

Reversed Photoswitching of Intramolecular Magnetic Interaction Using A Photochromic Bis(2-thienyl)ethene Spin Coupler

Kenji Matsuda,* Mitsuyoshi Matsuo, Shinji Mizoguti, Kenji Higashiguchi, and Masahiro Irie*

Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, and CREST, Japan Science and Technology Corporation, 6-10-1 Hakozaiki, Higashi-ku, Fukuoka 812-8581, Japan

Received: July 18, 2002; In Final Form: August 24, 2002

Bis(3-thienyl)- and bis(2-thienyl)ethenes having nitronyl nitroxide radicals at both ends of the molecules were synthesized. Bis(3-thienyl)ethene diradicals underwent a reversible photochromic reaction by irradiation with UV and visible light. Photoswitching of intramolecular magnetic interaction was proved by EPR spectroscopy. By choosing an appropriate spacer, the intramolecular exchange interaction in the closed-ring isomer was detected to be more than 150 times larger than that in the open-ring isomer. In the case of bis-(2-thienyl)ethene diradicals, the photocyclization reaction was prohibited, and only the cycloreversion reaction took place by irradiation with visible light. The closed-ring isomers of the diradicals were synthesized from the closed-ring isomers of the precursors. From the analysis of the EPR spectra of the system with an appropriate spacer, it was found that on/off switching behavior was reversed by changing the substitution position of the thiophene rings to the ethene moiety from the 3- to the 2-position. The open-ring isomer had a larger interaction than the closed-ring isomer. These results were rationally explained by the switching of the connectivity of the π bonds.

Introduction

The use of photochromic compounds to photocontrol the physical properties of materials has started to attract the interest of many chemists.¹ Photochromic compounds are potential molecular-scale photoswitches. Among these compounds, diarylethenes are the most promising for several applications because of their fatigue-resistant and thermally irreversible photochromic performance.² The open-ring and closed-ring isomers of the diarylethenes differ from each other not only in their absorption spectra but also in various physical and chemical properties such as geometrical structure, refractive index, dielectric constant, and oxidation/reduction potentials.

When an unpaired electron is placed at both ends of a π -conjugated chain, the two spins of the unpaired electrons interact magnetically.³ On the basis of this principle, several kinds of molecule-based magnetic materials have been synthesized. Among them, photofunctionalized magnetic materials have attracted attention in recent years.⁴ If a π -conjugated chain length can be switched using a photochromic spin coupler, then the magnetic interaction is expected to be controlled by irradiation with light. For this purpose, diarylethenes are very effective because the π -conjugated chain length is switched by photoirradiation. π systems of the two aryl rings are separated in the open-ring isomer, whereas the π system is delocalized throughout the molecule in the closed-ring isomer. On the basis of this idea, we have demonstrated the photoswitching of intramolecular magnetic interaction by several detection methods (i.e., temperature dependence of the magnetic susceptibilities, temperature dependence of the EPR signal intensities at cryogenic temperatures, and EPR spectral changes at room temperature) (Figure 1).⁵

Because the magnetic interaction depends on the π conjugation length of the coupler, the on/off switching is regulated by cyclization/cycloreversion reactions of the diarylethene units.

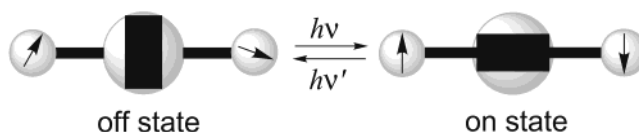


Figure 1. Photoswitching of the magnetic interaction.

In this work, we have synthesized bis(3-thienyl)- and bis(2-thienyl)ethenes having nitronyl nitroxide radicals at both ends of the molecule to reveal the effect of the substitution position of the thiophene rings to the ethene moiety on the photoreactivity and switching of the magnetic interaction.

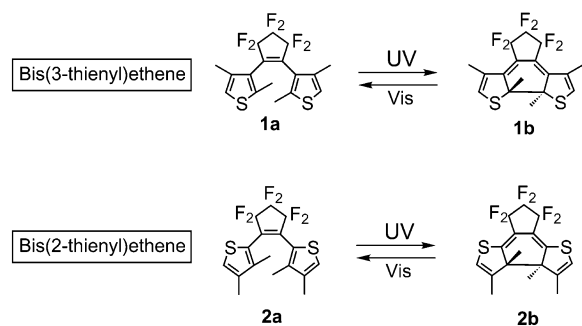
Results and Discussion

Molecular Design and Synthesis. We chose two kinds of diarylethenes as switching units. Scheme 1 shows the two kinds of diarylethene: 1,2-bis(2,4-dimethyl-3-thienyl)perfluorocyclopentene (**1a**) and 1,2-bis(3,4-dimethyl-2-thienyl)perfluorocyclopentene (**2a**). The thiophene rings are substituted onto the perfluorocyclopentene ring at the 3-position in **1a** and at the 2-position in **2a**.⁶

In the case of bis(3-thienyl)ethenes, the bond alternation is discontinued in the open-ring isomer, but in the closed-ring isomer, the π electron is delocalized throughout the molecule. So far we have reported the photoswitching of the magnetic interaction using bis(3-thienyl)ethenes as the spin coupler.⁵ When two unpaired electrons are placed at both 5-positions of the thiophene rings, the magnetic interaction in the closed-ring isomer is much larger than that in the open-ring isomer. In other words, the open-ring isomer is in the OFF state because of the disconnection of the π system, and the closed-ring isomer is in the ON state because of the delocalization of the π conjugated system.

The situation is reversed when thiophene rings are substituted onto the ethene moiety at the 2-position. The bond alternation is continued throughout the molecule in the open-ring isomer, whereas in the closed-ring isomer, two aryl rings are separated

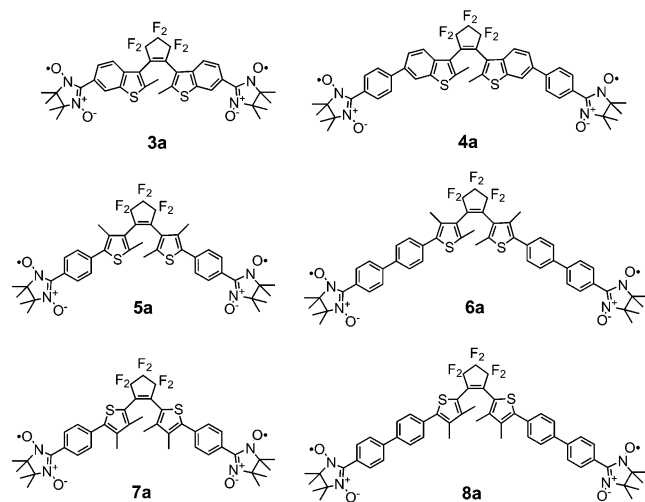
* Corresponding authors. E-mail: kmatsuda@cstf.kyushu-u.ac.jp; irie@cstf.kyushu-u.ac.jp.

SCHEME 1: Photochromism of Bis(3-thienyl)ethene 1a and Bis(2-thienyl)ethene 2a

by the sp^3 carbon and the sulfur atom. The magnetic interaction between the two unpaired electrons at the 5-positions in the closed-ring isomer is expected to become much smaller than that in the open-ring isomer. In other words, the open-ring isomer is in the ON state, and the closed-ring isomer is in the OFF state.

The nitronyl nitroxide radical was chosen for the spin source because this radical is π -conjugative. For the detection of magnetic switching, EPR spectroscopy was employed. Nitronyl nitroxide itself has two equivalent nitrogen atoms to give a five-line EPR spectrum with relative intensities of 1:2:3:2:1 and a 7.5-G spacing. When two nitronyl nitroxides are magnetically coupled with exchange interaction, the diradical gives a nine-line EPR spectrum with relative intensities of 1:4:10:16:19:16:10:4:1 and a 3.7-G spacing. If the exchange interaction is smaller than the hyperfine coupling in the diradical, two nitroxide radicals are magnetically independent and give the same spectrum as the isolated monoradical. In intermediate situations, the spectrum becomes complex.⁷

We have already reported the photoswitching of the intramolecular magnetic interaction in **3a** and **4a**. **4a** has *p*-phenylene spacers at both ends of the molecule, which modifies the exchange interaction. Any photoinduced EPR spectral change was not observed in **3a**, whereas in **4a**, an obvious photoinduced EPR spectral change was observed by alternate irradiation with UV and visible light.^{5c} The π -conjugated chain length in **3a** is too short, and the exchange interaction is strong enough even in the open-ring isomer state. However, the chain length of **4a** is long enough for us to detect the exchange interaction. Therefore, we have designed **5a**–**8a**, whose chain lengths are all longer than **3a**, to investigate the photoswitching of the magnetic interaction by EPR spectroscopy.

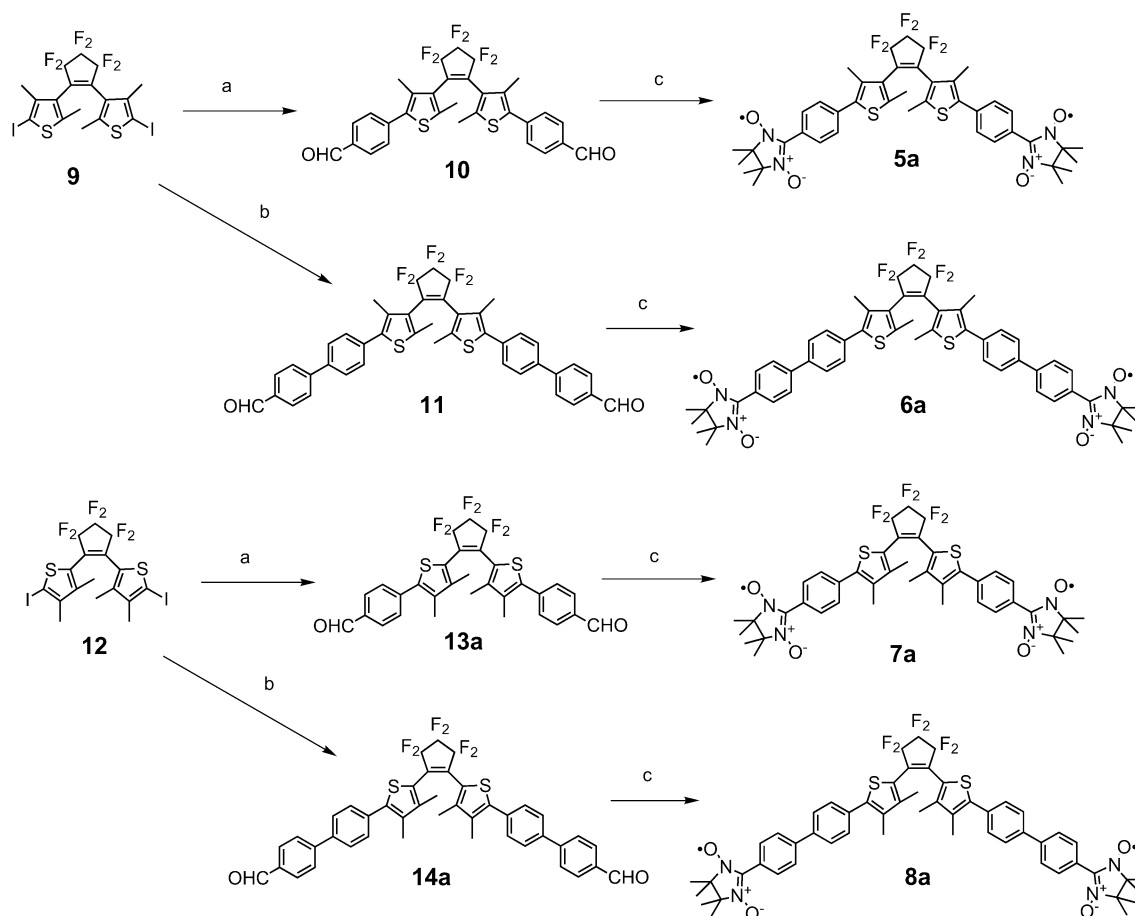


The synthesis was performed according to Scheme 2. **5a** and **6a** were synthesized from 1,2-bis(2,4-dimethyl-5-iodo-3-thienyl)hexafluorocyclopentene (**9**). Suzuki coupling with 4-formylphenylboronic acid gave diformyl compound **10**. Transformation of **9** to diboronic acid followed by Suzuki coupling with 4-formyl-4'-iodobiphenyl gave diformyl compound **11**. Condensation of diformyl compounds with 2,3-bis(hydroxyamino)-2,3-dimethylbutane sulfate and succeeding oxidation gave nitronyl nitroxides **5a** and **6a**. **7a** and **8a** were synthesized from 1,2-bis(3,4-dimethyl-5-iodo-2-thienyl)hexafluorocyclopentene (**12**). Suzuki coupling with 4-formylphenylboronic acid gave diformyl compound **13a**. Transformation of **12** to diboronic acid followed by Suzuki coupling with 4-formyl-4'-iodobiphenyl gave diformyl compound **14a**. The same treatment was employed for formyl compounds to convert nitronyl nitroxide radicals **7a** and **8a**. For all compounds, the structures were confirmed by NMR, EPR, and then elemental analysis or mass spectrometry.

Photochromic Reactions. **5a** and **6a** underwent photochromic reactions in ethyl acetate solution. Upon irradiation with UV light, the pale-blue solution turned blue-purple with the retention of isosbestic points at 337 and 341 nm (Figure 2). The color change is due to the formation of closed-ring isomers **5b** and **6b**. This blue-purple color disappeared upon irradiation with visible light. The absorption maximum of the closed-ring isomer **6b** was 583 nm, which is 5 nm shorter than that of **5b**. A hypsochromic shift with an increase in the π -conjugated chain length was observed. The conversion in the photostationary state under irradiation with UV light was 76% for **5** and 48% for **6**. The conversion was lowered with the increase in the π -conjugated chain length. Similar phenomena were also observed in **3a** and **4a** and have been discussed in detail.^{5e}

Although bis(3-thienyl)ethene **5a** and **6a** showed reversible photochromic reactions, bis(2-thienyl)ethene **7a** and **8a** did not show any photoreactivity. Their formyl precursors **13a** and **14a**, in which there is no radical substituent, underwent normal photochromic reactions. The radical substituents are considered to suppress photochromic reactivity. Therefore, the closed-ring isomers **7b** and **8b** were synthesized from the closed-ring isomers of the formyl precursors **13b** and **14b** (Scheme 3). The synthesized closed-ring isomers **7b** and **8b** underwent photocycloreversion reactions upon irradiation with visible light. The orange closed-ring isomers turned to pale green open-ring isomers. The bleached spectra were identical to the spectra of the corresponding open-ring isomers **7a** and **8a**. Figure 3 showed the absorption spectra of **7** and **8** before and after the cycloreversion reaction. The open-ring isomers of diarylethenes **7a** and **8a** had absorption bands at longer wavelengths than those of the corresponding open-ring isomers of bis(3-thienyl)ethenes **5a** and **6a**. However, the absorption bands of the closed-ring isomers **7b** and **8b** showed hypsochromic shifts in comparison with those of the corresponding closed-ring isomers of bis(3-thienyl)ethenes **5b** and **6b**.

As discussed in previous papers, the radical-containing closed-ring isomers of bis(3-thienyl)ethenes have a resonant quinoid structure.^{5b,e} For example, the closed-ring isomer **5b** has the resonant quinoid structure **5b'**, as shown in Scheme 4. The contribution of the quinoid structure stabilizes the closed-ring isomer and decreases the cycloreversion quantum yield. This effect gets weaker when the π -conjugated chain length becomes longer. The decrease in conversion in the photostationary state and the hypsochromic shift of the absorption maxima with the increase in the chain length from **5b** to **6b** can be explained as the decrease of the contribution of the quinoid structure. In the case of bis(2-thienyl)ethene, the open-ring isomer has the

SCHEME 2^a

^a Reagents and conditions: (a) $\text{Pd}(\text{PPh}_3)_4$, 4-formylphenylboronic acid, Na_2CO_3 , THF, and H_2O , 78–83%. (b) $n\text{-BuLi}$, $\text{B}(\text{O}i\text{Bu})_3$ and then $\text{Pd}(\text{PPh}_3)_4$, 4-formyl-4'-iodobiphenyl, Na_2CO_3 , THF, and H_2O , 21–26%. (c) 2,3-Dimethyl-2,3-bis(hydroxyamino)butane sulfate and methanol and then NaIO_4 and CH_2Cl_2 , 6–35%.

resonant quinoid structure. For example, the open-ring isomer **7a** has the resonant quinoid structure **7a'**, as shown in Scheme 4. However, the formyl precursor **13a** does not have such a resonant quinoid structure. The existence of the resonant quinoid structure in **7a** and **8a** may be the reason that **7a** and **8a** do not photocyclize. Closed-ring isomers **7b** and **8b** do not have such resonance structure. Therefore, they undergo normal photocycloreversion reactions. The photoreactivity of the open-shell diarylethenes was found to be largely affected by the substitution position of the thiophene rings.

Switching of EPR Spectra. The exchange interaction between two radical centers was investigated by means of EPR spectroscopy (Figures 4 and 5).⁸ In the case of **5**, any EPR spectral change was not observed along with the photochromism. Both the open- and closed-ring isomers of **5** have a nine-line spectrum, suggesting that in both isomers the exchange interactions are stronger than the hyperfine coupling constant. By the simulation of the spectrum, the exchange interaction $|2J/k_B|$ was estimated to be larger than 0.04 K. To see the change in the exchange interaction by EPR spectroscopy, the π -conjugated chain length should be longer than **5**. In the case of **6a**, a drastic spectral change was observed. The open-ring isomer **6a** showed a five-line spectrum, suggesting that the exchange interaction is smaller than the hyperfine coupling constant ($|2J/k_B| < 3 \times 10^{-4}$ K). On the contrary, the closed-ring isomer **6b** showed a nine-line spectrum. The π -conjugated chain length of **6** is appropriate for the detection of the exchange interaction change

by EPR spectroscopy. The change in the exchange interaction was estimated to be more than 150-fold.

The EPR spectra of **7** and **8** were also measured. In the case of **7**, both the open- and closed-ring isomer had a nine-line spectrum, suggesting the exchange interaction is too strong to be detected by EPR spectroscopy. Because **7** and **5** have the same number of carbon atoms between two nitronyl nitroxides, similar EPR spectra are expected, as observed in Figures 4a and 5a.

8a showed a complicated 15-line spectrum. In this case, the exchange interaction is comparable to the hyperfine coupling constant. This spectrum can be simulated by the superposition of two kinds of exchange interactions.⁹ The open-ring isomer of diarylethene has two atropisomers, which are parallel and antiparallel, and they should have different exchange interactions.¹⁰ The values were estimated to be $|2J/g\mu_B| = 24$ G ($|2J/k_B| = 0.0032$ K) and $|2J/g\mu_B| < 2$ G ($|2J/k_B| < 3 \times 10^{-4}$ K).

Although **8a** and **6a** have the same number of carbon atoms between two nitronyl nitroxides, the EPR spectrum of **8a** showed a stronger interaction than that of **6a**. The open-ring isomer of bis(2-thienyl)ethene has a delocalized π -conjugated system; therefore, it has a stronger interaction than bis(3-thienyl)ethene. Meanwhile, the closed-ring isomer **8b** had a five-line EPR spectrum. In this case, the exchange interaction is much smaller than the hyperfine coupling constant. The small interaction is due to the fact that the two nitronyl nitroxides are separated by four phenyl rings and by the sp^3 carbon and sulfur atoms.

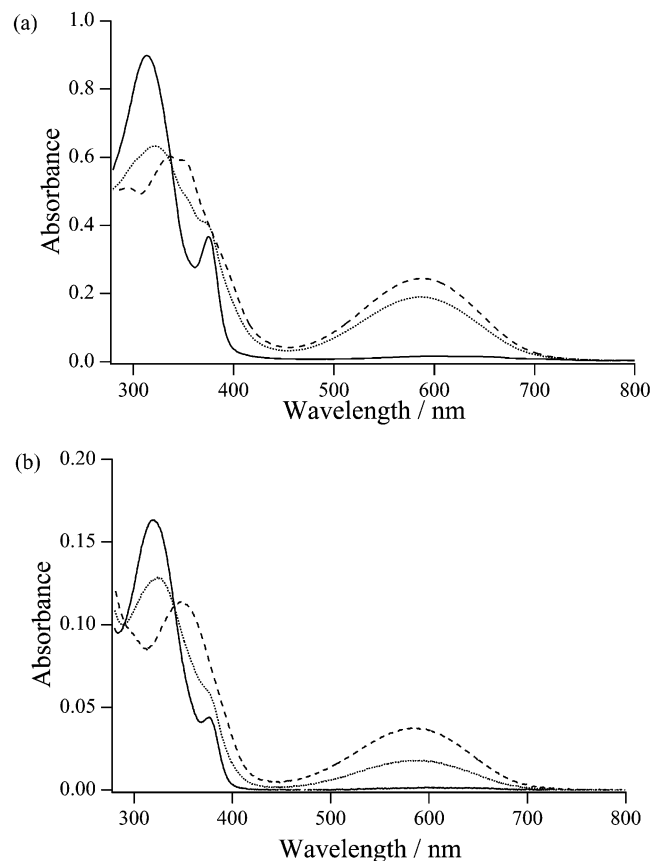


Figure 2. (a) UV-vis absorption spectra of **5** (2.6×10^{-5} M ethyl acetate solution): open-ring isomer **5a** (—), closed-ring isomer **5b** (---), and in the photostationary state under irradiation with 313-nm light (···). (b) UV-vis absorption spectra of **6** (2.6×10^{-6} M ethyl acetate solution): open-ring isomer **6a** (—), closed-ring isomer **6b** (---), and in the photostationary state under irradiation with 366-nm light (···).

The EPR spectral change and the estimated exchange interaction are summarized in Table 1 along with the absorption maxima. When a spacer of appropriate length was chosen, the change in the exchange interaction was detected by EPR. The exchange interaction change between the open- and closed-ring isomers is dependent on the substitution positions of the thiophene rings onto the ethene moiety. The closed-ring isomer has a larger interaction than the open-ring isomer in bis(3-thienyl)ethenes, whereas in bis(2-thienyl)ethenes, the open-ring isomer has a larger interaction. Although in both cases the closed-ring isomers had absorption maxima at longer wavelengths than the open-ring isomers, the magnetic interaction showed the reverse effect. This result indicates that the magnetic interaction and the absorption spectra have a different dependence on the π -conjugated structure. The bond alternation is connected throughout the molecule in both **6b** and **8a**, but **6b** had a stronger interaction than **8a**. This is attributable to the fact that the planarity of the closed-ring isomer **6b** is higher than that of **8a**.

Conclusions

Bis(3-thienyl)ethenes and bis(2-thienyl)ethenes having nitronyl nitroxide radicals at both ends of the molecule were synthesized, and the photochromic performance and EPR spectral change upon photoirradiation were investigated. Bis(3-thienyl)ethene diradicals underwent photochromic reactions by irradiation with UV and visible light. EPR spectral analysis

demonstrated that the exchange interaction changed more than 150-fold upon alternate irradiation with UV and visible light when an appropriate spacer was chosen. In the case of bis(2-thienyl)ethene diradicals, only cycloreversion reactions took place by irradiation with visible light. The closed-ring isomers of the diradicals were prepared from the closed-ring isomers of the precursors. When a biphenyl spacer was employed, it was found that the switching behavior is reversed by changing the substitution position of the thiophene rings to the ethene moiety. Although the bis(2-thienyl)ethene diradicals did not show reversibility, these results expand the possibility of using diarylethenes as photoswitching units in molecular devices.

Experimental Section

A. Materials. ^1H NMR spectra were recorded on Varian Gemini 200, Bruker AC-250P, and JEOL GSX-400 instruments. UV-vis spectra were recorded on a Hitachi U-3500 spectrophotometer. Mass spectra were obtained on JEOL JMS-HX110A and Applied Biosystems Voyager DE instruments. Melting points were not corrected.

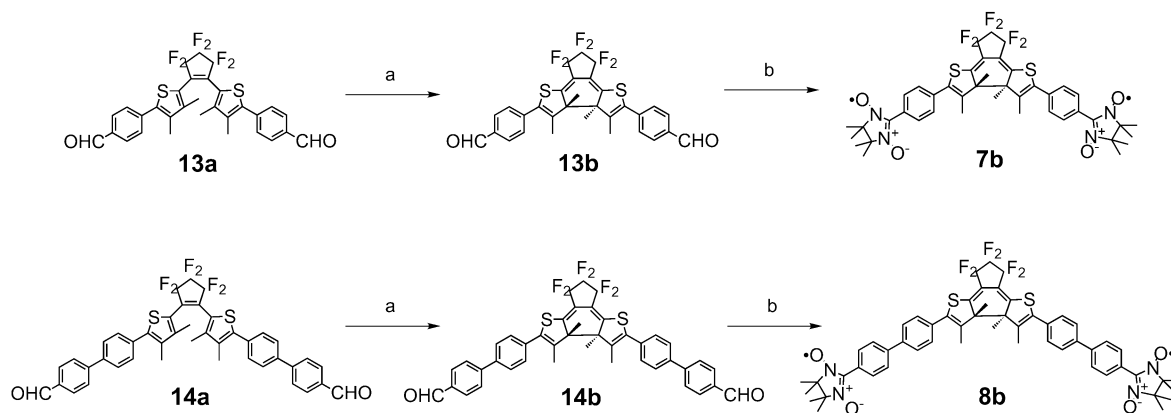
All reactions were monitored by thin-layer chromatography carried out on 0.2-mm E. Merck silica gel plates (60F-254). Column chromatography was performed on silica gel (E. Merck, 70–230 mesh).

1,2-Bis(5-formylphenyl)-2,4-dimethyl-3-thienylhexafluorocyclopentene (10). To a solution of **9** (400 mg, 0.62 mmol) in THF (10 mL) was added $\text{Pd}(\text{PPh}_3)_4$ (70 mg, 0.06 mmol), Na_2CO_3 (2.5 g), water (10 mL), and 4-formylphenylboronic acid (360 mg, 2.4 mmol). The reaction mixture was refluxed for 24 h and was then poured into water, extracted with Et_2O , washed with water, dried over magnesium sulfate, and concentrated. Column chromatography (silica, hexane/ Et_2O 3:1) gave diformyl compound **10** (290 mg, 78%) as a white powder: mp 143.9–145.7 °C; ^1H NMR (CDCl_3 , 250 MHz): δ 2.16 (s, 6H), 2.40 (s, 6H), 7.54 (d, $J = 8$ Hz, 4H), 7.90 (d, $J = 8$ Hz, 4H), 10.03 (s, 2H). Anal. Calcd for $\text{C}_{31}\text{H}_{22}\text{F}_6\text{O}_2\text{S}_2$: C, 61.58; H, 3.67. Found: C, 61.50; H, 3.84.

1,2-Bis[5-(4-(1-oxyl-3-oxide-4,4,5,5-tetramethylimidazolin-2-yl)phenyl)-2,4-dimethyl-3-thienyl]hexafluorocyclopentene (5a). A solution of **10** (1.4 g, 2.3 mmol), 2,3-bis-(hydroxyamino)-2,3-dimethylbutane sulfate (2.9 g, 12 mmol), and potassium carbonate (1.7 g, 12 mmol) in methanol (140 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 a yellow oil. Purification was not performed.

To a solution of tetrahydroxylamine in dichloromethane (300 mL) was added a solution of sodium periodate (1.7 g, 7.7 mmol) in water (300 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, chloroform/ $\text{AcOEt} = 10:1$). **5a** was obtained as dark-blue microcrystals (105 mg, 6%): mp 218.5–220.4 °C (dec); UV-vis (AcOEt) λ_{max} , nm (ϵ): 314 (3.5×10^4), 376 (1.5×10^4), 549 (sh), 600 (5.3×10^2), 645 (4.9×10^2), 718 (sh); EPR (benzene) 1:4:10:16:19:16:10:4:1, nine lines, $g = 2.006$, $a_N = 3.4$ G. Anal. Calcd for $\text{C}_{43}\text{H}_{44}\text{F}_6\text{N}_4\text{O}_4\text{S}_2$: C, 60.13; H, 5.16; N, 6.52. Found: C, 60.40; H, 5.43; N, 6.27.

Corresponding Closed-Ring Isomer 5b. UV-vis (AcOEt) λ_{max} , nm (ϵ): 294 (2.0×10^4), 337 (2.3×10^4), 352 (sh), 588 (9.5×10^3); EPR (benzene) 1:4:10:16:19:16:10:4:1, nine lines, $g = 2.006$, $a_N = 3.6$ G.

SCHEME 3^a

^a Reagents and conditions: (a) UV light ($340 \text{ nm} < \lambda < 440 \text{ nm}$), AcOEt. (b) 2,3-Dimethyl-2,3-bis(hydroxyamino)butane sulfate and methanol and then NaIO_4 and CH_2Cl_2 , 5–17%.

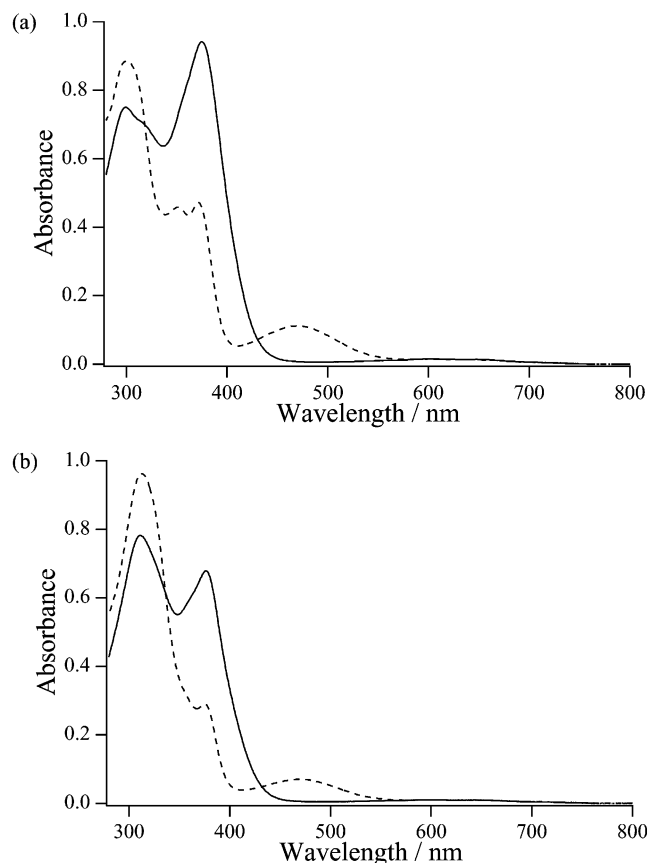
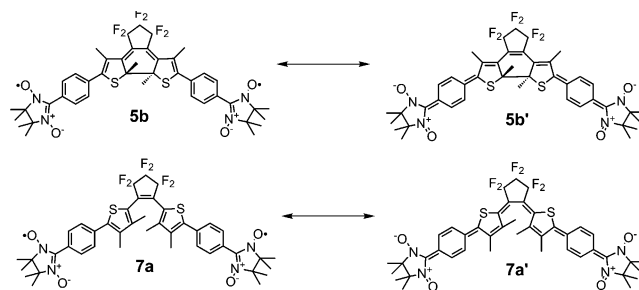


Figure 3. (a) UV-vis absorption spectra of **7** ($2.3 \times 10^{-5} \text{ M}$ ethyl acetate solution): open-ring isomer **7a** (—) and closed-ring isomer **7b** (---). (b) UV-vis absorption spectra of **8** ($1.4 \times 10^{-5} \text{ M}$ ethyl acetate solution): open-ring isomer **8a** (—) and closed-ring isomer **8b** (---).

1,2-Bis(5-(4-(4-formylphenyl)phenyl)-2,4-dimethyl-3-thienyl)hexafluorocyclopentene (11). To a solution of **9** (410 mg, 0.63 mmol) in THF (10 mL) was added 1.6 M *n*-butyllithium in hexane (0.9 mL, 1.6 mmol) at -78°C . After the mixture was stirred for 1 h at -78°C , tri-*n*-butylborate (0.8 mL, 3.0 mmol) was added. The solution was allowed to warm to 10°C with stirring. Water (3 mL) was added to the reaction mixture followed by the addition of $\text{Pd}(\text{PPh}_3)_4$ (80 mg, 0.07 mmol), Na_2CO_3 (2.4 g), water (10 mL), and 4-formyl-4'-iodobiphenyl (1.1 g, 3.6 mmol). The reaction mixture was refluxed for 12 h and then poured into water, extracted with Et_2O , washed with water,

SCHEME 4: Possible Resonant Quinoid Structure of **5b** and **7a**

dried over magnesium sulfate, and concentrated. Column chromatography (hexane/dichloromethane 20:1) gave compound **11** (100 mg, 21%) as a white wax: ^1H NMR (CDCl_3 , 200 MHz): δ 2.17 (s, 6H), 2.41 (s, 6H), 7.50 (d, $J = 8 \text{ Hz}$, 4H), 7.68 (d, $J = 8 \text{ Hz}$, 4H), 7.78 (d, $J = 8 \text{ Hz}$, 4H), 7.98 (d, $J = 8 \text{ Hz}$, 4H), 10.03 (s, 2H); FAB HRMS (m/z): $[\text{M}]^+$ calcd for $\text{C}_{43}\text{H}_{30}\text{F}_6\text{O}_2\text{S}_2$: 756.1591; found: 756.1596.

1,2-Bis[5-(4-(1-oxyl-3-oxide-4,4,5,5-tetramethylimidazolin-2-yl)phenyl)-2,4-dimethyl-3-thienyl]hexafluorocyclopentene (6a). A solution of **11** (100 mg, 0.13 mmol), 2,3-bis(hydroxyamino)-2,3-dimethylbutane sulfate (320 mg, 1.3 mmol), and potassium carbonate (180 mg, 1.3 mmol) in benzene (10 mL) and methanol (2 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 a yellow oil. Purification was not performed.

To a solution of tetrahydroxylamine in dichloromethane (30 mL) was added a solution of sodium periodate (85 mg, 0.40 mmol) in water (30 mL); the mixture was stirred for 15 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_2O 10:1). **6a** was obtained as a dark-green wax (40 mg, 30%): UV-vis (AcOEt) λ_{max} , nm (ϵ): 319 (6.4×10^4), 376 (1.8×10^4), 560 (sh), 599 (8.4×10^2), 650 (sh), 710 (sh); EPR (benzene) 1:2:3:2:1, five lines, $g = 2.007$, $a_N = 7.5 \text{ G}$; FAB MS (m/z): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{55}\text{H}_{53}\text{F}_6\text{N}_4\text{O}_4\text{S}_2$: 1011; found: 1011.

Corresponding Closed-Ring Isomer 6b. UV-vis (AcOEt) λ_{max} , nm (ϵ): 348 (4.4×10^4), 583 (1.5×10^4); EPR (benzene) 1:4:10:16:19:16:10:4:1, nine lines, $g = 2.007$, $a_N = 3.7 \text{ G}$.

1,2-Bis(5-iodo-3,4-dimethyl-2-thienyl)hexafluorocyclopentene (12). To a stirred solution of 1,2-bis(3,4-dimethyl-2-

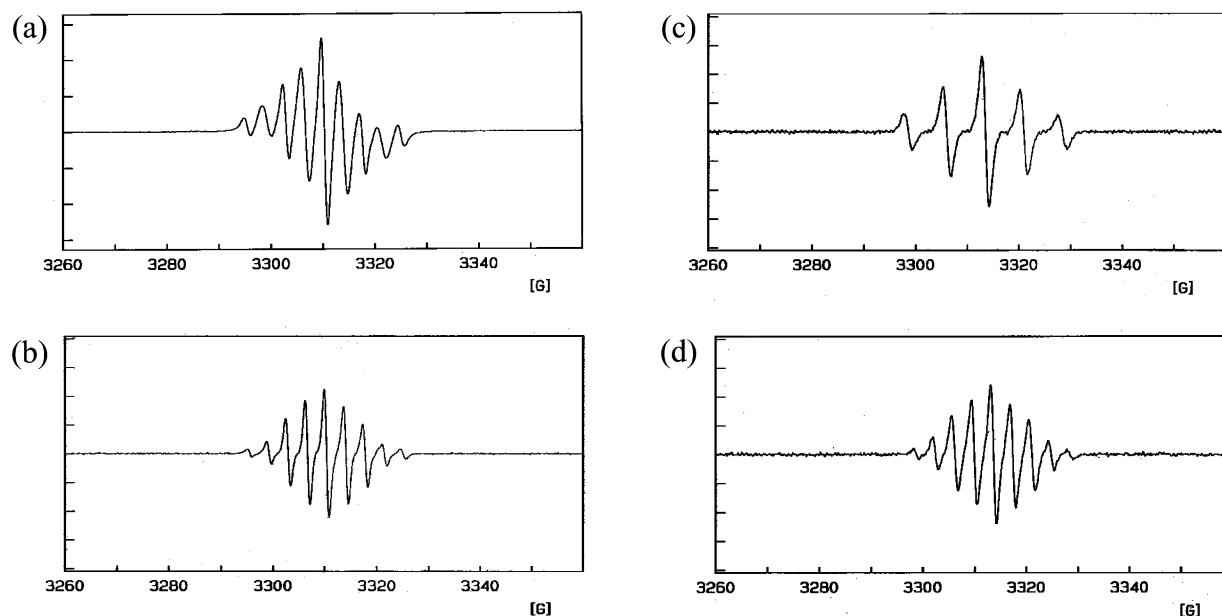


Figure 4. X-band EPR spectra of the diradical in benzene solution at room temperature (9.32 GHz). (a) **5a**. (b) **5b**. (c) **6a**. (d) **6b**.

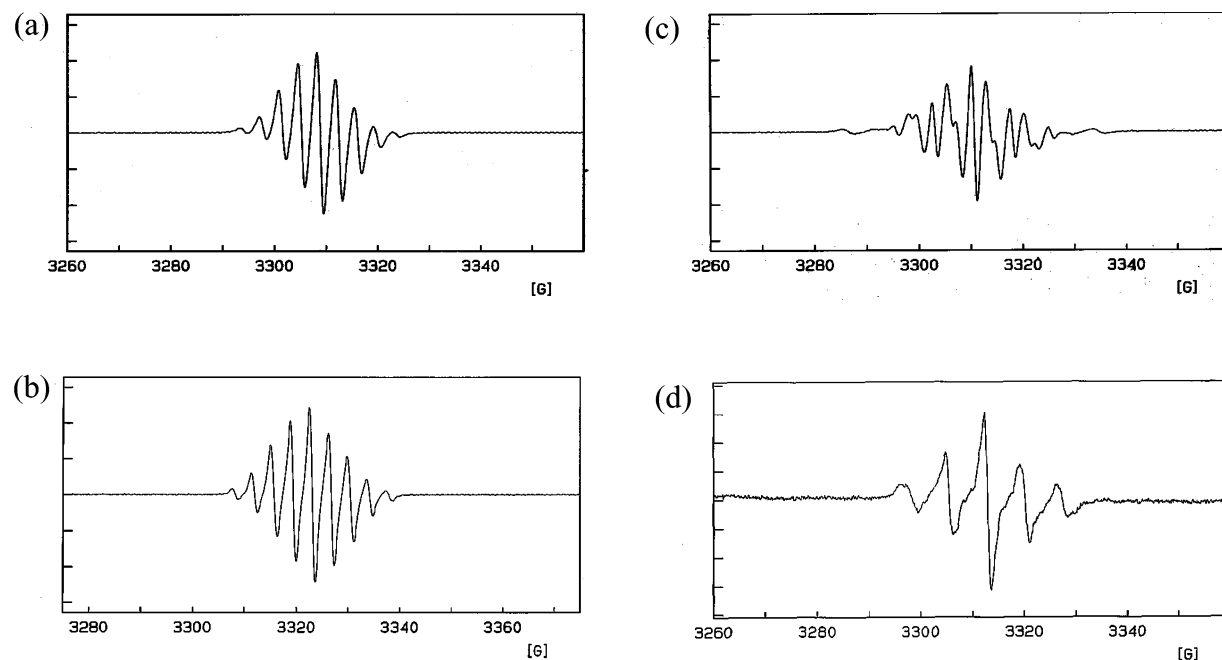


Figure 5. X-band EPR spectra of the diradical in benzene solution at room temperature (9.32 GHz). (a) **7a**. (b) **7b**. (c) **8a**. (d) **8b**.

TABLE 1: EPR Line Shapes and Exchange Interactions ($|2J/k_B \text{ K}|$) of Diradicals

open-ring isomer a			closed-ring isomer b		
EPR line	$ 2J/k_B \text{ K} $	$\lambda_{\text{max}}/\text{nm}$	EPR line	$ 2J/k_B \text{ K} $	$\lambda_{\text{max}}/\text{nm}$
shape			shape		
5 9 lines	>0.04	314	9 lines	>0.04	588
6 5 lines	$<3 \times 10^{-4}$	319	9 lines	>0.04	583
7 9 lines	>0.04	375	9 lines	>0.04	469
8 15 lines	0.0032, $<3 \times 10^{-4}$	377	5 lines	$<3 \times 10^{-4}$	467

thienyl)hexafluorocyclopentene (1.9 g, 4.8 mmol) in acetic acid (28 mL), sulfuric acid (5.2 mL), and water (12 mL) was added iodine (2.0 g, 7.9 mmol) and H_5IO_6 (0.8 g, 3.5 mmol), and the mixture was stirred for 5 h at 70 °C in the open air. The reaction mixture was poured into ice water and extracted with Et_2O , and the organic layer was washed with water, NaHCO_3 aqueous solution, and sodium thiosulfate aqueous solution and dried over

MgSO_4 . The solvent was evaporated, and the residue was purified by short-path column chromatography (silica, hexane). Diiodo compound **12** (2.2 g, 71%) was obtained as a yellow solid: mp 99.1–100.8 °C; ^1H NMR (CDCl_3 , 200 MHz): δ 1.75 (s, 6 H), 2.09 (s, 6 H); FAB HRMS (m/z): $[\text{M}]^+$ calcd for $\text{C}_{17}\text{H}_{12}\text{F}_6\text{I}_2\text{S}_2$: 647.8374; found: 647.8399.

1,2-Bis(5-(4-formylphenyl)-3,4-dimethyl-2-thienyl)hexafluorocyclopentene (13a). To a stirred solution of **12** (1.0 g, 1.5 mmol) in THF (15 mL) was added $\text{Pd}(\text{PPh}_3)_4$ (300 mg, 0.3 mmol), Na_2CO_3 (2.3 g), water (15 mL), and 4-formylphenylboronic acid (1.5 g, 10 mmol). The reaction mixture was refluxed for 30 h and then poured into water, extracted with Et_2O , washed with water, dried over magnesium sulfate, and concentrated. Column chromatography (silica, chloroform) gave diformyl compound **13a** (750 mg, 83%) as pale-yellow crystals: mp 151.3–152.9 °C; ^1H NMR (CDCl_3 , 200 MHz): δ 1.79 (s, 6 H), 2.20 (s, 6 H), 7.63 (d, $J = 7$ Hz, 4 H), 7.95 (d, $J = 8$

Hz, 4 H), 10.07 (s, 2 H); UV-vis (AcOEt) λ_{max} , nm: 301, 368; FAB HRMS (m/z): $[M+H]^+$ calcd for $C_{31}H_{23}F_6O_2S_2$: 605.1044; found: 605.1047. For the corresponding closed-ring isomer **13b**: UV-vis (AcOEt) λ_{max} , nm: 300, 476.

1,2-Bis[5-(4-(1-oxyl-3-oxide-4,4,5,5-tetramethylimidazolin-2-yl)phenyl)-3,4-dimethyl-2-thienyl]hexafluorocyclopentene (7a). A solution of **13a** (500 mg, 0.8 mmol), 2,3-bis(hydroxyamino)-2,3-dimethylbutane sulfate (1.0 g, 4.0 mmol), and potassium carbonate (0.8 g, 5.5 mmol) in methanol (20 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 a yellow oil. Purification was not performed.

To a solution of tetrahydroxylamine in dichloromethane (50 mL) was added a solution of sodium periodate (0.42 g, 2.0 mmol) in water (75 mL); the mixture was stirred for 15 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/Et₂O 1:1). **7a** was obtained as dark-green microcrystals (240 mg, 35%): mp 207 °C (dec); UV-vis (AcOEt) λ_{max} , nm (ϵ): 299 (3.2×10^4), 318 (sh), 375 (4.0×10^4), 556 (sh), 603 (6.1×10^2), 646 (5.7×10^2), 720 (sh); EPR (benzene) 1:4:10:16:19:16:10:4:1, nine lines, $g = 2.006$, $a_N = 3.6$ G. Anal. Calcd for $C_{43}H_{44}F_6N_4O_4S_2$: C, 60.13; H, 5.16; N, 6.52. Found: C, 60.45; H, 5.28; N, 6.54.

Corresponding Closed-Ring Isomer 7b. The following procedure was performed under red light. A solution of **13b** (100 mg, 0.17 mmol), 2,3-bis(hydroxyamino)-2,3-dimethylbutane sulfate (0.15 g, 0.61 mmol), and potassium carbonate (0.10 g, 0.72 mmol) in methanol (50 mL) was refluxed for 25 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 a yellow oil. Purification was not performed. To a solution of tetrahydroxylamine in dichloromethane (50 mL) was added a solution of sodium periodate (0.15 g, 0.70 mmol) in water (50 mL); the mixture stirred for 15 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, dichloromethane/Et₂O 1:1). **7b** was obtained as a brown wax (25 mg, 17%): UV-vis (AcOEt) λ_{max} , nm (ϵ): 300 (3.8×10^4), 351 (2.0×10^4), 372 (2.1×10^4), 469 (4.9×10^3); EPR (benzene) 1:4:10:16:19:16:10:4:1, nine lines, $g = 2.008$, $a_N = 3.6$ G; MALDI-TOF MS (m/z): $[M+H]^+$ calcd for $C_{43}H_{45}F_6N_4O_4S_2$: 859; found: 859.

1,2-Bis(5-(4-(4-formylphenyl)phenyl)-3,4-dimethyl-2-thienyl)hexafluorocyclopentene (14a). To a solution of **12** (500 mg, 0.75 mmol) in THF (10 mL) was added 1.6 M *n*-butyllithium in hexane (1.0 mL, 1.6 mmol) at -78 °C. After the mixture was stirred for 1 h at -78 °C, tri-*n*-butylborate (0.8 mL, 3.0 mmol) was added. The solution was allowed to warm to 10 °C with stirring. Water (3 mL) was added to the reaction mixture followed by the addition of Pd(PPh₃)₄ (80 mg, 0.07 mmol), Na₂CO₃ (2.4 g), water (10 mL), and 4-formyl-4'-iodobiphenyl (600 mg, 1.9 mmol). The reaction mixture was refluxed 12 h and then poured into water, extracted with Et₂O, washed with water, dried over magnesium sulfate, and concentrated. Column chromatography (hexane/dichloromethane = 9:1) gave compound **14a** (150 mg, 26%) as a yellow wax: ¹H NMR (CDCl₃, 400 MHz): δ 1.80 (s, 6H), 2.21 (s, 6H), 7.57 (d, $J = 8$ Hz, 4H), 7.71 (d, $J = 8$ Hz, 4H), 7.79 (d, $J = 8$ Hz, 4H), 7.98 (d, $J = 8$ Hz, 4H), 10.07 (s, 2H); UV-vis (AcOEt) λ_{max} , nm: 315, 367; MS (m/z): $[M]^+$ calcd for $C_{43}H_{30}F_6O_2S_2$: 756;

found: 756. Anal. Calcd for $C_{43}H_{30}F_6O_2S_2$: C, 68.24; H, 4.00. Found: C, 68.13; H, 4.07. Corresponding closed-ring isomer **14b**: UV-vis (AcOEt) λ_{max} , nm: 345, 468.

1,2-Bis[5-(4-(1-oxyl-3-oxide-4,4,5,5-tetramethylimidazolin-2-yl)phenyl)-3,4-dimethyl-2-thienyl]hexafluorocyclopentene (8a). A solution of **14a** (340 mg, 0.45 mmol), 2,3-bis(hydroxyamino)-2,3-dimethylbutane sulfate (800 mg, 3.2 mmol), and potassium carbonate (0.6 g, 4.3 mmol) in a mixed solvent of benzene (50 mL) and methanol (10 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 a yellow oil. Purification was not performed.

To a solution of tetrahydroxylamine in dichloromethane (50 mL) was added a solution of sodium periodate (0.4 g, 2.0 mmol) in water (80 mL); the mixture was stirred for 15 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/Et₂O 9:1). **8a** was obtained as a dark-green wax (100 mg, 21%): UV-vis (CH₂Cl₂) λ_{max} , nm (ϵ): 311 (5.6×10^4), 377 (5.2×10^4), 545 (sh), 597 (8.9×10^2), 630 (sh), 703 (sh); EPR (benzene) complicated 15 lines, $g = 2.007$. Anal. Calcd for $C_{55}H_{52}F_6N_4O_4S_2$: C, 65.35; H, 5.27; N, 5.53. Found: C, 65.33; H, 5.18; N, 5.54.

Corresponding Closed-Ring Isomer 8b. The following procedure was performed under red light. A solution of **14b** (140 mg, 0.19 mmol), 2,3-bis(hydroxyamino)-2,3-dimethylbutane sulfate (0.15 g, 0.61 mmol), and potassium carbonate (0.10 g, 0.72 mmol) in methanol (50 mL) and benzene (50 mL) was refluxed for 40 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 a yellow oil. Purification was not performed.

To a solution of tetrahydroxylamine in dichloromethane (100 mL) was added a solution of sodium periodate (0.15 g, 0.70 mmol) in water (100 mL); the mixture was stirred for 15 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, dichloromethane/Et₂O 1:1). **8b** was obtained as a brown wax (10 mg, 5.3%): UV-vis (AcOEt) λ_{max} , nm (ϵ): 313 (6.9×10^4), 376 (2.1×10^4), 467 (5.0×10^3), 602 (750); EPR (benzene) 1:4:10:16:19:16:10:4:1, nine lines, $g = 2.008$, $a_N = 7.5$ G. FAB HRMS (m/z): $[M+H]^+$ calcd for $C_{55}H_{53}F_6N_4O_4S_2$: 1011; found: 1011.

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 optical filters and monochromator (Ritsu MC-20L).

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

Acknowledgment. We thank Professor Paul M. Lahti and Professor B. Kirste for making the BIRADG program available to us. This work was supported by CREST of Japan Science and Technology Corporation and by a Grant-in Aid for Scientific Research on the Priority Area "Creation of Delocalized Electronic Systems" (no. 12020244) from the Ministry of Education, Science, Culture, and Sports, Japan.

References and Notes

- (1) Photocontrol of physical properties by photochromic molecules: (a) *Chem. Rev.* **2000**, 100(5); thematic issue on "Photochromism: Memories and Switches". (b) Brown, G. H. *Photochromism*; Wiley-Interscience: New York, 1971. (c) Dürr, H.; Bouas-Laurent, H. *Photochromism: Molecules and Systems*; Elsevier: Amsterdam, 1990. (d) Desvergne, J.-P.; Bouas-Laurent, H. *J. Chem. Soc., Chem. Commun.* **1978**, 403. (e) Shinkai, S. *Pure Appl. Chem.* **1987**, 59, 425. (f) Blank, M.; Soo, L. M.; Wasserman, N. H.; Erlanger, B. F. *Science (Washington, D.C.)* **1981**, 214, 70. (g) Irie, M.; Kato, M. *J. Am. Chem. Soc.* **1985**, 107, 1024. (h) Takeshita, M.; Irie, M. *J. Org. Chem.* **1998**, 63, 6643. (i) Irie, M.; Hirano, Y.; Hashimoto, S.; Hayashi, K. *Macromolecules* **1981**, 14, 262. (j) Irie, M. *Adv. Polym. Sci.* **1990**, 94, 27. (k) Irie, M. *Adv. Polym. Sci.* **1993**, 110, 49. (l) Ichimura, K.; Suzuki, Y.; Seki, T.; Hosoki, A.; Aoki, K. *Langmuir* **1988**, 4, 1214. (m) Ikeda, T.; Sasaki, T.; Ichimura, K. *Nature (London)* **1993**, 361, 428. (n) Atassi, Y.; Delaire, J. A.; Nakatani, K. *J. Phys. Chem.* **1995**, 99, 16320. (o) Gilat, S. L.; Kawai, S. H.; Lehn, J.-M. *J. Chem. Soc., Chem. Commun.* **1993**, 1439. (p) Gilat, S. L.; Kawai, S. H.; Lehn, J.-M. *Chem.—Eur. J.* **1995**, 1, 275. (q) Kawai, T.; Kunitake, T.; Irie, M. *Chem. Lett.* **1999**, 905. (r) Osuka, A.; Fujikane, D.; Shinmori, H.; Kobatake, S.; Irie, M. *J. Org. Chem.* **2001**, 66, 3913. (s) Irie, M.; Kobatake, S.; Horichi, M. *Science (Washington, D.C.)* **2001**, 291, 1769. (t) Maly, K.; Wand, M. D.; Lemieux, R. P. *J. Am. Chem. Soc.* **2002**, 124, 7898.
- (2) (a) Irie, M. *Chem. Rev.* **2000**, 100, 1685. (b) Irie, M.; Uchida, K. *Bull. Chem. Soc. Jpn.* **1998**, 71, 985.
- (3) (a) Iwamura, H. *Adv. Phys. Org. Chem.* **1990**, 26, 179. (b) Kahn, O. *Molecular Magnetism*; VCH: New York, 1993. (c) Rajca, A. *Chem. Rev.* **1994**, 94, 871.
- (4) Photocontrol of magnetic properties: (a) Decurtins, S.; Gülich, P.; Köhler, C. P.; Spiering, H.; Hauser, A. *Chem. Phys. Lett.* **1984**, 105, 1. (b) Hauser, A. *Chem. Phys. Lett.* **1986**, 124, 543. (c) Buchen, T.; Gülich, P.; Goodwin, H. A. *Inorg. Chem.* **1994**, 33, 4573. (d) Sato, O.; Iyoda, T.; Fujishima, A.; Hashimoto, K. *Science (Washington, D.C.)* **1996**, 272, 704. (e) Gu, Z.-Z.; Sato, O.; Iyoda, T.; Hashimoto, K.; Fujishima, A. *J. Phys. Chem.* **1996**, 100, 18289. (f) Boillot, M.-L.; Roux, C.; Audièr, J.-P.; Dausse, A.; Zarembowitch, J. *Inorg. Chem.* **1996**, 35, 3975. (g) Fujita, W.; Awaga, K. *J. Am. Chem. Soc.* **1997**, 119, 4563. (h) Hamachi, K.; Matsuda, K.; Itoh, T.; Iwamura, H. *Bull. Chem. Soc. Jpn.* **1998**, 71, 2937. (i) Létard, J.-F.; Guionneau, P.; Rabardel, L.; Howard, J. A. K.; Goeta, A. E.; Chasseau, D.; Kahn, O. *Inorg. Chem.* **1998**, 37, 4432. (j) Nakatsuji, S.; Ogawa, Y.; Takeuchi, S.; Akutsu, H.; Yamada, J.-i.; Naito, A.; Sudo, K.; Yasuoka, N. *J. Chem. Soc., Perkin Trans. 2* **2000**, 1969. (k) Hayami, S.; Gu, Z.-Z.; Shiro, M.; Einaga, Y.; Fujishima, A.; Sato, O. *J. Am. Chem. Soc.* **2000**, 122, 7126. (l) Breuning, E.; Ruben, M.; Lehn, J.-M.; Renz, F.; Garcia, Y.; Ksenofontov, V.; Gülich, P.; Wegelius, E. K.; Rissanen, K. *Angew. Chem., Int. Ed.* **2000**, 39, 2504. (m) Abe, J.; Sano, T.; Kawano, M.; Ohashi, Y.; Matsushita, M. M.; Iyoda, T. *Angew. Chem., Int. Ed.* **2001**, 40, 580. (n) Ratera, I.; Ruiz-Molina, D.; Vidal-Gancedo, J.; Wurst, K.; Daro, N.; Létard, J.-F.; Rivira, C.; Veciana, J. *Angew. Chem., Int. Ed.* **2001**, 40, 919. (o) Bénard, S.; Rivière, E.; Yu, P.; Nakatani, K.; Delouis, J. F. *Chem. Mater.* **2001**, 13, 159. (p) Bénard, S.; Léaustic, A.; Rivière, E.; Yu, P.; Clément, R. *Chem. Mater.* **2001**, 13, 3709. (q) Nakatsuji, S.; Ojima, T.; Akutsu, H.; Yamada, J.-i. *J. Org. Chem.* **2002**, 67, 916.
- (5) (a) Matsuda, K.; Irie, M. *Chem. Lett.* **2000**, 16. (b) Matsuda, K.; Irie, M. *J. Am. Chem. Soc.* **2000**, 122, 7195. (c) Matsuda, K.; Irie, M. *J. Am. Chem. Soc.* **2000**, 122, 8309. (d) Matsuda, K.; Matsuo, M.; Irie, M. *Chem. Lett.* **2001**, 436. (e) Matsuda, K.; Irie, M. *Chem.—Eur. J.* **2001**, 7, 3466. (f) Matsuda, K.; Irie, M. *J. Am. Chem. Soc.* **2001**, 123, 9896. (g) Matsuda, K.; Matsuo, M.; Irie, M. *J. Org. Chem.* **2001**, 66, 8799.
- (6) (a) Uchida, K.; Irie, M. *Chem. Lett.* **1995**, 969. (b) Uchida, K.; Matsuo, T.; Kobatake, S.; Yamaguchi, T.; Irie, M. *Tetrahedron* **2001**, 57, 4559.
- (7) (a) Brière, R.; Dupeyre R.-M.; Lemaire, H.; Morat, C.; Rassat, A.; Rey, P. *Bull. Soc. Chim. Fr.* **1965**, 11, 3290. (b) Glarum, S. H.; Marshall, J. H. *J. Chem. Phys.* **1967**, 47, 1374.
- (8) Although the magnetic susceptibility measurements could technically give direct information on the exchange interaction, the interaction in our system was too small to be measured accurately. See ref 5e.
- (9) Kriste, B. *Anal. Chim. Acta* **1992**, 265, 191.
- (10) Irie, M.; Lifka, T.; Kobatake, S.; Kato, N. *J. Am. Chem. Soc.* **2000**, 122, 4781.