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Dithienylethenes with a Novel Photochromic Performance

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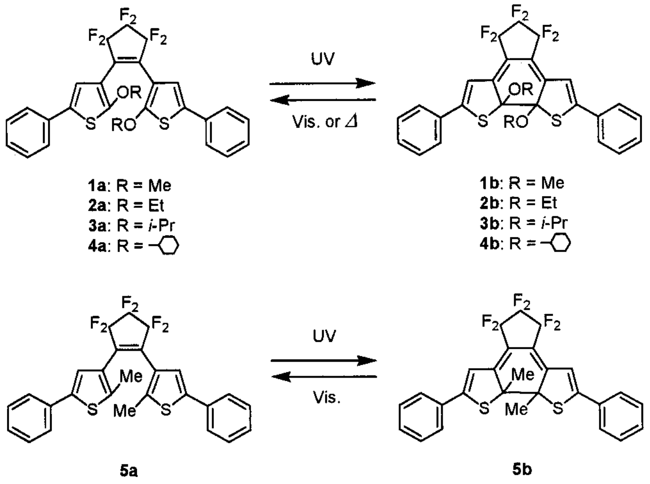
Dithienylethenes with low decoloration quantum yields and thermal reversibility at high temperature above 100 °C were prepared. Introduction of bulky alkoxy substituents at 2- and 2′-positions of the thiophene rings strongly suppressed the cycloreversion quantum yields. The quantum yields were lower than 10^{-3}, and the photogenerated color remained stable enough under room light. On the other hand, the bulky alkoxy substituent decreased the thermal stability of the colored closed-ring isomers at high temperature. The color of the dithienylethene with cyclohexyloxy substituents faded out in less than 1 min at 160 °C.

Introduction

Photochromic compounds undergo reversible photoisomerization between two isomers with different absorption spectra upon irradiation with appropriate wavelength of light.[1,2] Photogenerated colored isomers, in general, return to the initial colorless isomers either photochemically or thermally at room temperature.[3−6] In most cases thermally reversible photochromic compounds are also photochemically reactive.[5,6] Therefore, photogenerated colored isomers are unstable under room light at room temperature, and the compounds cannot be applied to image recording. For the recording application, the photochromic compounds should have very low photodecoloration quantum yields and thermal stability at room temperature. In addition, it is desired for the reusability that the colored isomers can return to the colorless isomers either thermally or photochemically at high temperature, for example above 100 °C. So far, such photochromic compounds have not yet been developed.

Scheme 1



We have synthesized a new class of photochromic compounds, named dithienylethenes, which undergo thermally irreversible and fatigue-resistant photochromic reactions.[7−10] The photogenerated colored isomer of a derivative, 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene (**5b**), is stable for more than 1900 years at 30 °C.[11] The colored isomer, however, returns to the colorless isomer by visible irradiation (the photodecoloration quantum yield = 0.013). Recently we have preliminary reported that the photodecoloration quantum yield is strongly suppressed by the introduction of methoxy groups at the reactive 2- and 2′-positions of the thiophene rings.[12] In the present study we have designed and synthesized dithienylethene molecules, which have both very low decoloration quantum yields and thermal reversibility at high temperature, though the colored isomers are stable enough at room temperature.

Results and Discussion

Synthesis. Dithienylethene derivatives with various types of alkoxy substituents at the reactive 2- and 2′-positions of the thiophene rings were prepared. Bulky alkoxy groups, such as ethoxy, isopropoxy, and cyclohexyloxy groups, were specially selected, because bulky substituents are known to enhance the thermal decoloration reactions at high temperature.[13,14]

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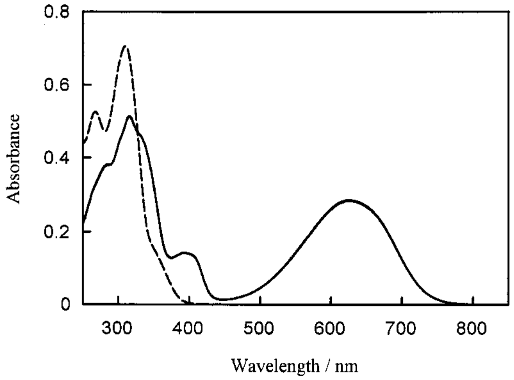
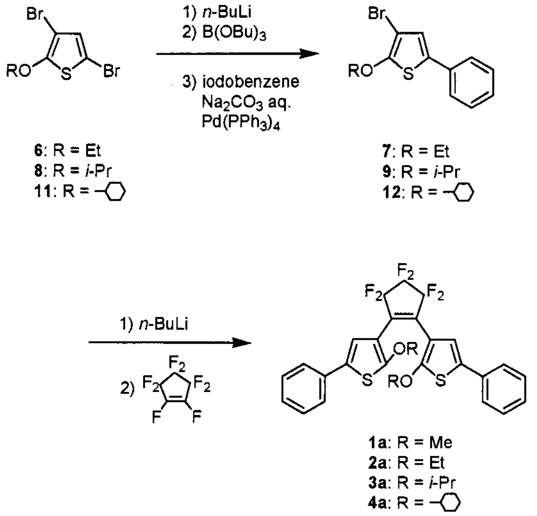


Figure 1. Absorption spectral change of **1** in hexane (2.1 × 10^{-5} M) by photoirradiation: **1a** (- - -), **1** in the photostationary state under irradiation with 313-nm light (—), and **1b** (—). The absorption spectrum in the photostationary state under irradiation with 313-nm light was overlapped with the spectrum of **1b**.[12]

Scheme 2



The synthetic procedure is shown in Scheme 2. The dithienylethene derivatives were synthesized from 2-alkoxy-3,5-dibromothiophenes by two-step procedures. **1a**–**4a** were purified by column chromatography and recrystallization (hexane or acetone). The structures of all compounds were confirmed by ^{1}H NMR, mass spectroscopy, and elemental analysis.

Absorption Spectra. Figure 1 shows the absorption spectral change of **1** by irradiation with 313-nm light.[12] **1a** has the absorption maximum at 267 and 309 nm in hexane. Upon irradiation with 313-nm light, the colorless hexane solution of **1a** turned blue, in which a visible absorption band was observed at 625 nm. The blue color is due to the closed-ring form isomer **1b**.[10] The colored isomer was stable in the dark at room temperature and could be isolated by high performance liquid chromatography (HPLC, silica gel column, hexane/ethyl acetate = 80:20). The closed-ring form isomer very slowly reformed the open-ring form isomer upon prolonged irradiation with visible light. The absorption spectrum returned to the original one after 4 h irradiation with an intense 500 W mercury lamp (λ > 500 nm). This indicates that the introduction of the methoxy groups strongly suppressed the cycloreversion reaction. The conversion from **1a** to **1b** in the photostationary state under irradiation with 313-nm light was 100%.

Table 1. Absorption Maxima and Coefficients of 1b–4b in Hexane

compd	λ_{max}/nm	$\epsilon/10^4$ M^{-1} cm^{-1}	volume[a]/Å^3
1b	625	1.5	62.8
2b	625	1.3	89.4
3b	635	1.3	116.0
4b	635	1.3	185.6

[a] Estimated for the alkoxy groups according to atomic increment method.[15]

Table 2. Cyclization and Cycloreversion Quantum Yields of 1–5 in Hexane

compd	cyclization[a]	cycloreversion[a]
1	0.44	~1.7 × 10^{-5}
2	0.48	2.5 × 10^{-4}
3	0.46	6.6 × 10^{-4}
4	0.43	6.4 × 10^{-4}
5[11]	0.59	1.3 × 10^{-2}

[a] Standard deviation of the experimental error: ±5%.

2a, **3a**, and **4a** also exhibited similar photochromism. Table 1 summarizes the main absorption bands of the closed-ring form isomers **1b**–**4b**. The visible absorption maxima of the closed-ring form isomers shifted to longer wavelengths by the introduction of bulky alkoxy groups. The absorption maxima of **1b** having methoxy substituents was observed at 625 nm, while it shifted to 635 nm when cyclohexyloxy substituents were introduced. The maximum wavelength of **4b** was 10 nm longer than that of **1b**. The absorption maximum shift agrees to the order of the bulkiness; MeO, EtO < *i*-PrO, cyclohexyloxy.[15] It is known that introduction of long π-conjugated aryl groups to dithienylethene derivatives results in the shift of the absorption maximum of the closed-ring form isomer to longer wavelengths.[16–18] The bulky alkoxy subutituent at 2- and 2′-positions of the thiophene rings gave a similar effect to shift the absorption maximum of the closed-ring isomer to longer wavelengths.

Absorption coefficients (ϵ, M^{-1} cm^{-1}) of the closed-ring form isomers were also affected by the alkoxy substituents. The values of ϵ for **1b**, **2b**, **3b**, and **4b** were 1.5 × 10^4, 1.3 × 10^4, 1.3 × 10^4, and 1.3 × 10^4 M^{-1} cm^{-1}, respectively. The alkoxy subustituents decreased ϵ-values as follows: MeO > EtO, *i*-PrO, cyclohexyloxy. This effect is opposite to ϵ-values observed in dithienylethene derivatives with long π-conjugated aryl groups. In the derivatives ϵ-values increased with the shift of the absorption maximum to longer wavelengths.[16,17]

Quantum Yields. The cyclization and cycloreversion quantum yields of **1**–**4** were measured in hexane at room temperature. As shown in Table 2, the cyclization quantum yields of **1a**, **2a**, **3a**, and **4a** were 0.44, 0.48, 0.46, and 0.43, respectively. The values were similar each other and slightly smaller than that of **5a** ($\Phi_{a\rightarrow b}$ = 0.59).[11] This means that these alkoxy substituents scarcely affect the cyclization reactions even when bulky cyclohexyloxy substituents were introduced.

On the other hand, the cycloreversion quantum yields of **1b**–**4b** were strongly suppressed by the alkoxy substituents. As shown in Table 2, the cycloreversion quan-

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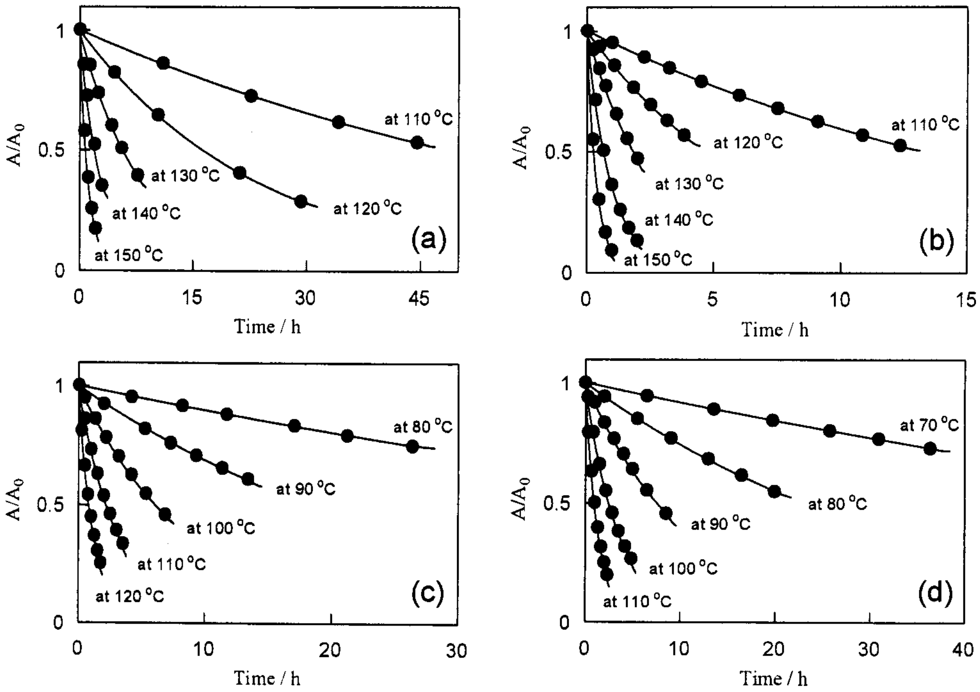

Figure 2. Thermal fading curves of **1b** (a), **2b** (b), **3b** (c), and **4b** (d) in decalin.

tum yields of **1b**, **2b**, **3b**, and **4b** were estimated to be $\sim 1.7 \times 10^{-5}$, 2.5×10^{-4}, 6.6×10^{-4}, and 6.4×10^{-4}, respectively. The cycloreversion quantum yields of the alkoxy-substituted dithienylethenes were lower than that of **5b** by a factor of 10^2–10^3. The decrease in the cycloreversion quantum yield is attributed based on molecular orbital theoretical calculations to the presence of activation barriers in the cycloreversion process in the singlet excited state.[19] When the bulkiness of the alkoxy groups increased, the cycloreversion quantum yields also increased. The quantum yield $\sim 1.7 \times 10^{-5}$ of **1b** increased to 6.4×10^{-4} when bulky cyclohexyloxy substituents were introduced. The increase is ascribable to the molecular strain of the closed-ring isomers by the bulky substituents.

Thermal Cycloreversion in Solution. **5** underwent thermally irreversible photochromism. **5b** was stable in the dark and had the half-life time of 1900 years at 30 °C.[11] Even at 100 °C **5b** was stable for more than 18 days. On the other hand, it was reported that dithienylethene derivatives having bulky substituents such as isopropyl groups at the reactive 2- and 2′-positions of the thiophene rings are thermally unstable above 80 °C and return to the open-ring isomers in 20 min at 100 °C.[14]

The thermal stability of the closed-ring form isomers **1b**–**4b** were examined at 70~150 °C in decalin. Figure 2 shows the decay curves of the absorbance of the closed-ring isomers at several temperatures. The absorbance of the closed-ring isomers decreases slowly above 70 °C. The decay curves followed the first-order kinetics. The absorption spectra of the thermal-bleached solutions after 10 times photocoloration/thermal-decoloration cycles remained almost same in shape and intensity with the initial spectra of the open-ring isomers. This indicates that the thermal fading of the color is due to the thermal cycloreversion to the open-ring isomer. The rates of thermal cycloreversion were dependent on the substituents and increased in the following order: MeO < EtO < *i*-PrO < cyclohexyloxy.

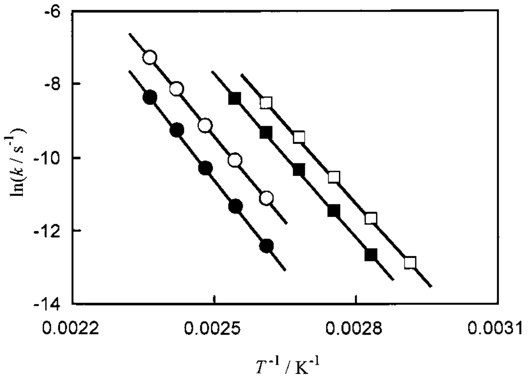

Figure 3. Temperature dependence of the thermal fading rates of **1b** (●), **2b** (○), **3b** (■), and **4b** (□).

Table 3. Arrhenius Parameters of Thermal Cycloreversions and Half-Life Times from the Closed- to the Open-Ring Isomers

compd	E_a/kJ mol^{-1}	A/s^{-1}	$t_{1/2}$(160 °C)	$t_{1/2}$(30 °C)
1b	137	2.1×10^{13}	18 min	420 y
2b	129	5.5×10^{12}	7.4 min	65 y
3b	123	5.5×10^{12}	1.6 min	7.0 y
4b	120	4.4×10^{12}	45 s	2.2 y
5b[11]	139	1.3×10^{13}	51 min	1900 y

Figure 3 shows the temperature dependences of the rates (k). The activation energy (E_a) and frequency factor (A) of the cycloreversion were estimated from the linear relation. The values are summarized in Table 3. When bulky alkoxy substituents were introduced, the values decreased as follows; MeO > EtO > *i*-PrO > cyclohexyloxy. The decrease in E_a values enhanced the thermal cycloreversion reaction at higher temperature. Bulky substituents at the central bond induce the strain in the

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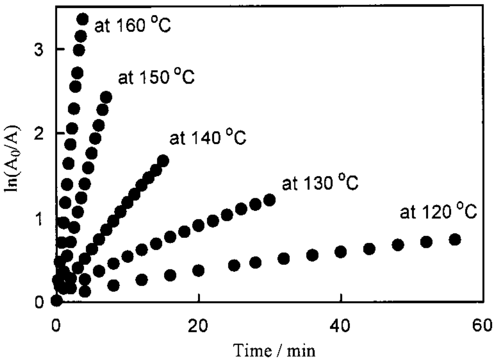

Figure 4. Thermal fading of **4b** in a polymer film. The film was prepared by casting the toluene solution containing **4b** and poly[oxycarbonyloxy-1,4-phenylene(methyl)phenylmethylene-1,4-phenylene] (1/10 wt/wt) on the slide glass. The thickness of the film was ca. 3 μm.

molecular structure of the closed-ring isomers, resulting in the decrease in E_a values.

Table 3 also shows the estimated half-life times of the thermal cycloreversion reactions for the closed-ring isomers **1b**−**4b** at 160 and 30 °C obtained by the extrapolation of the temperature dependence. The half-life times of **1b**, **2b**, **3b**, and **4b**, at 160 °C were 18 min, 7.4 min, 1.6 min, and 45 s, respectively. **4b** has both reasonable thermal cycloreversion rate at high temperature and thermal stability at room temperature. In addition, **4b** has a very low photodecoloration quantum yield.

Thermal Cycloreversion in Polymer Films. **4b** satisfies both requirements of photostability and thermally reversibility at higher temperature. We measured thermal cycloreversion of **4b** in a polymer film. The polymer film was prepared by casting the toluene solution containing **4a** and poly[oxycarbonyloxy-1,4-phenylene(methyl)phenylmethylene-1,4-phenylene] (1/10 wt/wt) on the slide glass. The polymer film underwent photocoloration upon irradiation with UV light (366 nm). The thermal stability was measured between 120 °C and 160 °C. Figure 4 shows the first-order plots of the decoloration rate at several temperatures. The decoloration curves deviated from the first-order kinetics. This kind of phenomenon is often observed in polymer systems and ascribed to distribution of first-order constant rates due to existence of various microenvironments.[20] Apparently, the values are similar to those in solution. The absorbance of **4b** decreased to 50% of the initial value in less than 1 min at 160 °C.

Figure 5 shows the color changes of **4b** and **5b** by heat and light. The samples were prepared by casting the toluene solutions containing the dithienylethenes and the polymer as used in the previous experiment. The sample in the left side is **4** and right side is **5** on the paper. The colorless open-ring isomers (Figure 5a and 5d) turned blue upon UV irradiation (Figure 5b and 5e). Then, the samples were kept at 160 °C in the dark. After storage for 5 min, the blue color of **4b** disappeared, while the blue color of **5b** remained the original color (Figure 5c). When the colored sample (Figure 5e) was irradiated with visible light (>520 nm) for 10 min, the blue color of **5b** disappeared, while the color of **4b** remained (Figure 5f). **4b** is photochemically stable but thermally reversible.

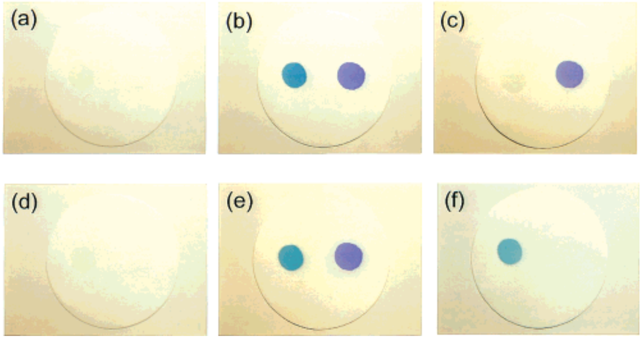

Figure 5. Photocoloration and thermal and photochemical fading of **4** (left side on the paper) and **5** (right side) in the polymer film. Samples a and d are the colorless open-ring isomers. Samples b and e are the colored isomers upon UV irradiation. When the colored sample b was kept at 160 °C in the dark for 5 min, sample b changed to sample c. The blue color of **4b** disappeared, while the blue color of **5b** remained the original color. When the colored sample e was irradiated with visible light (>520 nm) for 10 min, sample e changed to f. The blue color of **5b** disappeared, while the color of **4b** remained.

Conclusion

This paper has demonstrated design and synthesis of dithienylethenes, which have both very low decoloration quantum yields and thermal reversibility at high temperature. Introduction of the alkoxy groups at the reacting positions of the dithienylethenes extraordinarily decreased the photocycloreversion quantum yields. The bulky alkoxy substituents shifted the absorption maximum to longer wavelength and increased the thermal cycloreversion rate at high temperature. Photochromic compounds with such a new photochromic reactivity are applicable for image recording.

Experimental Section

General. Solvents used were spectroscopic grade and purified by distillation. ^{1}H NMR spectra were recorded on at 200 MHz. A high-temperature chamber was used to maintain constant temperature of the solution. Absorption spectra of the polymer film were measured using a microscope connected with a PMA-11 photodetector. A hot stage was used to maintain constant temperature of the polymer film. Photoirradiation was carried out using a 500 W super-high-pressure mercury lump or a 500 W xenon lamp as the light sources. Monochromic light was obtained by passing the light through a monochromator. The quantum yields were determined by comparing the reaction yields of the dithienylethenes in hexane against furyl fulgide in hexane or toluene.[21,22] The samples were not degassed. The films were prepared by casting the toluene solution containing **4a** and poly[oxycarbonyloxy-1,4-phenylene(methyl)phenylmethylene-1,4-phenylene] (1/10 wt/wt) on the glass substrate.

1,2-Bis(2-methoxy-5-phenyl-3-thienyl)perfluorocyclopentene (1a). **1a** was prepared according to the method described in the literature.[12]

3,5-Dibromo-2-ethoxythiophene (6). To a stirred solution of 2-ethoxythiophene[23] (3.1 g; 24 mmol) in dichloromethane (48 mL) at 0 °C was slowly added *N*-bromosuccinimide (NBS) (8.5 g, 48 mmol). The reaction mixture was stirred overnight at room temperature. The mixture was cooled on the ice bath

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and then filtered. The filtrate was neutralized and extracted with chloroform. The chloroform extract was dried over $MgSO_4$, filtered, and concentrated. The residue was purified by silica gel column chromatography using hexane as the eluent. **6** was obtained as colorless oil of 6.5 g in 94% yield: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.43 (t, $J = 7$ Hz, 3H), 4.13 (q, $J = 7$ Hz, 2H), 6.75 (s, 1H); MS m/z (M^+) 284, 286, 288. Anal. Calcd for $C_6H_6Br_2OS$: C, 25.20; H, 2.11. Found: C, 25.50; H, 2.14.

3-Bromo-2-ethoxy-5-phenylthiophene (7). To 150 mL of dry THF containing **6** (6.5 g; 23 mmol) was added 15% *n*-BuLi hexane solution (15 mL; 25 mmol) at −78 °C under argon atmosphere, and the solution was stirred for 1 h at the low temperature. Tri-*n*-butyl borate (9.1 mL; 34 mmol) was slowly added to the reaction mixture at −78 °C, and the mixture was stirred for 1.5 h at that temperature. After warming the solution up to room temperature, 20 wt % Na_2CO_3(aq) (53 mL), iodobenzene (4.6 g; 23 mmol), and tetrakis(triphenylphosphine)palladium(0) (1.1 g; 0.95 mmol) were added to the reaction mixture. The mixture was refluxed overnight at 70 °C. The product was extracted with ether. The organic layer was dried over $MgSO_4$, filtered, and concentrated. The residue was purified by silica gel column chromatography using hexane as the eluent to give 4.9 g of **7** in 76% yield as colorless oil: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.48 (t, $J = 7$ Hz, 3H), 4.21 (q, $J = 7$ Hz, 2H), 6.98 (s, 1H), 7.2−7.5 (m, 5H); MS m/z (M^+) 282, 284. Anal. Calcd for $C_{12}H_{11}BrOS$: C, 50.90; H, 3.92. Found: C, 51.17; H, 3.89.

1,2-Bis(2-ethoxy-5-phenyl-3-thienyl)perfluorocyclopentene (2a). To 50 mL of dry THF solution containing **7** (4.9 g; 17 mmol) was added 15% *n*-BuLi hexane solution (12 mL; 19 mmol) at −78 °C under argon atmosphere, and the solution was stirred for 1.5 h at that low temperature. Octafluorocyclopentene (1.2 mL; 8.6 mmol, Nippon Zeon) was slowly added to the reaction mixture at −78 °C, and the mixture was stirred for 3 h at that temperature. The reaction was stopped by the addition of water. The product was extracted with ether. The organic layer was dried over $MgSO_4$, filtered, and concentrated. The residue was purified by silica gel column chromatography using hexane/chloroform (7:3) as the eluent and by recrystallization from acetone to give 1.8 g of **2a** in 36% yield as pale yellow crystals: mp 199.6−200.6 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.08 (t, $J = 7$ Hz, 6H), 3.92 (q, $J = 7$ Hz, 4H), 7.22 (s, 2H), 7.2−7.5 (m, 10H); MS m/z (M^+) 580. Anal. Calcd for $C_{29}H_{22}F_6O_2S_2$: C, 59.99; H, 3.82. Found: C, 60.03; H, 3.80.

3,5-Dibromo-2-isopropoxythiophene (8). **8** was prepared from 2-isopropoxythiophene[24] (3.5 g; 24 mmol) by a procedure similar to that used for **6**. The crude product was purified by silica gel column chromatography using hexane as the eluent to give 4.5 g of **8** in 62% yield as pale yellow oil: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.39 (d, $J = 6$ Hz, 6H), 4.32 (sep, $J = 6$ Hz, 1H), 6.74 (s, 1H); MS m/z ($M^+ - CH_2{=}CHCH_3$) 256, 258, 260. Anal. Calcd for $C_7H_8Br_2OS$: C, 28.02; H, 2.69. Found: C, 27.95; H, 2.63.

3-Bromo-2-isopropoxy-5-phenylthiophene (9). **9** was prepared from **8** (4.3 g; 14 mmol) by a procedure similar to that used for **7**. The crude product was purified by silica gel column chromatography using hexane as the eluent to give 3.0 g of **9** in 70% yield as pale yellow oil: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.43 (d, $J = 6$ Hz, 6H), 4.42 (sep, $J = 6$ Hz, 1H), 6.97 (s, 1H), 7.2−7.5 (m, 5H); MS m/z (M^+) 296, 298. Anal. Calcd for $C_{13}H_{13}BrOS$: C, 52.53; H, 4.41. Found: C, 52.62; H, 4.52.

1,2-Bis(2-isopropoxy-5-phenyl-3-thienyl)perfluorocyclopentene (3a). **3a** was prepared from **9** (2.0 g; 6.7 mol) by a procedure similar to that used for **2a**. The crude product was purified by silica gel column chromatography using hexane/chloroform (7:3) as the eluent to give 0.70 g of **3a** in 35% yield as pale yellow crystals: mp 191.3−192.3 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.15 (d, $J = 6$ Hz, 12H), 4.26 (sep, $J = 6$ Hz, 2H), 7.16 (s, 2H), 7.2−7.5 (m, 10H); MS m/z (M^+) 608. Anal. Calcd for $C_{31}H_{26}F_6O_2S_2$: C, 61.17; H, 4.31. Found: C, 61.20; H, 4.33.

2-Cyclohexyloxythiophene (10). Sodium (1.6 g; 71 mmol) was added into a flask containing dry cyclohexanol (100 mL) under argon atmosphere and was completely dissolved by stirring at 120 °C. 2-Iodothiophene (5.3 mL; 48 mmol), CuO (1.9 g; 24 mmol), and KI (4.0 g; 24 mmol) were added to the solution and stirred for 2 h at 130 °C. The product was extracted with ether. The organic layer was dried over $MgSO_4$, filtered, and concentrated. The residue was purified by silica gel column chromatography using hexane as the eluent to give 0.64 g of **10** in 7.4% yield as pale yellow oil: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.3−2.0 (m, 11H), 4.06 (tt, $J = 9$, 4 Hz, 1H), 6.24 (d, $J = 4$ Hz, 1H), 6.56 (d, $J = 6$ Hz, 1H), 6.70 (dd, $J = 4$ and 6 Hz, 1H); MS m/z (M^+) 182. Anal. Calcd for $C_{10}H_{14}OS$: C, 65.89; H, 7.74. Found: C, 65.73; H, 7.64.

3,5-Dibromo-2-cyclohexyloxythiophene (11). **11** was prepared from **10** (0.60 g; 3.3 mmol) by a procedure similar to that used for **6**. The crude product was purified by silica gel column chromatography using hexane as the eluent to give 0.94 g of **11** in 84% yield as pale yellow oil: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.3−2.0 (m, 11H), 4.05 (tt, $J = 9$, 4 Hz, 1H), 6.73 (s, 1H); MS m/z (M^+ − cyclohexene) 256, 258, 260. Anal. Calcd for $C_{10}H_{12}Br_2OS$: C, 35.32; H, 3.56. Found: C, 35.39; H, 3.58.

3-Bromo-2-cyclohexyloxy-5-phenylthiophene (12). **12** was prepared from **11** (1.6 g; 4.7 mmol) by a procedure similar to that used for **7**. The crude product was purified by silica gel column chromatography using hexane as the eluent to give 0.96 g of **12** in 61% yield as pale yellow crystals: mp 58.3−59.3 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.3−2.0 (m, 11H), 4.15 (tt, $J = 9$, 4 Hz, 1H), 6.96 (s, 1H), 7.2−7.5 (m, 5H); MS m/z (M^+) 336, 338. Anal. Calcd for $C_{16}H_{17}BrOS$: C, 56.98; H, 5.08. Found: C, 56.94; H, 5.08.

1,2-Bis(2-cyclohexyloxy-5-phenyl-3-thienyl)perfluorocyclopentene (4a). **4a** was prepared from **12** (0.90 g; 2.7 mol) by a procedure similar to that used for **2a**. The crude product was purified by silica gel column chromatography using hexane/chloroform (7:3) as the eluent to give 0.41 g of **4a** in 44% yield as pale yellow crystals: mp 134.3−135.3 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.2−1.8 (m, 22H), 4.03 (br, 2H), 7.14 (s, 2H), 7.2−7.5 (m, 10H); MS m/z (M^+) 688. Anal. Calcd for $C_{37}H_{34}F_6O_2S_2$: C, 64.52; H, 4.98. Found: C, 64.30; H, 5.00.

1,2-Bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene (5a). **5a** was prepared according to the method described in the literature.[11]

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Supporting Information Available: ^{1}H NMR spectra of **2a**, **3a**, and **4a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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