Photochromism of Diarylethenes with Two Nitronyl Nitroxides: Photoswitching of an Intramolecular Magnetic Interaction

Kenji Matsuda* and Masahiro Irie*[a]

Abstract: Photochromic diarylethenes that have *p*-phenylene-substituted benzothiophene aryl groups with and without nitronyl nitroxide radicals at both ends of the molecules were synthesized. The absorption maxima of the closed-ring isomers showed a hypsochromic shift with the increase in the π-conjugated chain length. The unique behavior was attributed to the stabilization by the resonant quinoid structures. Both photocyclization and photocycloreversion quantum yields of the diarylethene with nitronyl nitroxide radicals were found to increase with the increase in the π-conjugated chain length. Photoswitching of the magnetic interaction between two nitronyl nitroxide radicals was studied by means of ESR spectroscopy. The change in exchange interaction between open- and closed-ring isomers of 1,2-bis{6-{4-[4-(1-oxyl-3-oxide-4,4,5,5-tetramethylimidazolin-2-yl)phenyl]phenyl}-2-methyl-1-benzothiophen-3-yl}hexafluorocyclopentene was determined to be more than 30-fold.

Keywords: EPR spectroscopy · magnetic properties · photochemistry · photochromism · pi-conjugated chain

Introduction

Photochromic compounds reversibly change their molecular properties upon photoirradiation, such as absorption and fluorescence spectra, refractive indices, geometrical structures, dielectric constants, oxidation/reduction potentials, and chiroptical properties. These property changes have been widely used to switch the physical and chemical functions of molecular systems that contain photochromic units.[1] Although various types of photochromic compounds have been so far adopted as the switching units, diarylethenes are among the most promising compounds for molecular-scale memory and switch devices, because of their fatigue-resistant and thermally irreversible photochromic performance.[2] The open- and closed-ring isomers of the diarylethenes are substantially different in electronic and geometrical structures. The most striking difference is that while the π systems of the two aryl rings are separated in the open-ring isomer, the closed-ring isomer has olefinic electronic structure and the two π systems are connected to each other and delocalize throughout the molecule.

When two unpaired electrons are placed at both ends of a π-conjugated chain, the two spins of the unpaired electrons interact magnetically.[3] If the π-conjugated chain length can be switched by using a photochromic spin coupler, the magnetic interaction can be controlled upon photoirradiation.[4] For this purpose, diarylethenes are very effective because the π-conjugated chain length is switched by the photoirradiation (Figure 1). So far we have reported the photoswitching of intramolecular magnetic interaction using diarylethene spin couplers evidenced by several methods, that is, temperature dependence of the magnetic susceptibilities,[5] temperature dependence of the ESR signal intensities at cryogenic temperatures,[5] and ESR spectral change at room temperature.[6] During the course of this study it was found that the photochromic reactivity was affected by the introduction of the radical moiety.[7] The cycloreversion reaction of the diarylethenes with two nitronyl nitroxide radicals was remarkably suppressed due to the contribution of the resonant quinoid structure in the closed-ring isomer.

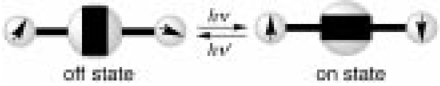

Figure 1. Photoswitching of magnetic interaction.

In this work, we have synthesized several photochromic diarylethenes that have different π-conjugated chain lengths with and without nitronyl nitroxides and studied the photoswitching of the magnetic interaction between two nitronyl nitroxide radicals by an ESR method. Their photochromic reactivity was also investigated.

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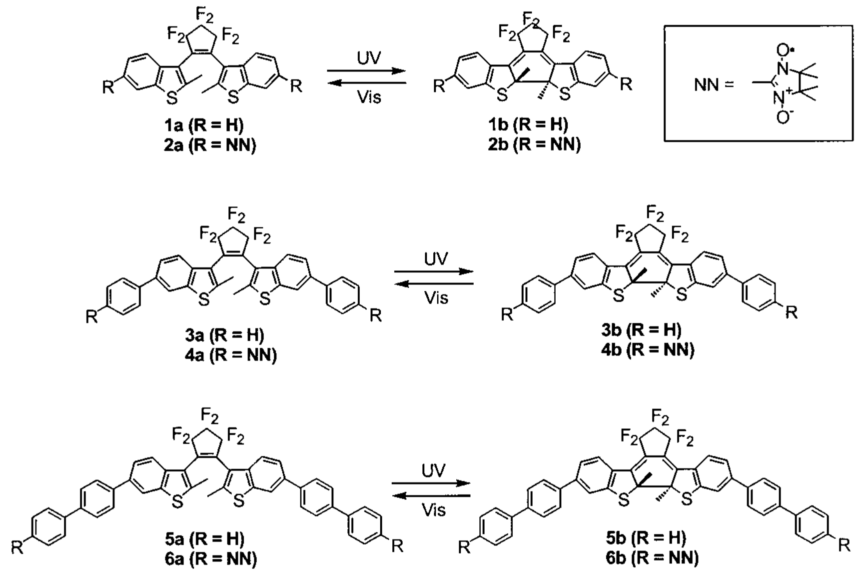
Results and Discussion

Molecular design and synthesis: For the core photochromic spin coupler we chose 1,2-bis(2-methyl-1-benzothiophen-3-yl)perfluorocyclopentene, which is one of the most robust photochromic units. One or two *p*-phenylene spacers were introduced at the both ends. Nitronyl nitroxide was used as the spin source because the radical is π-conjugative. The molecules synthesized are listed in Scheme 1.

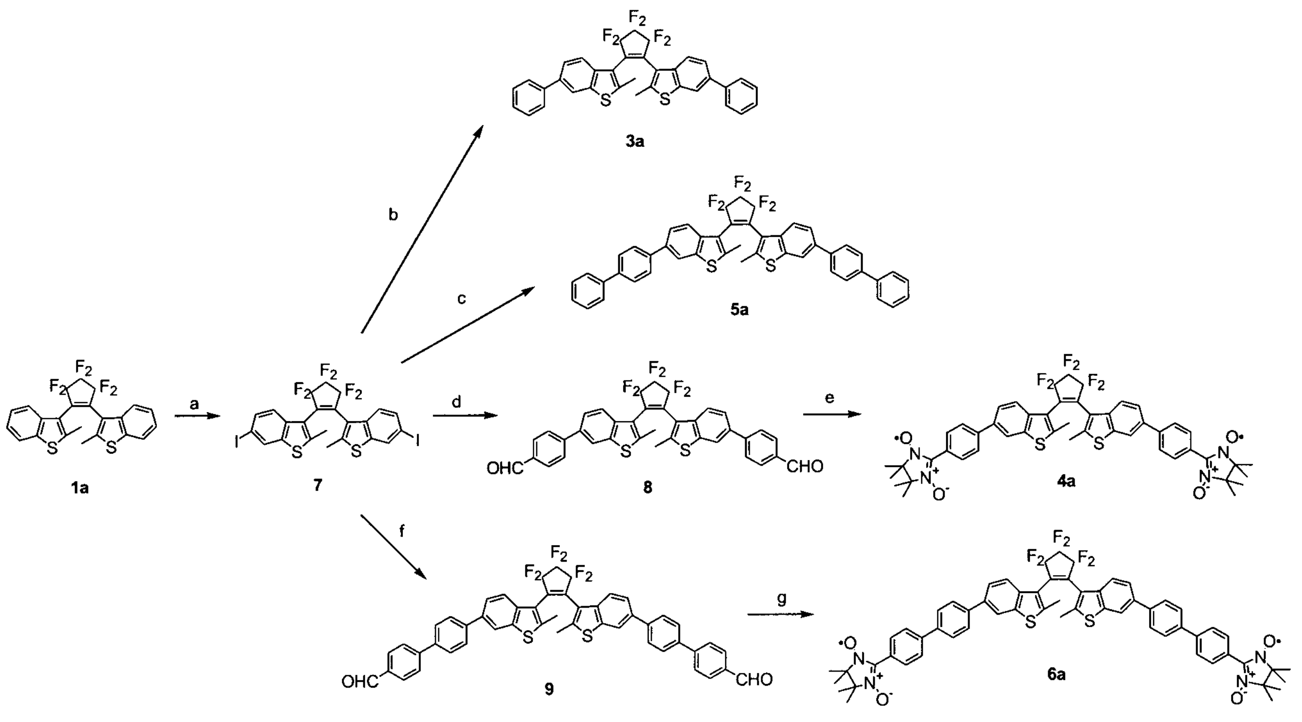
Nitronyl nitroxide itself has two identical nitrogen atoms to give a five-line ESR spectrum with relative intensities 1:2:3:2:1 and a 7.5 G spacing. When two nitronyl nitroxides are magnetically coupled with an exchange interaction, the diradical gives a nine-line ESR spectrum with relative intensities 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 spectrum that is the same as the independent monoradical. In intermediate situations the spectrum becomes complex.[8]

In a previous report we found that the antiferromagnetic interaction between two nitronyl nitroxides remarkably increased from $2J/k_B = -2.2$ K to $2J/k_B = -11.6$ K upon photoirradiation when the nitronyl nitroxides are introduced to both ends of **2** (Scheme 1), while any photoinduced ESR spectral change was not observed, because the exchange interaction between the two radicals was much stronger than the hyperfine coupling constant.[5b] To decrease the intramolecular magnetic interaction it is effective to elongate the π-conjugated chain.

Compounds **3a**–**6a** were synthesized according to Scheme 2. The synthesis of **1a** and **2a** has been described previously.[5b, 9] Diiodo compound **7** was used as a common inter-



Scheme 1. Photochromic diarylethenes with two nitronyl nitroxides.



Scheme 2. Reagents and conditions: a) I_2, H_5IO_6, H_2SO_4, AcOH, H_2O, 76%. b) [Pd(PPh_3)$_4$], phenylboronic acid, Na_2CO_3, THF, H_2O, 29%. c) [Pd(PPh_3)$_4$], 4-biphenylboronic acid, Na_2CO_3, THF, H_2O, 32%. d) [Pd(PPh_3)$_4$], 4-formylphenylboronic acid, Na_2CO_3, THF, H_2O, 49%. e) 2,3-Dimethyl-2,3-bis(hydroxyamino)butane sulfate, methanol then $NaIO_4$, CH_2Cl_2, 13%. f) *n*-BuLi, B(OBu)$_3$, [Pd(PPh_3)$_4$], 4-formyl-4′-iodobiphenyl, Na_2CO_3, THF, H_2O, 60%. g) 2,3-Dimethyl-2,3-bis(hydroxyamino)butane, benzene/methanol, $NaIO_4$, CH_2Cl_2, 15%.

mediate for the syntheses of **3a**–**6a**. Suzuki coupling of **7** with phenylboronic acid, 4-biphenylboronic acid, and 4-formylphenylboronic acid afforded **3a**, **5a**, and **8**, respectively. Transformation of **7** to diboronic acid followed by Suzuki coupling with 4-formyl-4′-iodobiphenyl gave diformyl compound **9**. The diformyl compounds were transformed to the bis(nitronyl nitroxide) derivatives. It should be noted that diarylethene skeleton is so persistent that many chemical transformations can be applied. This is an advantage of diarylethenes as building blocks of functional molecules. For all compounds, the structures were confirmed by NMR and ESR spectroscopy, and elementary analysis or mass spectrometry.

Photochromic reaction: All synthesized diarylethenes **1a**–**6a** underwent reversible photochromic reactions in ethyl acetate by alternative irradiation with 313 nm UV light and 578 nm visible light with retention of isosbestic points. Figures 2 and 3 illustrate absorption spectra of the open- and closed-ring isomers, and of the photostationary state under irradiation with 313 nm light for **3**–**6**. The color of the solutions changed from colorless (**1a**, **3a**, and **5a**) or pale blue (**2a**, **4a**, and **6a**) to red-purple (**1b**–**6b**). Although nitronyl nitroxide has absorption around 550–700 nm, it did not prohibit the photochromic reactions. Absorption maxima and coefficients of the open- and closed-ring isomers are summarized in Tables 1 and 2.

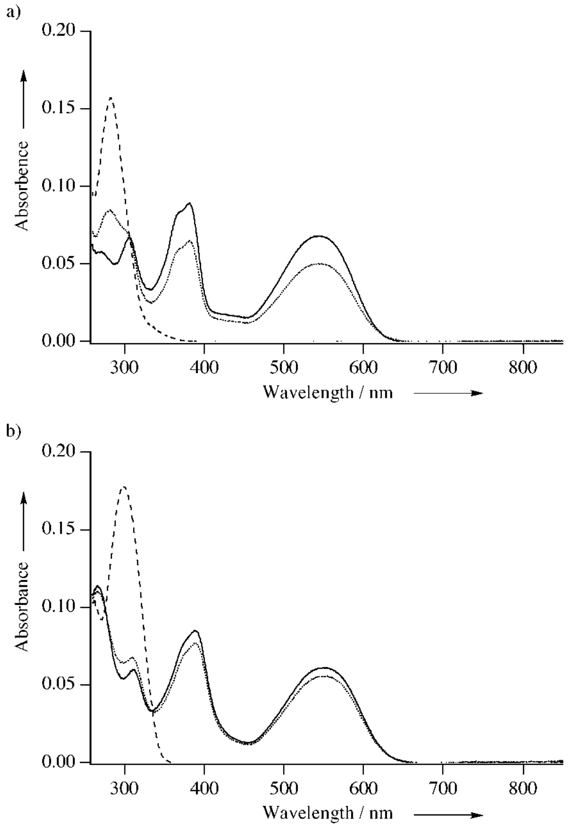


Figure 2. Absorption spectral changes of a) **3** (3.3×10^{-6} M) and b) **5** (2.6×10^{-6} M) in ethyl acetate solution by photoirradiation: (solid line) open-ring isomer, (dashed line) closed-ring isomer, and (dotted line) in the photostationary state under irradiation with 313 nm light.

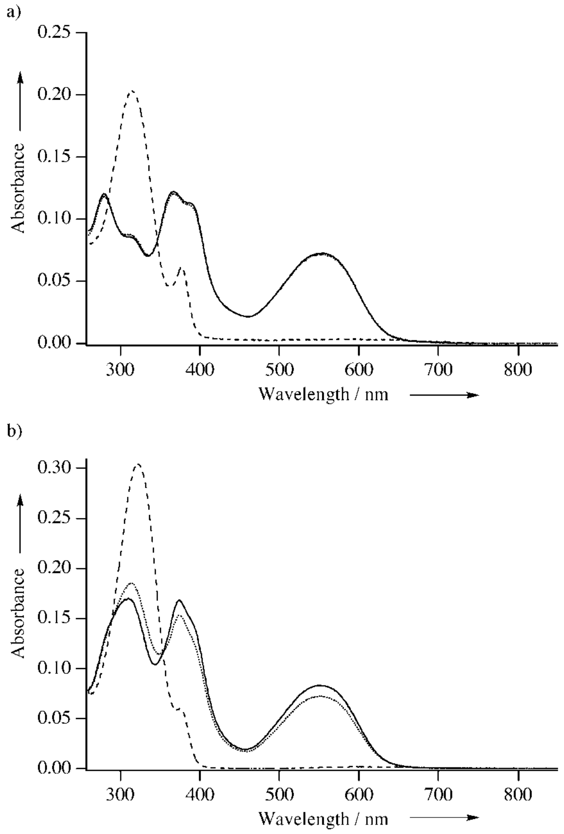


Figure 3. Absorption spectral changes of a) **4** (2.8×10^{-6} M) and b) **6** (2.9×10^{-6} M) in ethyl acetate solution by photoirradiation: (solid line) open-ring isomer, (dashed line) closed-ring isomer, and (dotted line) in the photostationary state under irradiation with 313 nm light.

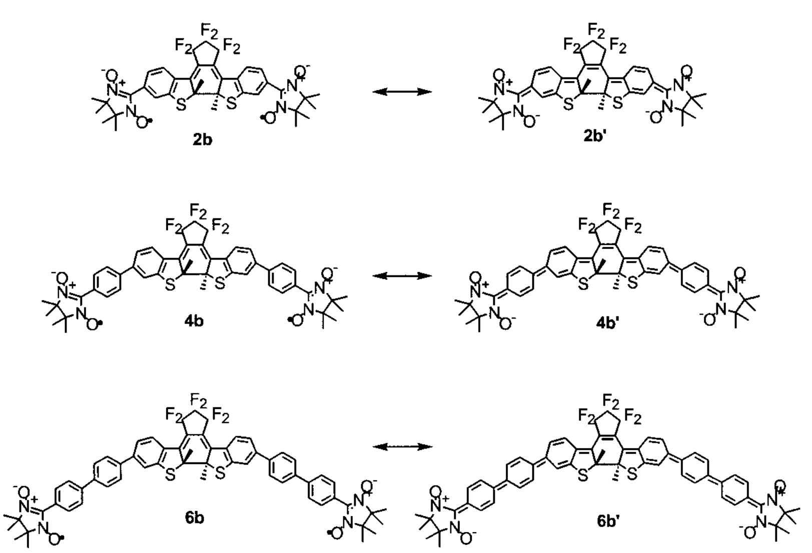
Table 1. Absorption maxima and coefficients of the open-ring isomers **1a**–**6a** in ethyl acetate.

	λ_{max} [nm] (ε [$M^{-1}cm^{-1}$])
1a	258 (16000), 290 (6200), 299 (6800)
2a	309 (34000), 377 (16000), 553 (sh), 598 (630), 646 (630), 706 (sh)
3a	284 (48000)
4a	313 (76000), 377 (22000), 555 (sh), 600 (790), 644 (740), 718 (sh)
5a	298 (69000)
6a	320 (104000), 375 (sh), 550 (sh), 601 (720), 647 (690), 720 (sh)

Table 2. Absorption maxima and coefficients of the closed-ring isomers **1b**–**6b** in ethyl acetate.

	λ_{max} [nm] (ε [$M^{-1}cm^{-1}$])
1b	276 (14000), 352 (12000), 523 (10000)
2b	280 (17000), 348 (19000), 385 (sh), 400 (20000), 565 (15000)
3b	307 (20000), 381 (27000), 543 (21000)
4b	280 (43000), 367 (44000), 553 (26000)
5b	313 (23000), 389 (33000), 549 (24000)
6b	311 (58000), 374 (58000), 548 (28000)

The absorption maxima of the diarylethenes without radicals (**1**, **3**, and **5**) shifted to longer wavelengths with increasing π-conjugated chain length in both open- and closed-ring isomers. On the other hand, in the case of diarylethenes with two nitronyl nitroxide radicals (**2**, **4**, and **6**) the visible absorption maxima of the closed-ring isomers showed a hypsochromic shift with the increase in the chain length. This phenomenon is attributed to the fact that the contribution of the resonant quinoid structure becomes smaller as the chain length becomes longer (Scheme 3). The absorption spectrum of the visible band of **6b** is similar to that of **5b**. This indicates that the contribution of the resonant quinoid structure **6b**′ shown in Scheme 3 is very small in the closed-ring isomer.



Scheme 3. The resonant stabilization of the closed-ring isomers with two nitronyl nitroxide radicals.

Quantum-yield measurements: The quantum yields of cyclization and cycloreversion reactions of **3**–**6** were measured in ethyl acetate by using **1** as a reference.[10] The conversions under irradiation with 313 nm light were determined by comparing the UV-visible spectra of the isolated closed-ring isomers and the sample at the photostationary state. The results are summarized in Table 3.

Table 3. The quantum yields and conversions of cyclization and cycloreversion reactions in ethyl acetate.

	Cyclization (313 nm)		Cycloreversion[a] (517 nm)
	Φ	Conversion	Φ
1	0.31[b]	0.43[b]	0.28[b]
2	0.040[b]	1.00[b]	0.0010[b]
3	0.31	0.74	0.14
4	0.10	0.99	0.012
5	0.49	0.91	0.14
6	0.13	0.87	0.062

[a] For all compounds the conversions of the cycloreversion reaction were 1.00. [b] Taken from ref. [5b].

The quantum yields of the cyclization reactions of the diarylethenes with two nitronyl nitroxide radicals increased from 0.040 to 0.13 with the increase in the π-conjugated chain length. The energy transfer from the central diarylethene to the radical moiety is considered to reduce the quantum yield of **2a**. More interestingly, it is clearly shown that the cycloreversion quantum yield increased from 0.0010 to 0.062 with increasing the π-conjugated chain length. In this case besides the effect of the energy transfer, the contribution of the resonant quinoid structure of **2b**′ to the closed-ring isomer is considered to suppress the cycloreversion reaction.

The conversion in the photostationary state was also dependent on the chain length. In the case of diarylethenes without radicals, the conversions increased with the increase in the chain length. In contrast, in the case of diarylethenes with two nitronyl nitroxide radicals, the longer chain length gave smaller conversions. Since the conversions are related to the quantum yields by Equation (1), the difference in conversions originates from the difference in the quantum yields. The calculated conversions agreed well with the experimental values.

$$\text{conversion}_{\mathrm{O}\rightarrow\mathrm{C}} = \frac{\Phi_{\mathrm{O}\rightarrow\mathrm{C}}\varepsilon_{\mathrm{O}}}{\Phi_{\mathrm{O}\rightarrow\mathrm{C}}\varepsilon_{\mathrm{O}} + \Phi_{\mathrm{C}\rightarrow\mathrm{O}}\varepsilon_{\mathrm{O}}} \qquad (1)$$

Switching of ESR spectra: The changes in the ESR spectra along with the photochromism were examined in diarylethenes **4** and **6**. A solution of **4a** in benzene was irradiated with UV or visible light in the ESR cavity and their ESR spectral changes were measured at room temperature. Figure 4 shows the ESR spectra at different stages of the photochromic reaction. The ESR spectrum of **4a** is complex with 15 lines. This result suggests that the two spins of nitronyl nitroxide radicals are coupled by the exchange interaction that is comparable to the hyperfine coupling constant. Upon

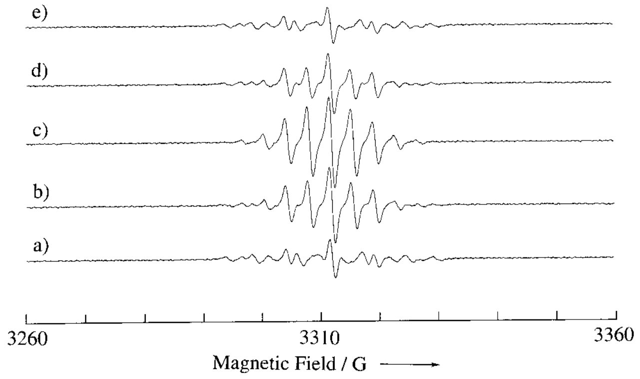


Figure 4. X-band ESR spectra measured at room temperature at different stages of the photochromic reaction starting from open-ring isomer **4a** (1.1×10^{-4} M benzene solution, 9.32 GHz). a) Initial, b) after irradiation with 366 nm light for 1 min, c) 4 min, d) after irradiation with $\lambda > 520$ nm light for 20 min, e) 50 min.

irradiation with 366 nm light, the signal of nine lines at the center grew, and after four minutes the spectrum reached the photostationary state. The nine-line spectrum corresponds to the closed-ring isomer **4b**. The spectrum indicates that the exchange interaction between the two spins in **4b** is much larger than the hyperfine coupling constant.

At the photostationary state the 15-line spectrum originating from **4a** disappeared; this is consistent with the high conversion as observed in the UV-visible absorption spectral changes upon UV irradiation. When the sample was irradiated with $\lambda > 520$ nm light, the spectrum returned to the original one. 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 (Figure 5). This also indicates that the closed-ring isomer maintains the biradical character and so the contribution of the mesomeric form **4b′** is very small.

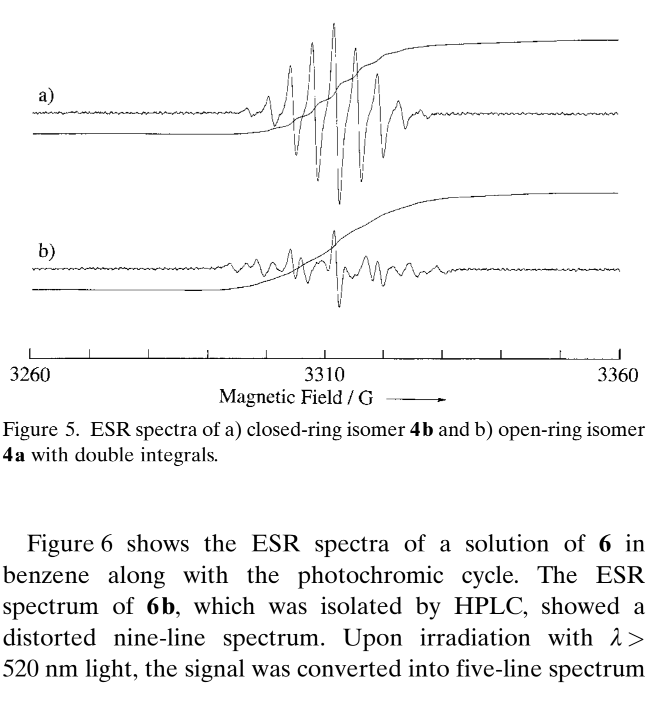


Figure 5. ESR spectra of a) closed-ring isomer **4b** and b) open-ring isomer **4a** with double integrals.

Figure 6 shows the ESR spectra of a solution of **6** in benzene along with the photochromic cycle. The ESR spectrum of **6b**, which was isolated by HPLC, showed a distorted nine-line spectrum. Upon irradiation with $\lambda >$ 520 nm light, the signal was converted into five-line spectrum and after two minutes there were no additional signals. This five-line spectrum corresponds to the open-ring isomer **6a**. This spectrum indicates that the exchange interaction between the two spins in **6a** is much smaller than the hyperfine coupling constant. Then the sample was irradiated with 366 nm light. After ten minutes the sample reached the photostationary state. The spectrum in the photostationary state was very similar but not identical to that of closed-ring isomer **6b**. This is because the cyclization conversion in the photostationary state was 87 %. The cycle could be repeated several times. The open-ring isomer **6a**, the closed-ring isomer **6b**, and the sample in the photostationary state had same signal intensity determined by the double integral of the spectra, indicating the conservation of the total number of the spins (Figure 7).

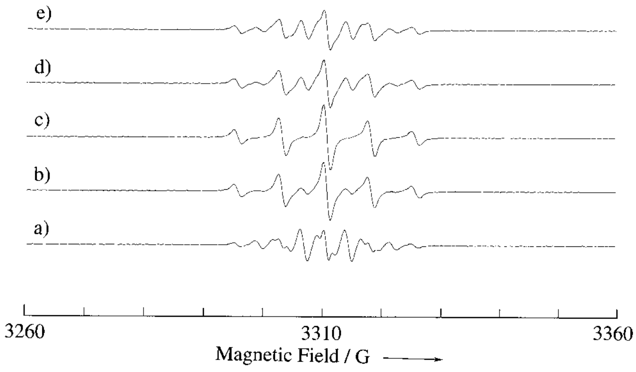


Figure 6. X-band ESR spectra measured at room temperature at different stages of the photochromic reaction starting from closed-ring isomer **6b** (1.9×10^{-4} M benzene solution, 9.32 GHz). a) Initial, b) after irradiation with $\lambda > 520$ nm light for 1 min, c) 2 min, d) after irradiation with 366 nm light for 1 min, e) 10 min.

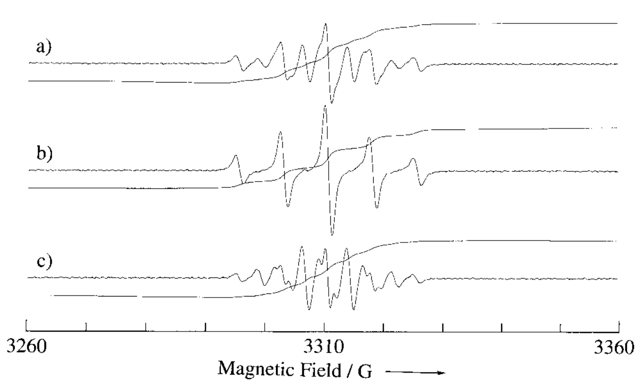


Figure 7. ESR spectra of a) **6** in the photostationary state under irradiation with 366 nm light, b) open-ring isomer **6a**, and c) closed-ring isomer **6b** with double integrals.

The simulation of the ESR spectra was performed by using the BIRADG program written by Dr. B. Kirste[11] in order to estimate the exchange interaction. The nine-line spectrum of **4b** and five-line spectrum of **6a** were reproduced as $|2J/g\mu_B| > 300$ G ($|2J/k_B| > 0.04$ K) and $|2J/g\mu_B| < 2$ G ($|2J/k_B| < 3 \times 10^{-4}$ K), respectively. The ESR spectra of **4a** and **6b** were complicated because the exchange interactions were comparable to the hyperfine coupling constants. Even in such cases, the simulation of the spectra can afford the value of the exchange interaction. Figure 8 shows the experimental and simulated spectra of **4a** and **6b**. The ESR spectrum of **6b** was reproduced with an exchange interaction of $|2J/g\mu_B| = 76$ G ($|2J/k_B| = 0.010$ K).

In the case of **4a**, two kinds of exchange interaction were required 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, which are parallel and antiparallel conformers, in the NMR timescale (Figure 9).[12] The parallel and antiparallel isomers should have different exchange interactions between spins. The ratio between parallel and antiparallel conformers was 35:65 for 1,2-bis(2-methyl-1-benzothiophen-3-yl)perfluorocyclopentene. By taking this ratio into account, the exchange interaction was determined to be $|2J/g\mu_B| = 9.0$ G ($|2J/k_B| = 1.2 \times 10^{-3}$ K) for the antiparallel conformer and $|2J/g\mu_B| < 2$ G ($|2J/k_B| < 3 \times 10^{-4}$ K) for the parallel conformer.

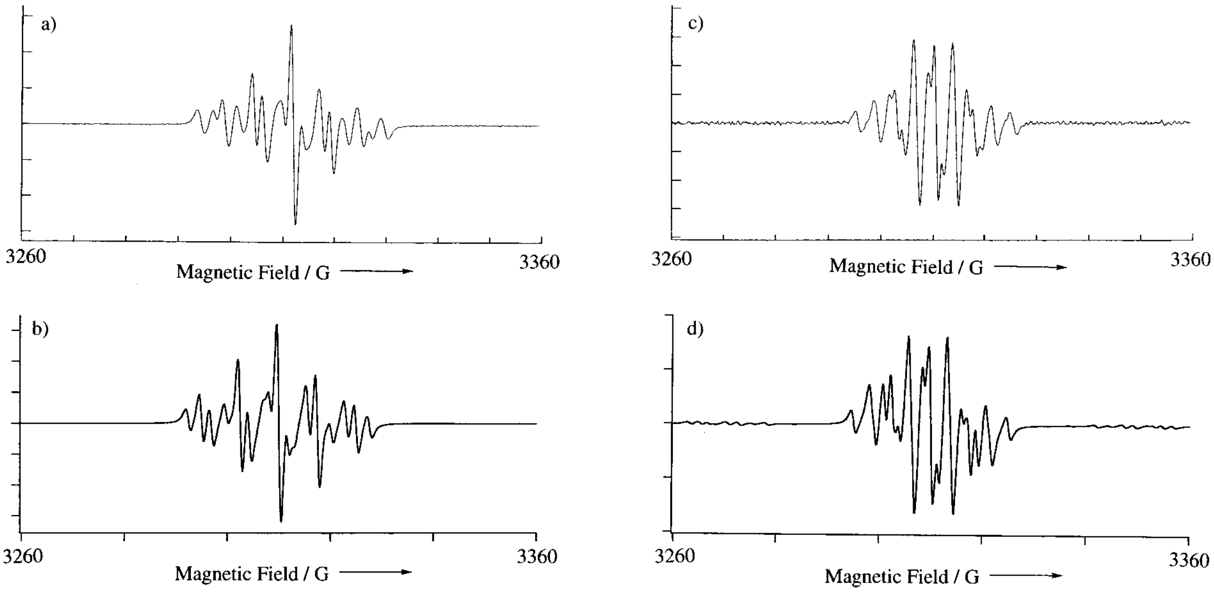


Figure 8. a) ESR spectra of open-ring isomer **4a** (1.1×10^{-4} M benzene solution, 9.32 GHz). b) Simulated spectrum of **4a** (see text). c) ESR spectra of open-ring isomer **6b** (1.9×10^{-4} M benzene solution, 9.32 GHz). d) Simulated spectrum of **6b** (see text).

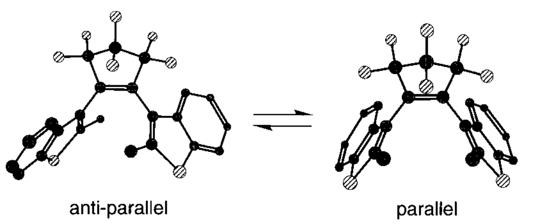


Figure 9. Parallel and antiparallel conformations of an open-ring isomer of 1,2-bis(2-methyl-benzothiophen-3-yl)perfluorocyclopentene.

The simulation of the ESR spectra does not afford the sign of the exchange interaction, that is, whether the interaction is ferromagnetic or antiferromagnetic. A spin polarization model suggested that all the interactions in **2**, **4**, and **6** were antiferromagnetic. The SQUID measurement of **2a** and **2b** showed antiferromagnetic interaction between spins. Based on these results we can infer all the interactions are antiferromagnetic. In this photoswiching, the sign of the interaction did not changed.

Table 4 lists the exchange interaction between two nitronyl nitroxide radicals bridged by diarylethenes. The exchange interaction decreases with increasing π-conjugated chain length. By incorporating *p*-phenylene spacers, the interaction could be detected by ESR spectroscopy. For all three diradicals closed-ring isomers have stronger interaction than open-ring isomers. The exchange interaction change in **2** was only fivefold, while more than 30-fold change was observed in **6**. Although the SQUID measurement is not sensitive for the weakly coupled diradicals, the value of the exchange interaction could be precisely determined by simulating the ESR spectrum of the diradical, in which the exchange interactions are comparable to the hyperfine coupling constants. The intrinsic change between open- and closed-ring isomers was estimated to be more than 30-fold. This result shows a very large switching effect of diarylethenes and consolidates the superiority of diarylethenes as molecular switching units. Although the absolute value of the exchange interaction is small, the information of the spins can be clearly transmitted through the closed-ring isomer and the switching can be detected by ESR spectroscopy.

Table 4. The change of the ESR line shapes and exchange interactions ($|2J/k_BK|$) between the open- and closed-ring isomers.

	Open-ring isomer		Closed-ring isomer	
	ESR line shape	$\lvert 2J/k_BK \rvert$	ESR line shape	$\lvert 2J/k_BK \rvert$
2	9 lines[a]	2.2[a,b]	9 lines[a]	11.6[a,b]
4	15 lines	1.2×10^{-3}, $< 3 \times 10^{-4}$	9 lines	> 0.04
6	5 lines	$< 3 \times 10^{-4}$	distorted 9 lines	0.010

[a] Taken from ref. [5b]. [b] Determined by magnetic susceptibility measurement.

Conclusion

The diarylethenes with open-shell radical moieties were synthesized and investigated photochemically and magnetochemically. It was proved that the photoreactivity was perturbed by incorporating the open-shell moieties into the diarylethenes. The photocycloreversion quantum yields of the closed-ring isomers with two radicals was strongly suppressed by the resonant quinoid structure. The considerably large ESR spectral change, as large as 30-fold, upon photoirradiation was observed due to the change in the exchange interaction.

Experimental Section

Materials: ^{1}H NMR spectra were recorded on a Varian Gemini 200 and JEOL GSX400 instruments. UV-visible 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 Merck silica gel plates (60F-254). Column chromatography was performed on silica gel (Merck, 70–230 mesh).

1,2-Bis(6-iodo-2-methyl-1-benzothiophen-3-yl)hexafluorocyclopentene (7): Iodine (1.2 g, 4.0 mmol) and H_5IO_6 (0.39 g, 1.5 mmol) was added to a stirred solution of **1a** (2.0 g, 4.3 mmol) in acetic acid (150 mL), sulfuric acid (3 mL), and water (7 mL), and the mixture was stirred for 3 h at 70 °C in the open air. The reaction mixture was poured into 500 mL of ice-water. The mixture was extracted with AcOEt, and the organic layer was washed with water, an aqueous solution of $NaHCO_3$, and an aqueous solution sodium thiosulfate, and dried over $MgSO_4$. The solvent was evaporated, and the residue was purified by short-path column chromatography (silica, hexane) and successively by digestion from hexane. Diiodo compound **7** (2.3 g, 76%) was obtained as a white solid. M.p. 194.5–195.0 °C; ^1H NMR ($CDCl_3$, 200 MHz) parallel conformer: $\delta = 2.46$ (s, 6H), 7.22, (d, $J = 9$ Hz, 2H), 7.48 (d, $J = 9$ Hz, 2H), 7.96 (s, 2H); antiparallel conformer: $\delta = 2.18$ (s, 6H), 7.36 (d, $J = 9$ Hz, 2H), 7.65 (d, $J = 9$ Hz, 2H), 8.03(s, 2H); parallel/antiparallel = 35:65; FAB HRMS (*m/z*) $[M]^+$ calcd for $C_{23}H_{12}F_6I_2S_2$: 719.8374; found 719.8376.

1,2-Bis(6-phenyl-2-methyl-1-benzothiophen-3-yl)hexafluorocyclopentene (3a): $[Pd(PPh_3)_4]$ (175 mg, 0.15 mmol), Na_2CO_3 (2.5 g), water (10 mL), and phenylboronic acid (600 mg, 4.0 mmol) was added to a solution of **7** (1.2 g, 1.1 mmol) in THF (10 mL). The reaction mixture was heated under reflux 24 h. The reaction mixture was poured into water, extracted with Et_2O, washed with water, dried over magnesium sulfate, and concentrated. Column chromatography (hexane/dichloromethane 3:1) gave **3a** (290 mg, 29%) as a white solid. ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 2.25$ (s, 3.9H), 2.50 (s, 2.1H), 7.3–7.9 (m, 16H); UV/Vis (AcOEt): λ_{max} (ε) = 284 nm (48000); FAB HRMS (*m/z*) $[M]^+$ calcd for $C_{35}H_{22}F_6S_2$: 620.1067; found 620.1059.

Closed-ring isomer 3b: ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 2.08$ (s, 6H), 7.3–8.0 (m, 16H); UV/Vis (AcOEt): λ_{max} (ε) = 307 (20000), 381 (27000), 543 nm (21000).

1,2-Bis[6-(4-biphenyl)-2-methyl-1-benzothiophen-3-yl]hexafluorocyclopentene (5a): $[Pd(PPh_3)_4]$ (80 mg, 0.07 mmol), Na_2CO_3 (1.2 g), water (5 mL), and 4-biphenylboronic acid (550 mg, 2.78 mmol) was added to a solution of **7** (500 mg, 0.69 mmol) in THF (5 mL). The reaction mixture was heated under reflux 24 h. The reaction mixture was poured into water, extracted with ethyl acetate, washed with water, dried over magnesium sulfate, and concentrated. Column chromatography (hexane/dichloromethane 4:1) gave **5a** (170 mg, 32%) as a white solid. M.p. 278.5–279.5 °C; ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 2.28$ (s, 3.9H), 2.54 (s, 2.1H), 7.3–8.0 (m, 24H); UV/Vis (AcOEt): λ_{max} (ε) = 298 nm (69000); FAB HRMS (*m/z*) $[M]^+$ calcd for $C_{47}H_{30}F_6S_2$: 772.1693; found 772.1690.

Closed-ring isomer 5b: ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 2.10$ (s, 6H), 7.3–8.1 (m, 24H); UV/Vis (AcOEt): λ_{max} (ε) = 313 (23000), 389 (33000), 549 nm (24000).

1,2-Bis[6-(4-formylphenyl)-2-methyl-1-benzothiophen-3-yl]hexafluorocyclopentene (8): $[Pd(PPh_3)_4]$ (175 mg, 0.15 mmol), Na_2CO_3 (2.5 g), water (10 mL), and 4-formylphenylboronic acid (600 mg, 4.0 mmol) was added to a solution of **7** (1.2 g, 1.1 mmol) in THF (10 mL). The reaction mixture was heated under reflux for 24 h. The reaction mixture was poured into water, extracted with Et_2O, washed with water, dried over magnesium sulfate, and concentrated. Column chromatography (silica, dichloromethane/Et_2O 3:1) gave diformyl compound **8** (540 mg, 49%) as a white solid. ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 2.28$ (s, 3.9H), 2.55 (s, 2.1H), 7.48–7.99 (m, 14H), 10.03 (s, 0.35H), 10.07 (s, 0.65H); FAB HRMS (*m/z*) $[M+H]^+$ calcd for $C_{37}H_{23}F_6O_2S_2$: 677.1044; found 677.1074.

1,2-Bis{6-[4-(1-oxyl-3-oxide-4,4,5,5-tetramethylimidazolin-2-yl)phenyl]-2-methyl-1-benzothiophen-3-yl}hexafluorocyclopentene (4a): A solution of **8** (540 mg, 0.80 mmol), 2,3-bis(hydroxyamino)-2,3-dimethylbutane sulfate (2 g, 8.0 mmol), and potassium carbonate (1.1 g, 8 mmol) in methanol (60 mL) was heated under reflux for 24 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. A solution of sodium periodate (520 mg, 2.4 mmol) in water (100 mL) was added to a solution of tetrahydroxylamine in dichloromethane (60 mL), and the reaction 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/Et_2O 9:1) followed by GPC, and then recrystallization from CH_2Cl_2/hexane by diffusion method in the dark. Compound **4a** was obtained as a dark blue solid (100 mg, 13%). M.p. 210.0–211.0 °C (decomp); UV/Vis (AcOEt): λ_{max} (ε) = 313 (76000), 377 (22000), 555 (sh), 600 (790), 644 (740), 718 nm (sh); ESR (benzene): complicated, 15 lines, $g = 2.007$; FAB HRMS (*m/z*) $[M+H]^+$ calcd for $C_{49}H_{45}F_6N_4O_4S_2$: 931.2786; found 931.2739; elemental analysis calcd (%) for $C_{49}H_{44}F_6N_4O_4S_2$: C 63.2, H 4.8, N, 6.0; found C 63.5, H 5.2, N 5.7.

Closed-ring isomer 4b: UV/Vis (AcOEt): λ_{max} (ε) = 280 (43000), 367 (44000), 553 (26000); ESR (benzene): 1:4:10:16:19:16:10:4:1, 9 lines, $g = 2.007$, $a_N = 3.7$ G.

1,2-Bis{6-[4-(4-formylphenyl)phenyl]-2-methyl-1-benzothiophen-3-yl}hexafluorocyclopentene (9): *n*-Butyllithium in hexane (1.6 M, 1.0 mL, 1.6 mmol) was added to a solution of **7** (510 mg, 0.71 mmol) in THF (10 mL) 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 addition of $[Pd(PPh_3)_4]$ (80 mg, 0.07 mmol), Na_2CO_3 (2.4 g), water (10 mL), and 4-formyl-4′-iodobiphenyl (1.1 g, 3.5 mmol). The reaction mixture was heated under reflux 12 h. The reaction mixture was poured into water, extracted with AcOEt, washed with water, dried over magnesium sulfate, and concentrated. Column chromatography (dichloromethane) gave compound **9** (350 mg, 60%) as a white powder. M.p. 263.0–264.0 °C; ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 2.29$ (s, 3.9H), 2.55 (s, 2.1H), 7.50–8.00 (m, 22H), 10.05 (s, 0.35H), 10.08 (s, 0.65H); FAB HRMS (*m/z*) $[M+H]^+$ calcd for $C_{49}H_{30}F_6O_2S_2$: 828.1591; found 828.1594.

1,2-Bis{6-{4-[4-(1-oxyl-3-oxide-4,4,5,5-tetramethylimidazolin-2-yl)phenyl]-phenyl}-2-methyl-1-benzothiophen-3-yl}exafluorocyclopentene (6a): A solution of **9** (100 mg, 0.12 mmol), 2,3-bis(hydroxyamino)-2,3-dimethylbutane sulfate (300 mg, 1.2 mmol), and potassium carbonate (170 mg, 1.2 mmol) in benzene (10 mL) and methanol (3 mL) was heated under reflux 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. A solution of sodium periodate (120 mg, 0.57 mmol) in water (30 mL) was added to a solution of tetrahydroxylamine in dichloromethane (30 mL), and the reaction 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/Et_2O 1:1). Compound **6a** was obtained as a dark blue solid (20 mg, 15%). UV/Vis (AcOEt): λ_{max} (ε) = 320 (104000), 375 (sh), 550 (sh), 601 (720), 647 (690), 720 nm (sh); ESR (benzene): 1:2:3:2:1, 5 lines, $g = 2.007$, $a_N = 7.5$ G; FAB MS (*m/z*) $[M+H]^+$ calcd for $C_{61}H_{53}F_6N_4O_4S_2$: 1083; found 1083.

Closed-ring isomer 6b: UV/Vis (AcOEt): λ_{max} (ε) = 311 (58000), 374 (58000), 553 nm (28000); ESR (benzene): 1:4:10:16:19:16:10:4:1, 9 lines, $g = 2.007$, $a_N = 3.9$ G.

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. Mercury lines of 313 and 578 nm were isolated by passing the light through a combination of Toshiba band-pass filter (UV-D33S) or sharp-cut filter (Y-52) and monochrometer (Ritsu MC-20L). Photoirradiation in the ESR cavity was performed by using a 200 W fiber mercury-Xe lamp with band-pass filter or sharp-cut filter.

ESR spectroscopy: A Bruker ESP300E 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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