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Photochromism of Dithienylethenes with Electron-Donating Substituents

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Bis(2,4-dimethyl-5-phenylthiophene-3-yl)perfluorocyclopentenes having hydrogen, methoxy, diethylamino, or cyano substituents at para-positions of the phenyl groups were synthesized to reveal the effect of the substitution on the absorption coefficient ϵ of the closed-ring forms and the photochemical reactivity. Electron-donating substituents, such as methoxy or diethylamino groups, were found to be effective to increase the absorption coefficient and to decrease the ring-opening quantum yield. The cyclization quantum yield was scarcely affected by the substitution. The conversion from the open- to the closed-ring forms of the diethylamino-substituted compound in the photostationary state under irradiation with 313 nm light was close to 100%.

Introduction

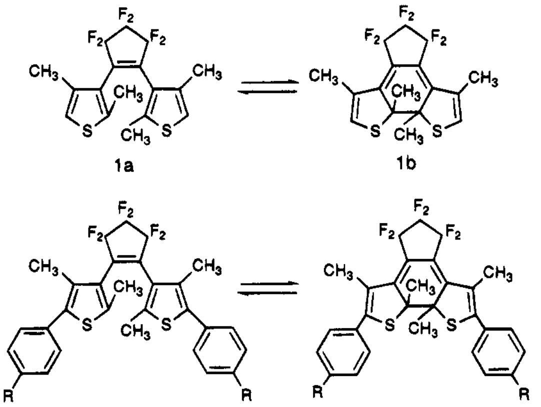
Recent renewal of interest in photochromism is ascribable to its potential capabilities for various optoelectronic devices.[1−5] Fundamental requirements for the application are thermal stability of both isomers and fatigue resistant characteristics. In general, photogenerated colored isomers are thermally unstable and return to the initial states in the dark. Recently, a few thermally irreversible photochromic compounds have been developed.[6−8] Among the compounds, 1,2-diarylethenes with heterocyclic rings are promising candidates for the optoelectronic application because both isomers of the compounds are stable for more than 3 months at 80 °C and the coloration/decoloration cycles can be repeated more than 10^4 times.[9,10]

Although the diarylethenes satisfy the minimum demands, other properties are also equally required for practical use, such as high cyclization quantum yields, low ring-opening quantum yields, and high absorption coefficients of the closed-ring forms. The low ring-opening quantum yield is specially desired for optical memory use in which many times readout without erasing the memory is required.

In this paper, we describe our effort to control the photochemical reactivity of diarylperfluorocyclopentenes by introducing electron-donating substituents to the aryl groups.

Results and Discussion

Absorption Spectra. The following diarylperfluorocyclopentenes **1−5**, with various electron-donating or -withdrawing substituents were synthesized. 1,2-Bis(2,4-dimethylthiophene-3-yl)perfluorocyclopentene (**1a**) has the absorption maximum at 234 nm (ϵ, 1.3×10^4 M^{-1} cm^{-1}) in hexane. Upon irradiation with 280 nm light, the open-ring form converted to the closed-ring form **1b** with the absorption maximum at 534 nm (ϵ, 5.0×10^3 M^{-1} cm^{-1}). The absorption coefficient ϵ of the colored form is rather low. The most convenient way to increase ϵ is to extend the polyene conjugation by introducing electron-rich chromophores into the molecule.[11] First, we replaced the hydrogens at the 5 and 5′ positions of the thiophene rings with phenyl groups.[12]



2a: R = H
3a: R = OCH3
4a: R = N $(C_2H_5)_2$
5a: R = CN

2b: R = H
3b: R = OCH3
4b: R = N $(C_2H_5)_2$
5b: R = CN

Figure 1 shows the absorption spectral change of 1,2-bis(2,4-dimethyl-5-phenylthiophene-3-yl)perfluorocyclopentene (**2**) in hexane. Upon irradiation with 313 nm light, a colorless hexane solution containing **2a** (3.3×10^{-5} mol/L) turned to blue-violet, in which the absorption

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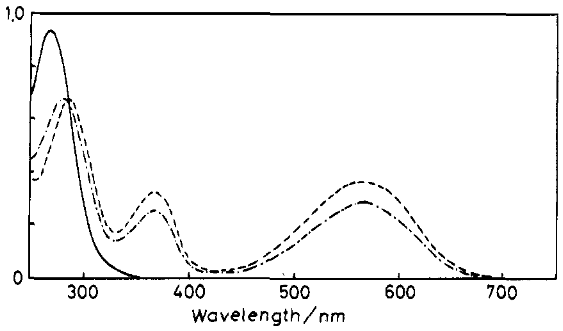

Figure 1. Absorption spectra of hexane solutions of **2a** (3.3×10^{-5} mol/L) (—), **2b** (– –), and **2b** in the photostationary state (—•—) under irradiation with 313 nm light.

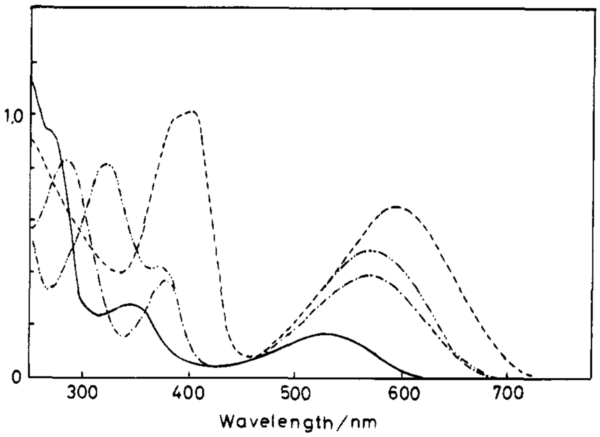

Figure 2. Absorption spectra of **1b** (—), **3b** (—••—), **4b** (– – –), and **5b** (—•—) in hexane (3.5×10^{-5} mol/L).

maximum was observed at 562 nm. The ϵ value at the absorption maximum, $1.1 \times 10^4\ M^{-1}\ cm^{-1}$, was twice as large as that of **1b**. Introduction of phenyl groups is effective to increase the coefficient. The blue-violet color disappeared upon irradiation with visible (λ > 550 nm) light.

Toward the goal of further increasing ϵ values, the effect of substitution at the para-positions of the phenyl rings with electron-donating or -withdrawing groups was examined. Compounds **3**–**5**, in which methoxy, diethylamino, or cyano groups were substituted at the para-positions of the phenyl rings, were prepared. The photochromic behavior of **3**–**5** was similar to that of **2**. Upon irradiation with UV light (313 nm light), colorless hexane solutions containing the compounds turned to blue and the blue color disappeared by irradiation with visible (λ > 550 nm) light. The colored isomers were stable and can be isolated by HPLC. Figure 2 shows the absorption spectra of the closed-ring isomers **3b**, **4b**, and **5b** along with the spectrum of **1b**. As can be seen from the spectra, the absorption maxima and the coefficients increase with an increasing electron-donating ability. The electron-withdrawing cyano substituents shifted the absorption maximum to a longer wavelength but did not increase the ϵ value. The absorption coefficient of **4b** is 3.6 times larger than that of unsubstituted closed-ring form **1b**. Table 1 summarizes the absorption maxima and the coefficients.

Quantum Yields. The cyclization and ring-opening quantum yields of **1**–**5** were measured in hexane at room temperature. Both cyclization and ring-opening quantum yields were found to depend on the substitution, as shown in Table 1. The cyclization quantum yields as high as 0.46 and 0.48 were observed for **2** and **3**, respectively. The quantum yields are much higher than the values so far measured for diarylmaleic anhydrides.[7,13] When strong electron-donating diethylamino groups were substituted at the para-positions of the phenyl groups such as **4**, the quantum yield decreased to some extent. Electron-withdrawing cyano substituents increased the cyclization quantum yield, and a yield as high as 0.50 was observed.

Table 1. Absorption Characteristics and Photoreactivity of Dithienylethenes

			quantum yield			
	$\epsilon/10^4\ M^{-1}\ cm^{-1}$ [a]			ring-opening		
compd	a	b	cyclization	22 °C	80 °C	convn[b]/%
1	1.3 (234 nm)	0.50 (534 nm)	0.21	0.13		62
2	2.8 (262 nm)	1.1 (562 nm)	0.46	0.015	0.037	79
3	3.3 (270 nm)	1.4 (597 nm)	0.48	0.0080	0.018	88
4	4.0 (305 nm)	1.8 (597 nm)	0.37	0.0025	0.010	>99
5	3.0 (300 nm)	1.1 (570 nm)	0.50	0.018	0.034	98

[a] Absorption coefficient at the absorption maximum. [b] Conversion from the open- to the closed-ring forms in the photostationary state under irradiation with 313 nm light.

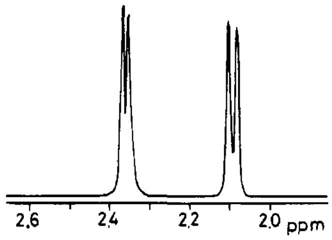

Figure 3. ^{1}NMR methyl signals of **2a** in $CDCl_3$.

Table 2. Conformation Ratio in the Ground State

compd	parallel	anti-parallel
2a	52	48
3a	52	48
4a	52	48
5a	50	50

Diarylperfluorocyclopentenes have two conformations, with the two aryl rings in mirror and C_2 symmetries, and the photocyclization reaction is allowed only from the conformation with the rings in C_2 symmetry.[14] The two conformations are in dynamic equilibrium, and the ratio can be estimated by NMR measurement. Figure 3 shows the methyl protons of **2a**. The doublet signals at 2.09 and 2.36 ppm are assigned to methyl protons at the 2 and 4 positions of the thiophene rings in anti-parallel and parallel conformations, respectively.[7,13] The intensity ratio of the doublet peaks indicates that the two conformations are in almost equal population. Table 2 shows the ratio of the two conformations of **2a**–**5a** determined by the NMR measurement. The two conformations exist in a 1:1 ratio.

The interconversion rate between the two conformations is estimated to be much slower than the lifetime of the photoexcited states.[13] Therefore, both conformers are

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excited independently, and only the photoexcited anti-parallel conformer has a chance to be converted to the closed-ring form. The closed-ring form is not produced from the photoexcited parallel conformer. This means that the maximum cyclization quantum yield is 0.5. The quantum yields of **2a**, **3a**, and **5a** are very close to the maximum value as shown in Table 1. In these compounds almost all photoexcited anti-parallel conformers convert to the closed-ring forms. In other words, the actual quantum yields are close to 1.0.

The ring-opening quantum yield was much more strongly dependent on the electron-donating substituents. Introduction of phenyl groups at the 5 and 5′ positions of the thiophene rings decreased the ring-opening quantum yield from 0.13 to 0.015. The quantum yield was further decreased by substituting the para-positions of the phenyl rings with electron-donating groups. The ring-opening quantum yield of **4b** was 1/6 of that of **2b**. The quantum yield of **5b** was almost the same as that of **2b**. Electron-withdrawing cyano groups did not affect the ring-opening quantum yield.

The percent conversion from the open-ring to the closed-ring isomers at the photostationary state is dependent on the following ratio under the conditions of $\epsilon_o C_o$, $\epsilon_c C_c \ll 1$

$$\text{conversion (\%)} = \frac{\Phi_{o\to c}\epsilon_o}{\Phi_{o\to c}\epsilon_o + \Phi_{c\to o}\epsilon_c}100$$

where ϵ_o and ϵ_c are the absorption coefficients of the open- and closed-ring isomers at the irradiation wavelength, respectively. $\Phi_{o\to c}$ and $\Phi_{c\to o}$ express cyclization and ring-opening quantum yields, respectively. When the quantum yield ratio of $\Phi_{o\to c}\epsilon_o/\Phi_{c\to o}\epsilon_c$ is high, the conversion increases. The conversion close to 100% was observed for **4** upon irradiation with 313 nm light.

The ring-opening quantum yield was found to depend on the reaction temperature as shown in Table 1. At 80 °C the yield of **4b** was four times larger than the value at 22 °C. The high yield is not due to the thermal reverse reaction, because the closed-ring isomers were stable and did not return to the open ring isomers even at 100 °C.

The ring-opening quantum yield of **1b** was much larger than those of phenyl ring substituted compounds. The extension of π-conjugation to the phenyl rings is considered to decrease the yield. At higher temperature the extension of π-conjugation is considered to be suppressed to some extent by the phenyl ring rotation. This may increase the quantum yield. This interpretation was supported by the blue shift in the absorption maximum of the closed-ring isomer at higher temperature. The absorption maximum of **4b** shifted from 618 nm at 22 °C to 605 nm at 80 °C in toluene. Destabilization of the excited state caused the increase in the quantum yield.

The Effect of Protonation—A Multi-Colored System. When the diethylamino groups of **4** are protonated, the electron-donating property is lost. The protonation can be reversibly carried out by the addition of strong acid (or base). Such a reversible chemical modification of **4** is expected to change the color and the reactivity of the compound. Figure 4 shows the absorption spectra of **4b** in the presence and absence of trifluoroacetic acid in ethyl acetate. By the addition of 30 times molar of trifluoroacetic acid the absorption maximum of the closed-ring form shifted from 618 nm to 582 nm and the ϵ value decreased to 55% of the neutral form. The absorption coefficient is almost similar to that of the unsubstituted compounds **2b**. The decrease is not due to the decomposition of the compound, because the absorption intensity is recovered by the addition of excess amines, such as triethylamine.

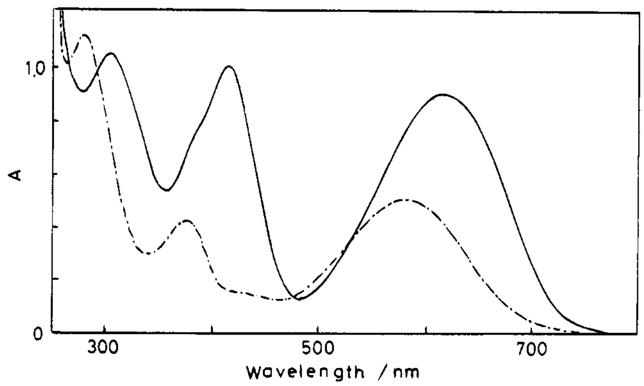
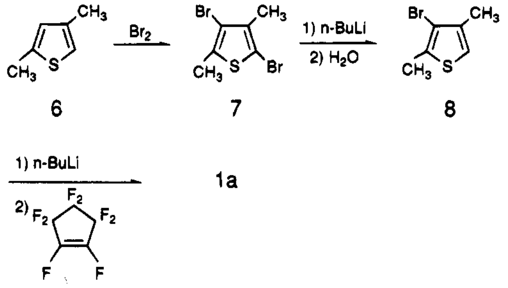


Figure 4. Absorption spectra of ethyl acetate solutions containing **4b** (5.0×10^{-5} mol/L) in the absence (—) and presence (—•—) of trifluoroacetic acid (1.5×10^{-3} mol/L).

Scheme 1



Not only the absorption characteristics but also the photoreactivity changed by the protonation. Both cyclization and ring-opening quantum yields increased. The increase in the ring-opening quantum yield was as much as four times. These results support the conclusion so far described that electron-donating substituents are effective to increase the absorption coefficient and to decrease the ring-opening quantum yield.

Experimental Section

General. Absorption spectra were measured with an absorption spectrometer (Hitachi U-3410). ^{1}H NMR spectra were recorded on Varian-Gemini-200 (200 MHz) spectrometer. Chemical shifts were reported in parts per million. Photoirradiation was carried out in the thermostat by using a USHIO 500 W high-pressure mercury lamp as the exciting light source. Mercury lines at 280, 313, and 546 nm were isolated by passing the light through a monochrometer (Ritsu MC-10N). Quantum yields were determined by comparing the reaction yields of the diarylethenes in hexane against furyl fulgide in toluene.[15,16] The samples were not degassed.

Materials. Compounds **1a–5a** were synthesized according to Schemes 1 and 2.

2,4-Dibromo-3,5-dimethylthiophene (7). To 50 mL of an acetic acid solution containing 2,4-dimethylthiophene (**6**) (5 g, 44.6 mmol) was added 5 mL (97 mmol) of bromine at 0 °C, and the solution was stirred overnight. The reaction mixture was poured into water (saturated with NaCl) and extracted with chloroform. The organic layer was washed with a sodium carbonate aqueous solution and water. Bromine was eliminated by washing the chloroform layer with a sodium thiosulfate aqueous solution. The organic layer was washed again

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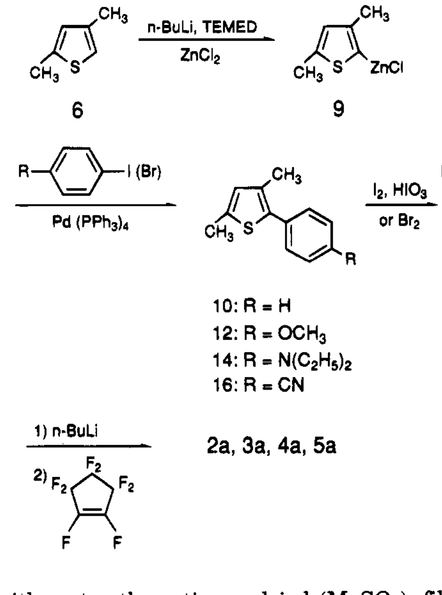
Scheme 2



with water three times, dried (MgSO$_4$), filtered, and evaporated. The residue was purified by column chromatography on silica gel (hexane) to give 7.8 g 2,4-dibromo-3,5-dimethylthiophene (**7**) in 65% yield. **7**: ^{1}H NMR (200 MHz, CDCl$_3$, TMS) δ 2.17 (s, 3H), 2.34 (s, 3H); MS *m/z* 270 (M$^+$). Anal. Calcd for C$_6$H$_6$Br$_2$S: C, 26.69; H, 2.24. Found: C, 26.98; H, 2.21.

3-Bromo-2,4-dimethylthiophene (8). To 25 mL of an ether solution containing compound **7** (2.85 g, 10.5 mmol) was added 10 mL of a *n*-butyllithium (BuLi) hexane solution (1.6 M, 16.0 mmol) at −60 °C in 5 min, and the solution was stirred for 2 h at the low temperature. Lithium at the 5-position of thiophene was replaced with hydrogen by the addition of water at room temperature. The reaction mixture was extracted with ether, and the organic layer was washed with water, dried (MgSO$_4$), filtered, and evaporated. The residue was purified by column chromatography on silica gel (hexane) to give 1.76 g of 3-bromo-2,4-dimethylthiophene (**8**) in 88% yield. **8**: ^{1}H NMR (200 MHz, CDCl$_3$, TMS) δ 2.19 (s, 3H), 2.39 (s, 3H), 6.70 (s, 3H); MS *m/z* 191 (M$^+$). Anal. Calcd for C$_6$H$_7$BrS: C, 37.71; H, 3.69. Found: C, 37.78; H, 3.53.

1,2-Bis(2,4-dimethylthiophen-3-yl)perfluorocyclopentene (1a). To 50 mL of a tetrahydrofuran solution containing compound **8** (1.09 g, 5.70 mmol) was added 4.3 mL of a *n*-BuLi hexane solution (1.6 M, 6.88 mmol) at −60 °C under nitrogen atmosphere during 2 min, and the solution was stirred for 15 min at the low temperature. Then, 0.35 mL of perfluorocyclopentene (2.61 mmol) was added to the reaction mixture at −60 °C, and the solution was further stirred for 3 h at that temperature. The reaction was stopped by the addition of a dilute HCl aqueous solution. The reaction product was extracted with ether. The organic layer was washed with water, dried (MgSO$_4$), filtered, and evaporated. The residue was purified by column chromatography on silica gel (hexane) to give 580 mg of 1,2-bis(2,4-dimethylthiophen-3-yl)perfluorocyclopentene (**1a**) in 56% yield as a white solid. **1a**: mp 133−134 °C; ^{1}H NMR (200 MHz, CDCl$_3$, TMS) δ 2.04 (s, 6H), 2.29 (s, 6H), 6.70 (s, 2H); MS *m/z* 396 (M$^+$). Anal. Calcd for C$_{17}$H$_{14}$F$_6$S$_2$: C, 51.51; H, 3.53. Found: C, 51.46; H, 3.62.

3,5-Dimethyl-2-phenylthiophene (10). To 20 mL of an ether solution containing 2.24 g (20.0 mmol) of 2,4-dimethylthiophene and 2.55 g (22.0 mmol) of *N,N,N′,N′*-tetramethylethylenediamine (TEMED) was added 13.7 mL of a BuLi hexane solution (1.6 M, 22.0 mmol) under nitrogen atmosphere at room temperature. The reaction mixture was stirred for 2 h. To this reaction mixture, was added 20 mL of an ether solution of zinc chloride (1.0 M) and the resulting mixture stirred for 4 h. In another reaction flask, 4.08 g (20.0 mmol) of iodobenzene and 231 mg of tetrakis(triphenylphosphine)palladium(0) were added to 20 mL of anhydrous tetrahydrofuran (THF), and the solution was stirred. To the THF solution was added the previous ether solution dropwise at room temperature. The reaction mixture was heated for 2 h at 50 °C and allowed to stir overnight at room temperature. Water was added to the reaction mixture, and the reaction product was extracted with ether. The organic layer was washed with water, dried (MgSO$_4$), filtered, and evaporated. The residue was purified by column chromatography on silica gel (hexane) to give 3.66 g of 3,5-dimethyl-2-phenylthiophene in 97% yield. **10**: ^{1}H NMR (200 MHz, CDCl$_3$, TMS) δ 2.22 (s, 3H), 2.40 (s, 3H), 6.48 (s, 1H), 7.09−7.38 (m, 5H); MS *m/z* 188 (M$^+$). Anal. Calcd for C$_{12}$H$_{12}$S: C, 76.55; H, 6.42. Found: C, 76.49; H, 6.60.

3-Iodo-2,4-dimethyl-5-phenylthiophene (11). To a mixture of 1.83 g (9.73 mmol) of compound **10**, 6.3 mL of acetic acid, and 6.3 mL of carbon tetrachloride were added an iodic acid solution (0.370 g (2.10 mmol) of iodic acid in 1 mL of water) and 0.850 g (3.35 mmol) of iodine. The solution was refluxed for 2 h. The reaction mixture was poured into ice-cold water and extracted with chloroform. The organic layer was washed with a sodium carbonate aqueous solution, a sodium thiosulfate aqueous solution, and water. Then, the chloroform layer was dried over MgSO$_4$ and evaporated. The residue was purified by column chromatography on silica gel (hexane) to give 2.36 g of 3-iodo-2,4-dimethyl-5-phenylthiophene(11) in 77% yield. **11**: ^{1}H NMR (200 MHz, CDCl$_3$, TMS) δ 2.27 (s, 3H), 2.43 (s, 3H), 7.36 (m, 5H); MS *m/z* 315 (M$^+$). Anal. Calcd for C$_{12}$H$_{11}$IS: C, 45.87; H, 3.53. Found: C, 46.04; H, 3.54.

1,2-Bis(2,4-dimethyl-5-phenylthiophen-3-yl)perfluorocyclopentene (2a). To a stirred THF solution (15 mL) containing compound **11** (2.08 g, 6.60 mmol) was slowly added 6.21 mL of BuLi hexane solution (1.6 M, 9.94 mmol) at −78 °C under nitrogen atmosphere, and the solution was stirred for 1 h. Perfluorocyclopentene (0.222 mL, 1.65 mmol) was added to the THF solution twice (for a total of 0.444 mL), and the mixture was stirred overnight at the low temperature. The reaction mixture was poured into water and extracted with ether. The organic layer was washed with 1 N HCl aqueous solution and water. The organic layer was dried (MgSO$_4$), filtered, and evaporated. The residue was purified by column chromatography on silica gel (hexane) to give 948 mg of 1,2-bis(2,4-dimethyl-5-phenylthiophen-3-yl)perfluorocyclopentene (**2a**) in 52% yield as a white solid. **2a**: mp 136−137 °C; ^{1}H NMR (200 MHz, CDCl$_3$, TMS) δ 2.09 (s, 6H) 2.36 (s, 6H), 7.35 (m, 10H); MS *m/z* 548 (M$^+$). Anal. Calcd for C$_{29}$H$_{22}$F$_6$S$_2$: C, 63.49; H, 4.04. Found: C, 63.58; H, 4.28.

3,5-Dimethyl-2-(4-methoxyphenyl)thiophene (12). The coupling reaction of 2,4-dimethylthiophene (**6**) (1.12 g, 10.0 mmol) and 4-iodoanisole (2.34 g, 10.0 mmol) was performed by the procedure as described for compound **10**. The crude product was purified by column chromatography on silica gel (hexane/chloroform = 1/1) to give 1.99 g of 3,5-dimethyl-2-(4-methoxyphenyl)thiophene (**12**) in 91% yield. **12**: ^{1}H NMR (200 MHz, CDCl$_3$, TMS) δ 2.22 (s, 3H), 2.40 (s, 3H), 3.83 (s, 3H), 6.48 (s, 1H), 7.09−7.38 (m, 4H); MS *m/z* 218 (M$^+$). Anal. Calcd for C$_{13}$H$_{14}$OS: C, 71.52; H, 6.46. Found: C, 71.47; H, 6.57.

3-Iodo-2,4-dimethyl-5-(4-methoxyphenyl)thiophene (13). Compound **12** (800 mg, 3.67 mmol) was iodized by the procedure as described for compound **11**. The crude product was purified by silica gel column chromatography (hexane/chloroform = 3/1) to give 900 mg of 3-iodo-2,4-dimethyl-5-(4-methoxyphenyl)thiophene (**13**) in 71% yield. **13**: ^{1}H NMR (200 MHz, CDCl$_3$, TMS) δ 2.23 (s, 3H), 2.44 (s, 3H), 3.83 (s, 3H), 7.25−7.36 (m, 4H); MS *m/z* 344 (M$^+$). Anal. Calcd for C$_{13}$H$_{13}$OIS: C, 45.36; H, 3.81. Found: C, 45.89; H, 3.91.

1,2-Bis(2,4-dimethyl-5-(4-methoxyphenyl)thiophene-3-yl)perfluorocyclopentene (3a). The coupling reaction of compound **13** (3.44 g, 10 mmol) and perfluorocyclopentene (0.671 mL, 5.00 mmol) was performed by the procedure as described for **2a**. The crude product was purified by silica gel chromatography (hexane/ethyl acetate = 10/1) to give 1.40 g of 1,2-bis(2,4-dimethyl-5-(4-methoxyphenyl)thiophene-3-yl)perfluorocyclopentene (**3a**) in 46% yield as a white solid. **3a**: mp 100−101 °C; ^{1}H NMR (CDCl$_3$) δ 2.05 (s, 6H), 2.33 (s, 6H), 3.83 (s, 6H), 6.90−7.27 (m, 8H); MS *m/z* 608 (M$^+$). Anal. Calcd for C$_{31}$H$_{26}$F$_6$O$_2$S$_2$: C, 61.17; H, 4.31. Found: C, 61.34; H, 4.55.

4-Iodo-*N*,*N*-diethylaniline (18). To a mixture of 1.47 g (10 mmol) of *N*,*N*-diethylaniline, 6.30 mL of acetic acid, and 6.30 mL of carbon tetrachloride were added iodic acid solution (0.370 g (2.10 mmol) of iodic acid in 0.900 mL of water) and 0.850 g (3.35 mmol) of iodine, and the solution was refluxed for 2 h. The reaction mixture was poured into ice-cold water and extracted with chloroform. The organic layer was washed with a sodium carbonate aqueous solution, sodium thiosulfate aqueous solution, and water. Then the chloroform layer was dried over $MgSO_4$ and evaporated. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate = 20/1) to give 1.82 g of 4-iodo-*N*,*N*-diethylaniline in 66% yield. **18**: ^1H NMR (200 MHz, $CDCl_3$, TMS) δ 1.14 (t, 6H, $J = 7$ Hz), 3.31 (q, 4H, $J = 7$ Hz), 7.36 (m, 4H); MS *m/z* 275 (M^+). Anal. Calcd for $C_{10}H_{14}NI$: C, 43.66; H, 5.13; N, 5.09. Found: C, 43.48; H, 5.05; N, 5.26.

3,5-Dimethyl-2-(4-(*N*,*N*-diethylamino)phenyl)thiophene (14). The coupling reaction of 2,4-dimethylthiophene (**6**) (1.12 g, 10 mmol) and compound **18** (2.75 g, 10 mmol) was performed as described above for compound **10**. The crude product was purified by silica gel chromatography(hexane/ethyl acetate = 30/1) to give 1.85 g of 3,5-dimethyl-2-(4-(*N*,*N*-diethylamino)phenyl)thiophene (**14**) in 71% yield. **14**: ^1H NMR (200 MHz, $CDCl_3$, TMS) δ 1.27 (t, 6H, $J = 7$ Hz), 2.24 (s, 3H), 2.43 (s, 3H), 3.38 (q, 4H, $J = 7$ Hz), 6.55–7.41 (m, 5H); MS *m/z* 259 (M^+). Anal. Calcd for $C_{16}H_{21}NS$: C, 74.08; H, 8.16; N, 5.40. Found: C, 74.10; H, 8.30; N, 5.50.

3-Bromo-2,4-dimethyl-5-(4-(*N*,*N*-diethylamino)phenyl)thiophene (15). To a stirred solution of compound **14** (1.00 g, 3.86 mmol) in 10 mL of carbon disulfide was added 0.200 mL (3.88 mmol) of bromine, and the solution was allowed to stir for 48 h. The reaction mixture was poured into water and extracted with chloroform. The organic layer was washed with a sodium thiosulfate aqueous solution and water. Then the organic layer was dried over $MgSO_4$ and evaporated. The crude product was purified by silica gel chromatography (hexane/benzene = 3/2) to give 1.12 g of 3-bromo-2,4-dimethyl-5-(4-(*N*,*N*-diethylamino)phenyl)thiophene (**15**) in 86% yield. **15**: ^1H NMR (200 MHz, $CDCl_3$, TMS) δ 1.17 (t, 6H, $J = 7$ Hz), 2.22 (s, 3H), 2.38 (s, 3H), 3.35 (q, 4H, $J = 7$ Hz), 6.61–7.41 (m, 4H); MS *m/z* 337 (M^+) 339 ($M^+ + 2$). Anal. Calcd for $C_{16}H_{20}NBrS$: C, 56.80; H, 5.96; N, 4.14. Found: C, 56.24; H, 5.46; N, 3.90.

1,2-Bis(2,4-dimethyl-5-(4-(*N*,*N*-diethylamino)phenyl)thiophene-3-yl)perfluorocyclopentene (4a). The coupling reaction of compound **15** (1.76 g, 5.22 mmol) and perfluorocyclopentene (0.340 mL, 2.53 mmol) was performed by the procedure as described for compound **2a**. The crude product was purified by silica gel chromatography (hexane/ethyl acetate = 15/1) to give 740 mg of 1,2-bis(2,4-dimethyl-5-(4-(*N*,*N*-diethylamino)phenyl)thiophene-3-yl)perfluorocyclopentene (**4a**) in 42% yield as a pale yellow solid. **4a**: mp 63–64 °C; ^1H NMR (200 MHz, $CDCl_3$, TMS) δ 1.17 (t, 12H, $J = 7$ Hz), 2.06 (s, 6H), 2.31 (s, 6H), 3.35 (q, 8H, $J = 7$ Hz), 6.61–7.24 (m, 8H); MS *m/z* 690 (M^+). Anal. Calcd for $C_{37}H_{40}F_6N_2S_2$: C, 64.33; H, 5.84; N, 4.05. Found: C, 64.23; H, 6.03; N, 4.23.

3,5-Dimethyl-2-(4-cyanophenyl)thiophene (16). The coupling reaction of 2.69 g (24.0 mmol) of 2,4-dimethylthiophene (**6**) and 3.64 g (20.0 mmol) of 4-bromobenzonitrile was performed by the same procedure as described for compound **10**. The crude product was purified by column chromatography on silica gel (hexane) to give 4.14 g of 3,5-dimethyl-2-(4-cyanophenyl)thiophene (**16**) in 97% yield. **16**: mp 71–72 °C; ^1H NMR (200 MHz, $CDCl_3$, TMS) δ 2.12 (s, 3H), 2.39 (s, 3H), 6.48 (s, 1H), 7.45–7.69 (m, 4H); MS *m/z* 213 (M^+). Anal. Calcd for $C_{13}H_{11}NS$: C, 73.20; H, 5.20; N, 6.57. Found: C, 72.91; H, 5.04; N, 6.48.

3-Iodo-2,4-dimethyl-5-(4-cyanophenyl)thiophene (17). Compound **16** (3.97 g, 18.6 mmol) was iodized by the procedure used for compound **11**. The crude product was purified by column chromatography on silica gel (hexane) to give 3.06 g of 3-iodo-2,4-dimethyl-5-(4-cyanophenyl)thiophene (**17**) in 49% yield. **17**: mp 136–137 °C; ^1H NMR (200 MHz, $CDCl_3$, TMS) δ 2.12 (s, 3H), 2.39 (s, 3H), 7.45–7.69 (m, 4H); MS *m/z* 339 (M^+). Anal. Calcd for $C_{13}H_{10}NSI$: C, 46.03; H, 2.97; N, 4.13. Found: C, 46.08; H, 2.95; N, 4.09.

1,2-Bis(2,4-dimethyl-5-(4-cyanophenyl)thiophene-3-yl)perfluorocyclopentene (5a). The coupling reaction of compound **17** (3.06 g, 9.03 mmol) and perfluorocyclopentene (0.600 mL, 4.47 mmol) was performed by the procedure as used for compound **2a**. The crude product was purified by column chromatography on silica gel (hexane) to give yield 540 mg of 1,2-bis(2,4-dimethyl-5-(4-cyanophenyl)thiophene-3-yl)perfluorocyclopentene (**5a**) in 20% yield as a white solid. **5a**: mp 188–189 °C; ^1H NMR (200 MHz, $CDCl_3$, TMS) δ 2.12 (s, 6H), 2.39 (s, 6H), 7.45–7.69 (m, 8H); IR (KBr) 2230 cm^{-1} (CN); MS *m/z* 598 (M^+). Anal. Calcd for $C_{31}H_{20}F_6N_2S_2$: C, 62.20; H, 3.37; N, 4.68. Found: C, 62.48; H, 3.67; N, 4.43.

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