

## Photochromic diarylethene as an information processing unit: Magnetic and electric switching\*

Kenji Matsuda

Department of Chemistry and Biochemistry, Graduate School of Engineering,  
Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan

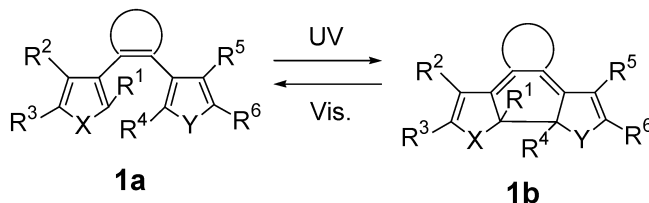
**Abstract:** Photochromic compounds reversibly change not only the absorption spectra but also their geometrical and electronic structures. This principle can be applied for the photo-switching of the physical properties of the molecular materials. In particular, photoswitching of the flow of information through the molecule is interesting because information processing using molecular devices is attracting interest in the molecular electronics field. The photoswitchings of the magnetic exchange interaction and the electrical conductance using photochromic diarylethene are described.

**Keywords:** photochromism; magnetism; exchange interaction; electric conductance; gold nanoparticles.

### INTRODUCTION

Photochromism is a reversible phototransformation of a chemical species between two forms having different absorption spectra [1–4]. Photochromic compounds reversibly change not only the absorption spectra but also their geometrical and electronic structures. The geometrical and electronic structural changes induce some changes in physical properties, such as fluorescence, refractive index, polarizability, and electric conductivity.

Diarylethenes with heterocyclic aryl groups are well known as thermally irreversible, highly sensitive, and fatigue-resistant photochromic compounds [5,6]. The photochromic reaction is based on a reversible transformation between an open-ring isomer with hexatriene structure and a closed-ring isomer with cyclohexadiene structure according to the Woodward–Hoffmann rule as shown in Fig. 1. While the open-ring isomer **1a** is colorless in most cases, the closed-ring isomer **1b** has the color of yellow, red, or blue, depending on the molecular structure.



**Fig. 1** Photochromism of diarylethene.

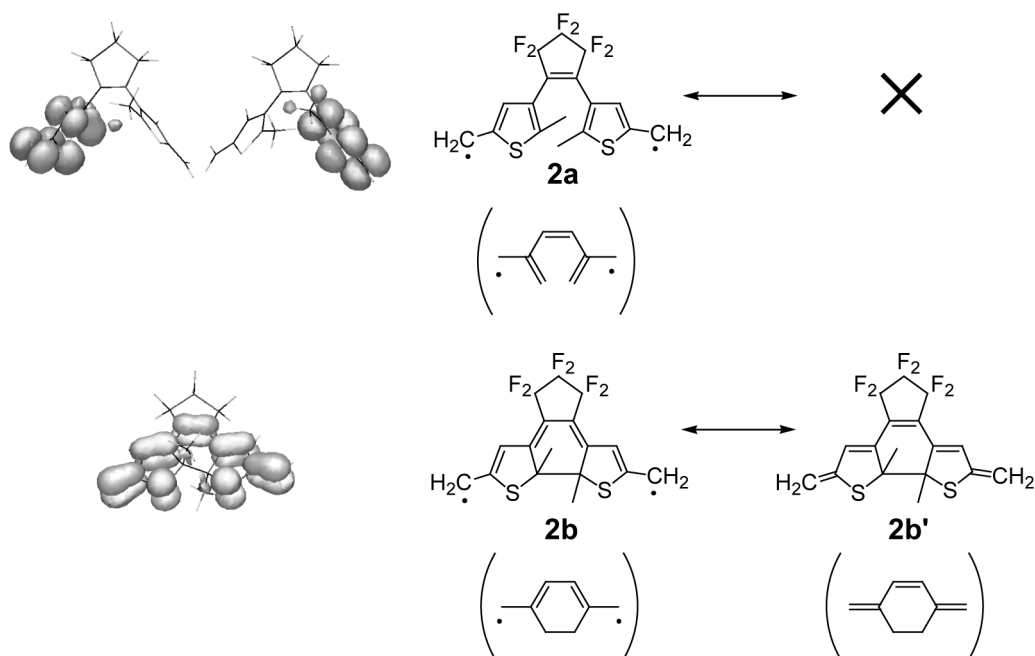
\*Paper based on a presentation at the 12<sup>th</sup> International Symposium on Novel Aromatic Compounds (ISNA-12), 22–27 July 2007, Awaji Island, Japan. Other presentations are published in this issue, pp. 411–667.

In the open-ring isomer,  $\pi$ -electrons are localized in the two aryl groups. On the other hand, the closed-ring isomer has a bond-alternative polyene structure and the  $\pi$ -electrons are delocalized throughout the molecule. These geometrical and electronic structural differences resulted in some differences in their physical properties. For example, the closed-ring isomer has a higher polarizability, because the closed-ring isomer has more delocalized  $\pi$ -electrons [7,8].

The  $\pi$ -conjugated system was reversibly switched by the photochromic reaction. In this paper, the utilization of this switching to the photoswitching of the flow of the information is described, featuring the magnetic exchange interaction and the electrical conductance.

## MAGNETIC SWITCHING

With regard to the magnetic interaction, there is a characteristic feature in the electronic structural changes between the two isomers of diarylethene. Figure 2 shows model structures of a radical-substituted diarylethene, the open-ring isomer **2a**, and closed-ring isomer **2b**. While there is no resonant closed-shell structure for **2a**, there does exist **2b'** as the resonant quinoid-type closed-shell structure for **2b**. **2a** is a non-Kekulé biradical, and **2b** is a normal Kekulé molecule. In other words, **2a** has two unpaired electrons, while **2b** has no unpaired electrons. Moreover, the calculated shapes of two singly occupied molecular orbitals (SOMOs) of **2a** are separated in the molecule and there is no overlap [9]. Therefore, the configuration of biradical **2a** is classified as a disjoint biradical, in which the intra-molecular radical–radical interaction is weak [10,11]. On the other hand, the closed-ring isomer **2b'** is a normal Kekulé molecule. In this case, the ground electronic state has no unpaired electrons. In the singlet ground state, the magnetic interaction is strongly antiferromagnetic. Judging from the above consideration, the interaction between spins in the open-ring isomer of diarylethene is weak, while significant antiferromagnetic interaction takes place in the closed-ring isomer. In other words, the open-ring isomer is in the “OFF” state and the closed-ring isomer is in the “ON” state.



**Fig. 2** The open-ring isomer **2a** and the closed-ring isomer **2b** of the radical-substituted diarylethene. Two SOMOs of **2a** and HOMO of **2b** are also shown.

According to the above guiding principle, the molecule which exhibits photoswitching of the magnetic interaction was synthesized. 1,2-Bis(2-methyl-1-benzothiophen-3-yl)perfluorocyclopentene was employed as a photochromic spin coupler. Nitronyl nitroxide was chosen for the spin source, because this radical is  $\pi$ -conjugative. Thus, molecule **3a** was designed, which is an embodiment of the simplified model **2a** [9] (Fig. 3). The open-ring isomer **3a** has a twisted molecular structure and a disjoint electronic configuration. The measurement of the temperature dependence of the magnetic susceptibility revealed that while in the open-ring isomer **3a**, only small exchange interaction was detected between the two spins, the significant antiferromagnetic interaction was observed for the closed-ring isomer **3b**. The photoinduced change in magnetism agrees well with the prediction that the open-ring isomer has an “OFF” state and the closed-ring isomer has an “ON” state.

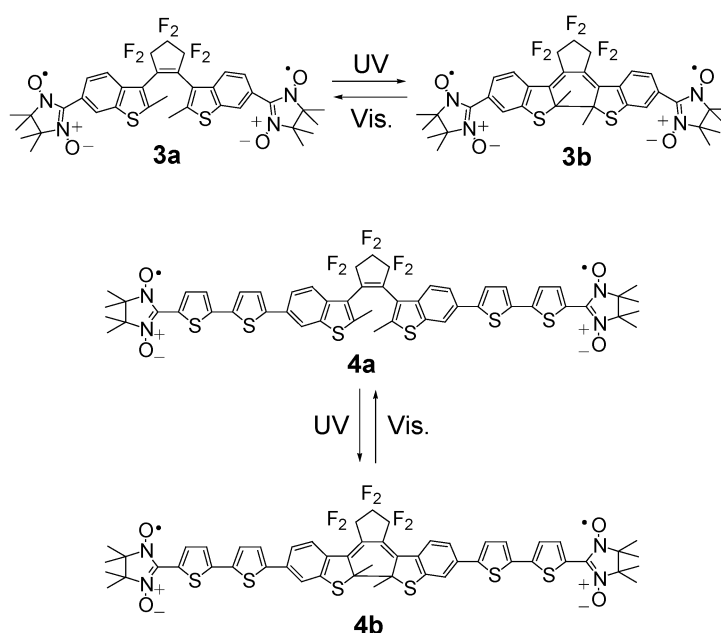
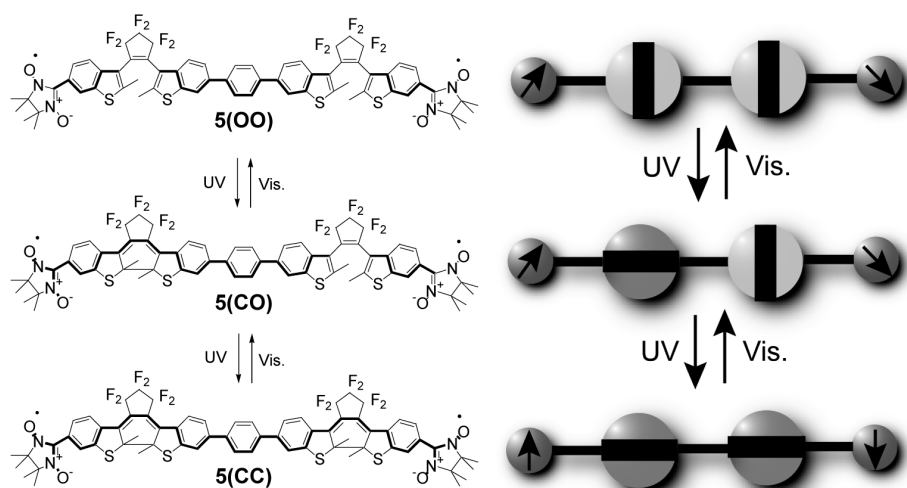


Fig. 3 Photochromism of diarylethene having two nitronyl nitroxide organic radicals.

Oligothiophenes are good candidates for conductive molecular wires. Diarylethene **4a** having one nitronyl nitroxide radical at each end of a molecule containing oligothiophene spacers was synthesized. The measurement of the electron spin resonance (ESR) spectrum at room temperature revealed the clear photoswitching of the magnetic exchange interaction. In the case of bithiophene spacers, the difference in exchange interaction between the open- and the closed-ring isomers was estimated to be more than 150-fold [12].

Photoswitching of an intramolecular magnetic interaction using a diarylethene dimer was also investigated [13] (Fig. 4). 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). Diarylethene dimer **5** was synthesized and ESR spectra of isolated **5(OO)**, **5(CO)**, and **5(CC)** were measured. The spectra of **5(OO)** and **5(CO)** are 5-line spectra, suggesting that the exchange interaction between the two nitronyl nitroxide radicals is much weaker than the hyperfine coupling constant. However, the spectrum of **5(CC)** has a clear 9-line spectrum, indicating that the exchange interaction between the two spins is much stronger than the hyperfine coupling constant. The result indicates that each diarylethene chromophore serves as a switching unit to control the magnetic interaction. The magnetic interaction between terminal nitronyl nitroxide radicals was controlled by the switching units in series.



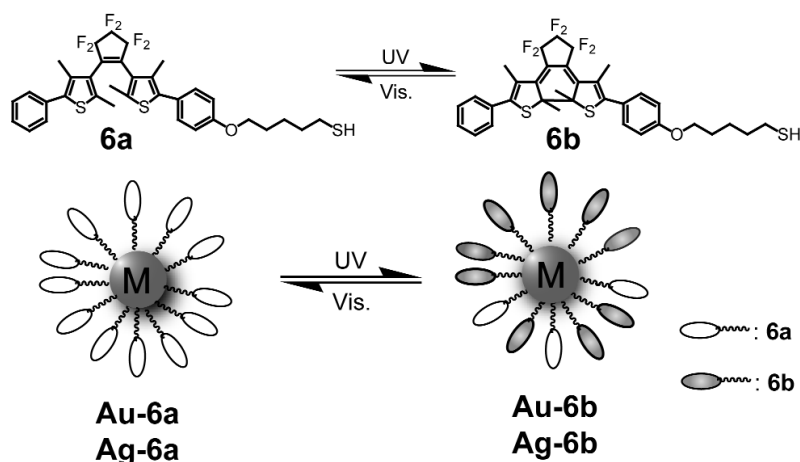
**Fig. 4** Photochromic reaction and schematic illustration of diarylethene **5**. The bold line represents the pathway of  $\pi$ -conjugation.

### ELECTRIC SWITCHING

“Molecular electronics” is a rapidly expanding field in nanoscience and nanotechnology. Molecular electronics can be defined narrowly as the study of electrical and electronic processes by accessing the individual molecules with electrodes and exploiting the molecular structure to control the flow of electrical signals through them.

Although there are increasing numbers of reports dealing with the conductance of the single molecules, studies on the photoswitchable molecule are very rare [14–17]. Besides, the studies on the conductance of the network prepared with organic molecules and Au nanoparticles on the interdigitated nanogapped electrode are attracting interest because of the relatively easy preparation and the applicability to the small number of molecules [18–20].

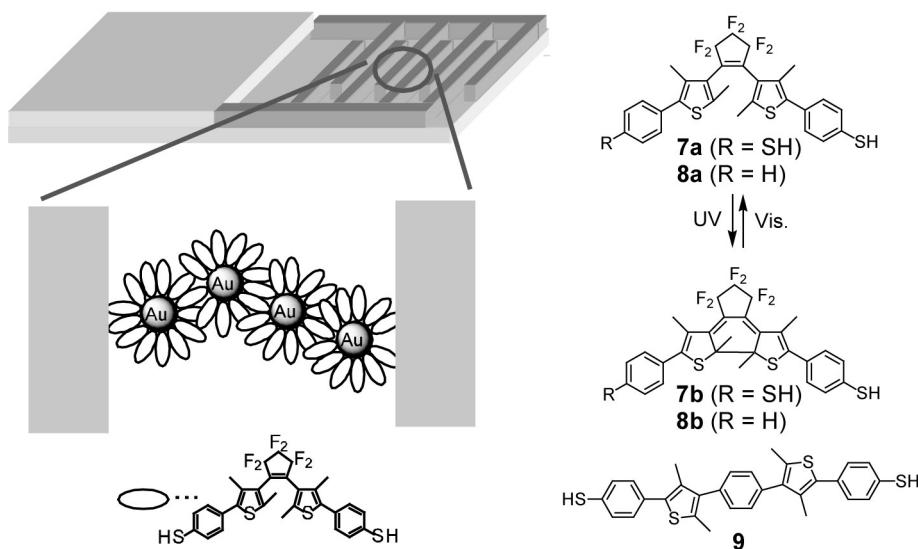
The excited state of the organic molecules on noble metal surface is considered to be easily quenched by the surface plasmon resonance. Therefore, the photochromism of diarylethene on the Au and Ag nanoparticle was first investigated (Fig. 5). Synthesized Au and Ag nanoparticles capped with



**Fig. 5** Photochromic reaction of diarylethene **6** and Au- and Ag-**6**.

a diarylethene derivative (**Au-6a**) showed reversible photochromism [21,22]. This is attributed to the fast photoreaction of diarylethenes in comparison with the quenching by the Au metal surface.

Considering that the conjugated molecule has much better conductance than nonconjugated molecule [23], sulfur atom should be attached directly to the  $\pi$ -conjugated system despite the anticipated quenching of the excited state. Thus, diarylethene dithiophenol **7a** was designed and synthesized [24]. The introduced two thiophenol units bridge the Au nanoparticles and make a conducting path between electrodes (Fig. 6). Au nanoparticles capped with monothiophenol **8a** were synthesized to see the effect of the direct attachment on the photoreactivity. For reference, nonphotoreactive dithiophenol **9** was also prepared.

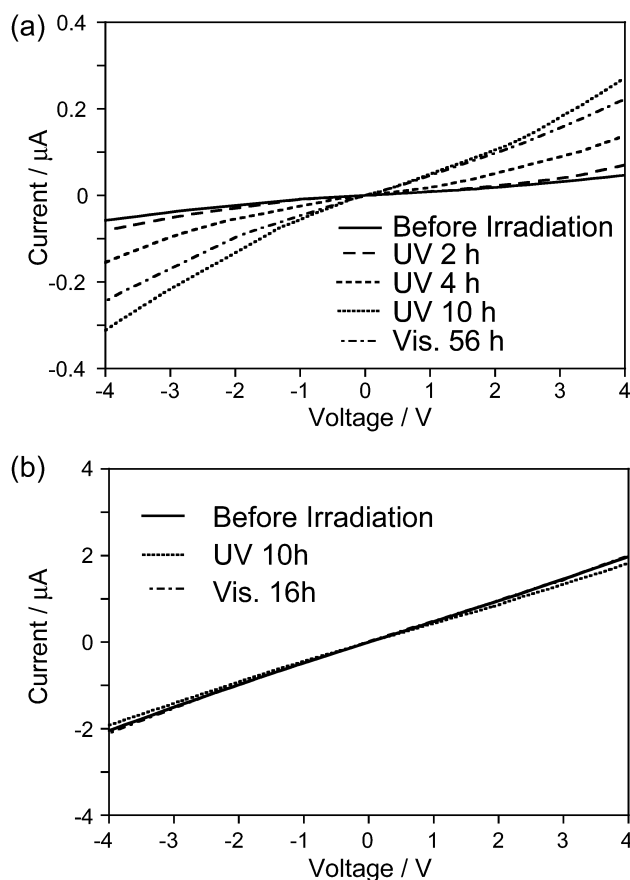


**Fig. 6** Schematic drawing of the diarylethene-Au nanoparticle network on an interdigitated nanogapped Au electrode.

The **Au-7** network showed photochromism in the solid state. The absorption spectra of **Au-7** network were measured in KBr. The spectrum showed reversible change along with the photochromism. From the difference spectra, the absorption maximum of the closed-ring isomer **Au-7b** exhibited the large bathochromic shift compared with free **7b**, indicating the perturbation of the electronic structure of the closed-ring isomer **7b** by Au. The gold nanoparticles prepared from monothiophenol **8a** also showed photochromism, though it was less reactive than the alkyl-containing analog **Au-6a** [21]. The absorption maximum of **Au-8b** measured in ethyl acetate also showed bathochromic shift on the Au surface.

The **Au-7a** nanoparticle network was prepared on the interdigitated nanogapped Au electrode (5  $\mu\text{m}$ ). The preparation of the network was performed on the electrode by mixing the tetraoctylammonium bromide (TOAB)-protected Au nanoparticle and the freshly prepared **7a** solution. Transmission electron microscopy (TEM) revealed the formation of the Au nanoparticles of  $3.6 \pm 0.7$  nm. Scanning electron microscopy (SEM) measurement showed the formation of the bridging between the electrodes.

Conductance was measured along with the alternate irradiation with UV and visible light (Fig. 7). Upon irradiation with UV light ( $290 \text{ nm} < \lambda < 380 \text{ nm}$ ), the conductance increased significantly and the conductance decreased by the irradiation with visible light ( $560 \text{ nm} < \lambda$ ). The **Au-9** network, prepared for reference, did not show any change upon photoirradiation (Fig. 7b). The photoreaction of the **Au-7a** nanoparticle network was very slow especially for the ring-opening reaction due to the severe quench-



**Fig. 7** Change of the I-V curve of (a) **Au-7** network and (b) **Au-9** network on the interdigitated Au nanogapped electrode. UV light ( $290\text{ nm} < \lambda < 380\text{ nm}$ ) and visible light ( $560\text{ nm} < \lambda$ ) were used for the experiment.

ing, which is also observed in the **Au-8a** nanoparticles. When the UV irradiation was carried out for 10 h, the maximum ON/OFF ratio of the conductance was more than fivefold, but the conductance was not completely restored by the visible irradiation. To check the reversibility, the same measurement was performed with 30 min of the UV irradiation, which is shorter than the previous experiment. In this case, the ON/OFF ratio was as small as 1.2-fold, but the complete reversibility was observed. The absolute value of the conductance varied with the different setups because the network formed on the electrode varied with the different setups. But the photochemical change of the conductance did not vary.

## CONCLUSIONS

In conclusion, information processing using photochromic diarylethenes was described. When the two organic radicals were placed at each end of the diarylethene molecule, the magnetic exchange interaction between two spins was photoswitched efficiently. By preparing the diarylethene-Au nanoparticles network made of diarylethene dithiophenol, the photoswitching of conductance through the organic molecule has been achieved.

## ACKNOWLEDGMENTS

The author greatly acknowledges Prof. Masahiro Irie for his extensive advice. We acknowledge PRESTO, Japan Science and Technology Agency, and a Grant-in-Aid for Scientific Research on Priority Areas (769) from the Ministry of Education, Culture, Sports, Science, and Technology for financial support.

## REFERENCES

1. B. L. Feringa (Ed.). *Molecular Switches*, Wiley-VCH, Weinheim (2001).
2. G. H. Brown. *Photochromism*, Wiley-Interscience, New York (1971).
3. H. Dürr, H. Bouas-Laurent (Eds.). *Photochromism: Molecules and Systems*, Elsevier, Amsterdam (2003).
4. H. Bouas-Laurent, H. Dürr. *Pure Appl. Chem.* **73**, 639 (2001).
5. M. Irie. *Chem. Rev.* **100**, 1685 (2000).
6. K. Matsuda, M. Irie. *J. Photochem. Photobiol., C* **5**, 169 (2004).
7. T. Kawai, N. Fukuda, D. Dröschl, S. Kobatake, M. Irie. *Jpn. J. Appl. Phys.* **38**, L1194 (1999).
8. J. Chauvin, T. Kawai, M. Irie. *Jpn. J. Appl. Phys.* **40**, 2518 (2001).
9. K. Matsuda, M. Irie. *J. Am. Chem. Soc.* **122**, 7195 (2000).
10. W. T. Borden, E. R. Davidson. *J. Am. Chem. Soc.* **99**, 4587 (1977).
11. K. Matsuda, H. Iwamura. *J. Am. Chem. Soc.* **119**, 7412 (1997).
12. K. Matsuda, M. Matsuo, M. Irie. *J. Org. Chem.* **66**, 8799 (2001).
13. K. Matsuda, M. Irie. *J. Am. Chem. Soc.* **123**, 9896 (2001).
14. D. Dulić, S. J. van der Molen, T. Kudernac, H. T. Jonkman, J. J. D. de Jong, T. N. Bowden, J. van Esch, B. L. Feringa, B. J. van Wees. *Phys. Rev. Lett.* **91**, 207402 (2003).
15. J. He, F. Chen, P. A. Liddell, J. Andréasson, S. D. Straight, D. Gust, T. A. Moore, A. L. Moore, J. Li, O. F. Sankey, S. M. Lindsay. *Nanotechnology* **16**, 695 (2005).
16. N. Katsonis, T. Kudernac, M. Walko, S. J. van der Molen, B. J. van Wees, B. L. Feringa. *Adv. Mater.* **18**, 1397 (2006).
17. M. Taniguchi, Y. Nojima, K. Yokota, J. Terao, K. Sato, N. Kambe, T. Kawai. *J. Am. Chem. Soc.* **128**, 15062 (2006).
18. T. Ogawa, K. Kobayashi, G. Masuda, T. Takase, S. Maeda. *Thin Solid Films* **393**, 374 (2001).
19. H. Shigi, S. Tokonami, H. Yakabe, T. Nagaoka. *J. Am. Chem. Soc.* **127**, 3280 (2005).
20. M. Minamoto, M. M. Matsushita, T. Sugawara. *Polyhedron* **24**, 2263 (2005).
21. K. Matsuda, M. Ikeda, M. Irie. *Chem. Lett.* **33**, 456 (2004).
22. H. Yamaguchi, M. Ikeda, K. Matsuda, M. Irie. *Bull. Chem. Soc. Jpn.* **79**, 1413 (2006).
23. X. Xiao, B. Xu, N. J. Tao. *Nano Lett.* **4**, 267 (2004).
24. M. Ikeda, N. Tanifuji, H. Yamaguchi, M. Irie, K. Matsuda. *Chem. Commun.* 1355 (2007).