

Photoswitching of Intramolecular Magnetic Interaction Using a Photochromic Spin Coupler: An ESR Study

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Photochromic compounds reversibly change their absorption spectra by irradiation with light of appropriate wavelengths.^{1–3} Not only absorption spectra but also molecular geometric and electronic structures are altered along with the photochromism. This feature can be applied to fabricating molecular-scale switching devices.^{4–6} When two unpaired electrons are placed at both ends of a π -conjugated chain, the two spins of the unpaired electrons interact magnetically. If the π -conjugated chain length can be switched when using a photochromic spin coupler, the magnetic interaction can be controlled by irradiation with light (Figure 1).

On the basis of this concept, we have designed **1a**, in which two nitronyl nitroxides were located at the both ends of 1,2-bis-(6-phenyl-2-methyl-1-benzothiophen-3-yl)hexafluorocyclopentene (Scheme 1). To detect the change of the exchange interaction by ESR spectroscopy, the value of the interaction should be comparable to the hyperfine coupling constant. Therefore, the system should have a long π -conjugated chain. Two *p*-phenylene groups are introduced for this purpose.

We have reported the photoswitching of the intramolecular magnetic interaction in **2a**, in which there is no *p*-phenylene spacer. Although the antiferromagnetic interaction between two nitronyl nitroxides remarkably increased from $2J/k_B = -2.2$ K to $2J/k_B = -11.6$ K when the diarylethene spin coupler was switched from open-ring isomer **2a** to closed-ring isomer **2b** (Scheme 1), any photoinduced ESR spectral change was not observed, because the exchange interaction between the two radicals was much stronger than the hyperfine coupling constant.^{7,8} In this work we have demonstrated photoswitching of intramolecular magnetic interaction, which can be evidenced by ESR spectra at room temperature.

The synthesis of **1a** was performed starting from 1,2-bis-(2-methyl-1-benzothiophen-3-yl)hexafluorocyclopentene.⁹ 1,2-bis-(2-methyl-1-benzothiophen-3-yl)hexafluorocyclopentene was diiodinated by iodine and orthoperiodic acid to give diiodinated compound at 6,6'-position in a 76% yield. Suzuki coupling with 4-formylphenylboronic acid afforded diformyl derivative in a 49% yield. This diformyl derivative was refluxed in methanol with 2,3-bis(hydroxyamino)-2,3-dimethylbutane sulfate in the presence

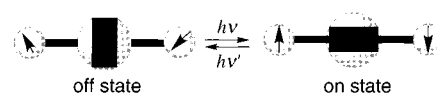


Figure 1. Photoswitching of magnetic interaction.

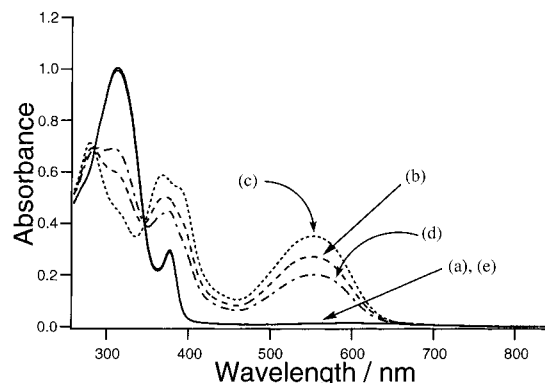


Figure 2. UV-vis absorption spectra measured at different stages of the photochromic reaction starting from open-ring isomer **1a** (1.3×10^{-5} M AcOEt solution). (a) Initial, (b) after irradiation with 313 nm light for 2 min, (c) 10 min, (d) after irradiation with 578 nm light for 2 min, (e) 20 min.

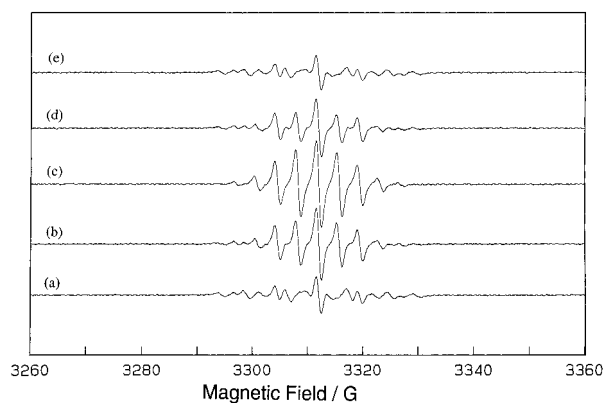


Figure 3. X-band ESR spectra measured at room temperature at different stages of the photochromic reaction starting from open-ring isomer **1a** (1.1×10^{-4} M benzene solution, 9.32 GHz). (a) Initial, (b) after irradiation with 366 nm light for 1 min, (c) 4 min, (d) after irradiation with $\lambda > 520$ nm light for 20 min, (e) 50 min.

of K_2CO_3 then oxidized with sodium periodate in dichloromethane and water to give nitronyl nitroxides **1a** in a 13% yield.¹⁰

Figure 2 shows the photochromic interconversion between **1a** and **1b**. The ethyl acetate solution of **1a** (1.3×10^{-5} M) was irradiated with 313 nm light. Upon irradiation the intense absorption at 553 nm grew and after 10 min it reached the photostationary state. The color of the solution was changed from pale blue to red purple. Clear isosbestic points were observed at 346 nm and 285 nm. The red purple solution was irradiated with 578 nm light for 20 min. The spectrum returned to the original one with retention of the isosbestic points at 346 nm and 285 nm. Although the radical moiety has absorption around 550–700 nm, the existence did not prohibit the photochromic reaction. The conversion at the photostationary state was 99%. The high conversion was estimated by comparison with the isolated closed-ring isomer.¹¹

(10) **1a**: blue solid; mp 210.0–211.0 °C dec; UV-vis (AcOEt) (ϵ) 313 (7.6×10^4), 377 (2.2×10^4), 555 (sh), 600 (7.9×10^3), 644 (7.4×10^3), 718 (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; Anal. 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.

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Scheme 1

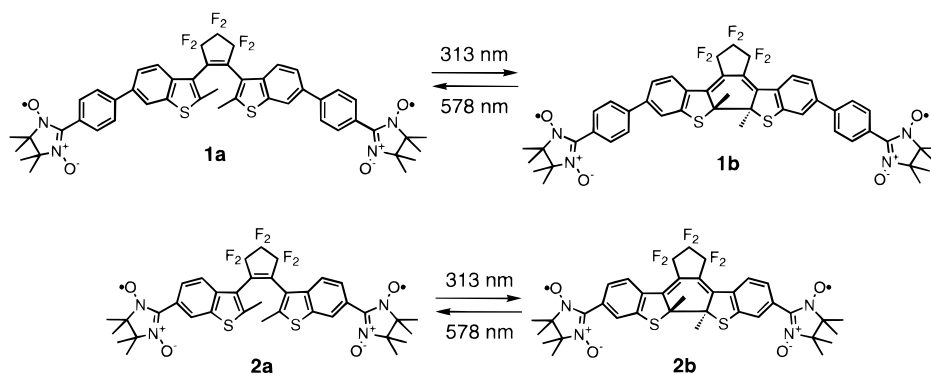


Figure 3 shows the ESR spectra of **1a** at room temperature at different stages of the photochromic reaction. The irradiation was performed in the ESR cavity. The ESR spectrum of **1a** showed a complex of 15 lines. This result suggests that the two spins of nitronyl nitroxide are coupled by the exchange interaction that is comparable to the hyperfine coupling constant. Upon irradiation with 366 nm light, the signal of 9 lines at the center grew, and after 4 min the spectrum reached the photostationary state. This 9-line spectrum corresponds to closed-ring isomer **1b**. The 9-line spectrum indicates that the exchange interaction between the two spins in **1b** is much larger than the hyperfine coupling constant.

At the photostationary state the 15-line spectrum originating from **1a** disappeared, which is consistent with the high conversion proved by the measurement of UV-vis absorption spectra. When the sample was irradiated with $\lambda > 520$ nm light, the spectrum completely returned to the original one. The double integrals 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 4).

To estimate the value of the exchange interaction, the simulation of the spectra was performed according to the formulation of Rassat et al.^{12,13} It was revealed that the antiferromagnetic interaction between two nitronyl nitroxides remarkably increased from $|2J/g\mu_B| \approx 8$ G ($|2J/k_B| \approx 1 \times 10^{-3}$ K) to $|2J/g\mu_B| > 600$ G ($|2J/k_B| > 0.08$ K) when the diarylethene spin coupler was switched from the open-ring isomer **1a** to the closed-ring isomer **1b**. The strength of exchange interaction was switched by more than 2 orders of magnitude.

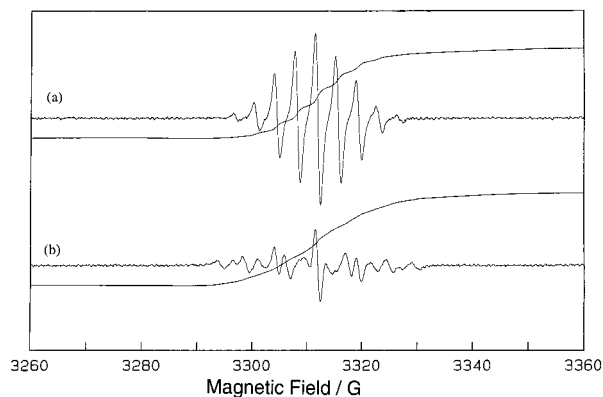


Figure 4. ESR spectra of (a) closed-ring isomer **1b** and (b) open-ring isomer **1a** with double integrals.

In conclusion the photoswitching of intramolecular magnetic interaction was detected by ESR spectroscopy at room temperature in solution. By introducing a *p*-phenylene spacer to the dibenzothienylethene aryl groups, the strength of the exchange interaction was successfully regulated so that the switching could be detected by ESR spectroscopy. This method is applicable to develop more complicated logic circuits.

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(11) **1b**: UV-vis (AcOEt) (ϵ) 280 (4.3×10^4), 367 (4.4×10^4), 553 (2.6×10^4); ESR (benzene) 1:4:10:16:19:16:10:4:1, 9 lines, $g = 2.007$, $a_N = 3.7$ G.

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