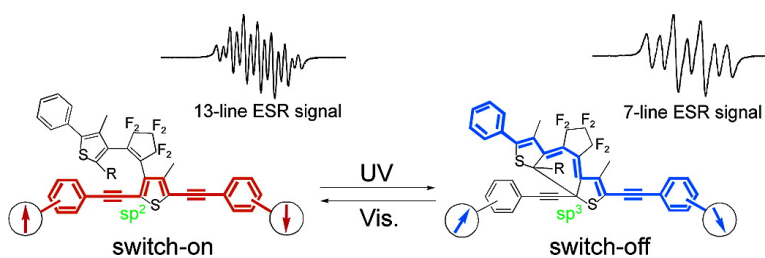


New Photoswitching Unit for Magnetic Interaction: Diarylethene with 2,5-Bis(arylethynyl)-3-thienyl Group

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New Photoswitching Unit for Magnetic Interaction: Diarylethene with 2,5-Bis(arylethynyl)-3-thienyl Group

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Abstract: Photoswitching of the intramolecular magnetic interaction was demonstrated using diarylethenes with 2,5-bis(arylethynyl)-4-methyl-3-thienyl side group. Two nitroxide radicals were placed at each end of the 2,5-bis(arylethynyl)-4-methyl-3-thienyl group. Three kinds of aryl groups, 2,5-thienylene, *p*-phenylene, and *m*-phenylene groups, were used in the arylethynyl moiety. The diarylethene photoswitching units have an extended π -conjugated chain on one side of the diarylethene. The photochromic reactivity was dependent on the arylethynyl group. Diarylethenes with *m*-phenylene group showed an efficient photochromic reactivity. Along with the photochromic reaction the diarylethenes showed photoswitching of an ESR spectrum originating from the change in the magnetic interaction between two unpaired electrons. The open-ring isomer showed stronger exchange interaction than the photogenerated closed-ring isomer. The magnetic interaction between two radicals via the π -conjugated chain was altered by photocyclization due to the change of the hybrid orbital at the 2-position of the thiophene ring from sp^2 to sp^3 .

Introduction

Photochromic compounds undergo reversible isomerization between two discrete states that have different colors by irradiation with light of appropriate wavelengths. The bistable molecules can be used as photoswitching units to control chemical and physical properties of the molecular systems.¹ Among various types of photochromic compounds, diarylethene is superior to other photochromic compounds with respect to their fatigue-resistant and thermally irreversible photochromic performance.² Photoswitching of diarylethene derivatives has been applied to control not only the absorption spectrum but also many various properties, such as liquid-crystalline phases,³ sol–gel transition,⁴ surface morphology of single crystals,⁵ fluorescence resonance energy transfer (FRET),⁶ fluorescence,⁷ electric conductivity,⁸ and refractive index.⁹

Molecular magnetism can be photocontrolled by using spin crossover phenomena, which are light-induced excited spin state trapping (LIESST), light-induced thermal hysteresis (LITH), and ligand-driven light-induced spin change (LD-LISC).¹⁰ In addition to spin crossover systems, several systems using photo-

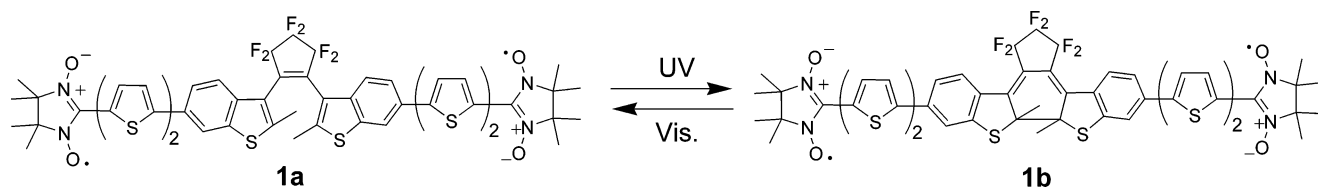
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[‡] Kyushu University.

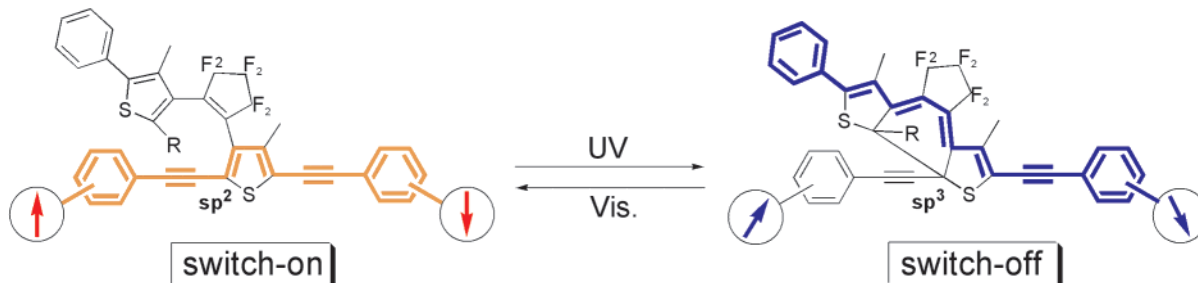
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Scheme 1



Scheme 2. Photochromism of Diarylethene Having 2,5-Arylethynyl-3-thienyl Unit



chromic units are also reported.¹¹ Among them, the most effective photoswitching of intramolecular magnetic interaction has been observed by using diarylethene derivatives as photo-switching units (Figure 1).¹² It has been demonstrated that the

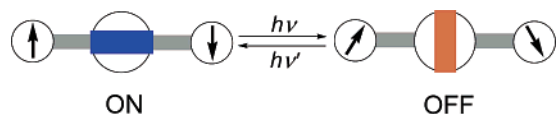


Figure 1. Photoswitching of the intramolecular magnetic interaction.

exchange interaction between two nitronyl nitroxide radicals, which are located at each end of diarylethene, is photoswitched reversibly by alternate irradiation with ultraviolet and visible light. While the conventional spin crossover system has a bistability in the spin state of the metal center, the molecular systems have a bistability based on molecular photoisomerization.

The switching of molecular magnetism is based on the molecular structure change of the diarylethene unit; the opening isomer of the biradical has a disjoint configuration while the closed-ring isomer has a resonant quinoid structure. This difference in the electronic structure brought about the change in the exchange interaction. The change of the exchange

interaction was found to be more than 150-fold between **1a** and **1b** (Scheme 1).^{12h}

In these photoswitches, radical units are placed at each side of the diarylethene photoswitching unit and separated by an extended π -conjugated chain. When the π -conjugated chain length between the radicals becomes longer, both photocyclization and cycloreversion reactivities are reduced. This can be attributed to the reduced excitation density at the central diarylethene unit.¹³ The excitation density localized at the center of both sides of the π -conjugated aryl unit such as oligothiophene. To solve the problem, it is necessary to develop new switching systems, in which the excitation density at the switching unit is not strongly reduced. The proposed new switching molecule has its switching unit located in the middle of the π -conjugated chain.

In this paper, we propose a new switching unit, in which two radicals are placed in the same aryl unit and the π -conjugated chain is extended from 2- and 5-positions of the thiophene ring in one aryl unit of the diarylethene. The photochromic reactivity and magnetic switching of the new diarylethene derivatives will be discussed.

Results and Discussion

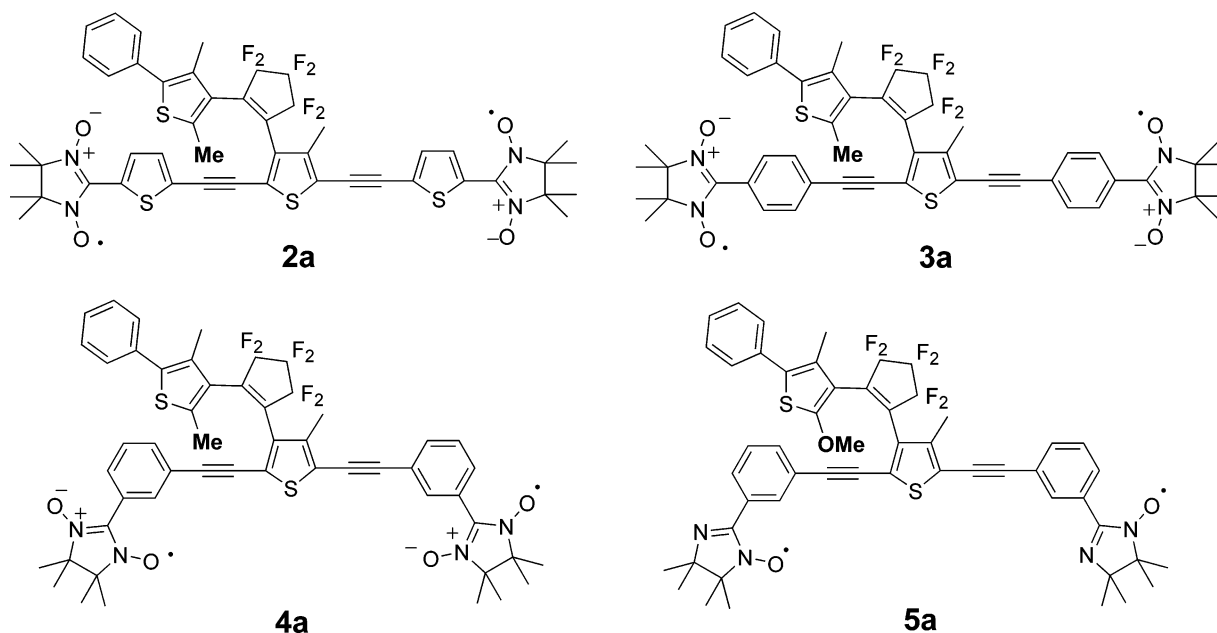
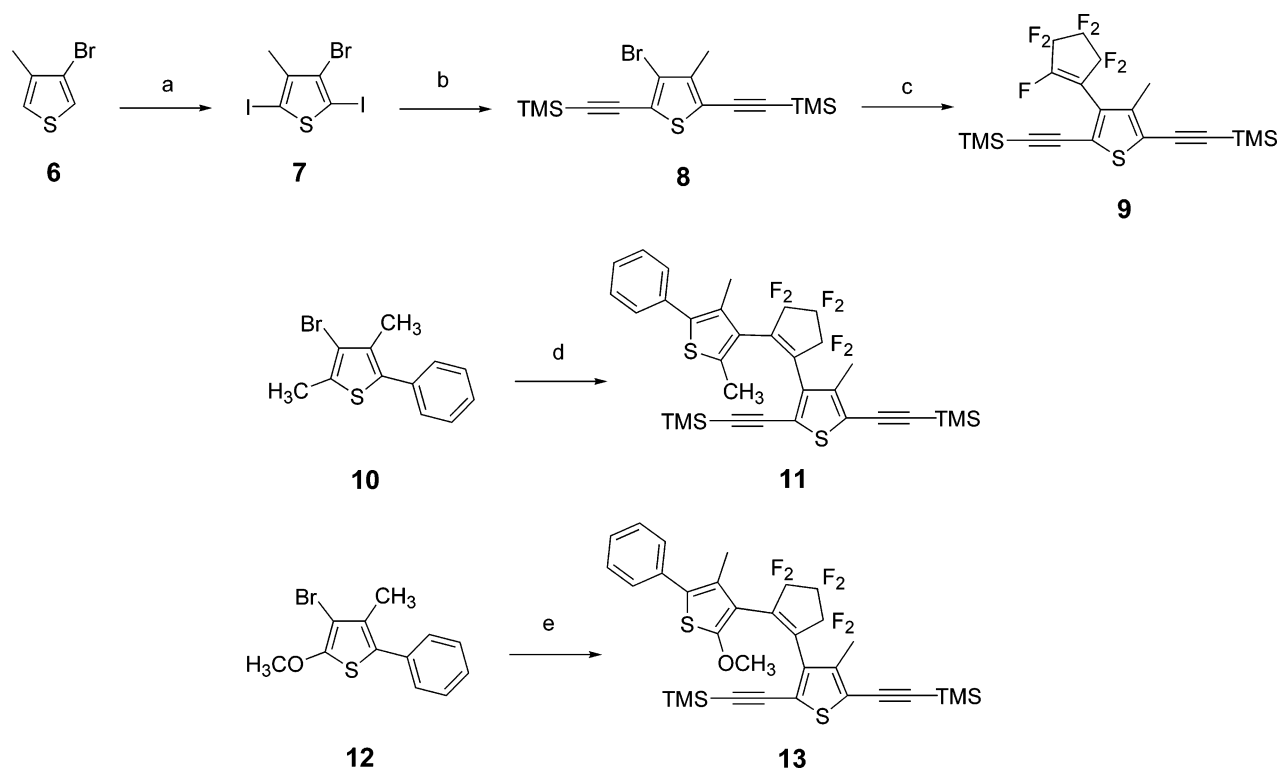
Molecular Design. Scheme 2 shows the photochromic behavior of the newly developed diarylethenes. The photocyclization reaction of the diarylethene unit breaks the π -conjugation in the 2,5-bis(arylethynyl)-3-thienyl unit due to the change of the orbital hybridization from sp^2 to sp^3 at the 2-position of the thiophene ring. Branda et al. used the switching of the orbital hybridization for the control of the absorption spectrum.¹⁴ Nitronyl or imino nitroxide radicals are introduced at both ends of the 2,5-bis(arylethynyl)thiophene π -conjugated chain. The designed molecules **2a–5a** are listed in Chart 1. The magnetic interaction between the two radicals via the π -conjugated chain can be altered by the photocyclization. The open-ring isomer represents the “ON” state because the π -conjugated system is delocalized between two radicals, while the closed-ring isomer represents the “OFF” state because the π -conjugated system is

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Chart 1

Scheme 3^a

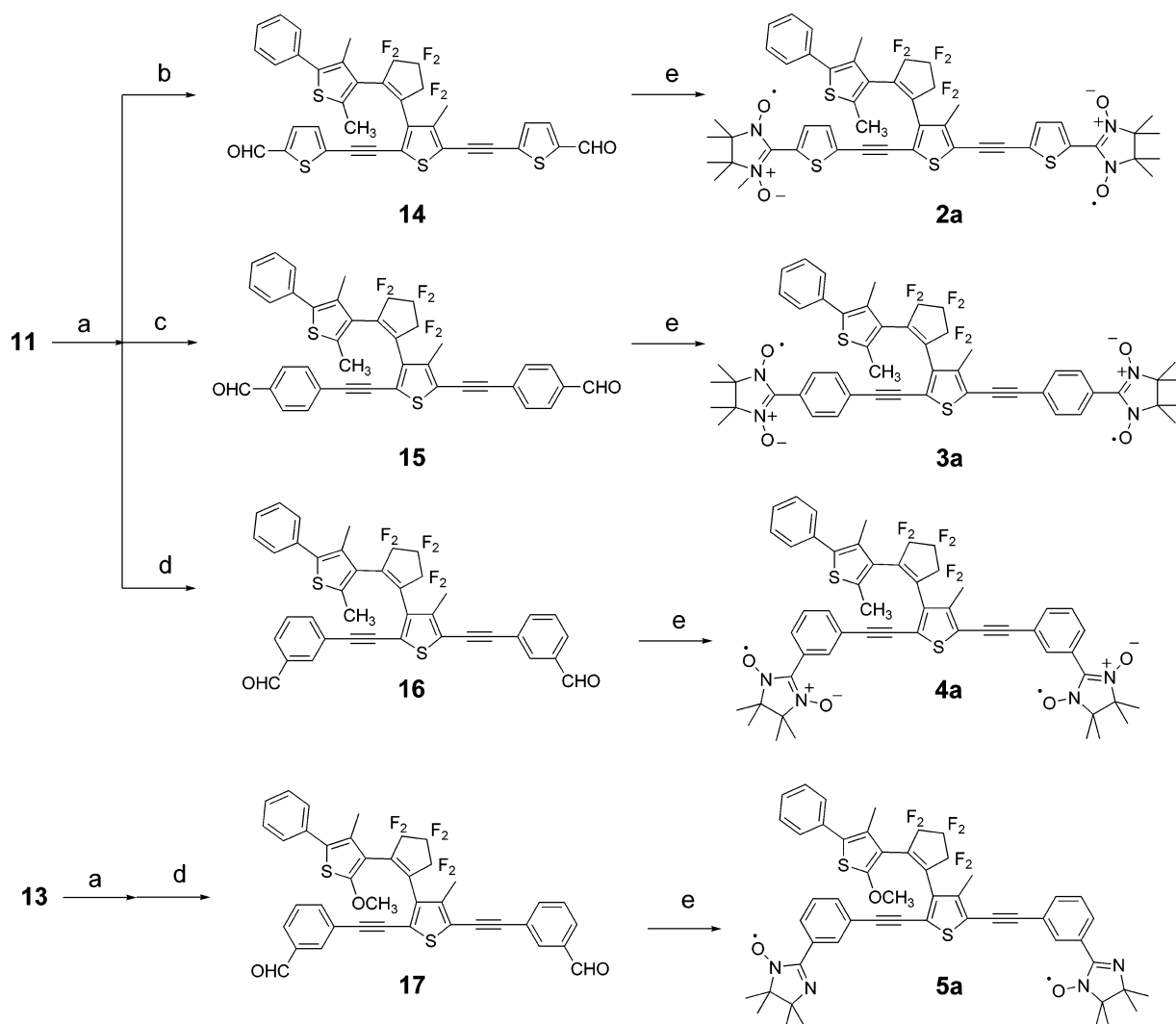
^a Reagents and conditions: (a) I₂, H₅IO₆, CH₃COOH, H₂SO₄, H₂O, 96%; (b) Pd(PPh₃)₂Cl₂, CuI, trimethylsilylacetylene, Et₃N, 40%; (c) *n*-BuLi, THF, and then perfluorocyclopentene, 81%; (d) THF, *n*-BuLi, and then **9**, 79%; (e) THF, *n*-BuLi, and then **9**, 90%.

disconnected at the 2-position of the thiophene ring. This switching direction is the opposite of the regular diarylethenes such as **1a**.

2,5-Thienylene (**2a**), *p*-phenylene (**3a**), and *m*-phenylene (**4a** and **5a**) were chosen as the spacer between the radicals and reactive center. **2a**, **3a**, and **4a** have nitronyl nitroxides and **5a** has imino nitroxides. **5a** has a methoxy group at the reactive carbon. These spacers have different features in respect to conjugation and magnetic interaction. While 2,5-thienylene and *p*-phenylene are strong antiferromagnetic spin couplers, *m*-

phenylene is a ferromagnetic spin coupler. The absolute value of the exchange interaction decreases in the following order: 2,5-thienylene, *p*-phenylene, and *m*-phenylene. In other words, the π -conjugation in 2,5-thienylene is more effective than *m*-phenylene. In addition, there is a possible resonant quinoid structure for the spacer of 2,5-thienylene and *p*-phenylene. The quinoid structure plays an important role in the photoreactivity.

Synthesis. The syntheses of **2a–5a** were performed according to Schemes 3 and 4. (4-Methyl-2,5-bis(trimethylsilylethynyl)-3-thienyl)heptafluorocyclopentene **9** was prepared from 3-bromo-

Scheme 4^a

^a Reagents and conditions: (a) 20% KOH aq., MeOH, THF, 86%; (b) Pd(PPh₃)₂Cl₂, CuI, 2-bromo-5-thiophenecarboxaldehyde, diisopropylamine, 20%; (c) Pd(PPh₃)₂Cl₂, CuI, 4-bromobenzaldehyde, diisopropylamine, 38%; (d) Pd(PPh₃)₂Cl₂, CuI, 3-bromobenzaldehyde, diisopropylamine, 54%; (e) 2,3-dimethyl-2,3-bis(hydroxyamino)butane sulfate and methanol and then NaIO₄ and CH₂Cl₂, 9–25%.

4-methylthiophene **6** by two steps. 3-Bromo-2,4-dimethyl-5-phenylthiophene **10**¹⁵ and 3-bromo-2-methoxy-4-methyl-5-phenylthiophene **12**¹⁶ were prepared according to the method described in the literature. Unsymmetrical diarylethenes, 2'-methyl derivative **11** and 2'-methoxy derivative **13**, were synthesized by the coupling of **9** with lithiated **10** and **12** in 79% and 90% yield, respectively. After desilylation by KOH, Sonogashira coupling with bromoformyl compounds gave bisformylated diarylethenes **14**–**17**. Formyl derivatives **14**–**17** were converted into nitroxide radicals **2a**–**5a** in 9–25% yield. When the substituent at the 2'-position of the thiophene ring is a methyl group, a major product of the final step was a nitronyl nitroxide radical. But when the substituent at the 2'-position of the thiophene ring is a methoxy group, a major product was an imino nitroxide radical. In general the oxidation of bis(hydroxy)amine affords both nitronyl and imino nitroxide radicals. Therefore, the difference in the products between methyl- and methoxy-substituted radicals was simply the difference in the product ratio between nitronyl and imino

nitroxide. The structures of the synthesized biradicals were confirmed by UV, ESR, and high-resolution mass spectroscopy. The structure of the key intermediate **11** was also confirmed by X-ray crystallography.¹⁷

Photochromic Reactions. The photochromic reactivity of diarylethene **2a**–**5a** was studied in ethyl acetate solution (Figure 2). Diarylethene **2a** did not show any photoreactivity by irradiation with light of any wavelength. On the other hand, compounds **3a**–**5a** underwent photochromic reactions upon alternate irradiation with UV and visible light. Before irradiation, the solutions showed pale green, pale blue, and pale yellow for **3a**, **4a**, and **5a**, respectively. The solutions of **4a** and **5a** turned blue by irradiation with 365 nm light. This blue color is due to the formation of the closed-ring isomers **4b** and **5b**. The blue color was bleached by irradiation with 578 nm light. The color change of the solution of **3a** was much less than the solutions of **4a** and **5a**. Absorption maxima, coefficients, and conversions from the open- to the closed-ring isomers under irradiation with

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(17) Crystallographic data for compound **11**: C₃₂H₃₂F₆OS₂Si₂, FW = 650.89, monoclinic *P*2₁/*n*, *a* = 17.833(4) Å, *b* = 9.664(2) Å, *c* = 20.097(4) Å, β = 104.716(4)°, *V* = 3349.8(13) Å³, *Z* = 4, *R*1 = 0.062 (*I* > 2σ), *wR*2 = 0.157 (all data). For the detail of the structure, see Supporting Information.

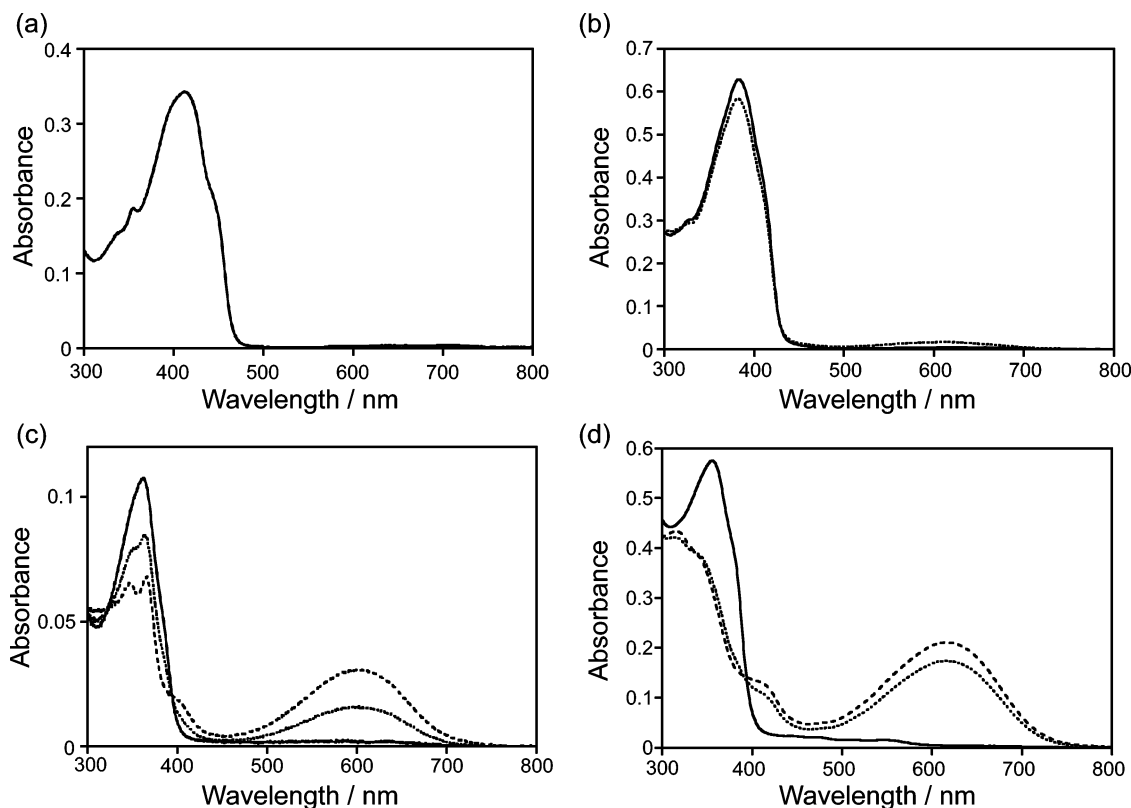


Figure 2. Absorption spectra of diarylethenes along with photochromism in ethyl acetate: (a) **2** (8.7×10^{-6} M); (b) **3** (1.3×10^{-5} M); (c) **4** (1.9×10^{-6} M); (d) **5** (1.0×10^{-5} M). The open-ring isomer (solid line), the closed-ring isomer (dashed line) and in the photostationary state under irradiation with 365 nm light (dotted line).

Table 1. Absorption Maxima of the Open- and the Closed-Ring Isomers and the Conversion from the Open- to the Closed-Ring Isomers under Irradiation with 365 nm Light

compound	open-ring isomer λ_{max} (ϵ)/nm	closed-ring isomer λ_{max} (ϵ)/nm	conversion/%
2	409 (3.9×10^4), 646 (450), 708 (500)	N/A	0
3	383 (4.9×10^4), 628 (420), 674 (360)	608 (N/A)	<10
4	361 (5.5×10^4), 590 (500), 633 (300)	606 (1.6×10^4), 410 (sh)	58
5	356 (3.3×10^4), 550 (sh)	616 (1.2×10^4), 410 (sh)	82

Table 2. Cyclization and Cycloreversion Quantum Yields of **4** and **5**

compound	quantum yield	
	$\Phi_{\text{O} \rightarrow \text{C}}$ (365 nm)	$\Phi_{\text{C} \rightarrow \text{O}}$ (578 nm)
4	0.011	0.048
5	0.055	0.0041

365 nm light are summarized in Table 1. Thiophene-2,5-diyl has the strongest π -conjugation so that the absorption maximum of the open-ring isomer was the longest. The conversion from the open- to the closed-ring isomers decreases as the π -conjugation between radicals gets stronger. The low conversion is ascribed to the low cyclization quantum yields or the high cycloreversion quantum yield. In the next section the relationship between the quantum yield and the structure will be discussed.

Quantum-Yield Measurements. Cyclization and cycloreversion quantum yields were measured in ethyl acetate using 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene as a reference.¹⁸ The quantum yields were summarized in Table 2. Compound **4**, which has a methyl group at the reactive carbon

and nitronyl nitroxide radical units, has a cycloreversion quantum yield larger than a cyclization quantum yield. This is the reason why the conversion is as low as 58%.

In the case of compound **5**, which has a methoxy group at the reactive carbon, it has a cyclization quantum yield larger than a cycloreversion quantum yield. The methoxy substituent suppresses the cycloreversion reaction.¹⁹ Therefore compound **5** has a smaller cycloreversion quantum yield than that of compound **4**, resulting in the high conversion of 82%. Compound **5** also has a larger cyclization quantum yield than that of compound **4**. Since the methoxy substitution is known not to affect the cyclization quantum yield,¹⁹ the difference in cyclization quantum yield is attributed to the difference in the radical species. Compound **5** has two imino nitroxide radicals instead of nitronyl nitroxide radicals. Teki et al. reported 9,10-bis[3-(4,4,5,5-tetramethyl-1-yloxy-imidazoline-2-yl)phenyl]anthracene as a photoswitchable molecule for spin alignment in a π -conjugated spin system.²⁰ When nitronyl nitroxide groups were used as radical sources instead of two imino nitroxides, the photoswitching of ESR spectrum was not observed because

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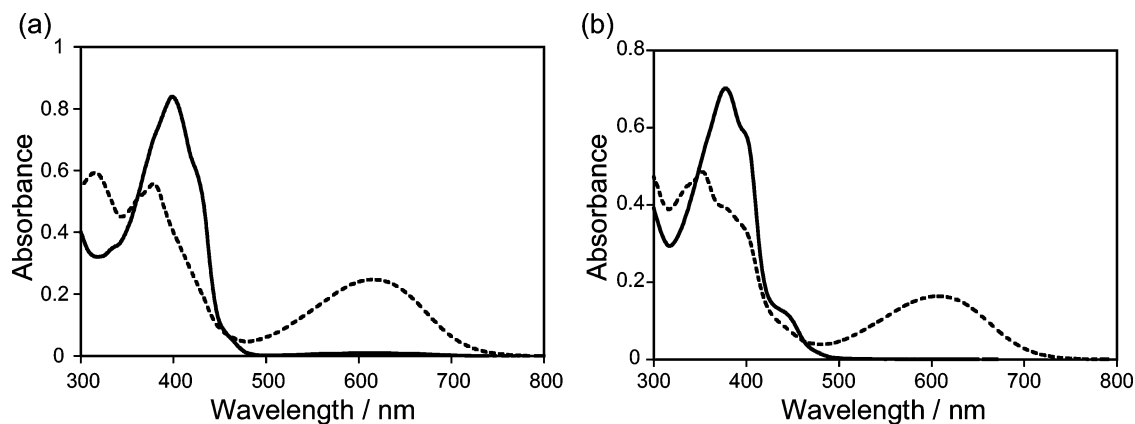
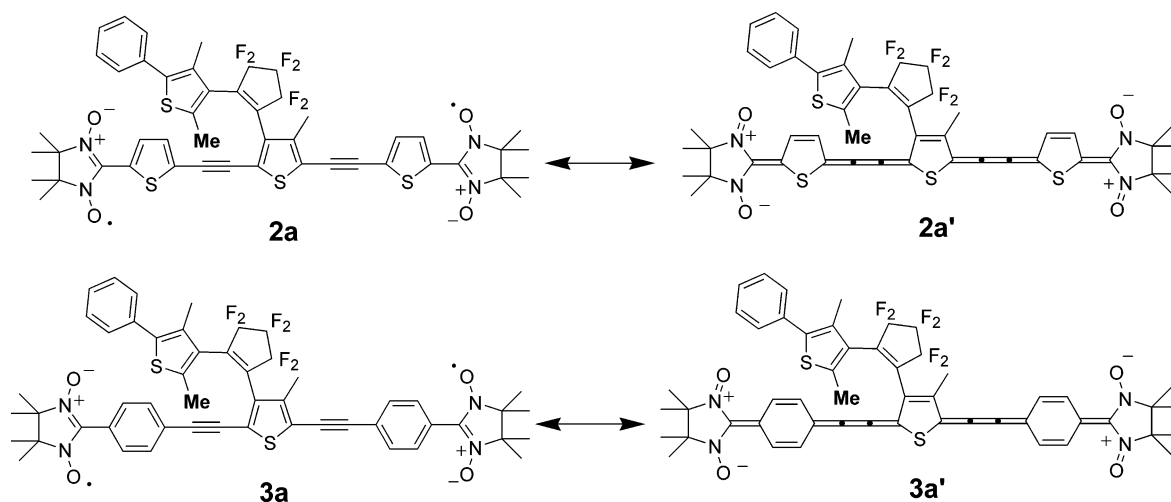


Figure 3. Absorption spectra of **14** and **15** along with photochromic reaction: (a) **14**; (b) **15**. The solid line denotes the open-ring isomer, and the dotted line denotes the spectra in the photostationary state under irradiation with 365 nm light.

Scheme 5. Possible Resonant Quinoid Structure of **2a** and **3a**



of the short lifetime of the excited state of the anthracene.²¹ With regard to the $\pi \rightarrow \pi^*$ transition band around 350 nm, the nitronyl nitroxide radical has a larger absorption band than that of the imino nitroxide radical. Therefore, nitronyl nitroxide radicals are anticipated to quench the excited state more effectively than imino nitroxide radicals. In other words, the energy transfer from the diarylethene to the nitronyl nitroxide radicals is more efficient than to the imino nitroxide.

The open-ring isomer **2a** and **3a** has a possible resonant quinoid structure **2a'** and **3a'** as shown in Scheme 5, while **4a** and **5a** cannot take such a quinoid structure. In a previous paper, it has been reported that the resonant quinoid structure suppresses the photocycloreversion quantum yield, and this effect is not discerned for the monosubstituted diarylethene.^{12b} By analogy, in **2a** and **3a** the quinoid structure in the open-ring isomer is anticipated to suppress the cyclization reaction.¹²ⁱ The low conversion of **2a** and **3a** is due to the contribution of the quinoid structure. In the case of precursors **14** and **15**, which are indifferent to the quinoid structure, the photocyclization reaction efficiently took place (Figure 3).

It has been discussed intensively whether a specific biradical adopts a biradical or quinoid structure.²² As the distance between

radical centers becomes longer, the biradical structure becomes more stable and the quinoidal effect becomes weaker. Although both nitronyl and imino nitroxides inherently do not have a strong quinoidal effect because of their allyl-like structure, the cyclization quantum yield was strongly suppressed when the radical is nitronyl nitroxide.

Switching of Magnetic Interaction. ESR spectroscopy is the most convenient way to detect weak changes in the magnetic interaction. Nitronyl nitroxide has two equivalent nitrogen atoms to give a 5-line ESR spectrum with a relative intensity of 1:2:3:2:1 and 7.5-G spacing. When two nitronyl nitroxide radicals are magnetically coupled with exchange interaction, the biradical gives a 9-line ESR spectrum with a relative intensity of 1:4:10:16:10:4:1 and 3.7-G spacing.²³ Imino nitroxide has a 7-line ESR spectrum for the isolated state due to the two inequivalent nitrogen atoms. When two imino nitroxide radicals interact, the spectrum gives 13 lines. The spectra of the specific interaction can be simulated, so that the ESR spectral change can be used as a probe to detect the exchange interaction.²⁴

The changes in the ESR spectra along with photochromism were examined in toluene solution for diarylethenes **2–5**. The

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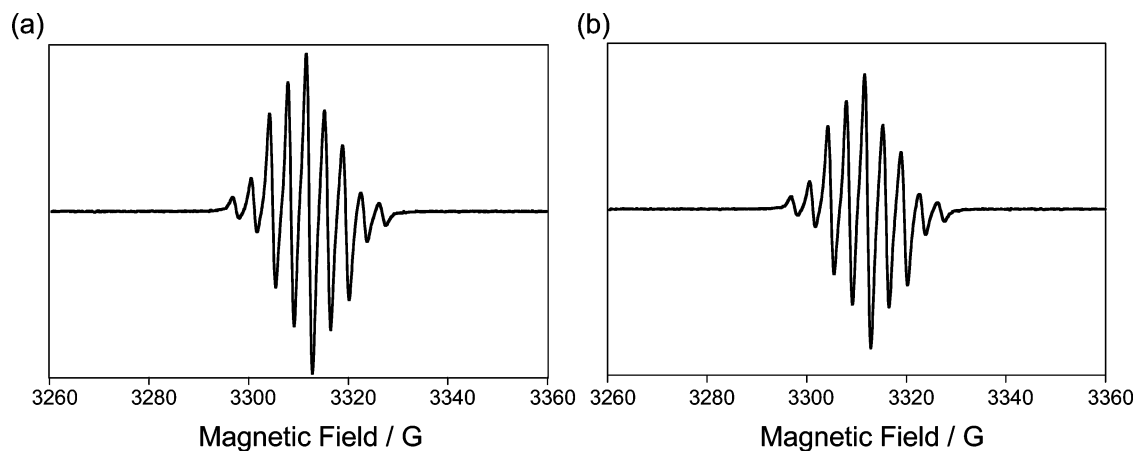


Figure 4. ESR spectra of biradicals measured in toluene at room temperature (9.32 GHz): (a) **2a**; (b) **3a**.

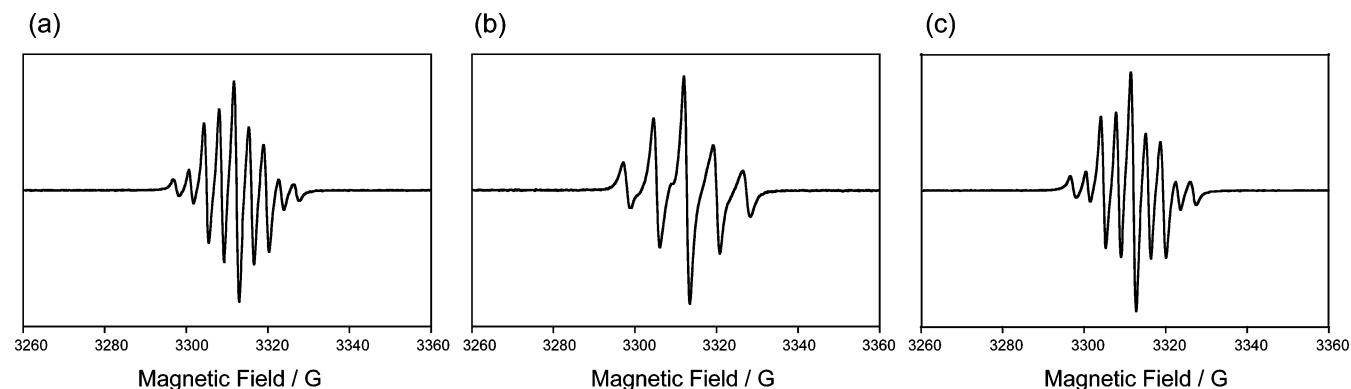


Figure 5. ESR spectra of biradicals measured in toluene at room temperature (9.33 GHz): (a) **4a**; (b) **4b**; (c) after irradiation with 365 nm light to **4a**.

ESR spectra of **2a** and **3a** are shown in Figure 4. Both spectra showed 9 lines, indicating that the exchange interaction between two radicals in **2a** and **3a** is larger than the coupling constant ($|2J/k_B| > 0.04$ K). As mentioned in the previous section, diarylethenes **2a** did not show any photoreactivity and the reactivity of **3a** was also limited. Therefore, the ESR spectra of **2a** and **3a** did not show any spectral change upon irradiation with UV light.

Figure 5 shows the ESR spectra of the open-ring isomer **4a**, the isolated closed-ring isomer **4b**, and the spectra after irradiation with 365 nm light to the open-ring isomer **4a**. The open-ring isomer has 9 lines, while the closed-ring isomer has 5 lines. This suggests that the exchange interaction between two radicals is much smaller in the closed-ring isomer ($|2J/k_B| < 3 \times 10^{-4}$ K) than in the open-ring isomer ($|2J/k_B| > 0.04$ K). Simulation of these spectra suggests that the change is more than 150-fold. The small interaction in the closed-ring isomer is attributed to the disconnection of the π -conjugated chain at the sp^3 carbon of the reactive center. In the photostationary state, the spectrum showed distorted 9 lines. This means that the spectrum after irradiation with UV light is the superposition of the 9-line and 5-line spectra. The low conversion ratio by irradiation with UV light could not cause obvious spectral change of the open-ring isomer.

ESR spectral change of the toluene solution containing compound **5** was followed with keeping the sample in the ESR cavity during irradiation with UV and visible light (Figure 6). The photoreaction was started from the isolated closed-ring isomer **5b**. The closed-ring isomer **5b** showed a 7-line spectrum, which is a spectrum of an isolated imino nitroxide ($|2J/k_B| <$

3×10^{-4} K). Upon irradiation with 578 nm light, as the generation of the open-ring isomer **5a**, a 13-line spectrum with the ratio of 1:2:5:6:10:10:13:10:10:6:5:2:1 generated. Upon further irradiation, the spectrum was completely converted to the 13-line spectrum. The 13-line spectrum indicates that the exchange interaction takes place between the two radicals ($|2J/k_B| > 0.04$ K). Subsequent irradiation with 365 nm light regenerated the 7-line spectrum along with the regeneration of the closed-ring isomer **5b**. The double integral values of the spectra at initial and photostationary state were almost identical, indicating that there is no gain or loss of the amount of the spins during the photochromic reaction. The difference in the exchange interaction between the open- and the closed-ring isomers was estimated to be larger than 150-fold. The difference in the exchange interaction is attributed to the change of the hybridization of the carbon atom from an sp^2 to sp^3 atom at the reaction center. The interconversion between 7 and 13 lines can be repeated 10 times without degradation.

Conclusions

Control of the photoreactivity and switching of the magnetic interaction in diarylethenes with 2,5-bis(arylethynyl)-3-thienyl group and nitroxide radical were studied. The photochromic reactivity of the diarylethenes is dependent on the arylethynyl group. Diarylethenes with *m*-phenylene group showed an efficient photochromic reactivity, and diarylethenes with a methoxy substituent showed enhanced conversion. The diarylethenes with *m*-phenylene groups showed photoswitching of the ESR spectrum. As inferred from the ESR spectral changes, the open-ring isomer showed stronger exchange interaction than the

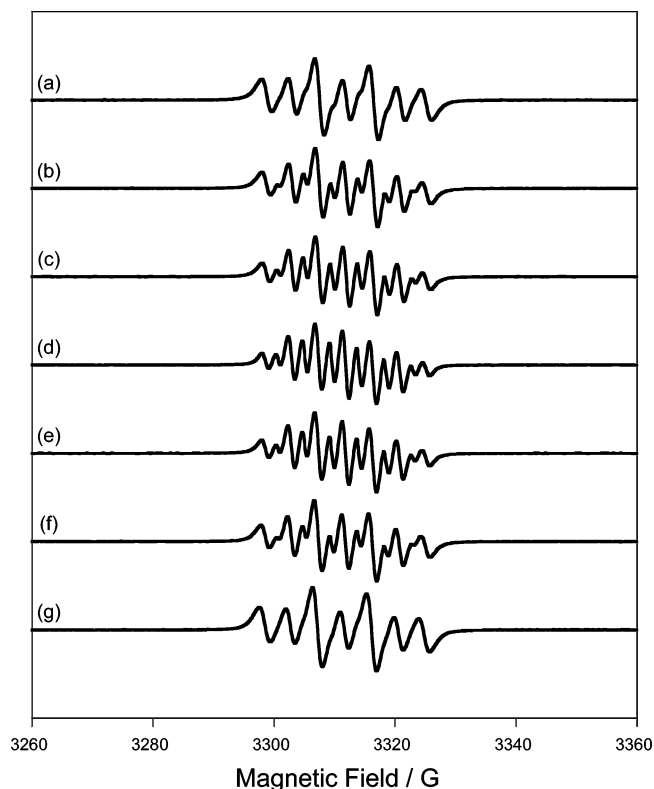


Figure 6. ESR spectra of biradical **5** along with photochromic reaction measured in toluene at room temperature (9.32 GHz): (a) the closed-ring isomer **5b**; (b) after irradiation with 578 nm light for 5 min; (c) for 7 min; (d) for 10 min, which is identical with the spectrum of **5a**; (e) after irradiation with 365 nm light for 1 min; (f) for 3 min; (g) for 5 min, which is identical with the spectrum of **5b**.

photogenerated closed-ring isomer. The magnetic interaction between two radicals via the π -conjugated chain was altered by photocyclization due to the change of the hybrid orbital at the 2-position of the thiophene ring from sp^2 to sp^3 .

Experimental Section

A. Materials. IR spectra were recorded on a Perkin-Elmer Spectrum One instrument by an ATR method. ^1H NMR spectra were recorded on a Varian Gemini 200 instrument. UV-vis spectra were recorded on a Hitachi U-3310 spectrophotometer. Mass spectra were obtained on a JEOL JMS-GCmate II. Melting points were 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 (Kanto, 63-210 mesh).

3-Bromo-2,5-diiodo-4-methylthiophene (7). To a solution of 3-bromo-4-methylthiophene **6** (5.0 g, 28.2 mmol) in acetic acid (30 mL) were added water (22 mL), concentrated H_2SO_4 (5.2 mL), orthoperiodic acid (2.0 g, 8.8 mmol), and iodine (6.76 g, 26.6 mmol). The reaction mixture was refluxed for 3 h and cooled to room temperature. After the addition of ice water, the reaction mixture was neutralized with sodium hydroxide, poured into water, extracted with ethyl acetate, washed with water, dried over magnesium sulfate, and concentrated. Column chromatography (silica, hexane/ethyl acetate = 5:1) gave compound **7** (11.19 g, 92%) as a colorless needle: mp 79.5–80.5 °C; ^1H NMR (CDCl_3 , 200 MHz) δ 2.34 (s, 3 H). Anal. Calcd for $\text{C}_6\text{H}_3\text{BrI}_2\text{S}$: C, 14.00; H, 0.71. Found: C, 14.05; H, 0.70.

3-Bromo-4-methyl-2,5-bis(trimethylsilylethynyl)thiophene (8). To a solution of diiodinated compound **7** (9.43 g, 22 mmol) in triethylamine (40 mL) were added $\text{Pd}(\text{Ph}_3\text{P})_2\text{Cl}_2$ (0.93 g, 1.3 mmol) and CuI (0.34 g, 1.8 mmol). A solution of trimethylsilylacetylene (4.32 g, 44 mmol) in triethylamine (440 mL) was added dropwise to the reaction mixture at

room temperature and stirred for 4 h at 60 °C. The reaction mixture was cooled to room temperature, filtered out brown solid. The solution was poured into water, extracted with ether, washed with water, dried over magnesium sulfate, and concentrated. Column chromatography (silica, hexane) gave compound **8** (3.42 g, 42%) as a colorless needle: mp 104.5–106.5 °C; ^1H NMR (CDCl_3 , 200 MHz) δ 0.26 (s, 9 H), 0.27 (s, 9 H), 2.25 (s, 3 H). Anal. Calcd for $\text{C}_{15}\text{H}_{21}\text{BrSSi}_2$: C, 48.76; H, 5.73. Found: C, 48.78; H, 5.73.

1-[4-Methyl-2,5-bis(trimethylsilylethynyl)-3-thienyl]heptafluorocyclopentene (9). *n*-Butyllithium in hexane (1.6 N, 4.59 mL, 7.04 mmol) was added to a solution of bromothiophene derivative **8** (2.59 g, 7.0 mmol) in THF (200 mL) at -78 °C under argon atmosphere. After the mixture was stirred for 30 min, perfluorocyclopentene (4.58 g, 21 mmol) was added in one portion. The solution was allowed to warm to 10 °C with stirring. Water was added to the reaction mixture. The reaction mixture was extracted with ether, washed with water, dried over magnesium sulfate, and concentrated. Column chromatography (silica, hexane) gave compound **9** (2.75 g, 79%) as a colorless wax: ^1H NMR (CDCl_3 , 200 MHz) δ 0.21 (s, 9 H), 0.26 (s, 9 H), 2.21 (s, 3 H). Anal. Calcd for $\text{C}_{20}\text{H}_{21}\text{F}_7\text{SSi}_2$: C, 49.77; H, 4.39. Found: C, 50.07; H, 4.50.

1-[2,4-Dimethyl-5-phenyl-3-thienyl]-2-[4-methyl-2,5-bis(trimethylsilylethynyl)-3-thienyl]hexafluorocyclopentene (11). *n*-Butyllithium in hexane (1.6 N, 3.03 mL, 4.84 mmol) was added to a solution of 3-bromo-2,4-dimethyl-5-phenylthiophene **10** (2.59 g, 4.4 mmol) in THF (25 mL) at -78 °C under argon atmosphere. After the mixture was stirred for 30 min, a solution of monosubstituted perfluorocyclopentene **9** (1.93 g, 3.95 mmol) in THF (10 mL) was added dropwise. The solution was allowed to warm to 10 °C with stirring. Water was added to the reaction mixture. The reaction mixture was extracted with ether, washed with water, dried over magnesium sulfate, and concentrated. Column chromatography (silica, hexane/ CH_2Cl_2 = 10:1) gave compound **11** (2.35 g, 76%) as a colorless powder: mp 57.5–59.5 °C; ^1H NMR (CDCl_3 , 200 MHz) δ 0.09–0.15 (m, 18 H), 1.95–2.52 (m, 9 H), 7.24–7.44 (m, 5 H). Anal. Calcd for $\text{C}_{32}\text{H}_{32}\text{F}_6\text{S}_2\text{Si}_2$: C, 59.05; H, 4.96. Found: C, 58.80; H, 4.99.

1-(2-Methoxy-4-methyl-5-phenyl-3-thienyl)-2-(4-methyl-2,5-bis(trimethylsilylethynyl)-3-thienyl)hexafluorocyclopentene (13). *n*-Butyllithium in hexane (1.6 N, 3.03 mL, 4.84 mmol) was added to a solution of 3-bromo-2-methoxy-4-methyl-5-phenyl thiophene **12** (566 mg, 2.0 mmol) in THF (10 mL) at -78 °C under argon atmosphere. After 30 min, the mixture was transferred to syringe and added dropwise to a solution of **9** (977 mg, 2.0 mmol) in THF (10 mL) at -78 °C under argon atmosphere. The solution was allowed to warm to 10 °C with stirring. Water was added to the reaction mixture. The reaction mixture was extracted with ether, washed with water, dried over magnesium sulfate, and concentrated. Column chromatography (silica, hexane:ethyl acetate = 10:1) gave compound **13** (1.19 g, 90%) as colorless powder: mp 114.0–115.5 °C; ^1H NMR(CDCl_3 , 200 MHz) δ 0.19 (s, 9 H), 0.24 (s, 9 H), 2.07 (s, 3 H), 2.14 (s, 3 H), 3.85 (s, 3 H), 7.25–7.42 (m, 5 H). Anal. Calcd for $\text{C}_{32}\text{H}_{32}\text{F}_6\text{OS}_2\text{Si}_2$: C, 57.63; H, 4.84. Found: C, 57.83 H, 4.91.

1-[2,5-Bis(5-formyl-2-thienylethynyl)-4-methyl-3-thienyl]-2-[2,4-dimethyl-5-phenyl-3-thienyl]hexafluorocyclopentene (14). To a solution of diarylethene **11** (651 mg, 1.0 mmol) in THF (20 mL) and methanol (10 mL) was added potassium hydroxide in water (20 wt %, 0.25 mL) with stirring. After the mixture was stirred for 30 min, the reaction mixture was extracted with ether, washed with water, dried over magnesium sulfate, and concentrated. Column chromatography (silica, hexane) gave the desilylated compound (461 mg, 86%) as a dark brown wax.

A solution of desilylated compound (461 mg, 0.86 mmol) in diisopropylamine (20 mL) was added to a solution of 2-bromo-5-thiophenecarboxaldehyde (172 mg, 0.9 mmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (151 mg, 0.22 mmol), and copper iodide (41 mg, 0.22 mmol) in diisopropylamine (10 mL) at room temperature under argon atmosphere and then stirred

for 5 h at 60 °C. The reaction mixture was cooled to room temperature, and a brown solid was filtered out. The solution was poured into water, extracted with ether, washed with water, dried over magnesium sulfate, and concentrated. Column chromatography (silica, hexane/ethyl acetate = 3:2) gave compound **14** (129 g, 20%) as a light green powder: mp 60.5–62.5 °C; ¹H NMR (CDCl₃, 200 MHz) δ 2.05–2.55 (m, 9 H), 7.20–7.50 (m, 7 H), 7.69 (d, *J* = 4.2 Hz, 2 H), 9.89 (s, 2 H). FAB HRMS [M]⁺ Calcd For C₃₆H₂₀F₆O₂S₄: 726.0250. Found 726.0231.

1-[2,4-Dimethyl-5-phenyl-3-thienyl]-2-[4-methyl-2,5-bis(1-oxyl-3-oxide-4,4,5,5-tetramethylimidazolin-2-yl)thienylethynyl]-3-thienyl]hexafluorocyclopentene (2a). A solution of bisformylated derivative **14** (129 mg, 0.18 mmol), 2,3-bis(hydroxyamino)-2,3-dimethylbutane sulfate (262 mg, 1.07 mmol), and potassium carbonate (152 mg, 1.10 mmol) in dry methanol (10 mL) and benzene (5 mL) was refluxed for 18 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 an orange solid. Purification was not performed.

To a solution of tetrahydroxylamine in dichloromethane (10 mL) was added a solution of sodium periodate (34 mg, 0.16 mmol) in water (20 mL). The mixture was stirred for 30 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, CH₂Cl₂/ethyl acetate = 100:1). **2a** was obtained as a green amorphous solid (15 mg, 9%): mp 98.5–100.5 °C; IR (Ge ATR) 2953, 2932, 2925, 1371, 1275, 1134 cm⁻¹; ESR (toluene) 1:4:10:16:19:16:10:4:1, 9 lines, *g* = 2.0065, *a_N* = 3.7 G (open-ring isomer **2a**); UV-vis (AcOEt) λ_{max}(ε) 409 (3.9 × 10⁴), 646 (450), 708 (500) nm. FAB HRMS (*m/z*) [M + 2]⁺ Calcd for C₄₈H₄₄F₆N₄O₄S₄: 982.2150. Found: 982.2166.

1-[2,5-Bis(4-formylphenylethynyl)-4-methyl-3-thienyl]-2-[2,4-dimethyl-5-phenyl-3-thienyl]hexafluorocyclopentene (15). Desilylated diarylethene, which was prepared from TMS-protected **11** (198 mg, 0.37 mmol) according to the same procedure for **14**, in diisopropylamine (20 mL) was added to a solution of 4-bromobenzaldehyde (205 mg, 1.11 mmol), Pd(PPh₃)₂Cl₂ (52 mg, 0.07 mmol), and copper iodide (10 mg, 0.07 mmol) in diisopropylamine (20 mL) at room temperature under argon atmosphere and then stirred for 5 h at 60 °C. The reaction mixture was cooled to room temperature, and a brown solid was filtered out. The solution was poured into water, extracted with ether, washed with water, dried over magnesium sulfate, and concentrated. Column chromatography (silica, hexane/ethyl acetate = 4:1) gave compound **15** (100 mg, 38%) as a light green powder: mp 80.0–81.5 °C; ¹H NMR (CDCl₃, 200 MHz) δ 2.00–2.56 (m, 9H), 7.20–7.50 (m, 5H), 7.50–7.98 (m, 8H), 10.03 (s, 2H). FAB HRMS [M]⁺ Calcd For C₄₀H₂₄F₆O₂S₂: 714.1122. Found 714.1117.

1-[2,4-Dimethyl-5-phenyl-3-thienyl]-2-[2,5-bis(4-(1-oxyl-3-oxide-4,4,5,5-tetramethylimidazolin-2-yl)phenylethynyl)-4-methyl-3-thienyl]hexafluorocyclopentene (3a). A solution of bisformylated diarylethene **15** (100 mg, 0.14 mmol), 2,3-bis(hydroxyamino)-2,3-dimethylbutane sulfate (208 mg, 1.07 mmol), and potassium carbonate (124 mg, 0.9 mmol) in dry methanol (10 mL) and benzene (5 mL) was refluxed for 18 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 an orange solid. Purification was not performed.

To a solution of tetrahydroxylamine in dichloromethane (10 mL) was added a solution of sodium periodate (107 mg, 0.5 mmol) in water (20 mL). The mixture was stirred for 30 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, CH₂Cl₂:ethyl acetate = 100:1). **3** was obtained as a dark-green wax (35 mg, 25%): IR (Ge ATR) 2676, 2925, 2853, 1368, 1275, 1140 cm⁻¹; ESR (toluene) 1:4:10:16:19:16:10:4:1, nine lines (open-ring isomer **3a**), *g* = 2.0065, *a_N* = 3.7 G; UV-vis (AcOEt) λ_{max}(ε)

383 (4.9 × 10⁴), 628 (420), 674 (360) nm. FAB HRMS (*m/z*) [M+2H]⁺ Calcd for C₄₈H₄₂F₆N₄O₄S₄: 970.3021. Found: 970.3047.

1-[2,5-Bis(3-formylphenylethynyl)-4-methyl-3-thienyl]-2-[2,4-dimethyl-5-phenyl-3-thienyl]hexafluorocyclopentene (16). Desilylated diarylethene, which was prepared from TMS-protected **11** (268 mg, 0.5 mmol) by the same procedure of **14**, in diisopropylamine (25 mL) was added to a solution of 3-iodobenzaldehyde (348 mg, 1.5 mmol), Pd(PPh₃)₂Cl₂ (70.2 mg, 0.1 mmol) and copper iodide (19 mg, 0.1 mmol) in diisopropylamine (20 mL) at room temperature under argon atmosphere and then stirred for 5 h at 60 °C. The reaction mixture was cooled to room temperature, filtered out brown solid. The solution was poured into water, extracted with ether, washed with water, dried over magnesium sulfate, and concentrated. Column chromatography (silica, hexane:ethyl acetate = 3:1) gave compound **16** (196 g, 54%) as a light green powder: mp 51.5–53.5 °C; ¹H NMR (CDCl₃, 200 MHz) δ 2.08–2.35 (m, 6 H), 2.38 (s, 3 H), 7.22–7.44 (m, 5 H), 7.56–7.74 (m, 4 H), 7.84–7.94 (m, 4 H), 10.00–10.10 (m, 2 H); FAB HRMS [M]⁺ Calcd For C₄₀H₂₄F₆O₂S₂: 714.1122. Found 714.1131.

1-[2,4-Dimethyl-5-phenyl-3-thienyl]-2-[2,5-bis(3-(1-oxyl-3-oxide-4,4,5,5-tetramethylimidazolin-2-yl)phenylethynyl)-4-methyl-3-thienyl]hexafluorocyclopentene (4a). A solution of bisformylated diarylethene **16** (143 mg, 0.2 mmol), 2,3-bis(hydroxyamino)-2,3-dimethylbutane sulfate (296 mg, 1.2 mmol), and potassium carbonate (180 mg, 1.3 mmol) in dry methanol (10 mL) and benzene (5 mL) was refluxed for 18 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 an orange solid. Purification was not performed.

To a solution of tetrahydroxylamine in dichloromethane (10 mL) was added a solution of sodium periodate (150 mg, 0.7 mmol) in water (20 mL). The mixture was stirred for 30 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, CH₂Cl₂/ethyl acetate = 100:1). **4a** was obtained as a dark-blue amorphous solid (31 mg, 16%): mp 127.5–129 °C; IR (Ge ATR) 2987, 2929, 2853, 1363, 1274, 1143 cm⁻¹; ESR (toluene) 1:4:10:16:19:16:10:4:1, 9 lines (open isomer **4a**), *g* = 2.0065, *a_N* = 3.7 G; UV-vis (AcOEt) λ_{max}(ε) 361 (5.5 × 10⁴), 590 (500), 633 (300) nm. FAB HRMS (*m/z*) [M + 2H]⁺ Calcd for C₄₈H₄₂F₆N₄O₄S₄: 970.3021. Found: 970.3025.

1-[2,5-Bis(3-formylphenylethynyl)-4-methyl-3-thienyl]-2-(2-methoxy-4-methyl-5-phenyl-3-thienyl)hexafluorocyclopentene (17). A solution of desilylated compound, which was prepared from **13** (551 mg, 1.0 mmol) by the same synthetic method of **14**, in diisopropylamine (50 mL) was added dropwise to a solution of 4-iodobenzaldehyde (945 mg, 3.0 mmol), Pd(PPh₃)₂Cl₂ (140 mg, 0.2 mmol), and copper iodide (38 mg, 0.2 mmol) in diisopropylamine (50 mL) at room temperature under argon atmosphere and then stirred for 12 h. The reaction mixture was filtered out to obtain a brown solid. The solution was poured into water, extracted with ether, washed with water, dried over magnesium sulfate, and concentrated. Column chromatography (silica, CH₂Cl₂) gave compound **17** (310 mg, 42%) as a green powder: mp 173.5–175.5 °C; ¹H NMR (CDCl₃, 200 MHz) δ 2.10 (s, 3H), 2.24 (s, 3H), 7.78 (s, 1H), 3.78 (s, 3H), 7.22–7.46 (m, 3H), 7.48–8.05 (m, 10H), 9.98 (s, 1H), 10.02 (s, 1H). Anal. Calcd for C₄₀H₂₄F₆O₃S₂: C, 66.12; H, 3.52. Found: C, 65.84; H, 3.54.

1-[2-Methoxy-4-methyl-5-phenyl-3-thienyl]-2-[2,5-bis(3-(1-oxyl-4,4,5,5-tetramethylimidazolin-2-yl)phenyl)-4-methyl-3-thienyl]hexafluorocyclopentene (5a). A solution of bisformylated diarylethene **17** (600 mg, 0.84 mmol), 2,3-bis(hydroxyamino)-2,3-dimethylbutane sulfate (1.24 g, 5.02 mmol), and potassium carbonate (760 mg, 5.50 mmol) in dry MeOH (20 mL) was refluxed for 72 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 an orange solid. Purification was not performed.

To a solution of tetrahydroxylamine in dichloromethane (10 mL) was added a solution of sodium periodate (718 mg, 3.36 mmol) in water (20 mL). The mixture was stirred for 2 h 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, CH₂Cl₂/ethyl acetate = 3:2). **5a** was obtained as a yellow brown solid (178 mg, 22%): mp 98.5–100.5 °C; IR (Ge ATR) 2973, 2931, 2864, 1274, 1140 cm⁻¹; ESR (toluene) 1:2:5:6:10:10:13:10:10:6:5:2:1, 13 lines, $g = 2.0065$, $a_N = 9.0$ G, 4.5 G; UV–vis (AcOEt) $\lambda_{\max}(\epsilon)$ 356 (3.3×10^4), 550 (sh) nm. FAB HRMS (m/z) [M + 2H]⁺ Calcd for C₅₂H₄₈F₆N₄O₃S₂: 954.3072. Found: 954.3078.

B. Photochemical Measurements. 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 with a combination of an optical filter and monochromator (Ritsu MC-20L).

Conditions for the separation of the isomers **3a** and **3b** were as follows: Pump, Hitachi L-2130; Detector, Hitachi L-2420; Column, Wakosil5SIL (Wako Chemical) 250–3 mm; Eluent, hexane/AcOEt = 98.5:1.5.

Conditions for the separation of the isomers **4a** and **4b** were as follows: Pump, Hitachi L-2130; Detector, Hitachi L-2420; Column, Wakosil5SIL (Wako Chemical) 250–3 mm; Eluent, hexane/AcOEt = 1:1.

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

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Supporting Information Available: Crystal Structures of **11** (PDF). X-ray structural data for **11** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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