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Award Accounts

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Photoswitching of Intramolecular Magnetic Interaction Using Diarylethene Photochromic Spin Couplers

Kenji Matsuda

Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University,
and PRESTO, JST, 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581

Received August 30, 2004; E-mail: kmatsuda@cstf.kyushu-u.ac.jp

Diarylethene is a photochromic molecule, which is potentially applicable to various optoelectronic devices. In diarylethenes the π-system of the two aryl rings is separated in the open-ring isomer, while the π-system is delocalized throughout the molecule in the closed-ring isomer. Based on this idea the exchange interaction between two nitronyl nitroxide radicals connected by a diarylethene unit was photocontrolled reversibly along with photochromism. The switching efficiency is more than 150-fold and thiophene spacer transmits the interaction more efficiently. When diarylethene dimer is used for the switching unit, the electric circuit-like behavior was observed. Moreover, reversed switching is achieved by reversing the thiophene ring. Magnetochemical and photochemical behavior of the radical-substituted diarylethene is described extensively.

Magnetism generally originates from the electron spin of an unpaired electron in a transition metal. When there is no interaction between individual spins, the electron spins behave independently. In such a case, the observed magnetism is paramagnetic. The exchange interaction makes the electron spins align parallel or antiparallel. When the exchange interaction is ferromagnetic ($J > 0$), the alignment is parallel, and when the exchange interaction is antiferromagnetic ($J < 0$), the alignment is antiparallel. When such alignment was achieved throughout the material, the electron spins have a long-range order and exhibit a cooperative phenomenon, such as ferromagnetism or ferrimagnetism.

Not only the electron spins of the transition metals but also the spins of the organic radicals can participate in the construction of magnetic materials. “Molecular Magnetism” is the field of science that deals with magnetic materials which are designed and synthesized from several kinds of metallic ions, organic radicals, and bridging units.[1–4] In this field, one of the ultimate goals was to make ferromagnets only from organic components. In 1991, Kinoshita et al. reported the first organic ferromagnet 2-(*p*-nitrophenyl)nitronyl nitroxide (4,4,5,5-tetramethyl-2-(4-nitrophenyl)imidazoline-1-oxyl-3-oxide) **1** (Chart 1).[5] However, this compound utilizes an intermolecular interaction that depends on the crystal structure. The magnetic property is controlled by the crystal structure, which is difficult to predict.

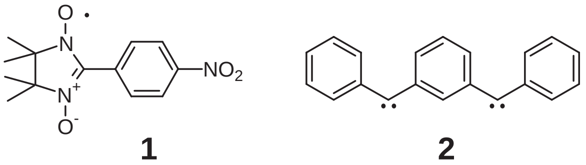

Chart 1.

The exchange interaction can also operate through chemical bonds within the molecule even more effectively. Dicarbene **2** is a classic example of this intramolecular interaction; it has a quintet ground state due to the ferromagnetic exchange interaction between two carbene centers.[6,7] The intramolecular interaction through the chemical bond depends on the molecular structure; therefore, the interaction can be regulated by molecular design. Organic molecules have advantages thanks to their various structures and functions. Organic compounds have been used in many fields, such as electroluminescent dyes, conductive polymers, and photochromic dyes. Therefore, by combinations of the organic radical and the functional organic molecule, highly integrated multi-functional magnetic materials will be constructed. In this account, the photofunctionalization of the organic magnetic material will be described. The background of the molecular design is also discussed intensively.

Intramolecular Magnetic Interaction

When two unpaired electrons are placed in proximity, the exchange interaction operates between the two electrons. The exchange interaction results in the separation of the energy of the singlet state (the spin quantum number equals zero) and that of the triplet state (the spin quantum number equals one). In the singlet state, the two spins align antiparallel, while the two spins align parallel in the triplet state. This means that

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the exchange interaction itself is the magnetic interaction. From the Heisenberg Hamiltonian (Eq. 1), the singlet–triplet energy gap $\Delta E_{\text{S–T}}$ can be expressed by the exchange interaction J as Eq. 2.

$$\hat{\mathbf{H}} = -2J\mathbf{S}_1 \cdot \mathbf{S}_2 \tag{1}$$

$$\Delta E_{\text{S–T}} = 2J. \tag{2}$$

When J is positive, the ground state is triplet; when J is negative, the ground state is singlet.

When an unpaired electron is placed at each end of a π-conjugated system, the two spins of the unpaired electrons interact magnetically through the π-system effectively. So, the π-conjugated system can be regarded as a "spin coupler".[8] The direction of the spin alignment and the sign of exchange interaction are regulated by the Ovchinnikov rule.[9] The interaction magnitude becomes weaker exponentially with an increase in the spacer length. In Fig. 1, several examples of bis(nitronyl nitroxide)s and the exchange interactions between two spins are shown. **3**,[10,11] **5**,[13] **7**,[14] and **8**[14] have even numbers of sp^2 carbon atoms between the two radicals, so the interaction is antiferromagnetic ($J < 0$). On the other hand, **4**[12] and **6**[13] have odd numbers of sp^2 carbon atoms between two radicals. In these cases, the interaction is ferromagnetic ($J > 0$). **7** and **8** have similar structures but **8** has a longer chain length, so **8** has a weaker interaction than **7**. When **3** and **5**, or **4** and **6** are compared, one may also recognize that the thiophene is superior to the phenylene as a spin coupler. The magnetic exchange interaction is dependent on the nature of the π-system placed between the spins.

To determine the magnetic interactions, there are several measuring methods. First of all, measuring the temperature dependence of the magnetic susceptibility is the most common method. When the two electron spins ($S = 1/2$) are coupled with exchange interaction J, the magnetic susceptibility χ values are expressed as a function of temperature T.[15]

$$\chi = \frac{2Ng^2\mu_{\text{B}}^2}{kT[3 + \exp(-2J/kT)]} \tag{3}$$

where g is the landé g factor, μ_{B} is the Bohr magneton, and k is the Boltzmann constant. When $J < 0$, χT decreases as the temperature decreases, and when $J > 0$, χT increases as the temperature decreases. This method can be used to determine rather strong interactions ($|J/k_{\text{B}}| >$ ca. 10 K), but can not be applied to measure weak interactions.

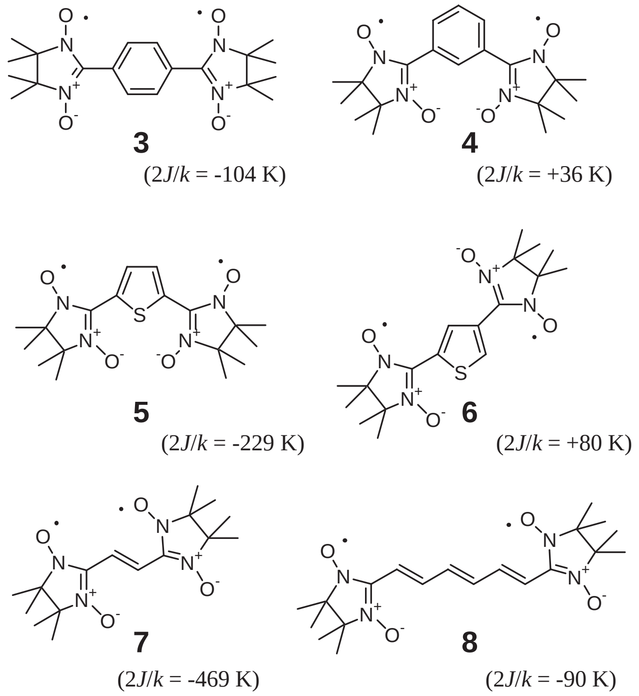


Fig. 1. Several bis(nitronyl nitroxide)s and the exchange interactions between two spins.

One method to detect weak interactions is to perform the ESR measurement in solution.[16,17] The hyperfine coupling in the ESR spectrum gives information concerning the magnetic interaction. For example, nitronyl nitroxides themselves have two identical nitrogen atoms; the molecules give 5-line ESR spectra with relative intensities 1:2:3:2:1 and a 7.5 G spacing. When two nitronyl nitroxides are magnetically coupled via an exchange interaction, the biradical gives a 9-line ESR spectrum with relative intensities 1:4:10:16:19:16:10:4:1 and a 3.7 G spacing. If the exchange interaction is weaker than the hyperfine coupling in the biradical, the two nitroxide radicals are magnetically independent and give the same spectrum as the independent monoradical. In intermediate situations, the spectrum becomes complex. This method is applicable to measure rather weak interactions ($|J/k| \sim$ ca. 0.01 K).

The measurement of the magnetic field dependence of the magnetization M is also a sensitive method for the determination of the singlet–triplet energy gap ($|J/k| \sim$ ca. 1 K).[18,19] If the Zeeman energy of the spins with an external magnetic field is not strong relative to the thermal energy kT, the magnetization of the paramagnetic species develops as the applied field is increased and/or the temperature is lowered. The resulting behavior is described by a Brillouin function. Furthermore, when the singlet–triplet energy gap ($2J$) of a biradical is comparable to the Zeeman splitting, the Brillouin function is expanded into Eq. 4. In this case, the magnetic susceptibility χ in Eq. 3 is $(\partial M/\partial H)_{\text{H}=0}$. Since χ only corresponds to the slope of Eq. 4 at very small applied magnetic fields, χ utilizes only a part of the information that is available by plotting the magnetization against the magnetic field strength.

$$M = Ng\mu_{\text{B}} \frac{\exp(g\mu_{\text{B}}H/kT) - \exp(-g\mu_{\text{B}}H/kT)}{\exp(g\mu_{\text{B}}H/kT) + 1 + \exp(-g\mu_{\text{B}}H/kT) + \exp(-2J/kT)}. \tag{4}$$

Disjoint and Non-disjoint Biradicals

The classification of biradicals (Fig. 2) should be noted here. If a biradical has no resonant closed-shell structure, the biradical is classified as a non-Kekulé biradical. The non-Kekulé biradical can be further classified into disjoint and non-disjoint biradicals.[20] Trimethylenemethane (TMM) **9** is a typical example of a non-disjoint biradical. The two singly occupied molecular orbitals (SOMOs) of **9** overlap in space. On the other hand, tetramethyleneethane (TME) **10** is a disjoint biradical. The two SOMOs of **10** do not overlap in space.

If a biradical has a resonant closed-shell structure, the closed-shell structure is more stable and the molecule therefore exists as a normal closed-shell Kekulé molecule. 1,3-Buta-

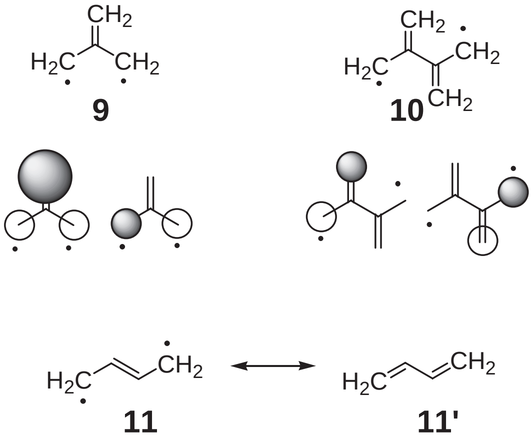


Fig. 2. The molecular structure and the shape of the orbitals of trimethylenemethane **9**, tetramethyleneethane **10**, and butadiene **11′**.

diene **11′** is an example of a normal Kekulé molecule; it has the resonant biradical structure, 2-butene-1,4-diyl **11**. In this case, the closed-shell structure **11′** is the ground state, so the ground electronic state has no unpaired electrons. In other words, the magnetic interaction between the two spins in the structure **11** is strongly antiferromagnetic.

The magnetic interactions in the disjoint and non-disjoint biradicals have been theoretically investigated by Borden and Davidson, who used perturbational MO theory. While TMM **9** should have a ground triplet state, the singlet and triplet states of TME **10** are nearly degenerate; and higher order terms favor a singlet ground state for planar TME **10**.[20] Ovchinnikov applied valence bond (VB) theory to conclude that the spin quantum number (S) is given by $S = (n^* - n)/2$, where n^* and n are the numbers of starred and unstarred carbon atoms, respectively. The S values of TMM **9** and TME **10** are predicted by this rule to be 1 and 0, respectively,[9] leading again to the prediction of a triplet ground state for TMM **9** but a singlet ground state for planar TME **10**.

The dependence of the singlet–triplet splitting in TME **10** on the dihedral angle ϕ between the two $(CH_2)_2C$ units has been calculated.[21–28] Based on the results of large CI calculations, Jordan et al. predicted that the triplet state would become more stable than the singlet state at the optimized triplet geometry of $\phi = 59°$; more planar or more twisted structures would favor a singlet ground state.[28]

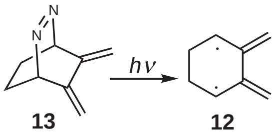
The triplet ground state of TMM **9**, predicted by theory, has been confirmed by experiments.[29–36] However, despite the predictions of a singlet ground state for planar TME **10** and even prior to these predictions, triplet EPR spectra had been observed for TME **10** by Dowd[37] and for 2,3-dimethylenecyclohexane-1,4-diyl (**12**), a conformationally restricted analog, by Roth and Erker.[38] Nevertheless, it was not clear until 1986 whether the triplet is the ground state or a thermally populated state of TME **10** and of **12**. In that year, Dowd et al. studied the temperature dependence of the EPR spectra of TME **10** and of **12** and found that the signal intensities obeyed Curie law in the temperature ranges 16–65[39] and 15–53 K,[40] respectively. Although these experiments allow the possibility that the singlet and triplet states are degenerated within 30–40 $cal\cdot mol^{-1}$ in both molecules, a triplet ground state was proposed. Such a conclusion was based on the hypothesis that it was clearly less likely that both TME **10** and the more conformationally restricted **12** had nearly degenerate singlet and triplet states.

The question of the energy separation between the singlet and triplet states of TME **10** and of **12** has attracted the interest of many theoretical[21–28] and experimental[37–43] chemists, has evoked some controversy, and therefore should be answered by proper methods.[8] As mentioned before, the measurement of the magnetic field dependence of the magnetization is very sensitive to the small singlet–triplet energy gap. We adopted this method to study the magnetic interactions in TME **10** and in its derivative **12**.

Determination of the Exchange Interaction in a TME Derivative

Diradical **12** was obtained by the photolysis of 5,6-dimethylene-2,3-diazabicyclo[2.2.2]oct-2-ene (**13**) (Eq. 5), which was the method for generating **12** that was employed by Dowd et al. (Fig. 3).[40] Magnetic measurements were performed on a SQUID susceptometer/magnetometer for samples of **12**. A solution of **13** in MTHF was placed in a quartz cell. Light ($\lambda > 320$ nm) was introduced to the SQUID susceptometer through an optical fiber introduced into a sample cell and the photolysis of **13** in MTHF was performed at 4–10 K for 14 h. The data before irradiation were subtracted as background data.

The field-dependence of the magnetization (M) of **12** is shown in Fig. 4. The fitting of Eq. 4 to the observed data by a least-squares method gave $2J/k = -0.76 \pm 0.16$ K ($= -1.5 \pm 0.3$ $cal\cdot mol^{-1}$ $= -6.3 \pm 1.3$ $J\cdot mol^{-1}$), indicating



13 **12**

Fig. 3. Photolytic generation of TME derivative **12**.

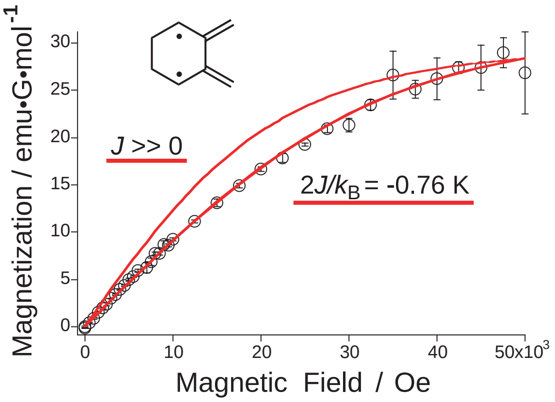


Fig. 4. Magnetic field dependence of magnetization of **12** measured at 2.0 K. Two solid curves are a theoretical $S = 1$ curve (top) and a best-fit curve (bottom) with a singlet–triplet gap of $2J/k = -0.76$ K (Eq. 4). Reprinted with permission from Ref. 18. Copyright 1997 American Chemical Society.

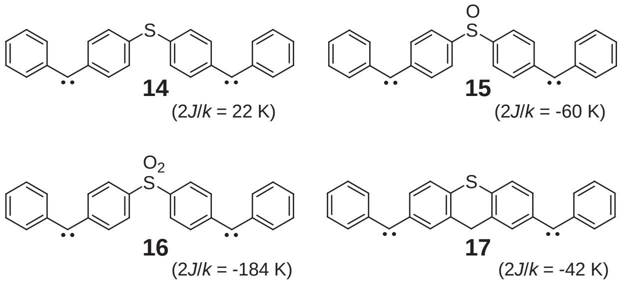


Fig. 5. Dicarbene with different kinds of sulfur-containing spin coupler.

that the singlet and triplet states are nearly degenerate in **12**. For a triplet ($S = 1$) ground state and $J \gg 0$, the last term in the denominator of Eq. 4 vanishes, and the corresponding theoretical curve does not fit the observed data at all. For $J \approx 0$, this term is equal to one, and therefore, the initial slope of the curve for $J \approx 0$ is $3/4$ of the curve for $J \gg 0$. The result was close to $3/4$, but the deviation from exact $3/4$ is due to the weak interaction $2J/k_B = -0.76$ K.

Control of the Magnetic Interaction by External Stimuli

Since the magnetic exchange interaction is dependent on the nature of the "spin coupler" connecting the two electron spins, the control of the magnetism is possible when the structure of the chain is perturbed by the external stimulus. On the basis of this idea, the author's group studied the exchange interaction between two triplet carbene centers through diphenyl sulfide 4,4′-diyl, its sulfoxide and sulfone analogs, and thiaxanthene 2,7-diyl coupling units (Fig. 5).[44] These dicarbenes were generated by the photolysis of the corresponding bis(diazo) precursors in MTHF matrices at cryogenic temperatures. Temperature dependence of the ESR signals showed that the dicarbene coupled by the diphenyl sulfide 4,4′-diyl group has a quintet ground state; it serves as a ferromagnetic coupler. On the other hand, as the oxidation state or the geometry of the sulfur atom was changed to sulfoxide, sulfone, and thiaxanthene groups, antiferromagnetic interaction was observed between the two diphenylcarbene units. The magnitude of the exchange interaction J/k was determined to be 11 K, -30 K, -92 K, and -21 K for diphenyl sulfide, sulfoxide, sulfone 4,4′-diyl, and thiaxanthene 2,7-diyl couplers, respectively. Such results demonstrated that the magnetic interaction could be tailored from ferro- to antiferromagnetic coupling by changing the oxidation state or the geometry of the sulfur atom.

Photochromic Spin Coupler

Photochromism is a reversible phototransformation of a chemical species between two forms having different absorption spectra.[45–48] 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. When the photochromic compounds are used as "spin couplers", the magnetic interaction can be controlled by photoirradiation. Not only our group but also others[49–54] have recently been interested in the photocontrol of magnetism of organic radical-based magnetic materials.

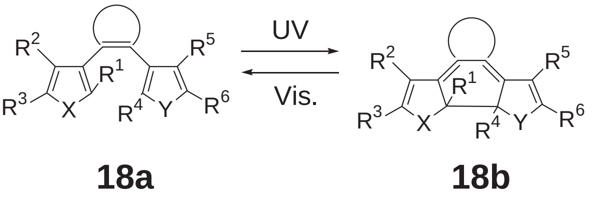


Fig. 6. Photochromism of diarylethene.

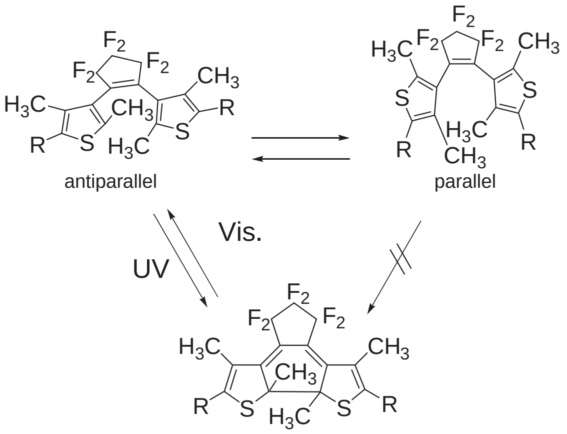


Fig. 7. Conformations of diarylethenes.

Diarylethenes with heterocyclic aryl groups are well known as thermally irreversible, highly sensitive, and fatigue-resistant photochromic compounds.[55,56] The photochromic reaction is based on a reversible transformation between the open-ring isomer with hexatriene structure and the closed-ring isomer with cyclohexadiene structure according to the Woodward–Hoffmann rule (Fig. 6). While the open-ring isomer **18a** is colorless in most cases, the closed-ring isomer has the color of yellow, red, or blue, depending on the molecular structure.

The difference in color is due to the differences in the geometrical and electronic structures. In the open-ring isomer, free rotation is possible between the ethene moiety and the aryl group. Therefore, the open-ring isomer is non-planar and the π-electrons are localized in the two aryl groups. Moreover, the open-ring isomer has two conformations: with the two rings in mirror symmetry (parallel conformation) or in C_2 symmetry (antiparallel conformation).[57] The photocyclization reaction can proceed only from the antiparallel conformation (Fig. 7). On the other hand, the closed-ring isomer has a planar structure, so there exist two enantiomers (*R*,*R* and *S*,*S*) originating from two asymmetric carbon atoms.[58–60] The closed-ring isomer has bond-alternative polyene structure and the π-electrons are delocalized throughout the molecule. These geometrical and electronic structural differences resulted in some differences in the physical properties. For example, the closed-ring isomer has a high polarizability, because the closed-ring isomer has more delocalized π-electrons.[61,62] Not only the change in polarizability, but also the switching in fluorescence[63–71] and electronic conduction[72–74] have been developed.

Diarylethene as a Photoswitch

There is a characteristic feature in the electronic structural

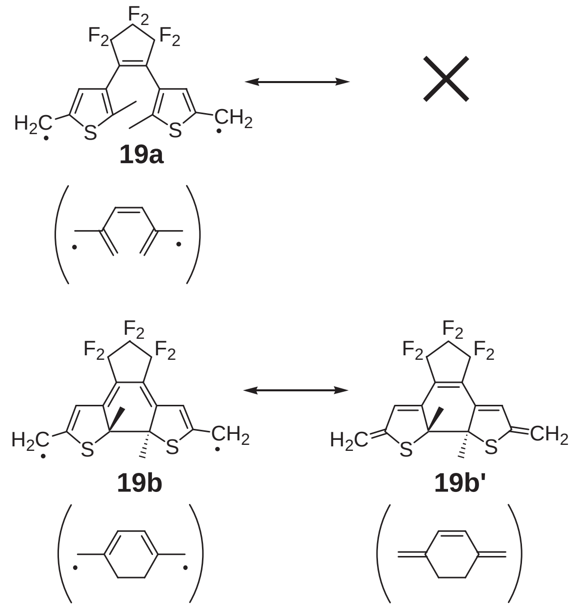


Fig. 8. The open-ring isomer **19a** and the closed-ring isomer **19b** of the radical-substituted diarylethene.

changes of diarylethenes. Figure 8 shows the open-ring isomer **19a** and closed-ring isomer **19b** of the radical-substituted diarylethenes with simplified structures. While there is no resonant closed-shell structure for **19a**, there does exist **19b′** as the resonant quinoid-type closed-shell structure for **19b**. **19a** is a non-Kekulé biradical, and **19b** is a normal Kekulé molecule. In other words, **19a** has two unpaired electrons, while **19b** has no unpaired electrons. The calculated shapes of two SOMOs of **19a** are separated in the molecule and there is no overlap.[75] This configuration is a typical disjoint biradical, in which the intramolecular radical–radical interaction is weak. In the open-ring isomer, the bond-alternation is discontinued at the 3-position of the thiophene rings. This is the origin of the disjoint nature of the electronic configuration of **19a**. **19a** is a disjoint non-Kekulé biradial and corresponds to tetramethyleneethane **10** in the former example. However, the closed-ring isomer **19b′** is a normal Kekulé molecule. In this case, the ground electronic state has no unpaired electrons. In this singlet ground state, the magnetic interaction is strongly antiferromagnetic. **19b′** corresponds to butadiene **11′** in the former example.

The electronic structural change of radical-substituted diarylethenes accompanying the photoisomerization is the transformation of a disjoint non-Kekulé structure to a closed-shell Kekulé structure. One may infer from the above consideration that 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 "OFF" state and the closed-ring isomer is "ON" state.

Photoswitching of Magnetic Interaction

Photochromic biradical **20a** was designed and synthesized by choosing 1,2-bis(2-methyl-1-benzothiophen-3-yl)perfluorocyclopentene as a photochromic spin coupler and nitronyl nitroxides as spin sources (Fig. 9).[75,76] The schematic representation is also shown in Fig. 9.

In solution, **20a** showed ideal photochromic behavior by irradiation with UV and visible light (Fig. 10). Although the radical moiety absorbed in the region from 550 to 700 nm, this did not prevent the photochromic reaction. Almost 100% photochemical conversions were observed in both the cyclization from open-ring isomer **20a** to closed-ring isomer **20b** and the cycloreversion from **20b** to **20a**. For the practical use of photochromic devices, high conversion is one of the most important characteristics.

Magnetic susceptibilities of **20a** and **20b** were measured on a SQUID susceptometer in microcrystalline form. χT–T plots are shown in Fig. 11. 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. The best-fit parameters obtained by means of a least-squares method were $2J/k_B = -2.2 \pm 0.04$ K for **20a** and $2J/k_B = -11.6 \pm 0.4$ K for **20b**. Although the interaction ($2J/k_B = -2.2$ K) between the two spins in the open-ring isomer **20a** was weak, the spins of **20b** have a remarkable antiferromagnetic interaction ($2J/k_B = -11.6$ K).

The open-ring isomer **20a** had a twisted molecular structure and a disjoint electronic configuration. On the other hand, the

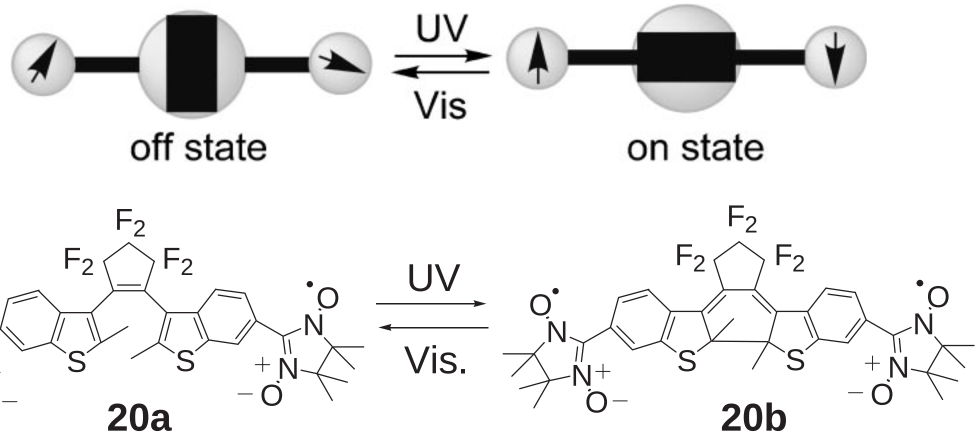


Fig. 9. Photoswitching of intramolecular magnetic interaction. Top: schematic representation, bottom: synthesized molecule.

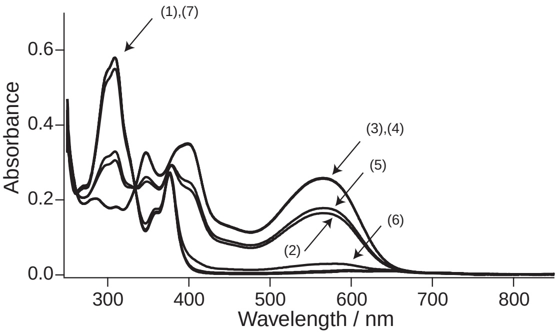


Fig. 10. The photochromic reaction of **20** (in EtOAc, 1.7×10^{-5} M): 1) the open-ring isomer; 2) irradiated with 313 nm light for 1 min; 3) for 5 min; 4) for 10 min; 5) irradiated with 578 nm light for 5 min; 6) for 30 min; 7) for 60 min (Ref. 76).

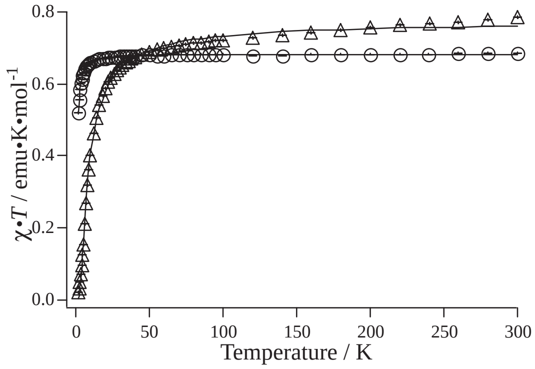


Fig. 11. Temperature dependence of the magnetic susceptibility of **20a** (○) and **20b** (△) (χT–T plot) (Ref. 76).

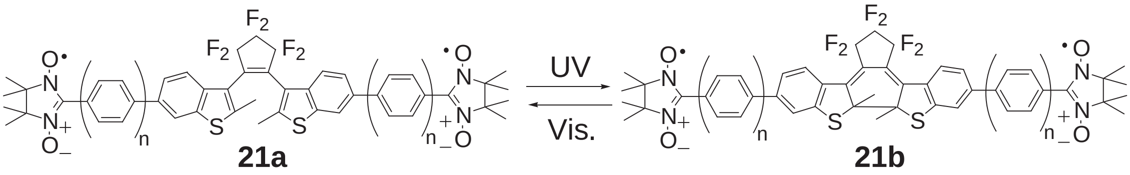


Fig. 12.

closed-ring isomer **20b** had a planar molecular structure and a non-disjoint electronic configuration. 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.

Although the switching of exchange interaction was detected by a susceptibility measurement of biradical **20**, both open- and closed-ring isomers **20a** and **20b** had 9-line ESR spectra because the exchange interaction between the two radicals was much stronger than the hyperfine coupling constant in both isomers. For one to detect the change of the exchange interaction by ESR spectroscopy, the value of the interaction should be comparable to the hyperfine coupling constant. Therefore, biradicals **21** (***n* = 1, 2**), in which *p*-phenylene spacers are introduced to control the strength of the exchange interaction, were designed and synthesized (Fig. 12).[77,78]

As described earlier, when two nitronyl nitroxides are magnetically coupled via an exchange interaction, the biradical gives a 9-line ESR spectrum. If the exchange interaction is weaker than the hyperfine coupling, the two nitroxide radicals are magnetically independent and give a 5-line spectrum. In intermediate situations, the spectrum becomes complex.[16,17]

Diarylethenes **21a** (***n* = 1, 2**) also underwent reversible photochromic reactions by alternative irradiation with UV and visible light. The changes in the ESR spectra accompanying the photochromic reaction were examined for diarylethenes **21a** (***n* = 1, 2**). Figure 13 shows the ESR spectra at different stages of the photochromic reaction of **21a** (***n* = 1**). The ESR spectrum of **21a** (***n* = 1**) showed a complex of 15 lines. This suggests that the two spins of nitronyl nitroxide radicals were coupled by an exchange interaction that is comparable to the hyperfine coupling constant. Upon irradiation with 366 nm light, the spectrum converted completely to a 9-line spectrum, corresponding to the closed-ring isomer **21b** (***n* = 1**). The 9-line spectrum indicates that the exchange interaction between the two spins in **21b** (***n* = 1**) is much stronger than the hyperfine coupling constant.

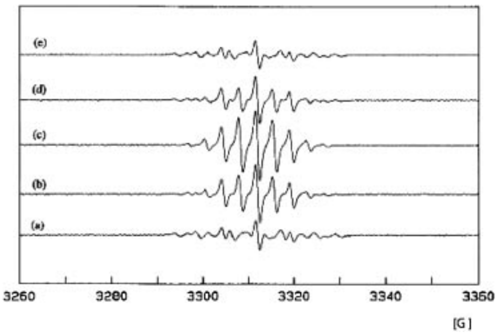


Fig. 13. ESR spectral change of **21a** (***n* = 1**) along with photochromism (benzene solution, 1.1×10^{-4} M): a) initial; b) irradiation with 366 nm light for 1 min; c) 4 min; d) irradiation with >520 nm light for 20 min; e) 50 min. Reprinted with permission from Ref. 77. Copyright 2000 American Chemical Society.

The ESR spectral change was also observed for **21a** (***n* = 2**). The open-ring isomer **21a** (***n* = 2**) had a 5-line spectrum, while the closed-ring isomer **21b** (***n* = 2**) had a distorted 9-line spectrum. A simulation of the ESR spectra was performed. The exchange interaction decreases with the increase in the π-conjugated chain length, as shown in Table 1. The exchange interaction change in **21a** (***n* = 1, 2**) upon photoirradiation was more than 30-fold. This result shows a very large switching effect of diarylethenes and suggests the superiority of diarylethenes as molecular switching units. Although the

Table 1. Magnetic Interaction between Two Nitronyl Nitroxide Connected by Diarylethene Photoswitches

	Open-ring isomer		Closed-ring isomer	
	ESR line shape	$\lvert 2J/k_B\mathrm{K}\rvert$	ESR line shape	$\lvert 2J/k_B\mathrm{K}\rvert$
20	9 lines	2.2	9 lines	11.6
21 (*n* = 1)	15 lines	1.2×10^{-3} $<3 \times 10^{-4}$	9 lines	>0.04
21 (*n* = 2)	5 lines	$<3 \times 10^{-4}$	Distorted 9 lines	0.010
22 (*n* = 1)	13 lines	5.6×10^{-3} $<3 \times 10^{-4}$	9 lines	>0.04
22 (*n* = 2)	5 lines	$<3 \times 10^{-4}$	9 lines	>0.04

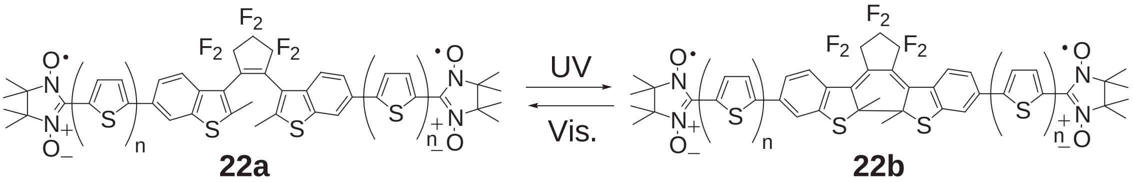


Fig. 14.

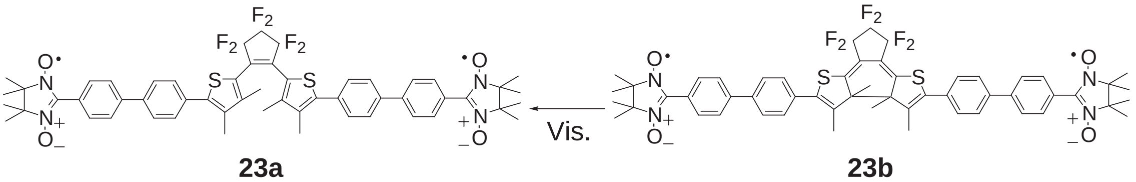


Fig. 15.

absolute value of the exchange interaction is small, the information of the spins can be clearly transmitted through the closed-ring isomer, and the switching can be detected by ESR spectroscopy.

Oligothiophenes are good candidates for conductive molecular wires. The thiophene-2,5-diyl moiety has been used as a molecular wire unit for energy and electron transfer and can serve as a stronger magnetic coupler than *p*-phenylene.[79,80] Therefore, diarylethenes **22a** (***n* = 1, 2**) having one nitronyl nitroxide radical at each end of a molecule containing oligothiophene spacers was synthesized and their photo- and magnetochemical properties were studied (Fig. 14).

Photochromic reactions and an ESR spectral change was also observed for **22a** (***n* = 1, 2**). Table 1 lists the exchange interaction between the two diarylethene-bridged nitronyl nitroxide radicals. For all five biradicals, the closed-ring isomers have stronger interactions than the open-ring isomers. The exchange interactions through oligothiophene spacers were stronger than the corresponding biradicals with oligophenylene spacers. The efficient π-conjugation in thiophene spacers resulted in strong exchange interactions between the two nitronyl nitroxide radicals. In the case of bithiophene spacers, the exchange interaction difference between open- and closed-ring isomers was estimated to be more than 150-fold.

Reversed Photoswitching Using Bis(2-thienyl)ethene

Photoswitching using bis(2-thienyl)ethene **23** (Fig. 15), in which 2-thienyl group is connected to the perfluorocyclopentene ring, was performed.[81] In the case of regular bis(3-thienyl)ethenes, the bond alternation is discontinued in the open-ring isomer, but in the closed-ring isomer, the π-electron is delocalized throughout the molecule. Therefore the open-ring isomer is in "OFF" state due to the disconnection of the π-system and the closed-ring isomer is in "ON" state due to the delocalization of the π-conjugated system. The situation is reversed when thiophene rings are substituted to the ethene moiety at 2-position. The bond alternation is continued throughout the molecule in the open-ring isomer, while in the closed-ring isomer two aryl rings are separated by the sp^3 carbon and sulfur atoms. The magnetic interaction between the two unpaired electrons at 5-positions in the closed-ring isomer is expected to become much weaker than that in the open-ring isomer. In other words, the open-ring isomer is in "ON" state and the closed-ring isomer in "OFF" state.

The synthesized bis(2-thienyl)ethene **23a** did not undergo photochromism, but the precursor underwent photochromic reaction. The closed-ring isomer of the precursor was obtained and the closed-ring isomer was transformed to the desired molecule. The obtained closed-ring isomer **23b** was converted to the open-ring isomer **23a** by irradiation with visible light. The ESR spectrum of the closed-ring isomer **23b** was a five-line spectrum, but the spectrum of the open-ring isomer **23a** was a distorted 9 lines. This suggests that there are stronger magnetic interaction in the open-ring isomer than in the

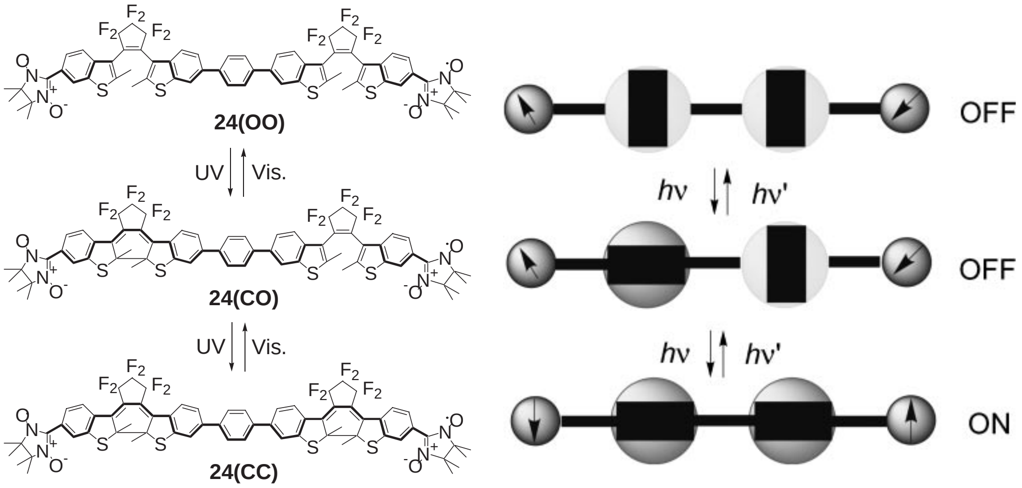


Fig. 16. Photochromic reaction and schematic illustration of diarylethene **24**.

closed-ring isomer. The switching direction is reversed by using bis(2-thienyl)ethene.

Photoswitching Using Array of Photochromic Molecules

In the previous section it was demonstrated that the exchange interaction between two nitronyl nitroxide radicals located at either end of a diarylethene was photoswitched reversibly by alternate irradiation with ultraviolet and visible light. The difference in the exchange interaction between the two switching states was more than 150-fold. ESR spectra can be used as a good tool for detecting small magnetic interaction changes in the molecular systems. In this section photoswitching of intramolecular magnetic interaction using a diarylethene dimer will be presented.[82]

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 an electric circuit, one may infer that the dimer has two switching units in series. Diarylethene dimer **24**, which has 28 carbon atoms between two nitronyl nitroxide radicals, was synthesized (Fig. 16). When the two radicals are separated by the 28 conjugated carbon atoms, the 5-line and 9-line spectra were clearly distinguishable upon irradiation. A *p*-phenylene spacer was introduced so that the cyclization reaction could occur at both diarylethene moieties. Bond alternation is discontinued at the open-ring moieties of **24(OO)** and **24(CO)**. As a result, the spins at either end of **24(OO)** and **24(CO)** cannot interact with each other. On the other hand, the π-system of **24(CC)** is delocalized throughout the molecule and the exchange interaction between the two radicals is expected to occur.

24(OO) underwent photochromic reaction by alternate irradiation with UV and visible light. Upon irradiation of the ethyl acetate solution of **24(OO)** with 313 nm light, an absorption at 560 nm appeared. This absorption grew and shifted and the system reached the photostationary state after 120 min. The color of the solution changed from pale blue to red-purple, and then to blue-purple. Such a red spectral shift suggests the formation of **24(CC)**. The isosbestic point was maintained at an initial stage of irradiation, but it later deviated. The blue-purple solution was completely bleached by irradiation with 578 nm light. **24(CO)** and **24(CC)** were isolated from the blue-purple solution by HPLC. **24(CC)** has an absorption maximum at 576 nm, which is red-shifted as much as 16 nm in comparison with its location in **24(CO)**.

ESR spectra of isolated **24(OO)**, **24(CO)**, and **24(CC)** were measured in benzene at room temperature (Fig. 17). The spectra of **24(OO)** and **24(CO)** are 5-line spectra, suggesting that the exchange interaction between the two nitronyl nitroxide radicals is much weaker than the hyperfine coupling constant ($2J/k_B < 3 \times 10^{-3}$ K).

However, the spectrum of **24(CC)** has clear 9-lines, indicating that the exchange interaction between the two spins is much stronger than the hyperfine coupling constant ($2J/k_B > 0.04$ K). 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.

Conclusion

Since the report of the quintet ground state of *m*-phenylenebis(phenylmethylene), the field of molecular magnetism has emerged. This inherently interdisciplinary field has developed by expanding its scope to organic, inorganic, physical chemistry, and solid state physics. In this account, starting from some basic considerations of the interaction mechanism, several aspects of the intramolecular magnetic interaction has been overviewed. The difference between the disjoint and non-disjoint biradicals brought to fruition the realization of the reversible photoswitching system. The one thing that should be stressed is that the photochromism of diarylethene is suitable for the switching system. This system has the possibility to be applied to the molecular-scale information processing system.[83–87]

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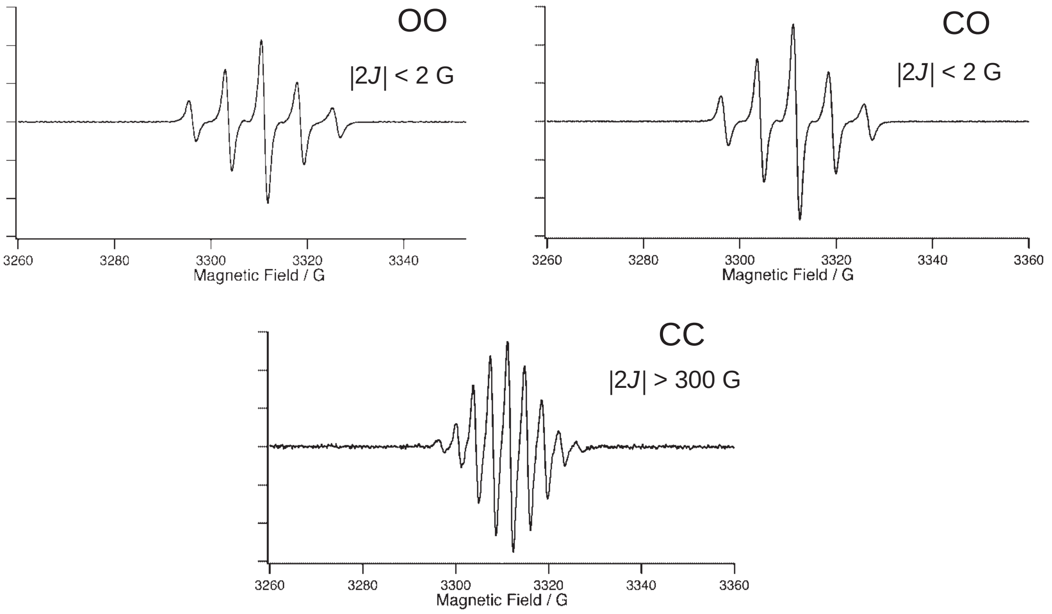

Fig. 17. ESR spectra of (a) **24(OO)**, (b) **24(CO)**, and (c) **24(CC)**. Reprinted with permission from Ref. 82. Copyright 2001 American Chemical Society.

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Kenji Matsuda was born in Nara in 1969. He received his B. S. (1992), M. S. (1994), and Ph. D. (1997) degrees from the University of Tokyo. In 1994, he joined the Faculty of Science, the University of Tokyo as a Research Associate and in 1995 he moved to Kyushu University at the Institute for Fundamental Research of Organic Chemistry. In 1998, he moved to the Graduate School of Engineering at the same university and was promoted to Associate Professor in 2004. In 2001–2002, he has been a JSPS researcher in University of Illinois, USA. He has been named the PRESTO project leader sponsored by JST since 2003. He received the Chemical Society of Japan Award for Young Scientist for 2003.