Photoswitching of Intramolecular Magnetic Interaction: A Diarylethene Photochromic Spin Coupler

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(Received September 27, 1999; CL-990831)

We have designed and synthesized 1,2-bis[6-(1-oxyl-3-oxide-4,4,5,5-tetramethylimidazolin-2-yl)-2-methylbenzo[*b*]thiophen-3-yl]hexafluorocyclopentene which shows photoswitching of intramolecular magnetic interaction by incorporating two nitronyl nitroxide into diarylethene photochromic spin coupler.

Photochromism is defined as light-induced reversible transformation of chemical species between two forms having different absorption spectra.[1] The two isomers differ from each other not only in the absorption spectra but also in various physical and chemical properties.[2] Molecular magnetism[3] can also be photocontrolled by incorporating photochromic moiety into the system. Although so far, intermolecular magnetic interaction has been photochemically controlled by several methods,[4] photocontrol of intramolecular magnetic interaction of discrete molecule has not yet been achieved.[5] Here we report that intramolecular magnetism is reversibly photoswitched by incorporating two radical moieties into a photochromic diarylethene spin coupler (Figure 1).

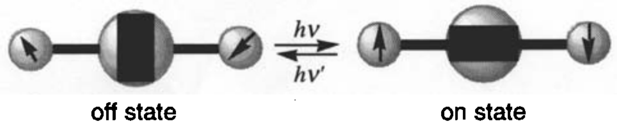
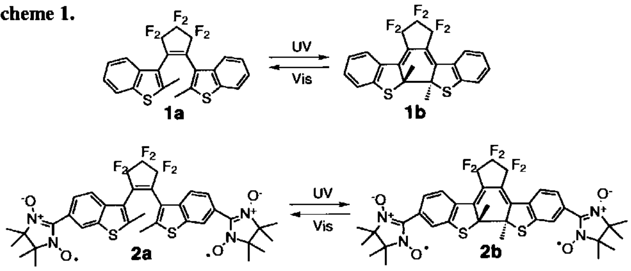


Figure 1. Photoswitching of magnetic interaction.

We have chosen 1,2-bis(2-methyl-benzo[*b*]thiophen-3-yl)perfluorocyclopentene[6] **1a** as a photochromic spin coupler (Scheme 1). **1a** is one of the photochromic diarylethenes, which undergo cyclization/ring-opening photochromic reactions, **1a** $\rightleftarrows$ **1b**, and have excellent photochromic performance:[1c] thermal stability of both isomers even at 100 °C, high fatigue resistance (>10^4 coloration/decoloration cycles), and very rapid response time (~1 ps). The interconversion between **1a** and **1b** of diarylethenes induces the change in aromaticity and in planarity of the π-systems, which are expected to influence the intramolecular magnetic interaction of two spins. For the spin source, we have chosen nitronyl nitroxide because this radical is π-conjugative and rather stable against UV-vis light. Thus we designed molecule **2a** which would show interconversion by light between two different spin states (Scheme 1).

Scheme 1.



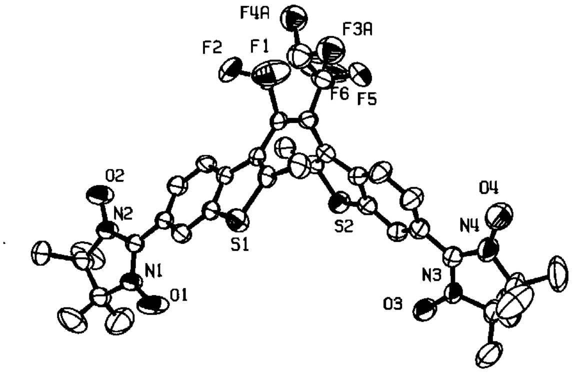


Figure 2. ORTEP drawing of **2a** with thermal ellipsoids (50% probability). The hydrogen atoms are omitted for clarity. Only one conformation of the disordered perfluorocyclopentene ring is shown.

The synthesis of **2a** was performed from **1a** via diformyl derivative. Dark blue plate crystal of **2a** was obtained by recrystallization from hexane-CH_2Cl_2.[7] The crystal structure was determined by X-ray crystallographic analysis (Figure 2).[8] The nearest intermolecular contact between oxygen atoms of nitroxide is 4.38 Å, which indicates intermolecular magnetic interaction is negligible. The average dihedral angle between benzothiophene ring and perfluorocyclopentene ring are 86.1°. The π-conjugation is disconnected between the two benzothiophene rings.

Figure 3 shows the photochromic reaction of compound **2a** and **2b**. The ethyl acetate solution of **2a** (1.7×10^{-5} M) was irradiated with 313 nm light. Upon irradiation the intense absorption at 565 nm grew and after 5 min it reached the photostationary state. The clear isosbestic point was observed at 334 nm. Then the sample was irradiated with 578 nm light for

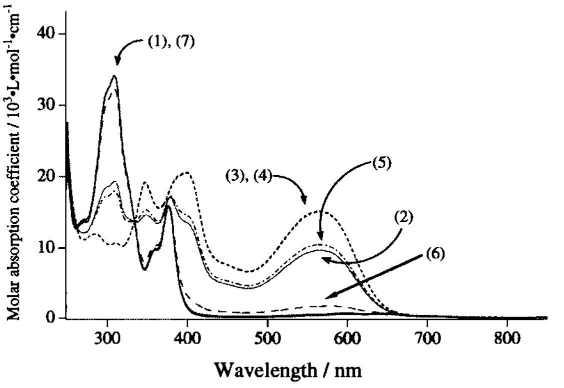


Figure 3. UV-vis absorption spectra measured at different stage of photochromic reaction starting from open form **2a** (1.7×10^{-5} M AcOEt solution). (1) initial (2) after irradiation with 313 nm light for 1 min (3) 5 min (4) 10 min (5) after irradiation with 578 nm light for 5 min (6) 30 min (7) 60 min.

60 min. The spectrum converted back to the original one with retention of isosbestic point at 334 nm. Although the radical moiety has absorption around 550-700 nm, its existence did not prohibit the photochromic reaction.

Both the degree of conversion of cyclization and ring-opening reaction were determined as >99% by HPLC. The perfect conversion of both cyclization and ring-opening reaction is ideal property for a switching device.

Both the isomers **2a** and **2b** can be isolated as microcrystals.[9] The magnetic susceptibility was measured on a SQUID susceptometer. χT-T plots are shown in Figure 4. The data were analyzed in terms of a modified singlet-triplet two-spin model (the Bleaney-Bowers-type) in which two spins (S = 1/2) couple antiferromagnetically within a biradical molecule by exchange interaction J (eq. 1).[10]

$$\chi_{\mathrm{mol}}T = f\frac{2Ng^2\mu_B T}{k_B(T-\theta)}\bullet\frac{1}{3+\exp(-2J/k_B T)} \qquad (1)$$

Where θ indicates a Weiss constant employed to describe the additional intermolecular interaction by a mean field theory. Correction factor f was introduced for the correction of the experimental error. The best fit parameters by means of a least-squares method were $2J/k_B$ = -2.2 ± 0.04 K, θ = 0.24 ± 0.01 K, and f = 0.91 for **2a** and $2J/k_B$ = -11.6 ± 0.4 K, θ = -2.4 ± 0.3 K, and f = 1.03 for **2b**. Though the two spins of open form **2a** have small interaction ($2J/k_B$ = -2.2 K) between spins due to the disconnection of the π-systems which was confirmed by X-ray crystal structure, spins of **2b** have remarkable antiferromagnetic interaction ($2J/k_B$ = -11.6 K).

We have measured the magnetic susceptibility of **2b** (3% w/w) dispersed in poly(n-butyl methacrylate) to know the contribution of the intermolecular interaction in the closed-ring form crystal.[11] The photochromic reaction could proceed in the polymer dispersed system. The measured intramolecular antiferromagnetic interaction[12] in the polymer dispersed system ($2J/k_B$ = -12.5 ± 0.5 K) was similar to that observed in the crystal. This clearly indicates that the increase in $|2J/k_B|$ is not due to intermolecular interaction but due to the intramolecular interaction. The photoinduced change in the molecular structure from twisted one to planer one resulted in the change of magnetic interaction. Recently Ziessel et al. reported that diradicals bridged by olefinic spacers showed stronger interaction than aromatic systems. The change from more aromatic open form **2a** to less aromatic **2b** also seemed to contribute to the change in interaction.[13]

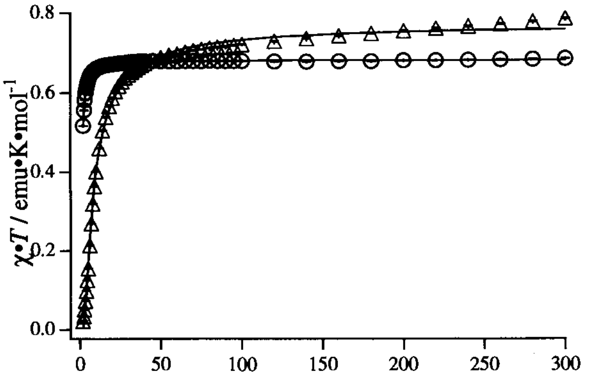


Figure 4. χT-T plot for (O) **2a** and (Δ) **2b** measured at 5000 G. Solid line represents the theoretical curve (see text).

Here we have reported the development of reversible photochromic system with the change of magnetic interaction. The conversion of both photoreaction was almost 100%. The change of the magnetization was attributed to the change of the planarity and aromaticity of the molecular structure. This system is one of the successful molecular switching device which can be applied for the development of logic operation circuit.

This work was partly supported by CREST of Japan Science and Technology Corporation and by a Grant-in Aid for Scientific Research on Priority Area "Creation of Delocalized Electronic Systems" (No. 11133249) from the Ministry of Education, Science, Culture, and Sports, Japan.

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7 **2a**: dark blue microcrystal; mp 231.0-232.0 °C (decomp.); UV-vis (AcOEt) λ_{max} (ε) 300 (sh), 309 (3.4×10^4), 359 (sh), 377 (1.6×10^4), 553 (sh), 598 (6.3×10^2), 646 (6.3×10^2), 706 (sh); EPR (benzene) 1:4:10:16:19:16:10:4:1, 9 lines, g = 2.007, a_N = 3.7 G; FAB HRMS (m/z) $[M+H]^+$ found 779.2173, calcd for $C_{37}H_{36}F_6N_4O_4S_2$ 779.2160.

8 Crystallographic data for **2a**: $C_{37}H_{36}F_6N_4O_4S_2$, FW = 778.82, triclinic (P 1, a = 11.537(5) Å, b = 12.256(5) Å, c = 14.568(6) Å, α = 85.023(8)°, β = 72.660(8)°, γ = 71.030(7)°, V = 1859.3(14) $Å^3$, Z = 2, μ(MoKα) = 0.218, R = 0.086, wR_2= 0.211.

9 **2b**: black microcrystal; UV-vis (AcOEt) λ_{max} (ε) 280 (1.7×10^4), 348 (1.9×10^4), 385 (sh), 400 (2.0×10^4), 565 (1.5×10^4); EPR (benzene) 1:4:10:16:19:16:10:4:1, 9 lines, g = 2.007, a_N = 3.7 G.

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11 Absorption maxima in solution and in film were same at 565 nm completely, while absorption maximum in solid was shifted to 581 nm, indicating the diradicals were molecularly dispersed in the film.

12 This fitting was performed without using parameter of intermolecular interaction.

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