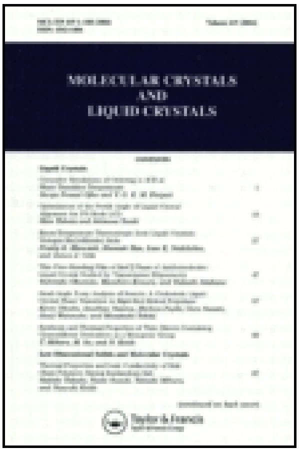


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Photoswitching of Magnetic Properties by using Diarylethene Photochromic Spin Coupler

Kenji Matsuda [a] & Masahiro Irie [a]

[a] Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, and CREST, Japan Science and Technology Corporation, Hakozaki 6-10-1, Higashi-ku, Fukuoka, 812-8581, Japan

To cite this article: Kenji Matsuda & Masahiro Irie (2000): Photoswitching of Magnetic Properties by using Diarylethene Photochromic Spin Coupler, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 345:1, 155-160

To link to this article: http://dx.doi.org/10.1080/10587250008023911

Mol. Cryst. and Liq. Cryst., 2000, Vol. 345, pp. 155-160
Reprints available directly from the publisher
Photocopying permitted by license only

Photoswitching of Magnetic Properties by using Diarylethene Photochromic Spin Coupler

KENJI MATSUDA and MASAHIRO IRIE

Department of Chemistry and Biochemistry, Graduate School of Engineering,
Kyushu University, and CREST, Japan Science and Technology Corporation,
Hakozaki 6–10–1, Higashi-ku, Fukuoka 812–8581, Japan

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 photo-switching of intramolecular magnetic interaction by incorporating two nitronyl nitroxide into diarylethene photochromic spin coupler.

Keywords: Photoswitching; Magnetism; Exchange Interaction

INTRODUCTION

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.[4] Here we report that intramolecular magnetism is reversibly photoswitched by incorporating two radical moieties into a photochromic diarylethene spin coupler (Figure 1).

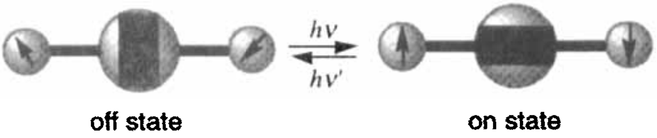


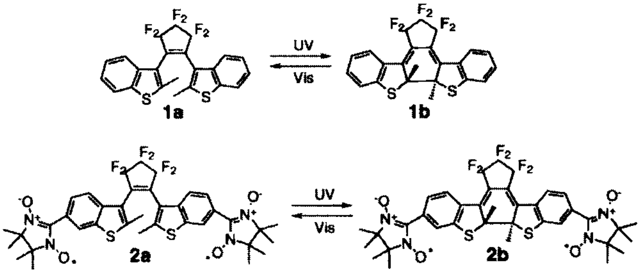
FIGURE 1 Photoswitching of magnetic interaction.

RESULTS AND DISCUSSIONS

Sample Preparation

We have chosen 1,2-bis(2-methyl-benzo[*b*]thiophen-3-yl)perfluorocyclopentene[5] **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] 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. Thus we designed molecule **2a** which would show interconversion by light between two different spin states (Scheme 1).

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. The crystal structure was determined by X-ray crystallographic analysis (Figure 2).



SCHEME 1

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.

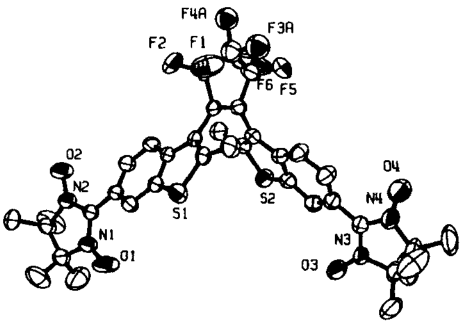


FIGURE 2 ORTEP drawing of **2a** with thermal ellipsoids (50% probability). The hydrogen atoms are omitted for clarity. Only one conformation of the disordered perfluorocyclopentene ring is shown.

Photochromic Reaction

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 60 min. The spectrum converted back to the original one with retention of isosbestic point at 334 nm. Both the degree of conversion of cyclization and ring-opening reaction were determined as >99% by HPLC.

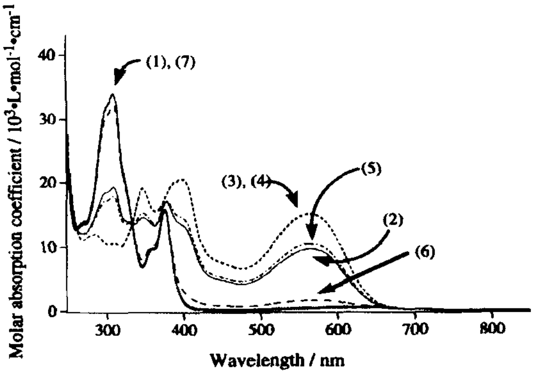


FIGURE 3 UV-vis absorption spectra measured at different stage of photochromic reaction starting from open form **2a** (1.7×10^{-5} M AcOEt solution). (1) initial (2) after irradiation with 313 nm light for 1 min (3) 5 min (4) 10 min (5) after irradiation with 578 nm light for 5 min (6) 30 min (7) 60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

Magnetic Measurement

Both the isomers **2a** and **2b** can be isolated as microcrystals. 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).[6]

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

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 $2J/k_{\mathrm{B}} = -2.2 \pm 0.04$ K, $\theta = 0.24 \pm 0.01$ K, and $f = 0.91$ for **2a** and $2J/k_{\mathrm{B}} = -11.6 \pm 0.4$ 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, 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. The photochromic reaction could proceed in the polymer dispersed system. The measured intramolecular antiferromagnetic interaction 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.

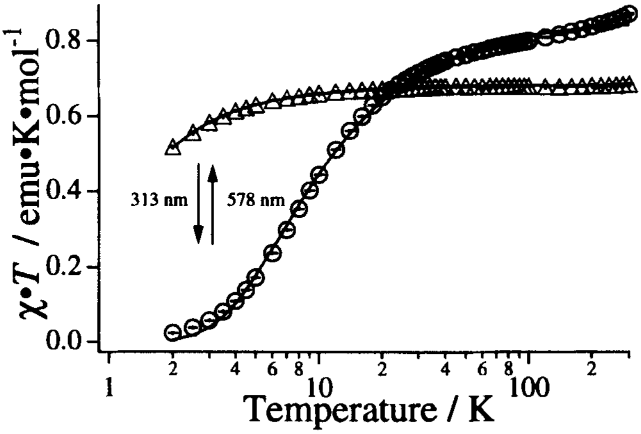


FIGURE 4 χT-T plot for (O) **2a** and (Δ) **2b** measured at 5000 G. Solid line represents the theoretical curve (see text).

CONCLUSION

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.

ACKNOWLEDGMENTS

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 (No. 11133249) from the Ministry of Education, Science, Culture, and Sports, Japan.

References

[1] a) G. H. Brown, "Photochromism", Wiley-Interscience, New York (1971). b) H. Dürr and H. Bouas-Laurent, "Photochromism: Molecules and Systems", Elsevier, Amsterdam (1990). c) M. Irie and K. Uchida, *Bull. Chem. Soc. Jpn.*, **71,** 985 (1998).

[2] a) J.-P. Desvergne and H. Bouas-Laurent, *J. Chem. Soc., Chem. Commun.*, **1978,** 403. b) S. Shinkai, *Pure Appl. Chem.*, **59,** 425 (1987). c) M. Irie and M. Kato, *J. Am. Chem. Soc.*, **107,** 1024 (1985). d) M. Irie, *Adv. Polymer Sci.*, **94,** 27 (1990). e) T. Ikeda, T. Sasaki, and K. Ichimura, *Nature*, **361,** 428 (1993). f) Y. Atassi, J. A. Delaire, and K. Nakatani, *J. Phys, Chem.*, **99,** 16320 (1995).

[3] O. Kahn, "Molecular Magnetism", VCH, New York (1993).

[4] a) O. Sato, T. Iyoda, A. Fujishima, and K. Hashimoto, *Science*, **272,** 704 (1996). b) Z.-Z. Gu, O. Sato, T. Iyoda, K. Hashimoto, and A. Fujishima, *J. Phys. Chem.*, **100,** 18289 (1996). c) M.-L. Boillot, C. Roux, J.-P. Audière, A. Dausse, and J. Zarembowitch, *Inorg. Chem.*, **35,** 3975 (1996). d) W. Fujita and K. Awaga, *J. Am. Chem. Soc.*, **119,** 4563 (1997). e) K. Hamachi, K. Matsuda, T. Itoh, and H. Iwamura, *Bull. Chem. Soc. Jpn.*, **71,** 2937 (1998).

[5] a) K. Uchida, Y. Nakayama, and M. Irie, *Bull. Chem. Soc. Jpn.*, **63,** 1311 (1990). b) M. Hanazawa, R. Sumiya, Y. Horikawa, and M. Irie, *J. Chem. Soc., Chem. Commun.*, **1992,** 206.

[6] B. Bleaney and K. D. Bowers, *Proc. R. Soc. London. ser. A*, **214,** 451 (1952).