Photoswitching of Intramolecular Magnetic Interaction Using Photochromic Diarylethene Spin Coupler: Introduction of Thiophene Spacer

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Photochromic 1,2-bis(2-methyl-1-benzothiophen-3-yl)perfluorocyclopentene having two nitronyl nitroxide radicals with a thiophene-2,5-diyl spacer was prepared and the intramolecular magnetic interaction was compared with the derivative having the radicals with a *p*-phenylene spacer. The stronger magnetic interaction was observed for the compound with the thiophene spacer.

Photochromic compounds have attracted much attention because of their potential ability for optical memory media and photo-optical switching devices.[1] Among them diarylethenes with heterocyclic aryl groups are the most promising compounds for the applications, because they undergo fatigue resistant and thermally irreversible photochromic reactions.[2] When two radicals were located at both ends of the diarylethene, the intramolecular magnetic interaction between two spins was switched by alternate irradiation with UV and visible light (Figure 1).[3] In this work, we will report on the photoswitching of intramolecular magnetic interaction of a diarylethene with two nitronyl nitroxide radicals with a thiophene-2,5-diyl spacer.

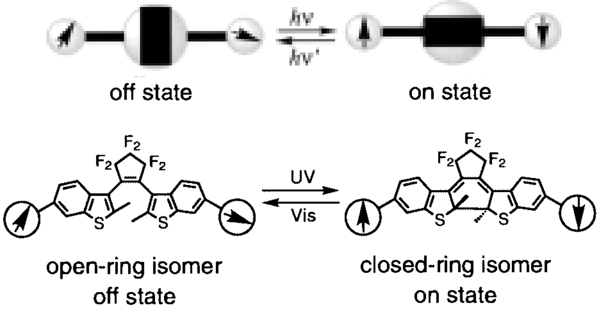
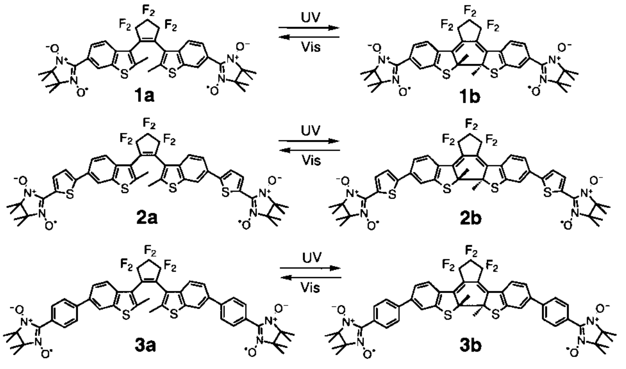


Figure 1. Photoswitching of magnetic interaction.

The synthesis of **2a** was performed using 1,2-bis(6-iodo-2-methyl-1-benzothiophen-3-yl)perfluorocyclopentene as the intermediate. Suzuki coupling of diiodo compound with 5-formyl-2-thiopheneboronic acid afforded diformyl derivative. This formyl derivative was refluxed in methanol and benzene with 2,3-bis(hydroxyamino)-2,3-dimethylbutane sulfate in the presence of K_2CO_3, and oxidized with sodium periodate in dichloromethane and water to give nitronyl nitroxides **2a**.[4] **1a** and **3a** were prepared according to the procedures described before (Scheme 1).[3]

Figure 2 shows the photochromic reaction of **2**. The open-ring form isomer **2a** in ethyl acetate was irradiated with 366 nm light. Upon irradiation absorption at 574 nm increased and reached photostationary state. The solution turned blue, which is the color of the closed-ring form isomer **2b**.[5] The conversion at the photostationary state was 71%, which was determined by comparison with the isolated closed-ring isomer. The conversion of **2** was less than that of **1** (100%) or **3** (99%).[3d] The absorption maximum of **2b** (λ_{max} = 571 nm) showed a bathochromic shift as much as 21 nm in comparison with the maximum of **3b** (λ_{max} = 553 nm).[3d] This large shift can be attributed to the planarity between benzothiophene ring and thiophene ring. Quantum yields of cyclization and cycloreversion reactions were measured in ethyl acetate. The cyclization quantum yield of **2** was 0.0015, which was ca. 1/70 of the cyclization quantum yield of **3** (0.10).[3e] The cycloreversion quantum yield of **2** was 0.0009, which was 1/10 of that of **3** (0.012).[3e] The extension of π-conjugation to nitronyl nitroxide radical through the thiophene ring is considered to strongly affect the reactivity.[6]



Scheme 1.

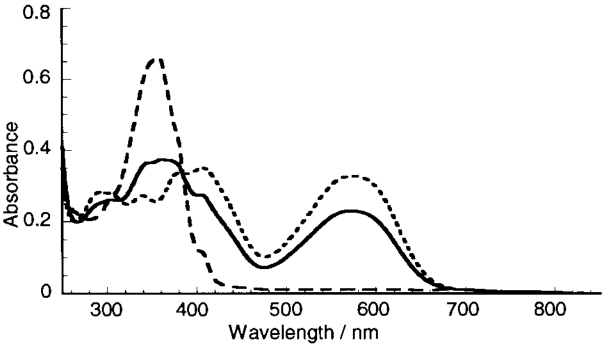


Figure 2. Absorption spectra of **2** in ethyl acetate (9.1 × 10^{-6} M). Open-ring form isomer (dashed line), closed-ring form isomer (dotted line), in the photostationary state (solid line).

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The photoswitching of magnetic interaction was investigated by ESR spectroscopy. The ESR spectrum of isolated closed-ring isomer **2b** is shown in Figure 3a. The spectrum showed 9 lines, indicating the intramolecular exchange interaction was much larger than the hyperfine coupling constant. The 9-line spectrum was reproduced as $|2J/g\mu_B| > 300$ G ($|2J/k_B| > 0.04$ K) by simulation using BIRADG program.[7]

Upon irradiation with 578 nm light the closed-ring isomer **2b** was completely converted to the open-ring isomer **2a**. The ESR spectrum of **2a** is shown in Figure 3b. The spectrum consists of complicated more than 13 lines, indicating the exchange interaction was comparable to the hyperfine coupling constant. When the open-ring form isomer **2a** was irradiated with 366 nm light the closed-ring isomer was regenerated. The ESR spectrum of the sample in the photostationary state showed distorted 9 lines. This cycle was reversible.

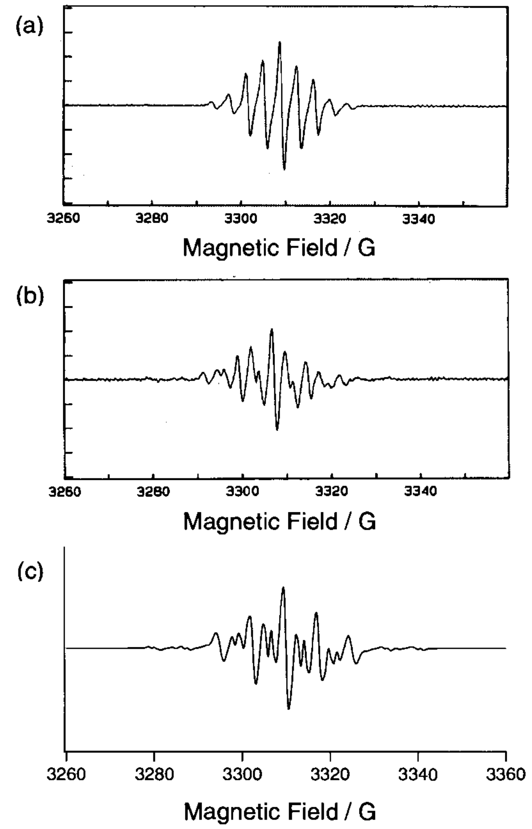

Figure 3. X-band ESR spectra (9.31 GHz, in dichloromethane) of (a) closed-ring form isomer **2b**, (b) open-ring form isomer **2a**, and (c) simulated spectrum of **2a** (see text).

In the case of **2a**, 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, parallel and antiparallel conformers, in the NMR time scale.[8] The parallel and antiparallel conformers are expected to have different exchange interactions between two spins. The ratio between parallel and antiparallel conformers was 35:65 for 1,2-bis(2-methyl-1-benzothiophen-3-yl)perfluorocyclopentene. Taking account of the same ratio (35:65) the exchange interaction was determined to be $|2J/g\mu_B| = 42$ G ($|2J/k_B| = 5.6 \times 10^{-3}$ K) for the antiparallel conformer and $|2J/g\mu_B| < 2$ G ($|2J/k_B| < 3 \times 10^{-4}$ K) for the parallel conformer (Figure 3c). For the open-ring form isomer with *p*-phenylene spacer **3a**, the exchange interaction was $|2J/g\mu_B| = 9.0$ 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.[3e] As expected, the exchange interaction through thiophene-2,5-diyl spacer is larger than that through *p*-phenylene spacer.

In conclusion, photochromic diarylethene having two nitronyl nitroxide radicals with thiophene-2,5-diyl spacers **2** was synthesized. It was found that the thiophene-2,5-diyl spacer serves as a stronger magnetic coupler than *p*-phenylene spacer. The photoinduced ESR spectral change indicates that the open-ring isomer has “OFF” state, while the closed-ring form isomer has “ON” state. This result indicates that thiophene-2,5-diyl spacer is useful for the design of strongly coupled spin systems.

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4 **2a**: dark blue form; UV–vis (AcOEt) λ_{max} (ε) 303 (sh), 358 (7.3×10^4), 407 (sh), 574 (sh), 629 (6.8×10^2), 688 (8.9×10^2), 762 (8.9×10^2) nm; EPR (dichloromethane) complicated more than 13 lines, $g = 2.007$; Anal. Found: C, 57.38; H, 4.56; N, 5.55%. Calcd for $C_{45}H_{40}F_6N_4O_4S_4$: C, 57.31; H, 4.28; N, 5.94%.

5 **2b**: UV–vis (AcOEt) λ_{max} (ε) 293 (3.1×10^4), 340 (3.0×10^4), 380 (3.7×10^4), 407 (3.8×10^4), 574 (3.6×10^4) nm; EPR (dichloromethane) 1:4:10:16:19:16:10:4:1, 9 lines, $g = 2.007$, $a_N = 3.8$ G.

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