.83 (m, 4H), 7.21–7.41 (m, 5H), 7.58–7.75 (m, 3H). ^{1}H NMR (400 MHz, CD_3OD, −90 °C) δ −0.46 (brs, 2H), 0.21 (brs, 1H), 0.32–0.39 (m, 6.8H), 0.62 (brs, 1H), 0.90–0.96 (m, 1.2H), 1.20 (brs, 2H), 2.00–2.05 (m, 1H), 2.24–2.37 (m, 2H), 2.56–2.86 (m, 1H), 7.10–7.26 (m, 0.1H), 7.37–7.58 (m, 4.9H), 7.77–7.79 (m, 2H), 7.94–7.97 (m, 1H). MS (EI) m/z 536 (M$^+$); Anal. Calcd for $C_{29}H_{26}F_6OS$: C, 64.91; H, 4.88%. Found: C, 64.94; H, 4.88%.

Crystallographic data have been deposited with Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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