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Communications to the Editor

Photoswitching of Intramolecular Magnetic Interaction Using a Diarylethene Dimer

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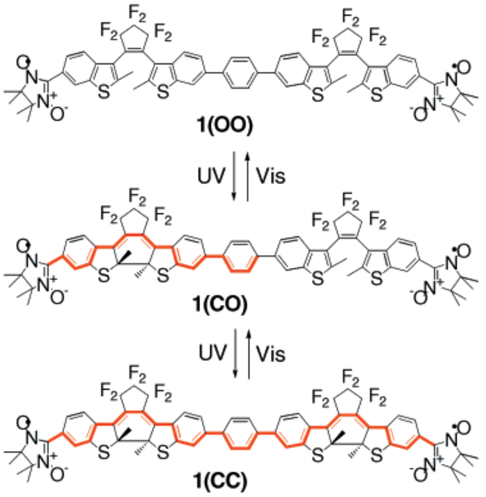
Photochromic molecules, which reversibly change their optical as well as electronic properties by irradiation with light of appropriate wavelengths, are potentially applicable to various optoelectronic devices, such as memories and switches.[1] The property changes are based on photoinduced electronic structural changes of the molecules. Therefore, the photochromic molecules can be used as molecular-scale switching units of electronic as well as magnetic interactions.[2] Among various photochromic molecules, diarylethenes are the most promising candidates for the applications because both isomers are thermally stable and fatigue-resistant.[3]

In previous papers[4] we have demonstrated that the exchange interaction between two nitronyl nitroxide radicals, which are located at both ends of a diarylethene, is photoswitched reversibly by alternate irradiation with ultraviolet and visible light. It was found that the change in the exchange interaction between the two switching states is more than 30-fold. For the detection of magnetic interaction changes, ESR spectroscopy was employed. When the exchange interaction is much smaller than the hyperfine coupling constant ($2J/k_B < 3 \times 10^{-4}$ K), the spectrum shows five lines. In the case that the exchange interaction is much larger than the hyperfine coupling constant ($2J/k_B > 0.04$ K), the spectrum is nine lines. ESR spectra can be used as a good tool for detecting small magnetic interaction changes in the molecular system. In this paper photoswitching of intramolecular magnetic interaction using a diarylethene dimer will be presented.

When a diarylethene dimer is used as a switching unit, there are three kinds of photochromic states; open−open (OO), closed−open (CO), and closed−closed (CC). From the analogy of electric circuit, it is inferred that the dimer has two switching units in series. We have designed the dimer **1**, which has 28 carbon atoms between two nitronyl nitroxide radicals (Scheme 1). When the two radicals are placed at both ends of a diarylethene and separated by conjugated 28 carbon atoms, the spectrum change was very clearly detected between five lines and distorted nine lines.[4f] *p*-Phenylene spacer was introduced so that the cyclization reaction can occur at both diarylethene moieties.[5] Bond alternation is disconnected at the open-ring form moieties of **1(OO)** and **1-(CO)**, so that the two spins at the both ends of **1(OO)** and **1-(CO)** cannot interact with each other. On the other hand the π-system of **1(CC)** is delocalized throughout the molecule, and the exchange interaction between two radicals is expected to take place.

Scheme 1. Photochromic Reaction of **1**[a]



[a] Red line indicates the connection of the bond alternation.

1(OO) was synthesized from 1,2-bis(6-iodo-2-methyl-1-benzothiophen-3-yl) hexafluorocyclopentene. Monoformylation followed by Suzuki coupling with phenylenebis-1,4-diboronic acid afforded diformyl intermediate. The diformyl intermediate was transformed to bis(nitronyl nitroxide) **1(OO)**. **1(OO)** was obtained as a blue amorphous solid. The blue color is due to the n−π* absorption from nitronyl nitroxide radicals. The structure of **1-(OO)** was confirmed by mass, UV, and ESR spectroscopy.[6]

1(OO) underwent photochromic reaction by alternate irradiation with UV and visible light. The ethyl acetate solution of **1(OO)** was irradiated with 313-nm light (Figure 1a). Upon irradiation the absorption at 560 nm appeared initially, then it grew with shifting the absorption maximum, and reached the photostationary state after 120 min. The color of the solution changed from pale blue to red-purple and then to purple. The red spectral shift suggests the formation of **1(CC)**. An isobestic point was maintained at an initial stage of irradiation, but later it deviated. The purple solution was completely bleached by irradiation with 578-nm light. **1(CO)** and **1(CC)** were isolated from the purple solution by HPLC.[7] The spectra of **1(OO)**, **1(CO)**, and **1(CC)**

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(6) **1(OO)**: blue solid; UV−vis (AcOEt) λ_{max} 311 , 377; ESR (benzene) 1:2:3:2:1, five lines, $g = 2.007$, $a_N = 7.5$ G.; FAB MS (*m/z*) $[M + H]^+$ calcd for $C_{66}H_{53}F_{12}N_4O_4S_4$, 1321, found 1321.

(7) **1(CO)**: UV−vis (AcOEt) λ_{max} 297, 379, 560; ESR (benzene) 1:2:3:2:1, five lines, $g = 2.007$, $a_N = 7.4$ G. **1(CC)**: UV−vis (AcOEt) λ_{max} 311, 344, 397, 576; ESR (benzene) 1:4:10:16:19:16:10:4:1, nine lines, $g = 2.007$, $a_N = 3.6$ G.

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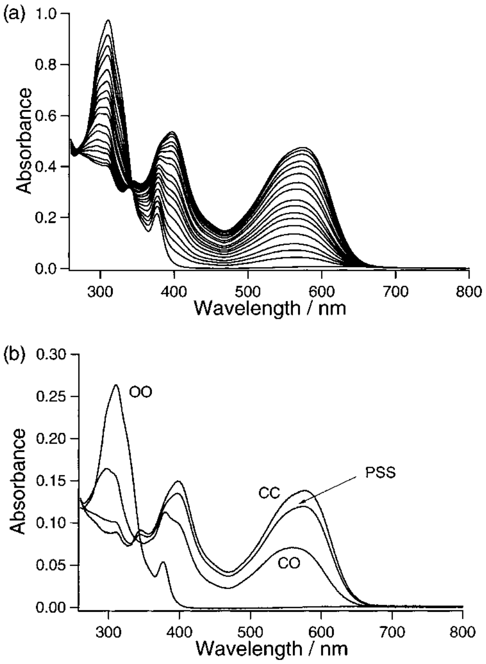

Figure 1. (a) Absorption spectral change of **1** under irradiation with 313-nm light. Initial, 20 s, 40 s, 60 s, 2 min, 3 min, 4 min, 5 min, 7 min, 9 min, 15 min, 20 min, 30 min, 40 min, 50 min, 70 min, 90 min, 120 min. (b) Absorption spectra of **1(OO)**, **1(CO)**, **1(CC)** and in the photostationary state under irradiation with 313-nm light.

are shown in Figure 1b with the spectrum in the photostationary state under irradiation with 313-nm light. **1(CC)** has absorption maximum at 576 nm, which is red-shifted as much as 16 nm in comparison with **1(CO)**.

The time course of the cyclization reaction starting from **1-(OO)** under irradiation with 313-nm light was followed by HPLC. At first **1(OO)** decreased and **1(CO)** increased, and then **1(CO)** decreased and **1(CC)** increased. The rate-determining step was the second cyclization reaction. As a result of the cyclization reaction, **1(CO)** was accumulated and reached a maximum value of 78%. In the photostationary state, the ratio was determined as **1(OO)**:**1(CO)**:**1(CC)** = 0:23:77. An efficient cyclization reaction from **1(OO)** to **1(CC)** was demonstrated. A cycloreversion reaction starting from **1(CC)** under irradiation with 578-nm light was also followed. In this case, the accumulation of **1(CO)** was not observed. The rate-determining step was the first cycloreversion reaction.

ESR spectra of isolated **1(OO)**, **1(CO)**, and **1(CC)** were measured in benzene at room temperature (Figure 2). The spectra of **1(OO)** and **1(CO)** were five lines, suggesting that the exchange interaction between two nitronyl nitroxide radicals was much smaller than the hyperfine coupling constant ($2J/k_B < 3 \times 10^{-4}$ K). However, the spectrum of **1(CC)** was a clear nine lines, indicating that the exchange interaction between two spins was much larger than the hyperfine coupling constant ($2J/k_B > 0.04$ K). The result indicates that each diarylethene chromophore served as a switching unit to control the magnetic interaction. The magnetic interaction between end nitronyl nitroxide radicals was controlled by the switching units in series.

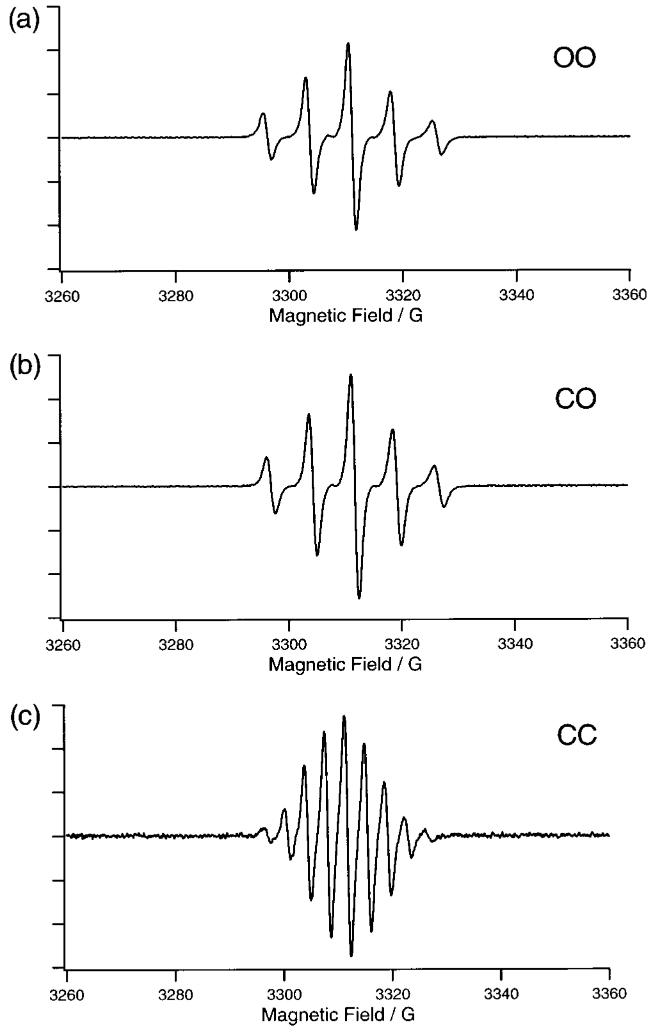

Figure 2. X-band ESR spectra measured at room temperature in benzene (9.32 GHz) (a) **1(OO)**, (b) **1(CO)**, and (c) **1(CC)**.

In conclusion we have synthesized bis(nitronyl nitroxide) with diarylethene dimer as a photoswitching core. The photochromic reaction proceeded effectively from open–open to closed–closed. The magnetic interaction in **1(OO)** and **1(CO)** was much smaller than **1(CC)**. While **1(OO)** and **1(CO)** were in the "OFF" state, **1(CC)** was in the "ON" state.

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