Photochromism of Dithienylethenes Containing Fluorinated Thiophene Rings

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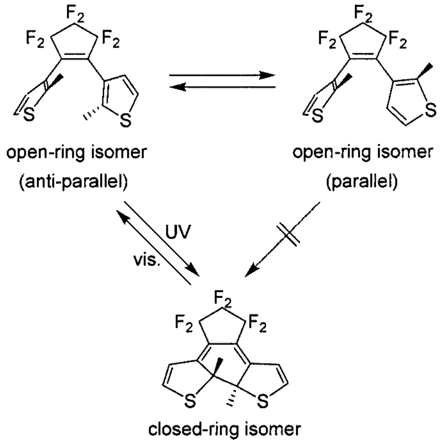
Bis(3-thienyl)perfluorocyclopentenes containing partially fluorinated thiophene rings were synthesized and their behaviors examined. Dithienylethenes containing chlorinated thiophene rings were also prepared as reference compounds. The absorption maxima of the closed-ring isomers, their thermal stabilities, and their quantum yields varied depending on the substitution position. The absorption maxima showed a red shift upon fluorine substitution at the 2- or 4-positions of the thiophene ring, whereas a blue shift was observed upon substitution at the 5-position. This shift was explained by the shape of the HOMO and LUMO and was well reproduced by theoretical calculations using time-dependent density-functional theory (TD-DFT). The cycloreversion quantum yield of the closed-ring isomer of 2-fluorine-substituted 1,2-bis(2-fluoro-3-thienyl)perfluorocyclopentene was about 130 times smaller than that of the closed-ring isomer of 5-fluorine-substituted 1,2-bis(5-fluoro-2-methyl-3-thienyl)perfluorocyclopentene. This low quantum yield was attributed to the change of the π-conjugation mode in the closed-ring isomer.

Introduction

Light-induced reversible isomerization between two forms having different absorption spectra is referred to as photochromism,[1] and compounds that are capable of these reactions are called photochromic compounds. Various types of photochromic compounds have been developed in an attempt to apply them to optoelectronic devices such as optical memories, photo-optical switches, and displays.[2] Thermal irreversibility is a necessary condition for above-mentioned applications, and several compounds, such as furylfulgides,[3] diarylethenes,[4] and phenoxynaphthacenequinone,[5] have been reported to exhibit such photochromic performance. Among these compounds, diarylethenes with heterocyclic aryl groups are the most promising candidates for applications because of their thermal irreversibility and high fatigue resistance.

Diarylethenes undergo the photochromic reactions shown in Scheme 1.[4] The open-ring isomer has two conformations — anti-parallel and parallel — and the conrotatory cyclization can proceed only from the anti-parallel conformation; the parallel conformer cannot undergo photocyclization. Upon irradiation with ultraviolet light, the open-ring anti-parallel conformer converts to the closed-ring isomer and changes the color. While the open-ring isomer does not absorb in the visible region, the closed-ring isomer does. Upon irradiation with visible light the colored closed-ring isomer returns to the initial colorless open-ring isomer.



Scheme 1

Compounds bearing fluorine atoms have unique characteristics since the fluorine atom has a strong inductive elec-

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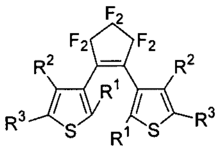
tron-withdrawing property.[6] Saturated fluorocarbons exhibit a high degree of thermal stability[7] and inertness to oxidation and reduction.[7b,8,9] The physical properties of saturated fluorocarbons are also unusual. For example, the boiling points of fluorocarbons are lower than those of hydrocarbons with a similar molecular weight.[10] Additionally, some of them have physiological effects. For example, 5-fluorouracil is widely used as an anticancer drug and fluoroquinolone acts as an antibacterial agent.[11]

In this paper, we have prepared bis(3-thienyl)perfluorocyclopentene **1**−**3**, containing fluorine atoms at the 2-, 4-, and 5-positions, respectively, of the thiophene rings, and examined their photochromic performance. Dithienylethenes containing chlorine- or methyl-substituted thiophene rings were also prepared as reference compounds. The photochromic performances of compounds **1**−**3** were compared with the chlorine-substituted ones (**4**−**6**), the methyl-substituted ones (**7**−**9**), and a single unsubstituted one (**10**).

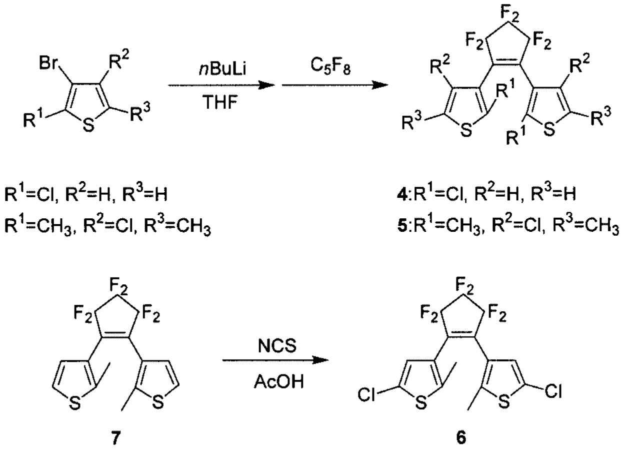


1: R^1 = F, R^2 = R^3 = H
2: R^1 = CH_3, R^2 = F, R^3 = CH_3
3: R^1 = CH_3, R^2 = H, R^3 = F
4: R^1 = Cl, R^2 = R^3 = H
5: R^1 = CH_3, R^2 = Cl, R^3 = CH_3
6: R^1 = CH_3, R^2 = H, R^3 = Cl
7: R^1 = CH_3, R^2 = R^3 = H
8: R^1 = R^2 = R^3 = CH_3
9: R^1 = CH_3, R^2 = H, R^3 = CH_3
10: R^1 = R^2 = R^3 = H

Results and Discussion

Synthesis

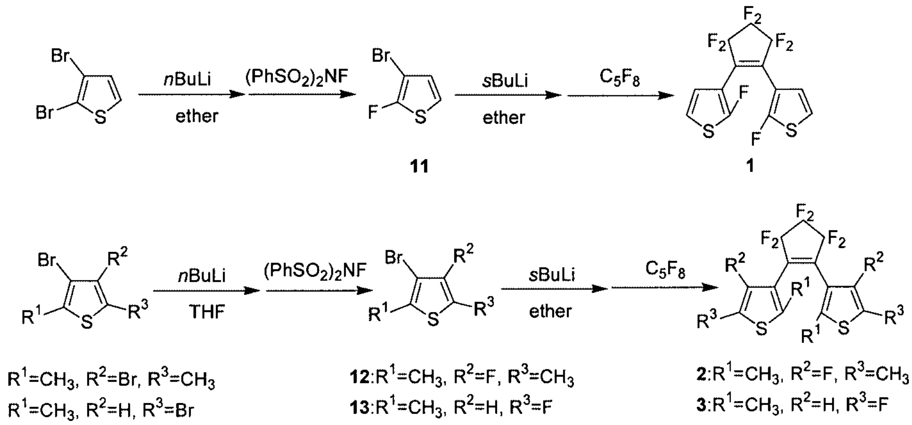
The syntheses of compounds **1**−**10** were carried out as detailed below. Compounds **6**,[12] **7**,[13] **8**,[14] **9**,[15] and **10**[16] are known compounds. Bromofluorothiophenes **11**−**13** were obtained by adding $(PhSO_2)_2NF$ to lithiated dibromothiophenes.[17] The coupling of perfluorocyclopentene with lithiated bromofluorothiophenes **11**−**13** gave diarylethenes containing fluorine atoms (Scheme 2). At first, we tried the synthesis of these fluorinated derivatives using *n*BuLi, but the results were very poor, so we used *s*BuLi instead. This may be because the fluorine substituent reduces the reactivity of the thiophene carbanion. The diarylethenes were purified by column chromatography and recrystallized from hexane solutions. Diarylethenes having chlorine atoms at the 2- and 4-positions (**4** and **5**, respectively) were synthesized by the coupling of perfluorocyclopentene with the corresponding lithiated bromochlorothiophenes. Chlorination at the 5-positions of 1,2-bis(2-methyl-3-thienyl)hexafluorocyclopentene (**7**) gave the 5-chlorinated diarylethene **6** (Scheme 3). All compounds were characterized by EI mass spectrometry, FAB-HR mass spectrometry, ^1H NMR spectroscopy, and elemental analysis.



Scheme 3

X-ray Crystallographic Analysis

Colorless crystals were obtained from appropriate solutions of the open-ring isomers of the compounds **1**−**6**. X-ray crystallographic analysis was carried out for all six com-



Scheme 2

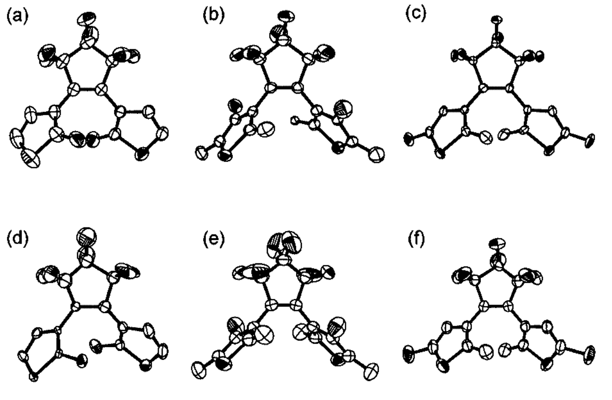


Figure 1. ORTEP drawings showing 50% probability displacement ellipsoids: (a) **1**, (b) **2**, (c) **3**, (d) **4**, (e) **5**, and (f) **6**; the perfluorocyclopentene moieties of **3**, **4**, and **6** and the thiophene moiety of **2** and **4** were disordered, therefore only one part of the disordered moiety is shown

pounds. Figure 1 shows the ORTEP drawings of the molecular structures.

Compounds **2** and **4** show disordered structures that include both anti-parallel and parallel conformations.[18] Only the anti-parallel conformers are discussed in the following studies. As can be seen from Figure 1, compounds **1**−**6** have different torsion angles between the two thiophene rings and the perfluorocyclopentene moiety, therefore the distances between the reactive carbons are different depending on the substitution positions. In the cases of diarylethenes substituted at the 2- or 4-positions, the distances between the reactive carbons depends on the size of the substituents at these positions: a larger substituent at the 2-position makes the two thiophene rings repel each other. The substituent at the 4-position is in close proximity to the fluorine atom of the perfluorocyclopentene ring, so this substituent causes the perfluorocyclopentene and the thiophene rings to be twisted. In the cases of diarylethenes substituted at the 5-positions the size of the substituent does not affect the distance.

Photochromic Reactions

Figure 2 shows the photoinduced spectral changes of compounds **1**−**3** in hexane. Upon irradiation with 313 nm light, the colorless solutions of the open-ring isomers **1**, **2**, and **3** turned violet, red, and yellow, respectively, with visible absorption bands at 539, 530, and 464 nm, respectively. This color is due to the closed-ring isomers **1c**−**3c** (**c** denotes the closed-ring isomer). Figure 2 also shows the spectra of the isolated closed-ring isomers **1c**−**3c**. The conversions from the open- to the closed-ring isomers were determined by comparing the absorbance of the isolated closed-ring isomer and the absorbance in the photostationary state. The conversion in the photostationary state under irradiation with 313 nm light was 42, 38, and 40% for **1**, **2**, and **3**, respectively. The color completely disappeared upon irradiation with visible light (>400 nm). The photochromic

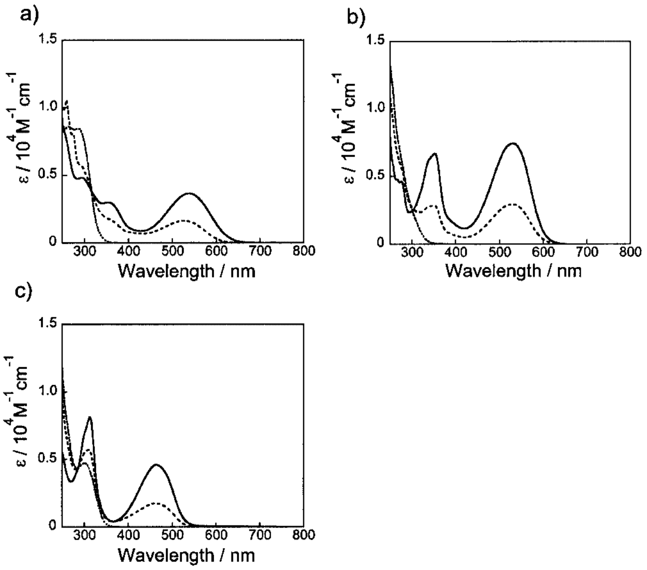


Figure 2. Absorption spectra of **1** (a), **2** (b), and **3** (c); (···) the open-ring isomer; (---) the closed-ring isomer; (—) in the photostationary state under irradiation with 313-nm light

Table 1. Physical properties of diarylethenes

Compound	λ_{max}[a] [nm]	ε[a] [10^3 $M^{-1}\cdot cm^{-1}$]	Calcd. λ_{max}[b] [nm]	Oscillator strength[b] (calcd.)	$\Phi_{O\text{-}C}$[c]	$\Phi_{C\text{-}O}$[c]	k[d] [min^{-1}]	Distance between reactive C atoms[e] [Å]
1	539	3.6	586	0.0734	0.30	0.0029	1.2×10^{-4}	3.23
2	530	7.4	528	0.1575	0.29	0.15	7.5×10^{-7}	4.30
3	464	4.6	477	0.1273	0.28	0.37	1.7×10^{-4}	3.54
4	–	–	646	0.0596	–	–	–	3.68
5	528	4.3	524	0.1527	0.16	0.22	stable	4.82
6	502	8.1	506	0.1652	0.47	0.13	stable	3.60
7	509	5.7	514	0.1037	0.50	0.27	stable	3.58
8	525	6.8	530	0.1423	0.02	0.096	stable	5.16[f]
9	503	8.0	509	0.1513	0.40[g]	0.12[g]	stable	3.57[h]
10	469	–	475	0.1455	–	–	2.4×10^{-3}	3.18

[a] Absorption maximum of the closed-ring isomer measured in hexane solution. [b] Calculated for the closed-ring isomer. [c] Quantum yield of cyclization ($\Phi_{O\text{-}C}$) and cycloreversion ($\Phi_{C\text{-}O}$) reactions. [d] Thermal stability of the closed-ring isomer measured at room temperature in hexane solution. [e] Obtained from the X-ray crystal structure. [f] Taken from ref.[13] [g] Taken from ref.[22] [h] Taken from ref.[14]

behavior of the other diarylethenes was similar, except for compound **4**, which did not show any photochromic reaction and decomposed upon excessive irradiation with UV light.

The absorption maxima and the molar-absorption coefficients of fluorinated (**1c**–**3c**), chlorinated (**4c**–**6c**), methyl-substituted (**7c**–**9c**), and unsubstituted (**10c**) closed-ring isomers are summarized in Table 1. The absorption maximum of the closed-ring isomer **1c** (539 nm), in which the 2-position is substituted by a fluorine atom, is at a longer wavelength than those of hydrogen-substituted **10c** (469 nm) or the methyl-substituted analogue **7c** (509 nm). This substituent effect of the fluorine atom is opposite to the effect observed for normal electron-withdrawing substituents.[19] This is due to the contribution of the lone pairs of the fluorine atom. A conjugative electron-donating effect is dominant for this absorption spectral change.

The closed-ring isomer with fluorine substituted at the 4-position, **2c** (530 nm), shows a bathochromic spectral shift with respect to hydrogen-substituted **9c** (503 nm) and methyl-substituted **8c** (525 nm). Chlorine-substituted **5c** shows a similar absorption band at 528 nm. On the other hand, when substituted at the 5-position by fluorine atoms, the absorption maximum of the closed-ring isomer, **3c** (464 nm), shows a hypsochromic shift with respect to hydrogen-substituted **7c** (509 nm) and methyl-substituted **9c** (503 nm).

The substituents also alter the cyclization quantum yields. One of the factors which determines the cyclization quantum yield is the distance between the reactive carbons. Although the thiophene rings can freely rotate about the single bond in solution, the distance in the crystal structure should reflect the equilibrium conformation in solution. In the case of a series of diarylethenes substituted at the 4-positions (**2**, **5**, **8** and **9**), the distance between the reactive carbons of the open-ring isomers depends on the substituents: the quantum yield of the cyclization reaction becomes larger as the distance between the reactive carbons becomes shorter.[20]

The cycloreversion quantum yield is also dependent on the substituents. A very low quantum yield was observed for 2-fluorine-substituted compound **1c**, whereas the value for compound **3c**, which has fluorine atoms at the 5-position, is larger than for the others. The difference between the values for **1c** and **3c** is as large as 130-fold. In the case of compound **2c**, which has fluorine atoms at the 4-positions, the yield is similar to the other compounds. The cycloreversion quantum yield is known to depend on the potential energy surface in the excited states,[19] and substitution at the 2- and 5-positions is considered to influence the excited energy surfaces.

Diarylethenes having thiophene and/or benzothiophene rings as the aryl groups are known to exhibit excellent thermal stability of the closed-ring isomers.[4] This is due to the small aromatic stabilization energy of the thiophene ring.[21] When fluorinated thiophene rings are used as the aryl groups, the diarylethenes **1**–**3** undergo thermally reversible photochromic reactions. This suggests that the energy surfaces in the ground state are influenced by the fluorine substitution.

Theoretical Calculations

The absorption spectra of the closed-ring isomers **1c**–**10c** were well reproduced by time-dependent density-functional theory (TD-DFT) calculations with the B3LYP functional and the 6-31G basis set,[23] as shown in Table 1.[24,25] These results suggest that it is possible to discuss the relationship between the substituents and the absorption spectra based on the theoretical calculations.

When the substitution position is the 4- and 5-position of the thiophene ring, the effect is well interpreted by the theoretical calculations, as the relative sizes of the lobes of the π-electrons influence the absorption maxima of the closed-ring isomers. Diarylethene **7c** was used as a model to see the shape of the HOMO and LUMO of the closed-ring isomer.[26] The sizes and signs of the lobes are illustrated in Figure 3. At the 5-position the LUMO has a larger lobe than the HOMO, whereas at the 4-position the HOMO has a larger lobe than the LUMO. Therefore, substitution at the 5- and 5′-positions with electron-donating groups and/or at the 4- and 4′-positions with electron-withdrawing groups gives rise to stabilization of the HOMO and destabilization of the LUMO. Thus, the energy gap between the HOMO and LUMO becomes larger and the absorption maximum shifts to shorter wavelengths. When the 5- and 5′-positions are substituted with electron-withdrawing groups and/or the 4- and 4′-positions are substituted with electron-donating groups, the energy gap becomes smaller and the absorption maximum shifts to longer wavelength.

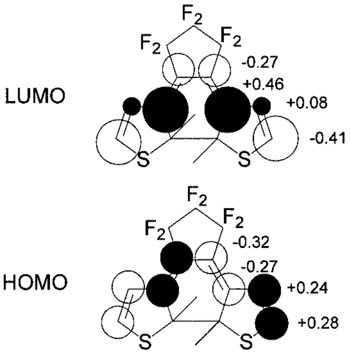


Figure 3. Orbital shapes of the HOMO and LUMO of the closed-ring isomer **7c**; the sizes and colors of the circles show the π-electron density and the signs of the lobes

Judging from the spectral shift, fluorine or chlorine substituents appear to serve as electron-donating groups. In order to determine the effect of a trifluoromethyl group, 1,2-bis(2,5-dimethyl-4-trifluoromethyl-3-thienyl)hexafluorocyclopentene (**14**) and 1,2-bis(2-methyl-5-trifluoromethyl-3-thienyl)hexafluorocyclopentene (**15**) were calculated by the same method. The calculation shows a blue-shift for the 4-trifluoromethyl-substituted closed-ring isomer **14c** (495 nm) compared with hydrogen-substituted **9**. A red-shift was observed for the 5-trifluoromethyl-substituted closed-ring isomer **15c** (545 nm) with respect to hydrogen-substituted **7**. In this case the trifluoromethyl group serves as an electron-withdrawing group. When halogen atoms are directly connected to the π-system, the unshared electrons can be delocalized into the π-conjugation system; the resonance effect of the halogen atoms contributes to the spectral shift.

Conclusions

The photochromic reactivity of bis(3-thienyl)perfluorocyclopentenes having fluorine atoms at the thiophene rings has been studied. The absorption maxima of the closed-ring isomers, the quantum yields of the photochromic reactions, and the thermal stability are dependent on the substituted groups and their positions. The absorption maximum changes by as much as 72 nm depending on the substitution position. The cyclization quantum yields are scarcely affected by the fluorination, while the cycloreversion quantum yields change dramatically with the substitution. The cycloreversion quantum yield of **1c** is about 130 times smaller than that of **3c**. Dithienylethenes with a fluorine substituent at the 2- or 5-positions of the thiophene ring (**1** or **3**) undergo a thermally reversible photochromic reaction. These results show that photochemical properties are dependent on both the kind and the position of the substituents.

Experimental Section

Photochemical Reaction: Hexane of spectroscopic grade was distilled before use. Absorption spectra of solutions were measured with a Hitachi U-3500 absorption spectrophotometer. Photoirradiation was carried out using a USHIO USH-500D 500 W high-pressure mercury lamp as the light source. Monochromatic light was obtained by passing the light through a Ritsu MC-20 L monochromator. Quantum yields for cyclization and cycloreversion reactions were determined by the methods described previously.[27] Hexane solutions of 1,2-bis(3,5-dimethyl-2-thienyl)perfluorocyclopentene[28] and 1,2-bis(2-methylbenzothiophene-3-yl)perfluorocyclopentene[29] were used as the references.

X-ray Crystallography: Data collection was performed with a Bruker SMART1000 CCD-based diffractometer (60 kV, 30 mA) with Mo-K_α radiation. Crystals of **2**, **3**, and **4** were cooled with a cryostat (RIGAKU GN2). The data were collected as a series of ω-scan frames, each with a width of 0.3°/frame. The crystal-to-detector distance was 5.118 cm. Crystal decay was monitored by repeating the 50 initial frames at the end of data collection and analyzing the duplicate reflections. Data reduction was performed using SAINT software,[30] which corrects for Lorentz and polarization effects, and decay. The cell constants were calculated by global refinement. The structure solved by direct methods using SHELXS-86 and refined by full least-squares on F^2 using SHELXL-97.[31] The positions of all hydrogen atoms were calculated geometrically and refined with a riding model. A disordered part with small occupancy was refined isotropically and the bond lengths and geometry were restrained in the refinement. A summary of the data collection and refinement parameters can be found in Table 2. CCDC-242212 to -242217 (**1−6**, respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Computational Methods: Preliminary calculations of molecular geometry optimization were done with the MM2 method. The absorption maxima and oscillator strengths were computed at the TD-DFT level with the B3LYP functional and the 6-31G basis set. The calculations were performed with the Gaussian 98 program package.[25]

Preparation of the Materials: ^{1}H NMR spectra were recorded with a Varian Gemini 200 spectrometer (200 MHz). Tetramethylsilane (TMS) was used as the internal standard. Mass spectra were measured with a Shimadzu GCMS-OP5050A (EI) or a JEOL JMS-GCmateII (FAB) mass spectrometer. The melting points were

Table 2. Crystallographic parameters for diarylethenes **1−6**

	1	**2**	**3**	**4**	**5**	**6**
Empirical formula	$C_{13}H_4F_8S_2$	$C_{17}H_{12}F_8S_2$	$C_{15}H_8F_8S_2$	$C_{13}H_4F_6S_2Cl_2$	$C_{17}H_{12}F_6S_2Cl_2$	$C_{15}H_8F_6S_2Cl_2$
Formula mass	376.28	432.39	404.33	409.18	465.29	437.23
Crystal color	colorless	colorless	colorless	colorless	colorless	colorless
Solvent	hexane	hexane	hexane	chloroform	hexane	hexane
Crystal system	monoclinic	triclinic	monoclinic	triclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$C2/c$	$C2/c$
a [Å]	15.509(4)	7.5685(15)	16.177(5)	7.348(4)	21.377(17)	19.947(6)
b [Å]	5.3688(13)	9.3401(18)	8.682(3)	9.987(5)	7.569(6)	8.805(3)
c [Å]	16.912(4)	12.977(3)	11.168(3)	10.985(6)	13.829(11)	11.709(4)
α [°]	90	90.004(3)	90	91.190(8)	90	90
β [°]	105.700(4)	94.005(3)	91.516(6)	102.104(8)	122.570(11)	122.695(4)
γ [°]	90	103.381(3)	90	107.000(8)	90	90
V [Å^3]	1355.6(6)	890.1(3)	1568.0(8)	750.8(7)	1886(3)	1730.7(9)
Z	4	2	4	2	4	4
T [K]	293	113	123	123	298	298
Data/constraints/parameters	2717/0/208	3540/0/242	3365/0/280	3008/17/252	1934/0/125	1818/0/146
R_1 [$I > 2\sigma(I)$]	0.0497	0.0790	0.0542	0.0829	0.0687	0.0539
wR_2 (all data)	0.1561	0.2333	0.1642	0.2371	0.2344	0.2057

measured with a Laboratory Devices MEL-TEMP II and are not corrected. Compounds **7**,[13] **8**,[14] **9**,[15] and **10**[16] were prepared by the methods described before. Elemental analyses were performed by the Microanalytical Laboratory at the Department of Chemistry, Faculty of Science, Kyushu University. Closed-ring isomers were isolated by passing the solution containing open- and closed-ring isomers through an HPLC (HITACHI L-7100 pump and an L-7400 UV detector). Silica-gel columns (Mightysil Si 60, Kanto, for normal phase or Mightysil RP-18, Kanto, for reversed phase) were used.

1,2-Bis(2-fluoro-3-thienyl)perfluorocyclopentene (1): *n*BuLi (1.6 M in hexane, 55 mL, 88 mmol) was added dropwise at a temperature below −60 °C to a solution of 2,3-dibromothiophene (20 g, 83 mmol) in dry diethyl ether (350 mL) under Ar. After stirring the mixture for 1 h, *N*-fluorobenzenesulfonimide (28 g, 88 mmol) in THF (125 mL) was added dropwise. The reaction mixture was allowed to warm to room temperature. Aqueous NH_4Cl was added to the reaction mixture and it was then extracted with Et_2O, washed with water, dried with $MgSO_4$, and concentrated. Column chromatography (silica, hexane) gave 3-bromo-2-fluorothiophene (**11**; 3.1 g, 21%). ^1H NMR ($CDCl_3$): δ = 6.70 (d, J = 1 Hz, 1 H), 6.72 (d, J = 1 Hz, 1 H) ppm. EI-MS: *m/z* = 180 [M^+], 182. *s*BuLi (0.96 M in hexane, 10 mL, 9.6 mmol) was added dropwise at a temperature below −95 °C to a solution of 3-bromo-2-fluorothiophene (**11**; 1.5 mg, 8.2 mmol) in dry diethyl ether (15 mL) under Ar. After stirring the mixture for 1 h, perfluorocyclopentene (0.54 mL, 4.1 mmol) was added in one portion. The reaction mixture was allowed to warm to room temperature. Aqueous NH_4Cl was added to the reaction mixture and it was then extracted with Et_2O, washed with water, dried with $MgSO_4$, and concentrated. Column chromatography (silica, hexane) gave 2-fluorodithienylethene **1** (152 mg, 5%). M.p. 54−55 °C. ^1H NMR ($CDCl_3$): δ = 6.68−6.83 (m, 4 H) ppm. UV/Vis (hexane): λ_{max} (ε) (open-ring isomer) = 286 (8400), 262 (8600) nm; λ_{max} (ε) (closed-ring isomer, separated by reversed-phase chromatography with acetonitrile) = 539 (3600), 353 (3000), 295 (4800) nm. FAB HRMS: calcd. for $C_{13}H_4F_8S_2$ [M^+] 375.9627; found 375.9641.

1,2-Bis(4-fluoro-2,5-dimethyl-3-thienyl)perfluorocyclopentene (2): *n*BuLi (1.6 M in hexane, 21 mL, 34 mmol) was added dropwise at a temperature below −60 °C to a solution of 3,4-dibromo-2,5-dimethylthiophene (8.6 g, 32 mmol) in THF (200 mL) under Ar. The mixture was stirred for 1 h. $(PhSO_2)_2NF$ (11 g, 34 mmol) in THF (50 mL) was added dropwise, and the resulting mixture was stirred at −65 °C for 1 h. Aqueous NH_4Cl was added to the reaction mixture and it was then extracted with Et_2O, washed with water, dried with $MgSO_4$, and concentrated. Column chromatography (silica, hexane) gave 3-bromo-4-fluoro-2,5-dimethylthiophene (**12**; 3.7 g, 55%): ^1H NMR ($CDCl_3$): δ = 2.30 (s, 3 H), 2.40 (s, 3 H) ppm. EI-MS: *m/z* = 208 $[M]^+$, 210. *s*BuLi (0.96 M in hexane, 10 mL, 9.6 mmol) was added dropwise at a temperature below −95 °C to a solution of 3-bromo-4-fluoro-2,5-dimethylthiophene (**12**; 1.7 g, 8.2 mmol) in dry diethyl ether (15 mL) under Ar. After stirring the mixture for 1 h, perfluorocyclopentene (0.54 mL, 4.1 mmol) was added in one portion. The reaction mixture was allowed to warm to room temperature. Aqueous NH_4Cl was added to the reaction mixture and it was then extracted with Et_2O, washed with water, dried with $MgSO_4$, and concentrated. Column chromatography (silica, hexane) gave 4-fluorodithienylethene **2** (192 mg, 5%). M.p. 150−151 °C. ^1H NMR ($CDCl_3$): δ = 2.13 (s, 6 H), 2.23 (s, 6 H). UV/Vis (hexane): λ_{max} (ε) (open-ring isomer) = no peaks (ε = 13000 at 250 nm); λ_{max} (ε) (closed-ring isomer, separated by normal-phase chromatography with hexane) = 530 (7400), 352 (6700), 276 (sh) nm. FAB HRMS: calcd. for $C_{17}H_{12}F_8S_2$ [M^+] 432.0253; found 432.0259.

1,2-Bis(5-fluoro-2-methyl-3-thienyl)perfluorocyclopentene (3): *n*BuLi (1.6 M in hexane, 53 mL) was added dropwise at a temperature below −60 °C to a solution of 2,4-dibromo-5-methylthiophene (20 g, 80 mmol) in THF (340 mL) under Ar. The mixture was stirred for 1 h. $(PhSO_2)_2NF$ (27 g, 84 mmol) in THF (125 mL) was added dropwise, and the resulting mixture was stirred at −65 °C for 1 h. Aqueous NH_4Cl was added to the reaction mixture and it was then extracted with Et_2O, washed with water, dried with $MgSO_4$, and concentrated. Column chromatography (silica, hexane) gave 3-bromo-5-fluoro-2-methylthiophene (**13**; 9.5 g, 61%). ^1H NMR ($CDCl_3$): δ = 2.28 (d, J = 3 Hz, 3 H), 6.31 (d, J = 1 Hz, 1 H) ppm. EI-MS: *m/z* = 194 [M^+], 196. *s*BuLi (0.96 M in hexane, 10 mL) was added dropwise at a temperature below −95 °C to a solution of 3-bromo-5-fluoro-2-methylthiophene (**13**; 1.6 g, 8.2 mmol) in dry diethyl ether (15 mL) under Ar. After stirring the mixture for 1 h, perfluorocyclopentene (0.54 mL, 4.1 mmol) was added in one portion. The reaction mixture was allowed to warm to room temperature. Aqueous NH_4Cl was added to the reaction mixture and it was then extracted with Et_2O, washed with water, dried with $MgSO_4$, and concentrated. Column chromatography (silica, hexane) gave 5-fluorodithienylethene **3** (530 mg, 16%). M.p. 83−84 °C. ^1H NMR ($CDCl_3$): δ = 1.87 (d, J = 3 Hz, 6 H), 6.46 (d, J = 2 Hz, 2 H) ppm. UV/Vis (hexane): λ_{max} (ε) (open-ring isomer) = 301 (4700) nm; λ_{max} (ε) (closed-ring isomer, separated by normal-phase chromatography with hexane/ethyl acetate, 95:5) = 464 (4600), 313 (8200) nm. FAB HRMS: calcd. for $C_{15}H_8F_8S_2$ [M^+]: 403.9940; found 403.9925.

1,2-Bis(2-chloro-3-thienyl)perfluorocyclopentene (4): *n*BuLi (1.6 M in hexane, 3.6 mL, 5.7 mmol) was added dropwise at a temperature below −60 °C to a solution of 3-bromo-2-chlorothiophene (905 mg, 5 mmol) in dry THF (45 mL) under Ar. Perfluorocyclopentene (1.6 mL, 2.5 mmol) was then added in one portion. The reaction mixture was allowed to warm to room temperature. Aqueous NH_4Cl was added to the reaction mixture and it was then extracted with Et_2O, washed with water, dried with $MgSO_4$, and concentrated. Column chromatography (silica, hexane) gave 2-chlorodithienylethene **4** (0.55 g, 27%). M.p. 49−50 °C. ^1H NMR ($CDCl_3$): δ = 7.09 (d, J = 6 Hz, 2 H), 7.22 (d, J = 6 Hz, 2 H) ppm. UV/Vis (hexane): λ_{max} (ε) (open-ring isomer) 312 (sh) nm. FAB HRMS: calcd. for $C_{13}H_4Cl_2F_6S_2$ [M^+] 407.9036; found 407.9057.

1,2-Bis(4-chloro-2,5-dimethyl-3-thienyl)perfluorocyclopentene (5): *n*BuLi (1.6 M in hexane, 6.8 mL) was added dropwise at a temperature below −95 °C to a solution of 3-bromo-4-chloro-2,5-dimethylthiophene (2.3 g, 10 mmol) in dry THF (15 mL) under Ar. After stirring the mixture for 1 h, perfluorocyclopentene (0.66 mL, 5.0 mmol) was added in one portion. The reaction mixture was allowed to warm to room temperature. Aqueous NH_4Cl was added to the reaction mixture and it was then extracted with Et_2O, washed with water, dried with $MgSO_4$, and concentrated. Column chromatography (silica, hexane) gave 4-chlorodithienylethene **5** (2.8 g, 60%). M.p. 165−166 °C. ^1H NMR (200 MHz, $CDCl_3$): δ = 2.29 (s, 2.3 H), 2.39 (s, 3.7 H) ppm. EI-MS: *m/z* = 464 [M^+]. UV/Vis (hexane): λ_{max} (ε) (open-ring isomer) = no peaks (ε = 12000 at 250 nm); λ_{max} (ε) (closed-ring isomer, separated by normal-phase chromatography with hexane) = 528 (4300), 357 (5000) nm. $C_{17}H_{12}Cl_2F_6S_2$ (465.30): calcd. C 43.88, H 2.60; found C 43.85, H 2.60.

1,2-Bis(5-chloro-2-methyl-3-thienyl)perfluorocyclopentene (6): NCS (0.11 g, 0.82 mmol) was added at 0 °C to a solution of 1,2-bis(2-

methyl-3-thienyl)perfluorocyclopentene (0.15 g, 0.41 mmol) in AcOH (2.0 mL). The mixture was stirred for 1 h and then aqueous NH$_4$Cl was added to the reaction mixture, which was extracted with Et$_2$O, washed with water, dried with MgSO$_4$, and concentrated. Column chromatography (silica, hexane) gave 5-chlorodithienylethene **6** (0.90 g, 50%). M.p. 138−139 °C (ref.[12] 132 °C). ^{1}H NMR (200 MHz, CDCl$_3$): δ = 1.89 (s, 3 H), 6.88 (s, 1 H) ppm. UV/Vis (hexane): λ_{max} (ε) (open-ring isomer) 302 (4500) nm; λ_{max} (ε) (closed-ring isomer, separated by normal phase with hexane) = 502 (8000), 339 (9500), 258 (10000) nm. FAB HRMS: calcd. for $C_{15}H_8Cl_2F_6S_2$ [M$^+$] 435.9349; found 435.9329.

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