# Photoswitching of Intramolecular Magnetic Interaction Using Diarylethene with Oligothiophene $\pi$-Conjugated Chain

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Diarylethenes having two nitronyl nitroxide radicals at both ends of the molecule with oligothiophene spacers were synthesized. The diradicals underwent photochromic reactions upon alternate irradiation with UV and visible light. ESR spectra of the diradicals reversibly changed with the photochromism. The magnetic interaction between spins through oligothiophene spacers was stronger than that through oligophenylene spacers, and the photochromic reactivity of the diradical diarylethenes with oligothiophene spacers was much reduced. The difference of the exchange interaction between open- and closed-ring form isomers was estimated to be more than 150-fold.

## Introduction

Photochromic molecules are now considered as effective building blocks for the nanoscale molecular photoswitching devices.[1] Among them, diarylethenes are the most promising candidates because of their fatigue resistance and thermal stability.[2] The two isomers of the diarylethenes are substantially different in electronic and geometrical structures. The most notable difference is that the $\pi$-system of the two aryl rings are separated in the open-ring form isomer, while the $\pi$-system is delocalized throughout the molecule in the closed-ring form isomer. When two unpaired electrons are placed at both ends of the $\pi$-conjugated chain, two spins interact magnetically.[3] Therefore, such a photochromic compound can serve as a switching unit for magnetic interactions.[4] On the basis of this concept, we have developed photoswitchable magnetic molecular devices using diarylethene photochromic spin couplers (Figure 1).[5] So far, it has been shown that the exchange interaction can be controlled as much as 30 times by photoirradiation.

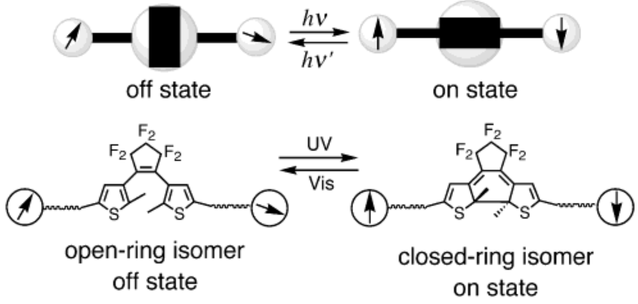

**Figure 1.** Photoswitching of magnetic interaction.

Oligothiophenes are the candidates for conductive molecular wires.[6] Thiophene-2,5-diyl group is known as a good molecular wire unit for energy and electron transfer and serve as a strong magnetic coupler than *p*-phenylene.[7] In this paper, we have synthesized diarylethenes having two nitronyl nitroxide radicals at both ends of the molecule with oligothiophene spacers and studied their photophysical and magnetochemical properties.

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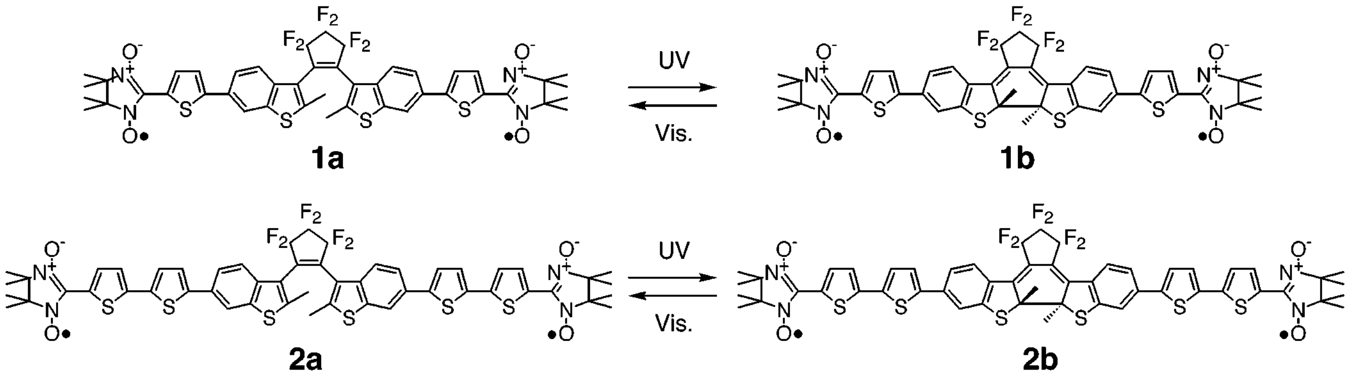
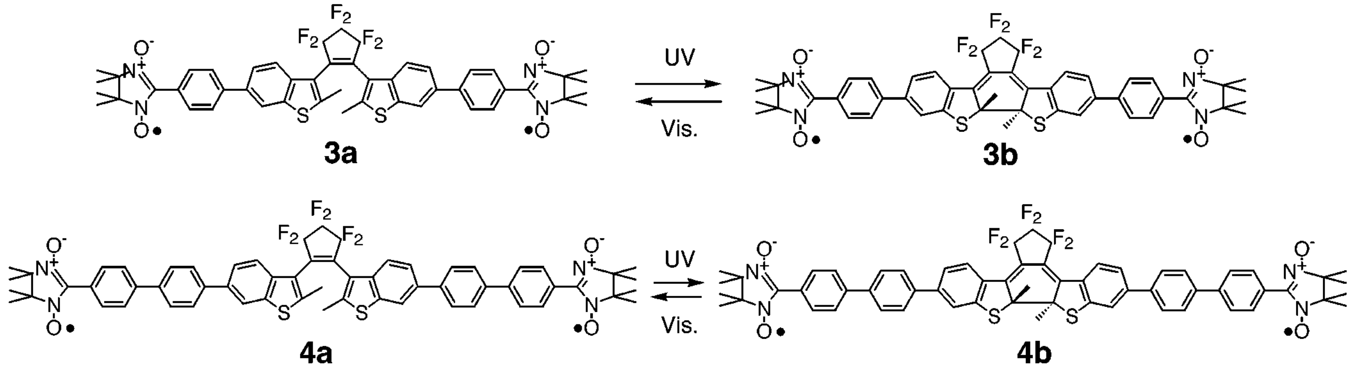
10.1021/jo010597g CCC: $20.00

**Scheme 1. Photochromic Diarylethenes Having Two Nitronyl Nitroxides with Oligothiophene Spacers**



**Scheme 2. Photochromic Diarylethenes Having Two Nitronyl Nitroxides with Oligophenylene Spacers**



## Results and Discussion

**Molecular Design and Synthesis.** 1,2-Bis(2-methyl-1-benzothiophen-3-yl)perfluorocyclopentene was chosen for the photochromic core because of its fatigue resistance. Two nitronyl nitroxide radicals were placed at both ends of the molecule. The photochromic core and the radical moiety were connected by one (**1a**) or two (**2a**) thiophene molecules, as shown in Scheme 1.

For the detection of switching of magnetic interaction, ESR spectroscopy was employed. When the exchange interaction is much smaller than the hyperfine coupling constant ($2J/k_B < 3 \times 10^{-4}$ K), the spectrum is five lines. In the case that the exchange interaction is much larger than the hyperfine coupling constant ($2J/k_B > 0.04$ K), the spectrum is nine lines. A complicated spectrum is expected in the intermediate case. For such cases, the exchange interaction can be estimated by simulation. The magnetic interaction changes of **1** and **2** were compared with those of **3** and **4**, which we have previously examined (Scheme 2).[5f]

The synthesis of **1a** and **2a** was performed according to Scheme 3. Diiodo compound **5** was used as a common starting material. Suzuki coupling of **5** with 2-formylthiophene-5-boronic acid afforded diformyl compound **6** in 50% yield. Transformation of **5** to diboronic acid followed by Suzuki coupling with 5-iodo-5′-formyl-2,2′-bithiophene gave diformyl compound **7** in 48% yield. The palladium-catalyzed coupling reaction, which is often used in the synthesis of oligothiophenes, could be employed in a similar way. Diformyl compounds were transformed to bis(nitronyl nitroxide) in 2−4% yield. These compounds were characterized by mass, UV, and ESR spectroscopy.

**Photochromic Reactions.** Both **1a** and **2a** underwent photochromic reactions by alternate irradiation with UV and visible light. The yellowish green solution of the open-ring form isomer **1a** and **2a** turned blue by irradiation with 366 nm light with retention of the isosbestic point at 384 and 428 nm. This is due to the formation of the closed-ring form isomers **1b** and **2b**. This blue color was bleached by irradiation with 578 nm light. Figure 2 shows the absorption spectra of the open-ring form isomers, the closed-ring form isomers, and in the photostationary state under irradiation with 366 nm light. Absorption maxima and coefficients of the closed-ring form isomer are summarized in Table 1. The absorption maxima of the closed-ring form isomers with oligothiophene spacers showed bathochromic shift with the increase in the $\pi$-conjugated chain length. On the contrary, in the case of the closed-ring form isomers with oligophenylene spacers, the absorption maxima showed hypsochromic shift with the increase in the $\pi$-conjugated chain length.[5f] The difference is due to strong $\pi$-conjugation owing to high planarity in the oligothiophene spacers.[8]

**Quantum Yield Measurements.** The quantum yields of both cyclization and cycloreversion reactions were measured in ethyl acetate using 1,2-bis(2-methyl-1-benzothiophen-3-yl)perfluorocyclopentene as a reference.[9] The results are summarized in Table 2.

The quantum yields of both cyclization and cycloreversion reactions of the diarylethenes with thiophene spacers were much smaller than those with *p*-phenylene spacers. Especially the cyclization quantum yield of **1** was about 70 times smaller than **3**. This large effect is attributable to the planarity between benzothiophene-oligothiophene-nitronyl nitroxide moieties.

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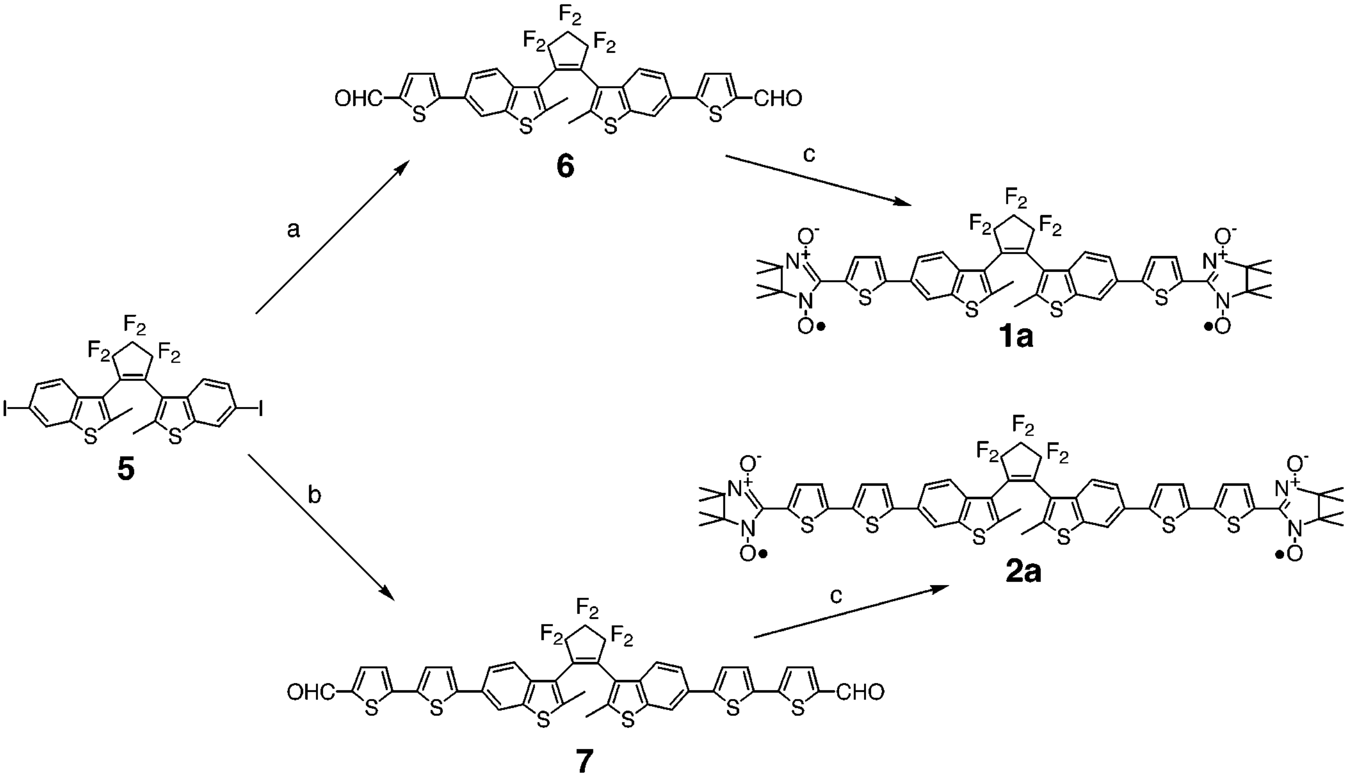
**Scheme 3**[a]



[a] Reagents and conditions: (a) $Pd(PPh_3)_4$, 2-formylthiophene-5-boronic acid, $Na_2CO_3$, THF, $H_2O$, 50%; (b) *n*-BuLi, $B(OBu)_3$, and then $Pd(PPh_3)_4$, 5-iodo-5′-formyl-2,2′-bithiophene, $Na_2CO_3$, THF, $H_2O$, 48%; (c) 2,3-dimethyl-2,3-bis(hydroxyamino)butane sulfate, methanol and then $NaIO_4$, $CH_2Cl_2$, 2−4%.

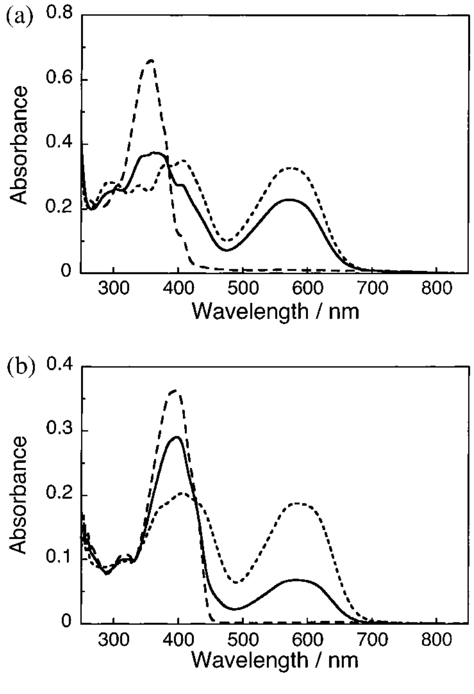


**Figure 2.** (a) Absorption spectra of **1a** ($9.1 \times 10^{-6}$ M ethyl acetate solution): open-ring form isomer (dashed line), closed-ring form isomer (dotted line), and in the photostationary state under irradiation with 366 nm light (solid line). (b) Absorption spectra of **2a** ($4.7 \times 10^{-6}$ M ethyl acetate solution): open-ring form isomer (dashed line), closed-ring form isomer (dotted line), and in the photostationary state under irradiation with 366 nm light (solid line).

**Table 1. Absorption Maxima and Coefficients of the Closed-ring Form Isomers**

| | $\lambda_{max}$ ($\epsilon$) |
|---|---|
| **1b** | 407 (38 000), 574 (36 000) |
| **2b** | 407 (40 000), 583 (37 000) |
| **3b**[a] | 280 (43 000), 367 (44 000), 553 (26 000) |
| **4b**[a] | 311 (58 000), 374 (58 000), 548 (28 000) |

[a] Reference 5f.

**Table 2. Quantum Yields of Cyclization and Cycloreversion Reactions in Ethyl Acetate**

| | cyclization | cycloreversion |
|---|---|---|
| **1** | 0.0015 | 0.0009 |
| **2** | 0.0054 | 0.0087 |
| **3**[a] | 0.10 | 0.012 |
| **4**[a] | 0.13 | 0.062 |

[a] Reference 5f.

The high planarity assists an effective energy transfer from the diarylethene moiety to the nitronyl nitroxide moiety resulting in the small cyclization quantum yield.

The conversions at the photostationary state of **1** (71%) and **2** (38%) were smaller than those of **3** (100%) and **4** (99%). The low conversions are due to the suppression of the cyclization quantum yields. The slight modification of the spacer from *p*-phenylene to thiophene-2,5-diyl showed a very large effect on the photoreactivities. The planarity of the oligothiophene spacers caused a lot of influence on the photoreactivity.

**Switching of ESR Spectra.** The changes of the ESR spectra with the photochromism were examined. Figure 3 shows the ESR spectra of **1a**, **1b**, **2a**, and **2b** measured in benzene solution at room temperature.

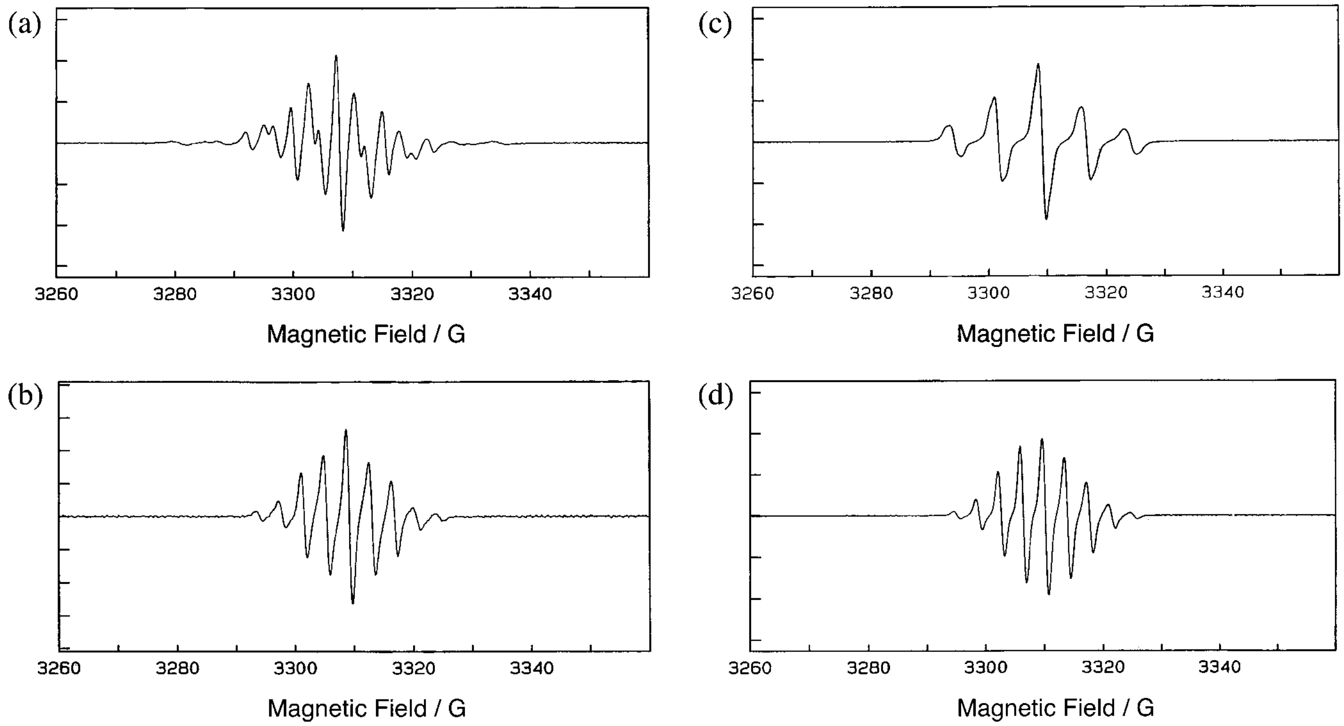


**Figure 3.** X-band ESR spectra of (a) **1a**, (b) **1b**, (c) **2a**, and (d) **2b** in benzene solution at room temperature (9.32 GHz).

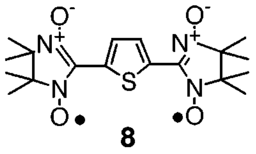
**Table 3. ESR Line Shapes and Exchange Interactions ($|2J/k_BK|$) of Diradicals**

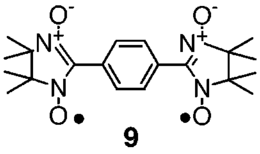
| | open-ring form isomer **a** | | closed-ring form isomer **b** | |
|---|---|---|---|---|
| | ESR line shape (lines) | $|2J/k_BK|$ | ESR line shape (lines) | $|2J/k_BK|$ |
| **1** | 13 | $5.6 \times 10^{-3}$, $<3 \times 10^{-4}$ | 9 | >0.04 |
| **2** | 5 | $<3 \times 10^{-4}$ | 9 | >0.04 |
| **3**[a] | 15 | $1.2 \times 10^{-3}$, $<3 \times 10^{-4}$ | 9 | >0.04 |
| **4**[a] | 5 | $< 3 \times 10^{-4}$ | distorted 9 | 0.010 |

The ESR spectrum of **1a** shows 13 lines. This suggests that the two spins of nitronyl nitroxide radicals are coupled by the exchange interaction that is comparable to the hyperfine coupling constant. On the contrary, the ESR spectrum of **1b** was nine lines. The nine-line spectrum indicates that the exchange interaction between the two spins in **1b** is much larger than the hyperfine coupling constant ($2J/k_B > 0.04$ K). To estimate the exchange interaction the spectrum of **1a** was simulated using BIRADG program.[10] In this case, two kinds of exchange interaction should be taken into account to reproduce the experimental spectrum. It is well-known that the open-ring isomer of 1,2-bis(2-methyl-1-benzothiophen-3-yl)perfluorocyclopentene has two atropisomers, parallel and antiparallel conformers, in the NMR time scale.[11] The parallel and antiparallel conformers are expected to have different exchange interactions between two spins. The ratio between parallel and antiparallel conformers was 35:65 for 1,2-bis(2-methyl-1-benzothiophen-3-yl)perfluorocyclopentene. Taking account of the ratio (35:65), the exchange interaction was determined to be $|2J/g\mu_B| = 42$ G ($|2J/k_B| = 5.6 \times 10^{-3}$ K) for the antiparallel conformer and $|2J/g\mu_B| < 2$ G ($|2J/k_B| < 3 \times 10^{-4}$ K) for the parallel conformer. Judging from the simulations using various $J$ values, the accuracy of the simulated value is estimated to be around ±10%. The photoinduced change indicates that the open-ring form isomer has "OFF" state, while the closed-ring form isomer has "ON" state.

The ESR spectrum of **2a**, in which two thiophene spacers were introduced, was 5 lines. This means the exchange interaction between two radicals was much smaller than the hyperfine coupling constant ($|2J/k_B| < 3 \times 10^{-4}$ K). On the contrary, the ESR spectrum of **2b** was nine lines, indicating that the exchange interaction was much larger than the hyperfine coupling constant ($|2J/k_B| > 0.04$ K). This result shows that the difference in the exchange interaction between open- (**2a**) and closed-ring form isomer (**2b**) is more than 150-fold.

The exchange interaction through oligothiophene spacer was larger than the corresponding diradicals with oligophenylene spacers (Table 3). The efficient $\pi$-conjugation in thiophene spacers resulted in the large exchange interaction between two nitronyl nitroxide radicals. The exchange interaction between two nitronyl nitroxide in **8** through thiophene-2,5-diyl spacer ($2J/k_B = -229$ K) has been reported to be 2.2 times stronger than the interaction in **9** through *p*-phenylene spacer ($2J/k_B = -104$ K[12]). **2b** has the interaction more than 4 times larger than **4b**. Thiophene-2,5-diyl spacers in series act as an effective spin coupler.


**8**


**9**

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## Conclusions

We have synthesized photochromic diarylethenes having two nitronyl nitroxide radicals at both ends of the molecule with oligothiophene spacers. The diradicals reversibly changed the ESR spectra by alternate irradiation with UV (366 nm) and visible (578 nm) light. The exchange interaction differences between open- and closed-ring form isomers were estimated from the ESR spectral changes as more than 150-fold. The quantum yields of both cyclization and cycloreversion reactions of diradicals with oligothiophene spacers were much smaller than those with oligophenylene spacers, while the magnetic interactions between spins of diarylethenes through oligothiophene spacers were stronger than those through oligophenylene spacers.

## Experimental Section

**A. Materials.** $^1$H NMR spectra were recorded on a JEOL GSX-400 instrument. UV−vis spectra were recorded on a Hitachi U-3500 Spectrophotometer. Mass spectra were obtained by a JEOL JMS-HX110A instrument. Melting points are not corrected. All reactions were monitored by thin-layer chromatography carried out on 0.2-mm E. Merck silica gel plates (60F-254). Column chromatography was performed on silica gel (E. Merck, 70−230 mesh).

**1,2-Bis(6-(5-formyl-2-thienyl)-2-methyl-1-benzothiophene-3-yl)hexafluorocyclopentene (6).** To a solution of 1,2-bis(6-iodo-2-methyl-1-benzothiophen-3-yl)hexafluorocyclopentene (**5**)[5f] (2.14 g, 3.0 mmol) in THF (30 mL) were added Pd(PPh$_3$)$_4$ (0.6 g, 0.6 mmol), NaCO$_3$ (4.6 g), water (30 mL), and 5-formylthiophene-2-boronic acid (1.0 g, 6.4 mmol). The solution was refluxed for 20 h. The reaction mixture was poured into water, extracted with ethyl acetate, washed with water, dried over MgSO$_4$, and concentrated. Column chromatography (silica, hexane/dichloromethane = 1:9) gave **6** (1.1 g, 50%) as a yellow solid: $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 2.27 (s, 3.9H), 2.54 (s, 2.1H), 7.38 (d, $J$ = 4 Hz, 0.7H), 7.46 (d, $J$ = 4 Hz, 1.3H), 7.5−7.8 (m, 6H), 7.93 (brs, 1.3H), 8.02 (brs, 0.7H), 9.87 (s, 0.7H), 9.92 (s, 1.3H); FAB HRMS calcd for $C_{33}H_{18}F_6O_2S_4$ 688.0094, found 688.0093.

**1,2-Bis(6-(5-(1-oxyl-3-oxide-4,4,5,5-tetramethylimidazolin-2-yl)-2-thienyl)-2-methyl-1-benzothiophene-3-yl)-hexafluorocyclopentene (1a).** A solution of **6** (1.0 g, 1.5 mmol), 2,3-bis(hydroxyamino)-2,3-dimethylbutane sulfate (1.6 g, 6.4 mmol), and potassium carbonate (1.2 g, 8.2 mmol) in benzene (100 mL) and methanol (20 mL) was refluxed for 23 h. The reaction mixture was poured into water, extracted with ethyl acetate, washed with water, dried over magnesium sulfate, and concentrated to give tetrahydroxylamine as yellow oil. Purification was not performed. To a solution of tetrahydroxylamine in dichloromethane (100 mL) was added a solution of sodium periodate (800 mg, 3.7 mmol) in water (160 mL) and the mixture stirred for 20 min in the open air. The organic layer was separated, washed with water, dried over magnesium sulfate, and concentrated. Purification was performed by column chromatography (silica, chloroform/Et$_2$O = 1:1) followed by GPC. **1a** was obtained as dark green solid (60 mg, 4%): mp >190 °C dec; UV−vis (AcOEt) $\lambda_{max}$ ($\epsilon$) 358 ($7.3 \times 10^4$), 574 (sh), 629 ($6.8 \times 10^2$), 688 ($8.9 \times 10^2$), 762 ($5.1 \times 10^2$); ESR (benzene) complicated 13 lines, $g$ = 2.007. Anal. Calcd for $C_{45}H_{40}F_6N_4O_4S_4$: C, 57.31; H, 4.28; N, 5.94. Found: C, 57.38; H, 4.56; N, 5.55. Corresponding closed-ring form isomer **1b**: UV−vis (AcOEt) 293 ($3.1 \times 10^4$), 340 ($3.0 \times 10^4$), 380 ($3.7 \times 10^4$), 407 ($3.8 \times 10^4$), 574 ($3.6 \times 10^4$); ESR (benzene) 9 lines, $g$ = 2.007, $a_N$ = 3.8 G.

**1,2-Bis(6-(5-(5-formyl-2-thienyl)-2-thienyl)-2-methyl-1-benzothiophene-3-yl)hexafluorocyclopentene (7).** To a solution of 1,2-bis(6-iodo-2-methyl-1-benzothiophen-3-yl)hexafluorocyclopentene (**5**) (700 mg, 0.97 mmol) in THF (10 mL) was added 1.6 M *n*-butyllithium in hexane (1.5 mL, 2.4 mmol) at −78 °C. After the mixture was stirred for 1 h at −78 °C, tri-*n*-butylborate (0.7 mL, 2.6 mmol) was added. The solution was allowed to warm to 10 °C with stirring. Water (5 mL) was added to the reaction mixture followed by addition of Pd(PPh$_3$)$_4$ (400 mg, 0.04 mmol), Na$_2$CO$_3$ (5 g), water (10 mL), and 5-formyl-5′-iodo-2,2′-bithiophene (650 mg, 2.0 mmol). The reaction mixture was refluxed 24 h. The reaction mixture was poured into water, extracted with AcOEt, washed with water, dried over magnesium sulfate, and concentrated. Column chromatography (silica, chloroform) gave compound **7** (390 mg, 48%) as a white solid: $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 2.25 (s, 3.9H), 2.52 (s, 2.1H), 7.2−7.7 (m, 12H), 7.82 (brs, 1.3H), 7.92-(brs, 0.7H), 9.84 (s, 0.7H), 9.87 (s, 1.3H); FAB HRMS ($m/z$) $[M + H]^+$ calcd for $C_{41}H_{22}F_6O_2S_6$ 851.9848, found 851.9846.

**1,2-Bis(6-(5-(5-(1-oxyl-3-oxide-4,4,5,5-tetramethylimidazolin-2-yl)-2-thienyl)-2-thienyl)-2-methyl-1-benzothiophene-3-yl)hexafluorocyclopentene (2a).** A solution of **7** (390 mg, 0.47 mmol), 2,3-bis(hydroxyamino)-2,3-dimethylbutane sulfate (0.8 g, 3.2 mmol), and potassium carbonate (0.6 g, 4.1 mmol) in benzene (20 mL) and methanol (10 mL) was refluxed for 15 h. The reaction mixture was poured into water, extracted with ethyl acetate, washed with water, dried over magnesium sulfate and concentrated to give tetrahydroxylamine as yellow oil. Purification was not performed. To a solution of tetrahydroxylamine in dichloromethane (50 mL) was added a solution of sodium periodate (400 mg, 1.9 mmol) in water (80 mL) and stirred for 10 min in the open air. The organic layer was separated, washed with water, dried over magnesium sulfate, and concentrated. Purification was performed by column chromatography (silica, chloroform:Et$_2$O = 95:5) followed by GPC. **2a** was obtained as dark green solid (30 mg, 2.4%): mp >190 °C dec; UV−vis (AcOEt for $\pi-\pi^*$ region, CH$_2$Cl$_2$ for $n-\pi^*$ region) $\lambda_{max}$ ($\epsilon$) 330 ($2.1 \times 10^4$), 395 ($7.1 \times 10^4$), 580 (sh), 639 ($7.0 \times 10^2$), 698 ($9.3 \times 10^2$), 770 ($5.7 \times 10^2$); ESR (benzene) 5 lines, $g$ = 2.006, $a_N$ = 7.5 G; MALDI MS ($m/z$) $[M + H]^+$ calcd for $C_{53}H_{45}F_6N_4O_4S_6$ 1107, found 1107. Anal. Calcd for $C_{53}H_{44}F_6N_4O_4S_6$: C, 57.49; H, 4.01; N, 5.06. Found: C, 57.16; H, 4.09; N, 4.71. Corresponding closed-ring form isomer **2b**: UV−vis (AcOEt) 407 ($4.0 \times 10^4$), 583 ($3.7 \times 10^4$); ESR (benzene) nine lines, $g$ = 2.007, $a_N$ = 3.8 G.

**B. Photochemical Measurement.** Absorption spectra were measured on a spectrophotometer (Hitachi U-3500). Photoirradiation was carried out by using a USHIO 500 W super-high-pressure mercury lamp or a USHIO 500 W xenon lamp. Mercury lines of 366 and 578 nm were isolated by passing the light through a combination of Toshiba band-pass filter (UV-D35) or sharp cut filter (UV-35, Y-51) and monochromator (Ritsu MC-20L).

**C. ESR Spectroscopy.** A Bruker ESP 300E spectrometer was used to obtain X-band ESR spectra. The sample was dissolved in benzene and degassed with Ar bubbling for 5 min.

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