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Photochromism of Bis(2-alkyl-1-benzofuran-3-yl)perfluorocyclopentene Derivatives

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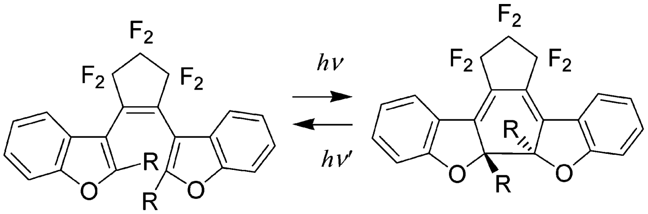

R= CH_3 or C_4H_9

Photochromic diarylethene derivatives having benzofuran heteroaryl groups, bis(2-methyl-1-benzofuran-3-yl)perfluorocyclopentene and bis(2-butyl-1-benzofuran-3-yl)perfluorocyclopentene, were synthesized, and their photochromic performance was examined in hexane solution as well as in the single-crystalline phase. The compounds exhibited photochromic reactivity even in the single-crystalline phase.

Introduction

Photochromic compounds have attracted considerable attention because of their potential application to photonic 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 thermally irreversible and fatigue-resistant photochromic performance.[3] Although many diarylethene derivatives have been synthesized, most of them are composed of thiophene or benzothiophene heteroaryl groups.[4−15] These compounds can be prepared by simple synthesis procedures, and their photochromic performance is superior to that of other derivatives having pyrrole or indole groups.[16] The latter derivatives undergo thermally reversible photochromic reactions and cannot be used for optical memories and switches.

1,2-Bis(2-methyl-1-benzothiophen-3-yl)perfluorocyclopentene **3a** undergoes a thermally irreversible and fatigue-resistant photochromic reaction in solution.[17] Although the benzothiophene heteroaryl moiety can provide the fatigue-resistant property to a diarylethene, the compound is photochemically inactive in the crystalline phase. The photochromic reactivity of diarylethene derivatives in the crystalline phase is controlled by their conformation and distance between reactive carbon atoms. An antiparallel conformation and a distance shorter than 0.42 nm are necessary conditions for the reaction to take place.[18] Although **3a** is packed in the antiparallel conformation in the crystal, the distance between reactive

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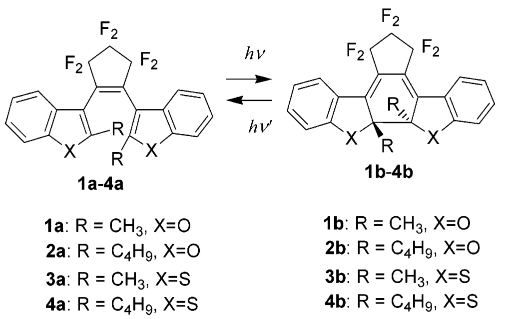
carbon atoms is as long as 0.435 nm. When nitro groups are substituted at the 6-position of the two benzothiophene rings, the distance decreases to as short as 0.385 nm and the compound shows a photochromic reactivity in the crystalline phase.[17]

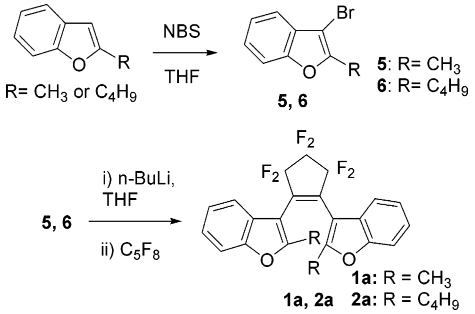
Furyl fulgide, which has a furan ring, undergoes photochromism in solution.[19,20] This suggests that diarylethene derivatives with furan rings are also expected to undergo photochromism. Theoretical calculation for 1,2-bis(3-furyl)ethene[21] predicts that the derivative undergoes a thermally irreversible photochromic reaction. In this work, we have synthesized 1,2-bis(2-alkyl-1-benzofuran-3-yl)perfluorocyclopentene derivatives and examined their photochromic reactivity in hexane as well as in the single-crystalline phase. Bis(2-methylbenzofuryl)ethene and bis(2-butylbenzofuryl)ethene were chosen because the starting chemicals are readily obtained from the commercial products.



Results and Discussion

Preparation of Diarylethene Derivatives. **1a** and **2a** were synthesized using the procedure shown in Scheme 1. 2-Methyl-1-benzofuran (1.0 equiv) in THF was reacted with *N*-bromosuccinimide (1.1 equiv) at room temperature to give 3-bromo-2-methyl-1-benzofuran **5** in 85% yield. A THF solution containing **5** (1.0 equiv) was cooled to −78 °C, and then 1.6 M *n*-BuLi hexane solution (1.1 equiv) was added to the solution dropwise at −78 °C. The reaction mixture was stirred for 30 min at −78 °C, and then octafluorocyclopentene (0.5 equiv) was added to the solution. The reaction mixture was stirred for 1 h at −78 °C, treated with water, extracted with ether, and purified by column chromatography (eluent/hexane) to give **1a** in 46% yield. The synthesis route for **2a** was the same as that for **1a**. **6** (1.0 equiv) was used instead of **5**. Compound **4a**, which has two 2-butyl-1-benzothiophene rings, was also synthesized as a reference.

SCHEME 1



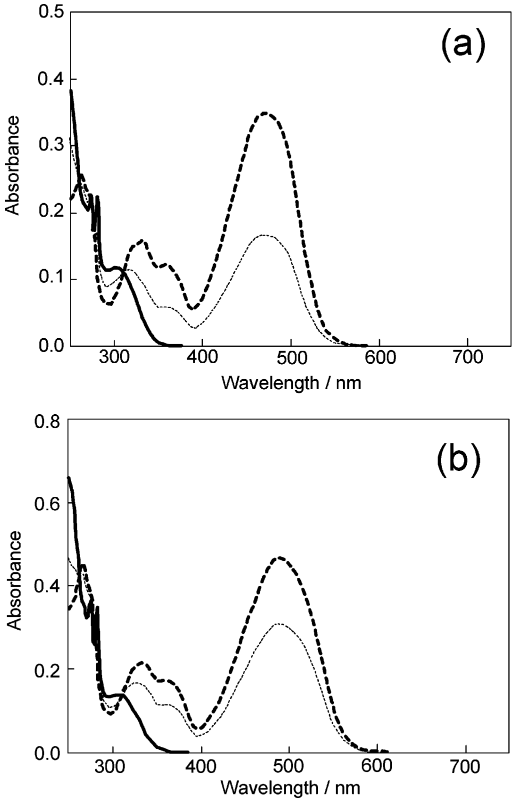


FIGURE 1. (a) Absorption spectra of **1a** (solid line) and **1b** (dashed line) and in the photostationary state (dotted line) under irradiation with 313 nm light in hexane (2.43×10^{-5} mol/L). (b) Absorption spectra of **2a** (solid line) and **2b** (dashed line) and in the photostationary state (dotted line) under irradiation with 313 nm light in hexane (3.16×10^{-5} mol/L).

Photochromism in Solution. Figure 1a shows the absorption spectral change of **1a** induced by photoirradiation in hexane. Upon irradiation with 313 nm light, a new absorption band due to the closed-ring isomer **1b** appeared at 469 nm. In the photostationary state, under irradiation with 313 nm light, 47% of the open-ring isomer **1a** converted to the closed-ring isomer **1b**. The closed-ring isomer has an absorption coefficient as large as 1.44×10^4 M^{-1} cm^{-1} (469 nm), which is 1.6 times as large as that of **3b** (ϵ_{517} 9.1×10^3 M^{-1} cm^{-1}). Upon irradiation with light of a wavelength longer than 550 nm, the closed-ring isomers reverted to **1a**.

As observed for **1a**, compound **2a** also underwent photochromism upon irradiation with UV and visible light in hexane solution. Figure 1b shows the spectral change of **2a** in hexane. In the photostationary state, upon irradiation with 313 nm light, 66% of the open-ring isomer **2a** converted to the closed-ring isomer **2b**, which has an absorption maximum at 489 nm. The absorption maximum of the closed-ring isomer showed a bathochromatic shift of as much as 20 nm by replacing methyl substituents with butyl substituents. Upon irradiation

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TABLE 1. Absorption Characteristics and Photochromic Reactivities of Diarylethene Derivatives 1−4 in Hexane

	$\epsilon/10^4$ dm^3 mol^{-1} cm^{-1} (wavelength/nm)		quantum yield	
compound	a	b	cyclization	cycloreversion
1	1.00 (274)	1.44 (469)	0.38 (313)	0.35 (469)
2	1.14 (275)	1.46 (489)	0.49 (313)	0.24 (489)
3	1.41 (258)	0.91 (517)	0.35 (313)	0.35 (517)
4	1.71 (258)	0.93 (536)	0.44 (313)	0.35 (536)

TABLE 2. Maximum Wavelengths (nm) of Closed-Ring Isomers 1−4 in Various Solvents

solvent (dielectric constant)	1	2	3	4
hexane (1.88)	469	489	517	535
ethyl acetate (6.02)	476	495	522	542
THF (7.58)	479	498	523	545
EtOH (24.55)	475	495	521	542
acetonitrile (37.50)	476	496	521	544

with light of a wavelength longer than 550 nm, the closed-ring isomers reverted to **2a**.

To determine the effect of substituents on the absorption maximum of the closed-ring isomer (**1b** and **2b**), compounds **3a** and **4a** were also synthesized and their absorption spectral characteristics were examined. Table 1 shows the absorption maxima of **1**−**4** in hexane. The absorption maximum of **4b** (536 nm) also showed a bathochromatic shift of as much as 19 nm upon replacement of methyl substituents with butyl substituents. The tendency was similar in all solvents examined, such as ethyl acetate, THF, ethanol, and acetonitrile, as shown in Table 2. The bulky butyl substituents are effective in shifting the absorption band of the closed-ring isomers to longer wavelengths. Similar behavior was reported for the closed-ring isomer of bis(2-*tert*-butyl-1-benzothiophen-3-yl)perfluorocyclopentene.[22]

Theoretical calculation for the absorption bands of the closed-ring isomers **1b** and **2b** was carried out with the Gaussian 98 and GAMESS program packages.[23] The calculated wavelengths of **1b** and **2b** are 492.06 nm (f = 0.3131) and 503.09 nm (f = 0.2701), respectively. The absorption wavelengths correlate well with those of experimental ones. Bulky substituents are considered to strain the π-conjugated structure and cause the bathochromatic shift of the absorption band of the closed-ring isomer.[24]

Thermal Stability and Fatigue Resistance. The thermal stability of both open- and closed-ring isomers is an indispensable property for the application to optical memory media. The closed-ring isomers of diarylethene derivatives having thiophene groups are thermally stable,[3] whereas diarylethene derivatives having pyrrol rings, such as 1,2-bis(2-cyano-1,5-dimethyl-4-pyrrolyl)perfluorocyclopentene,[25] are thermally unstable and return to the open-ring isomers even in the dark. Theoretical calculation[21] predicted that thermal stability is dependent on the aromatic stabilization energy of the aryl group. It is of interest to examine the thermal stability of diarylethene derivatives having benzofuran heteroaryl groups.

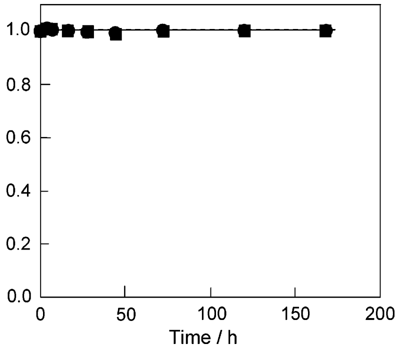

FIGURE 2. Thermal stability of closed-ring isomers **1b** (circles) and **2b** (squares) at 70 °C.

Figure 2 shows the thermal stability of the closed-ring isomers **1b** and **2b** in toluene at 70 °C. Both isomers are stable, and the absorption intensity remained constant even after 175 h. Fatigue resistance was also measured. The cyclization and cycloreversion could be repeated more than 1000 times in toluene in the presence of oxygen. Both **1** and **2** have high fatigue resistance comparable to that of 1,2-bis (2-methylbenzo-1-thiophen-3-yl)perfluorocyclopentene.

X-ray Crystallographic Analysis. Single crystals of **1a**, **1b**, **2a**, and **2b** were obtained by recrystallization in hexane. Figure 3 shows the ORTEP drawings based on the results of the X-ray crystallographic analyses. Both **1a** and **2b** are packed in the antiparallel conformation, and the distances between reactive carbons of **1a** and **2a** are 0.356 and 0.372 nm, respectively, which are sufficiently short for the molecules to undergo the photochromic reaction in the crystalline phase. As described in the Introduction, the distance between the reactive carbon atoms of **3a** is 0.435 nm, and **3a** does not show any photochromic reactivity in the crystalline phase.[13] The difference in the distances between the reactive carbon atoms is anticipated to affect the reactivity of these two crystals. The ORTEP drawings of **1b** and **2b** indicate that conrotatory photocyclization reactions take place in these compounds.

It was not easy to carry out the X-ray crystallographic analysis of **2b** because the **2b** crystal decomposes below −60 °C. Therefore, X-ray crystallographic measurement was carried out at room temperature. This is the reason why extremely large thermal disorder is observed, particularly in butyl and cyclopentene parts.

The difference between **1b** and **2b** is the angle of methyl(butyl)−carbon−oxygen. The angles of methyl and butyl derivatives are 111° and 116°, respectively. Bulky substituents increase the angles. As described in the calculation of the absorption spectrum of **1b** and **2b**, the constrained structure of **2b** shifts the absorption maximum to a longer wavelength.

Photochromism in the Single-Crystalline Phase. **1a** and **2a** showed photochromism in the single-crystalline phase. Figure 4 shows the photographs of the single-crystalline photochromism of **2a** observed under polarized

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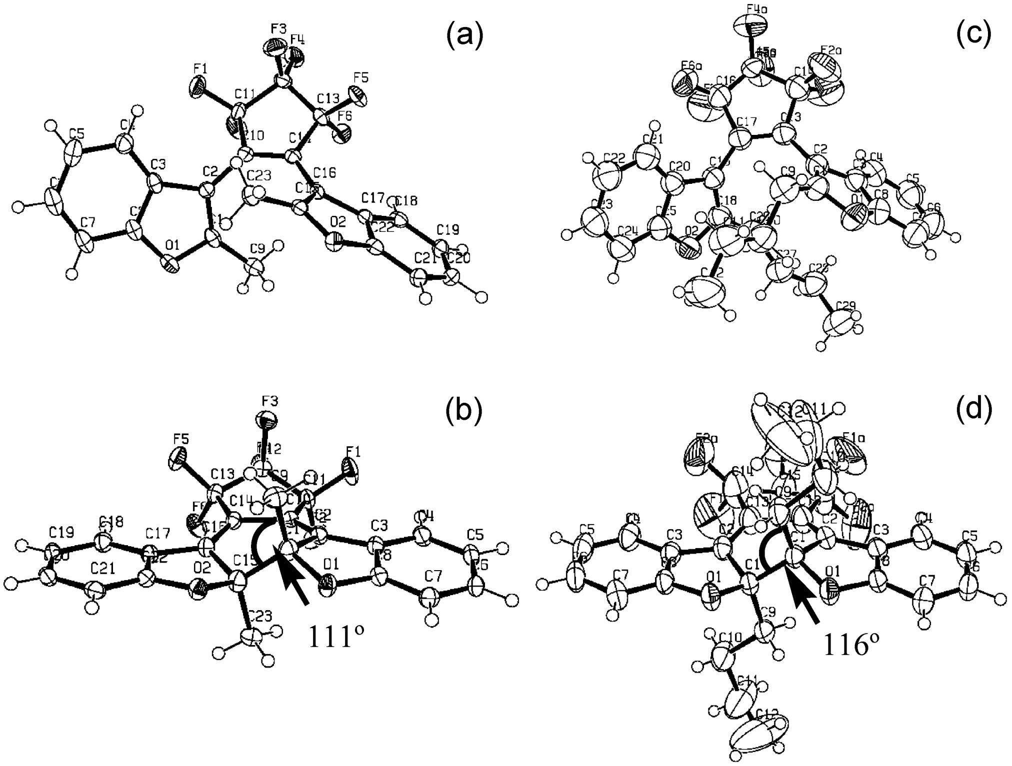

FIGURE 3. ORTEP drawings of (a) **1a**, (b) **1b**, (c) **2a**, and (d) **2b** showing 50% probability displacement ellipsoids.

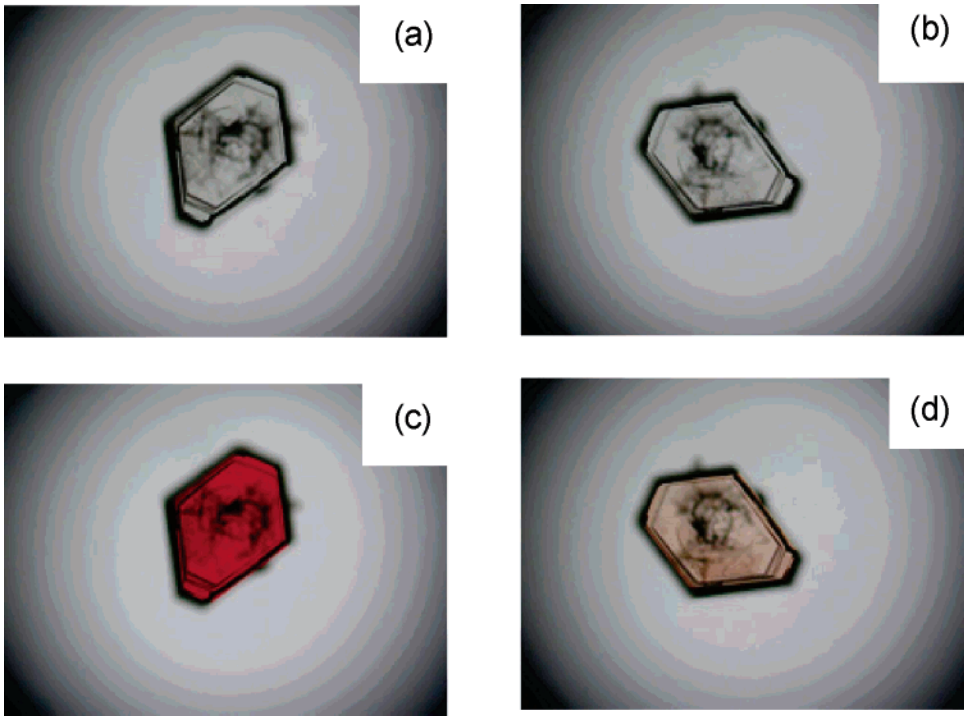

FIGURE 4. Photographs of single crystals of **2a** under polarized light before ((a) $\theta = 0°$; (b) $\theta = 90°$) and after ((c) $\theta = 0°$; (d) $\theta = 90°$) irradiation with 365 nm light. θ is the rotation angle of the crystal.

light. The crystal surface is (010) face. Before photoirradiation, the crystal was colorless (Figure 4a,b). Upon irradiation with 365 nm light, the crystal turned red at a certain angle (Figure 4c). When the crystal was rotated by as much as 90°, it turned to pale red. The red color reappeared at 270°. The clear dichroism indicates that the photochromic reaction proceeds in the crystal lattice. Upon irradiation with 400 nm light, the crystal became colorless.

Figure 5 shows the polarized absorption spectra of the UV-irradiated single crystal of **2** at (a) 0° and (b) 90° and the polar plots of the absorbance at 507 nm. The absorption maximum of the colored crystal **2b** is 507 nm. The absorption band of the colored isomer showed a

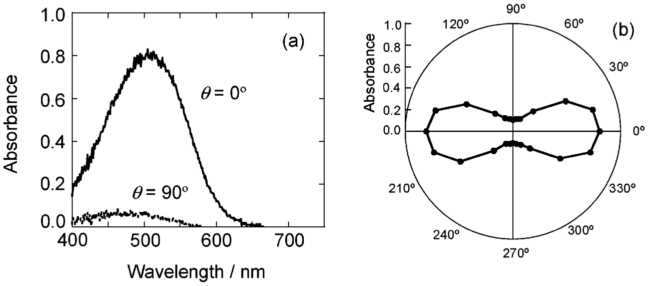

FIGURE 5. (a) Polarized absorption spectra of a photogenerated colored crystal of **2** and (b) polar plots of the absorbance of **2** at 507 nm.

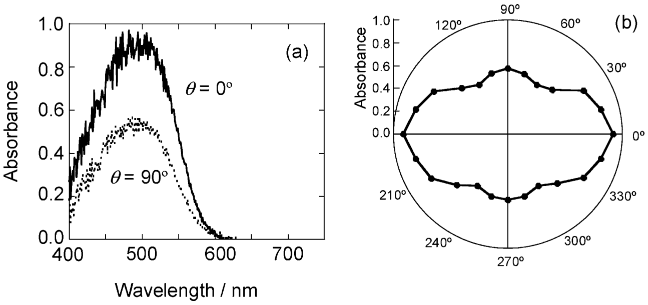

FIGURE 6. (a) Polarized absorption spectra of a photogenerated colored crystal of **1** and (b) polar plots of the absorbance of **1** at 504 nm.

bathochromic shift in comparison with the spectrum in hexane solution.

1a also showed photochromism in the single-crystalline phase. Upon irradiation with 365 nm light, the colorless single crystal turned orange. Upon irradiation with 400 nm light, the crystal turned colorless again. The photographs of **1** under polarized light are shown in the Supporting Information.

Figure 6 shows the polarized absorption spectra of the closed-ring form of the isomer of **1** at (a) 0° and (b) 90° and the polar plots of the absorbance at 504 nm. The crystal surface is (001) face, which is a well-developed face. The absorption maximum of the colored isomer was 504 nm at 0°. The color change by rotation was not as remarkable as that observed for single-crystal **2**. The low-order orientation of **1** is estimated by X-ray crystallographic analysis (the data are shown in the Supporting Information). Compound **3**, which has two benzothiophene units, did not show any photochromism in the single-crystalline phase. This result suggests that the difference in the nature between oxygen and sulfur atoms affects the conformation and photoreactivity of the molecules in the single-crystalline phase.

Conclusion

New photochromic compounds with benzofuran heteroaryl groups were synthesized, and their photochromic reactivity was examined in hexane solution as well as in the single-crystalline phase. The compounds underwent photochromic reactions even in the single-crystalline phase.

Experimental Section

3-Bromo-2-methy-1-benzofuran (5). To a stirred THF solution (30 mL) containing 2-methyl-1-benzofuran (1.0 g, 7.68 mmol) was slowly added 1.65 g of *N*-bromosuccinimide (9.30 mmol) at 5 °C. The reaction mixture was stirred for 15 h at room temperature. The reaction mixture was poured into sodium thiosulfate solution and extracted with diethyl ether. The organic phase 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 0.632 g of **5** in 39% yield.

5: colorless liquid; ^{1}H NMR (200 MHz) δ 2.50 (s, 3H), 7.27−7.34 (m, 2H), 7.40−7.49 (m, 2H); MS (EI) *m/z* [M$^+$] 210. Anal. Calcd for C_9H_7BrO: C, 51.22; H, 3.34%. Found: C, 51.21; H, 3.30%.

1,2-Bis(2-methyl-1-benzofuran-3-yl)perfluorocyclopentene (1a). To a stirred THF solution (40 mL) containing **5** (0.632 g, 2.99 mmol) was slowly added 1.97 mL of 1.6 M butyllithium hexane solution (3.14 mmol) at −78 °C, and the solution was stirred for 15 min at −78 °C. Then the octafluorocyclopentene (0.199 mL, 1.50 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 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 0.299 g of **1a** in 46% yield.

1a: colorless crystals; mp 102−103 °C; ^{1}H NMR (200 MHz) δ 2.07 (s, 3H), 2.16 (s, 3H), 7.14−7.30 (m, 4H), 7.36−7.48 (m, 2H), 7.59−7.77 (m, 2H); MS (EI) *m/z* (M$^+$) 436; Anal. Calcd for $C_{23}H_{14}F_6O_2$: C, 63.31; H, 3.23%. Found: C, 63.35; H, 3.19%.

3-Bromo-2-butyl-1-benzofuran (6). The bromination of 2-butyl-1-benzofuran (1.00 g, 5.74 mL) and NBS (1.30 g, 7.30 mmol) was performed as described for compound **5**. The crude product was purified by column chromatography on silica gel (hexane) to give 1.17 g of **6** in 81% yield.

6: colorless liquid; ^{1}H NMR (200 MHz) δ 0.95 (t, $J = 7$ Hz, 3H), 1.31−1.52 (m, 2H), 1.66−1.81 (m, 2H), 2.83 (t, $J = 7$ Hz, 2H), 7.24−7.30 (m, 2H), 7.35−7.46 (m, 2H); MS (EI) *m/z* [M$^+$] 252. Anal. Calcd for $C_{12}H_{13}BrO$: C, 56.94; H, 5.18%. Found: C, 56.84; H, 5.20%.

1,2-Bis(2-butyl-1-benzofuran-3-yl)perfluorocyclopentene (2a). The coupling of 3-bromo-2-butyl-1-benzofuran (1.17 g, 4.64 mmol) and octafluorocyclopentene (0.307 mL, 2.32 mmol) was performed as described for compound **1a**. The crude product was purified by column chromatography on silica gel (hexane) to give 0.351 g of **2a** in 29% yield.

2a: colorless crystals; mp 71−72 °C; ^{1}H NMR (200 MHz) δ 2.07 (s, 3H), 2.16 (s, 3H), 7.14−7.30 (m, 4H), 7.36−7.48 (m, 2H), 7.59−7.77 (m, 2H); MS (EI) *m/z* (M$^+$) 520. Anal. Calcd for $C_{29}H_{26}F_6O_2$: C, 66.92; H, 5.03%. Found: C, 67.02; H, 5.07%.

3-Bromo-2-butyl-1-benzothiophene (7). The bromination reaction of 2-butyl-1-benzothiophene (4.96 g, 26.1 mmol) and NBS (5.61 g, 31.3 mmol) was performed as described for compound **5**. The crude product was purified by column chromatography on silica gel (hexane) to give 5.28 g of **7** in 75% yield.

7: colorless liquid; ^{1}H NMR (200 MHz) δ 0.96 (t, $J = 7$ Hz, 3H), 1.35−1.53 (m, 2H), 1.65−1.80 (m, 2H), 2.94 (t, $J = 8$ Hz, 2H), 7.28−7.45 (m, 2H), 7.71−7.76 (m, 2H); MS (EI) *m/z* [M$^+$] 268. Anal. Calcd for $C_{12}H_{13}BrS$: C, 53.54; H, 4.87%. Found: C, 53.57; H, 4.88%.

1,2-Bis(2-butyl-1-benzothien-3-yl)perfluorocyclopentene (4a). The coupling of 2-butyl-3-bromo-1-benzothiophene (1.50 g, 5.57 mmol), 1.6 M *n*-BuLi (3.83 mL, 6.1 mmol), and octafluorocyclopentene (0.369 mL, 2.78 mmol) was performed as described for compound **1a**. The crude product was purified by column chromatography on silica gel (hexane) to give 0.508 g of **4a** in 33% yield.

4a: colorless crystals; mp 109−110 °C; ^{1}H NMR (200 MHz) δ 0.70 (t, $J = 7$ Hz, 6H), 0.82−1,12 (m, 4H), 1.27−1.50 (m, 4H), 2.18−2.31 (m, 1H), 2.55−2.70 (m, 1H), 7.14−7.42 (m, 6H), 7.54−7.74 (m, 2H); MS (FAB) *m/z* [M^+] 552. Anal. Calcd for $C_{29}H_{26}F_6S_2$: C, 63.03; H, 4.74%. Found: C, 63.02; H, 4.78%.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research (S) (No. 15105006) from the Japan Society of the Promotion of Science.

Supporting Information Available: Photographs of single crystals of **1** before and after irradiation with UV light and crystal structures of **1a** and **2a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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