The use of Diarylethene Derivatives for Photo-switching

Kenji Matsuda

Masahiro Irie

Department of Chemistry and Biochemistry, Graduate School of Engineering,
Kyushu University

1. Introduction

The process of reversible coloration changes induced at least in one-direction by photoirradiation is referred to as photochromism.[1] The two isomers of photochromic compounds differ in their geometrical and electrical structures. These geometrical and electrical differences lead to changes in the physical properties of the molecules, such as their absorption and fluorescence spectra, refractive index and electrical conductivity. Since the transformation between the isomers is induced by photoirradiation, optical-switching of the physical properties can be realized by using the photochromic units.

Diarylethene, which contains five-membered heterocyclic rings, is well known as a photochromic compound that is thermo-irreversible, has high-sensitivity and has fatigue resistance properties.[2] Photochromic reactions in diarylethene take place between two isomers, (hexatriene and cyclohexadiene) following the Woodward-Hoffmann rule (Figure 1). The open-ring isomer, hexatriene **1a**, is generally colorless, but the closed-ring, cyclohexadiene isomer **1b**, develops yellow, red and blue coloration, depending on the substituents.
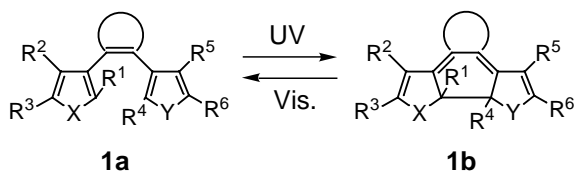
The color change is attributable to the different electrical structures between the open-ring and closed-ring isomers. In the open-ring isomers, free rotation exists at the ethene and aryl groups, so the isomer is non-planar and the π-electrons are localized in the two aryl groups. Furthermore, due to rotational energy barriers, two rotational isomers exist, namely, photo-reactive (anti-parallel) and photo-inactive (parallel) (Figure 2).[3] On the other hand, the closed ring isomer possesses high planarity, with asymmetrically arranged carbon atoms at the reaction site. It has a bond alternation polyene structure and a π-conjugated system spread throughout the molecule. Reflecting on the differences between these geometric and electrical structures, their physical properties vary in many ways.[4]

In this review, some of the physical properties that were photo-switched by using photochromic diarylethene units, i.e. the functions of fluorescent switching, dielectric switching and magnetic switching, are discussed in terms of molecular design and their correlation with the structural properties.
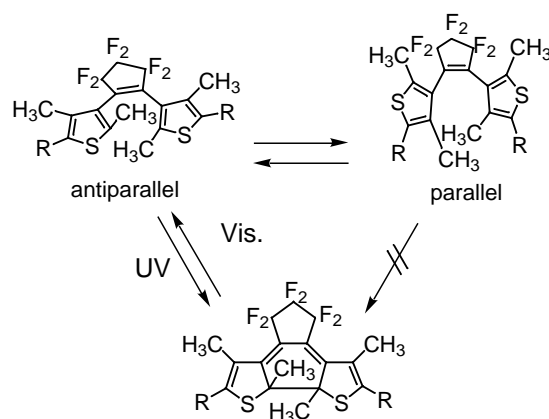

Figure 1. Photochromism in diarylethene.

Figure 2. Conformation of diarylethene.

2. Fluorescent Switches

2.1. Fluorescent Switching

For the application of photochromic compounds to optical memory media, one essential function that is required is a non-destructive readout capability. The conventional "transmittance readout method" could damage the recorded data due to the photochromic reactions that it might undergo, depending on the type of light that is used for the readout. On the other hand, "fluorescent readout method" is highly sensitive that is able to achieve detection with minimal damage to the data.[5]

Various fluorescent switching molecules have been synthesized. Figure 3 shows a fluorescent switching diarylethene that Lehn *et al.* developed.[6] In methanol, the open-ring isomer **2a** conversts to the closed-ring isomer **2b** when irradiated with light below 400 nm upto conversion rate of 92%. The closed-ring isomer **2b** quantitatively returned bade to the open-ring isomer **2a** upon irradiation with light of above 600 nm. The open-ring isomer emits fluorescence at 589 nm upon excitation with 459 nm light, which is the absorption maximum of pyridyl-diphenothiophen-thiophenes, while the closed-ring isomer does not emit any fluorescence. In short, the fluorescence is ON in the open-ring isomer but is OFF in the closed-ring isomer. Furthermore, both cyclization and cycloreversion reactions are hardly induced by excitation with 459 nm light. Therefore, it can be used as a non-destructive readout method.
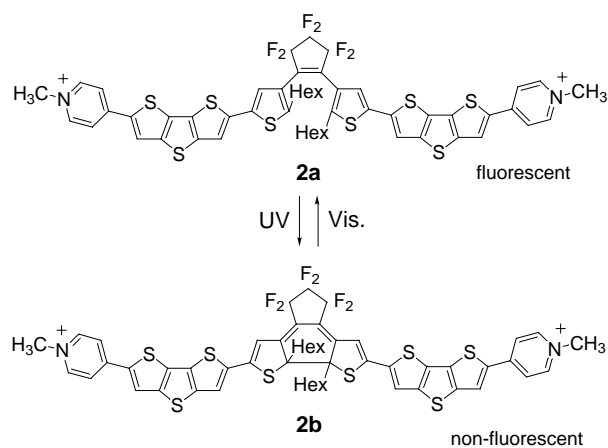

Figure 3. Diarylethane **2**.

Diarylethene with 4-formylphenylthiophene **3** (Figure 4) was also reported to show fluorescent switching behavior.[7] The open-ring isomer **3a** has a strong fluorescent emission at 420 nm when excited with 301 nm light, but the closed-ring isomer does not exhibit any fluorescence.
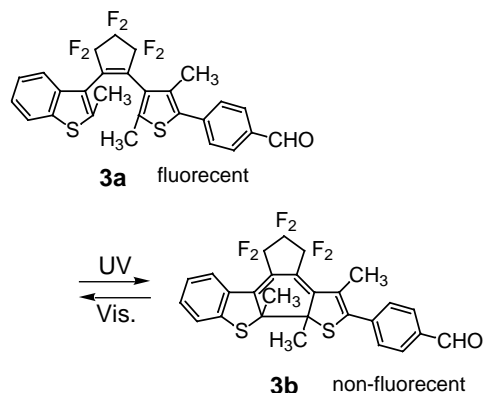

Figure 4.

Triphenylimidazole is a well-known compound that possesses a high fluorescent quantum yield (48%). Diarylethene **4** with triphenylimidazole as a substituent was synthesized. (Figure 5).[8] The open-ring isomer **4a** emitted fluorescence at 390 and 410 nm upon excitation with 313 nm light in hexane solution with a fluorescence quantum yield of 7.7%, while **4b** did not emit any fluorescence.
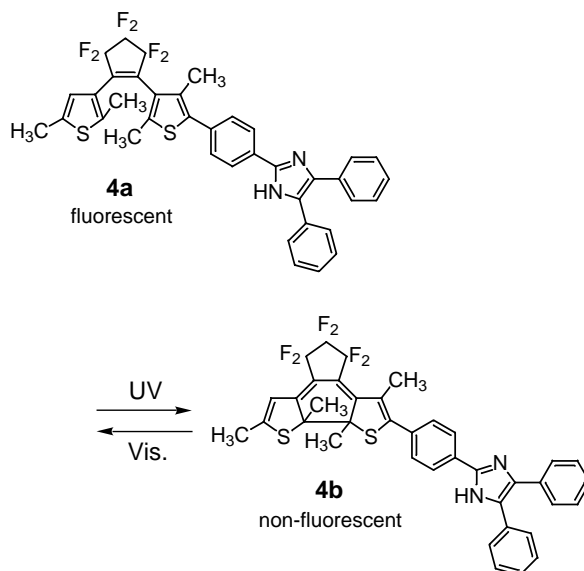

Figure 5. Diarylethene **4**.

Osuka *et al.* successfully synthesized diarylethene-substituted tetraphenylporphyrin **5** and reported its fluorescent behavior (Figure 6).[9] The open-ring form **5a** generated fluorescence at 650 nm and 717 nm upon excitation with 420 nm light. However, the intensity of the fluorescence became weaker for the closed ring form, **5b**. It was suggested that the excited energy of the diarylethene closed-ring form was transferred from the excited state of porphyrin. The conversion rate of the photostationary state upon irradiation with 330 nm light was determined as 75%. The cyclization and cycloreversion quantum yields were determined to be 4.3×10^{-2} and 1.8×10^{-3}, respectively.
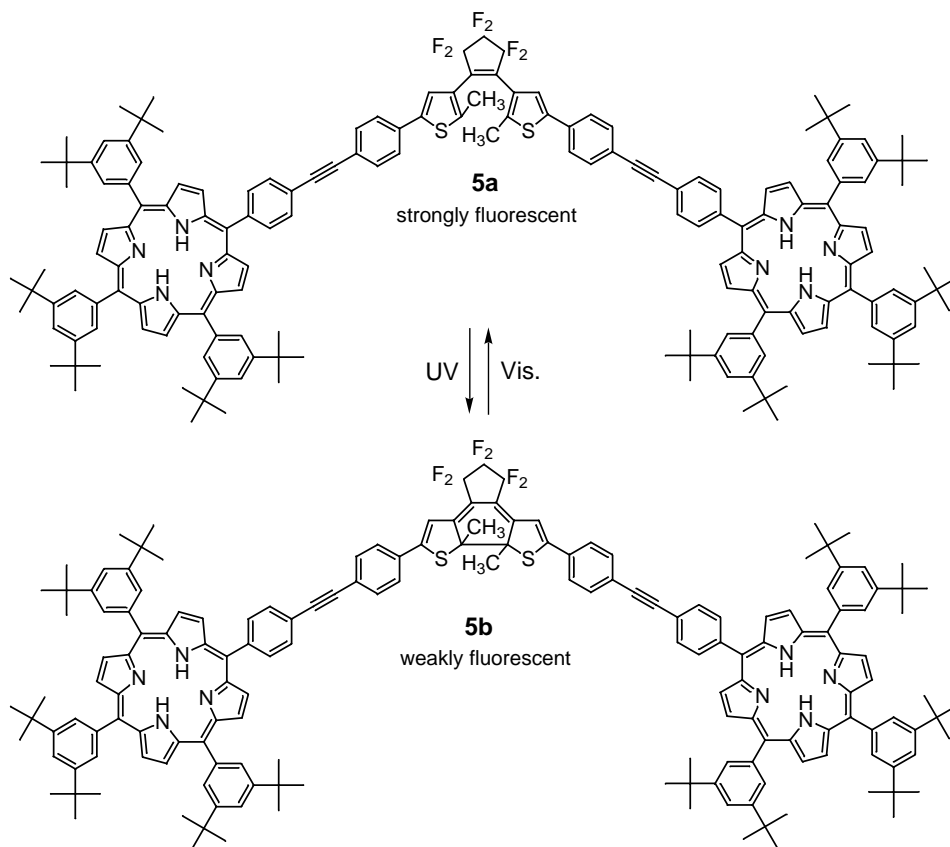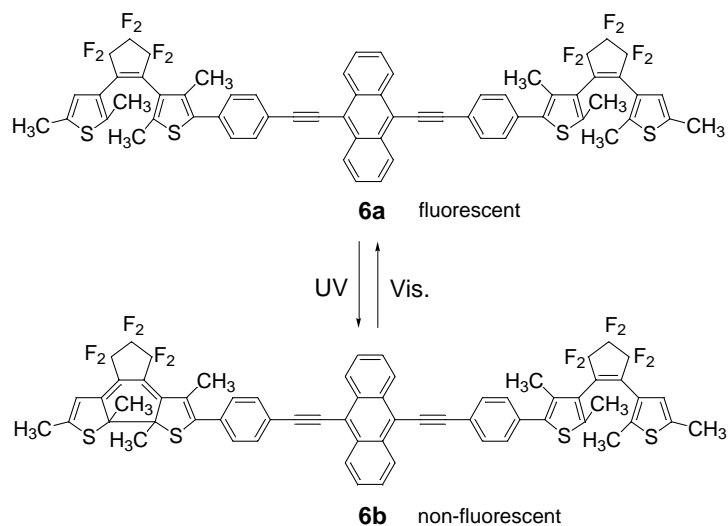
Figure 6. Diarylehtene **5**.

Figure 7. Diarylethene **6**.

Figure 7 shows fluorescent bis(phenylethynyl)anthracene **6**, which has two diarylethene groups.[10] The fluorescence quantum yield of the anthracene **6a** was 0.83, while ring-closure of the diarylethene ring decreased the quantum yield significantly to 0.001. Furthermore, the open-ring isomer **6a** underwent laser emission upon excitation with a 337.1 nm pulsed laser. The laser emission intensity could be photo-switched by the photoreaction of the diarylethene units.

2.2. Photoluminescence of Metal Complexes

Branda *et al.* reported the phosphorescence switching of a transition metal complex (Figure 8).[11] **7a** is a ruthenium complex, which is based on rutheniumporphyrins axially coordinated to pyridyl ligands. The open-ring isomer **7a** convered to the closed-ring isomer **7b** when irradiated with 365 nm light upto a conversion rate of 95%.
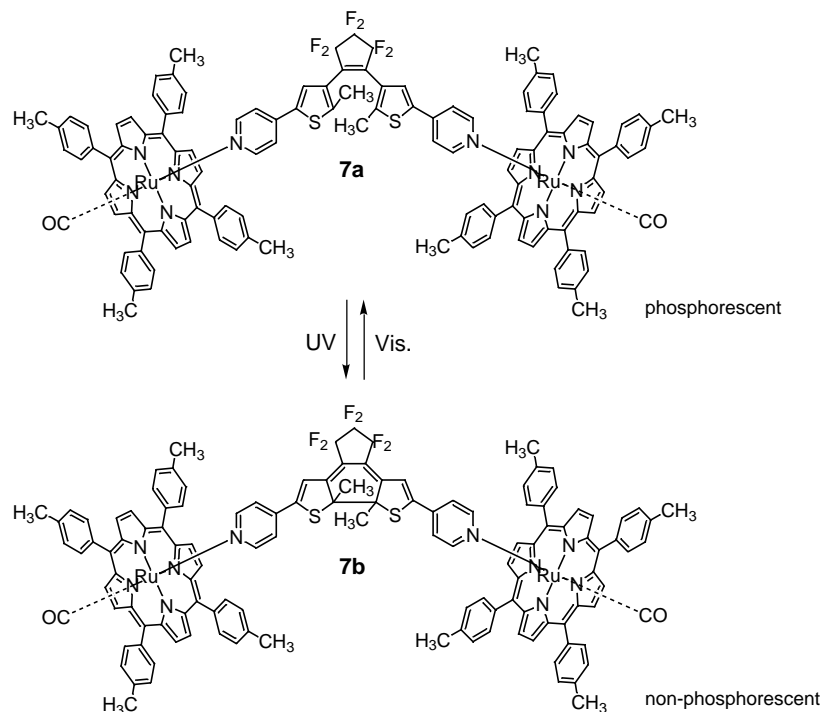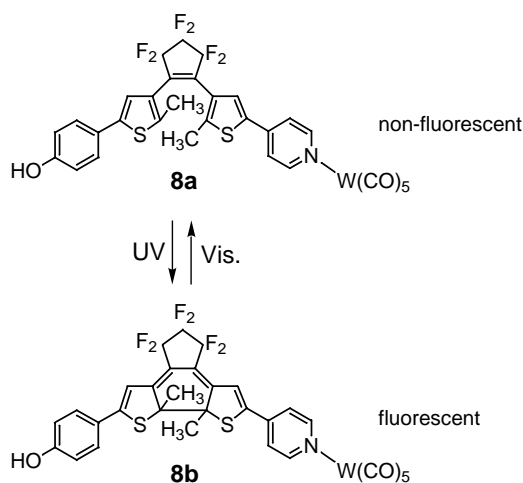
Figure 8. Diarylethene **7**.
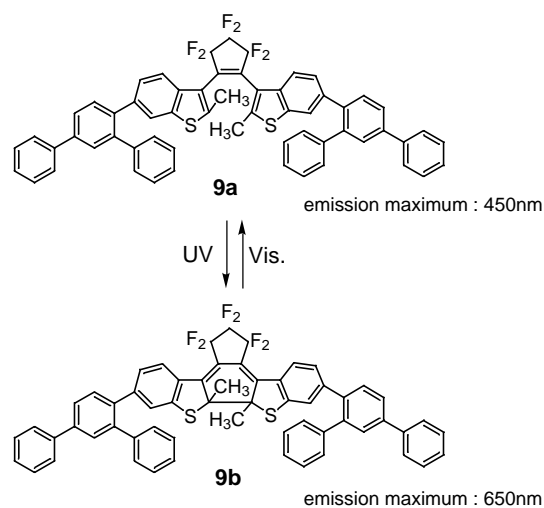

Figure 9. Diarylethene **8**.

Figure 10. Diarylethene **9**.

The closed-ring isomer reverted to the open-ring isomer upon irradiation with 470-685 nm light. The open-ring isomer **7a** phosphoresces at 730 nm when excited with 400-480 nm light. In contrast, the closed-ring isomer **7b** did not phosphoresce. Excitation with 400-480 nm light did not affect the photochromic reactions in either direction. Consequently, the compound can provide a non-destructive readout method.

The tungsten complex **8** showed a different response to those we have just described. The closed-ring form fluoresces more strongly than the open ring form (Figure 9).[12] The fluorescence quantum yield was 0.15 for the closed-ring isomer **8b**, and was 0.03 for the open-ring isomer **8a**.

Also, irradiation with 240 nm light has little effect on the photochromic reactions. This result demonstrates that the system is non-destructive under these conditions and could be applied to a non-destructive readout method.

Diarylethene **9** is also reported as a compound that photoluminesces in the closed ring form (Figure 10).[13] The open-ring isomer **9a** fluoresces with the emission maximum at 450 nm (fluorescence quantum yield of 1.1), but in the closed-ring isomer **9b**, the emission maximum shifted to 650 nm and the yield decreased significantly.

2.3. Photochromism at a Single-Molecule Level

Photochromic molecules can give useful performances even at the single-molecule level. If a single molecule worked as one bit of memory, then ultimately a high-density optical memory could be realized. As a first step to realizing this end, we synthesized a new fluorescent molecule with a photochromic diarylethene unit and evaluated the photoswitching behavior at the single-molecule level[14]. Detection of photoswitching of single molecules has not yet been realized due to the lack of robust photochromic molecules. Figure 10 shows the molecule **10**. Fatigue-resistant photochromic diarylethene is linked to a fluorescent phenylethynylanthracene through an adamantyl spacer. In the open-ring state of diarylethene, anthracene is strongly fluorescent. The fluorescence quantum yield is 0.73. The open-ring isomer is converted to the closed-ring isomer upon irradiation with ultraviolet light, and the fluorescence quantum yield is reduced to less than 0.001. In toluene solution, the intensity of the fluorescence grdually changes under irradiation with ultraviolet/visible light. However, at the single-molecule level the fluorescence is converted between ON and OFF states digitally in a reversible way by irradiation with ultraviolet/visible light, as shown in Figure 12. In the single-molecule system, it was observed that the photoresponse is stochastic in nature, and the response time fluctuates.
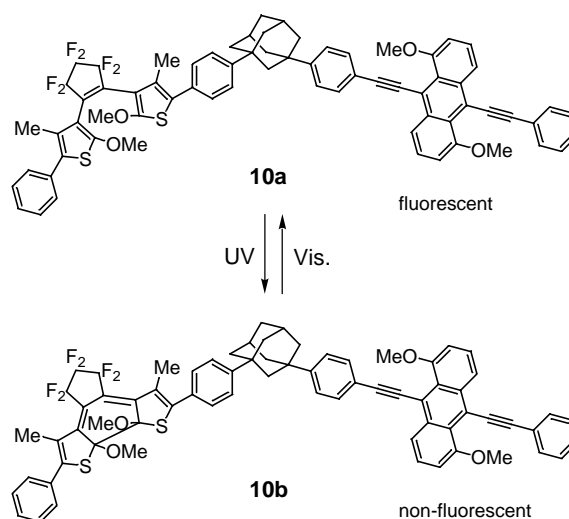
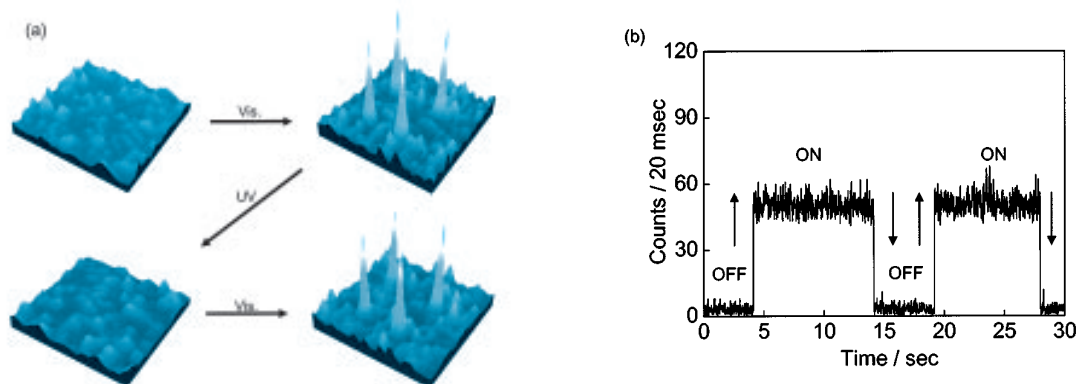

Figure 11. Diarylethene **10**.

Figure 12. Fluorescence switching of a single molecule.
(a) Photoresponsive behavior of four single molecules during alternating irradiation with ultraviolet/visible light.
(b) Digital-like ON/OFF behavior.

3. Conductive Switch

In conductive organic compounds, electrons flow within the π-conjugation system. Therefore, the conductivity can theoretically be controlled by manipulating the π-conjugation system. Lehn *et al.* introduced the concept of photo-switching the conductivity by photochromism using diarylethene (Figure 13).[15] The open-ring isomer **11a** quantitatively converted to the closed-ring isomer **11b** upon irradiation with 365 nm light and then reverted to the open-ring isomer upon irradiation with light above 600 nm.

In **11a** (open) a reduction wave was observed at −1.04 V (vs. SCE). On the other hand, for the closed ring form **11b**, a reversible single electron reduction wave was observed at −0.23 V (vs. SCE). It was considered that the positively charged sites were connected through π-conjugation due to photo-isomerization; consequently, the reduction electrical potential shifted.
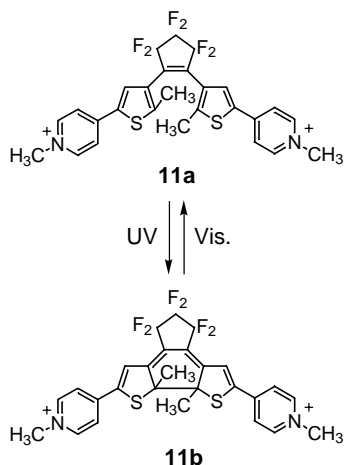
Figure 13. Diarylethene **11**.

A conductive polymer molecule was synthesized, which incorporated a main chain diarylethene group (Figure 14).[16] Upon irradiation with 313 nm ultraviolet light, the colorless open-ring isomer **12a** was converted to the closed-ring isomer **12b**, which had an absorption maximum at 560 nm. The conversion rate in THF solution was 35%. The conductivity of the open-ring isomer and the photo-steady state (closed-ring isomer 35%) films were 5.3×10^{-13} Scm^{-1} and 1.2×10^{-12} Scm^{-1}, respectively. The conductivity of the closed-ring isomer is twice as high as the open-ring isomer. This can be attributed to the changes in the π-conjugation system.
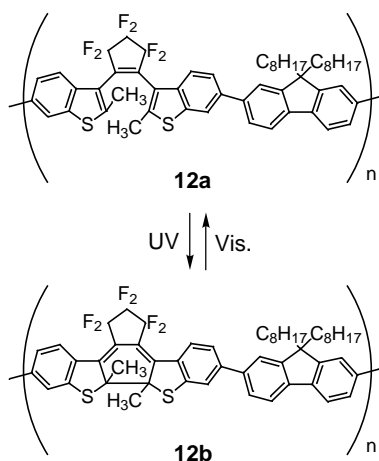

Figure 14. Diarylethene **12**.

4. Magnetic Switching

4.1. Biradical Molecules

In the field of molecular magnetism, studies have been conducted to investigate the magnetic interactions and magnetic behavior of the spins derived from the unpaired electrons that are incorporated in π-conjugation systems such as organic radicals and transition metals.[17] By linking organic radicals at both ends of the π-conjugation and by incorporating photochromic diarylethene in the π-conjugation system, magnetic photo-switching could be realized (Figure 15). Delocalized electrons in the π-conjugation system play an important roll in both photochromism and molecular magnetism. In other words, these two chemical and physical properties are compatible, and with effective molecular design, a compound could be formulated that possesses both of these attributes.
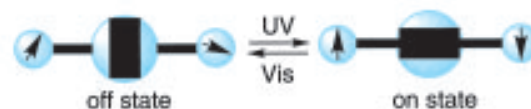

Figure 15. Conceptual diagram of magnetic photo-switching in photochromic molecules.

Firstly, we describe the classification of biradical molecules. A biradical without the closed shell resonance structure is called a non-Kekule structure. Conversely, in the case of biradicals with the resonance structure, they adopt the closed shell structure because they are more stable in energy. Non-Kekule biradicals can be further classified into the disjoint and non-disjoint forms.[18] Trimethylenemethane **13** is a typical non-disjoint form (Figure 16). Two of the SOMO (singly occupied molecular orbital) of **13** are spatially overlapped. In this case, the intramolecular magnetic interaction is strong, and it interacts ferromagnetically. On the other hand, tetramethylene-ethene **14** is a disjoint-type biradical. Two of the SOMO of **14** have no spatial overlap. In this case, the intramolecular magnetic interaction is very weak, and the singlet and triplet states are almost degenerate.[19] Butadiene **15′** is a typical Kekule molecule and possesses a 2-buten-1,4-diyl **15** resonance biradical structure. In this case, the closed shell structure **15′** is the ground state, which does not possess any unpaired electrons. In other words, the magnetic interaction is strong and it is anti-ferromagnetic. If the properties of the π-conjugation spacer could be controlled by a photochromic reaction, then the magnetic interaction could be switched by photo-irradiation.
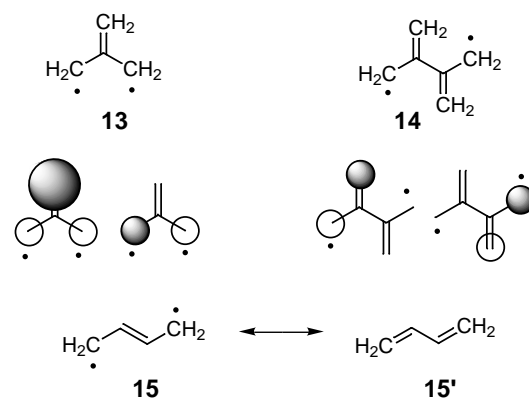

Figure 16. Molecular structures of trimethylenemethane **13**, tetramethyleneethene **14** and butadiene **15** and the SOMO orbitals of **13** and **14**.

4.2. Diarylethene Biradical

Figure 17 shows the structures of the open- and closed-ring isomers of a diarylethene with two radicals. Each structure is topologically equivalent to the structures parenthesized. The open-ring isomer **16a** has no closed shell structure. However, in the closed-ring isomer **16b**, the quinoid resonance structure **16b′** exists. **16a** is a non-Kekule biradical, while **16b** is a closed shell molecule. In other words, **16a** possesses two unpaired electrons, but **16b** does not. Furthermore, no overlap was found when calculating the two SOMO orbitals. This is a typical disjoint biradical, and the intramolecular magnetic interaction is very small. In the open-ring isomer, bond alternation was disconnected at the 3-position of the thiophene ring. This is why the open-ring isomer is of the disjoint type. **16a** corresponds to the tetramethyleneethene **14** in Figure 16.

On the other hand, the closed-ring isomer **16b′** is a typical closed shell structured molecule. In this case, the molecule does not possess any unpaired electrons in the ground state. In this singlet ground state, the two spins interact strongly antiferromagnetically. **16b′** corresponds to butadiene, **15** in Figure 16.

The change in the electronic state of the radical-substituted diarylethene with the photoirradiation can be considered to be a change from the disjoint, non-Kekule structure to a closed shell structure. Based on this concept, it can be considered that the interaction between spins in the open-ring isomer is weak, while a strong antiferromagnetic interaction will occur in the closed-ring isomer. In other words, the OFF state of the interaction in the open-ring iosmer changed to the ON state in the closed-ring isomer.
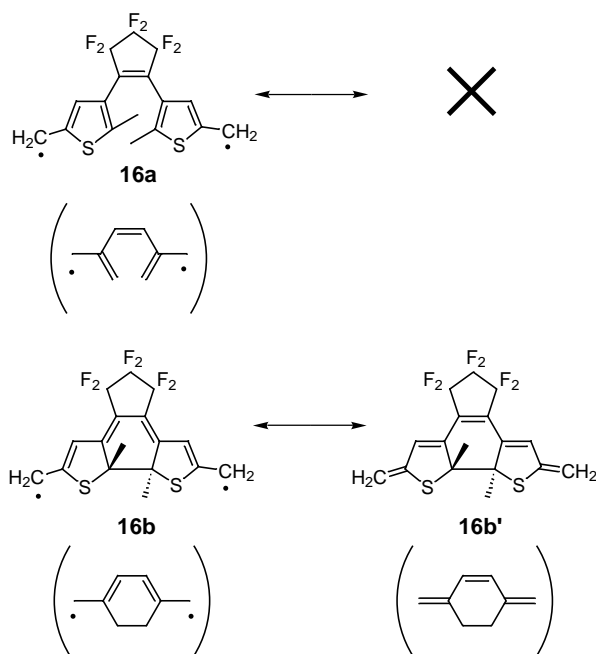
We have designed and synthesized a prototype molecule **17** (Figure 18).[20] We used photochromic bis(2-methylbenzothiophen-3-yl)perfluorocyclopentene (available at Tokyo Kasei Kogyo). These are excellent photochromic molecules, in that both isomers are thermally stable and photo-fatigue resistant. We chose to use nitronylnitroxide as the π-conjugated radical. This system is expected to switch to the ON state in the open-ring isomer and to the OFF state in the closed-ring isomer. In the case where nitronylnitroxide was used as the substituent group, the quinoid structure cannot be adopted completely. Therefore, conversion from the closed-ring isomer to the open-ring isomer could occur.

In ethyl acetate solution, the open-ring isomer **17a** could be converted to the closed-ring isomer **17b** by irradiation with ultraviolet light, and the reverse process from **17b** to **17a** occurred under irradiation with visible light, with a conversion rate of 100% (Figure 19). For diarylethene without the radical substituent group, the conversion rate of the cyclization reaction was just 43%, while the rate could be improved to 100% by introducing the radical substituent. This is considered to be because the resonant quinoid structure stabilizes the closed-ring isomer **17b** and contributed in the cycloreversion reaction to lower the quantum yield [21]. This high conversion rate will play an important roll in later development.

Figure 18. Diarylethene **17**.

Figure 19. Changes in the absorption spectra by photochromic reactions of **17** (ethyl acetate solution 1.7×10^{-5} M).
1) **1a** 2) irradiation with 313 nm light for 1 minutes 3) irradiated for 5 minutes 4) for 10 minutes 5) 5 minutes irradiation with 578 nm light for 5 minutes 6) 30 minutes 7) 60 minutes.

Figure 17. Resonance and topologically equivalent structures of the radical-substituted diarylethene open-ring isomer (**16a**) and closed-ring isomer (**16b**).

The magnetic properties of both isomers were characterized by measuring the magnetic susceptibility and by ESR spectra. As a result of SQUID measurements of the temperature dependency of the magnetic susceptibility, the open-ring isomer **17a** showed almost no intra-molecular magnetic interactions, $2J/k_B = -2.2$ K, while the closed-ring isomer **17b** showed significant interactions $2J/k_B = -11.6$ K (Figure 20). This result was confirmed by the temperature dependence of the signal intensity in cryogenic temperature ESR measurements in the MTHF matrices, which revealed that photo-switching of intramolecular magnetic interactions do exist.
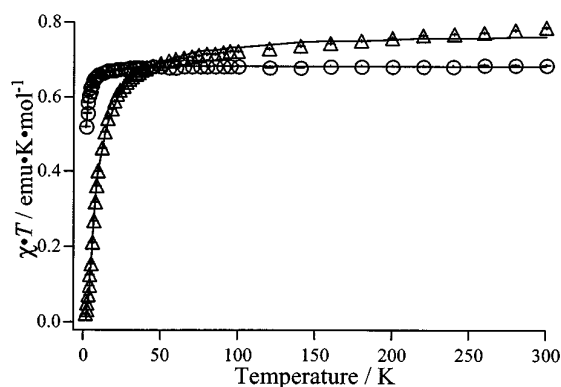
in the open-ring isomer **18a** (n =1) but became larger in the closed-ring isomer, and the changes were detected in the ESR spectrum. By performing simulations of the spectrum, it was revealed that the difference in the exchange interaction between the open and the closed-ring isomer was 30-fold. We adjusted the intensity of the exchange interaction to the same level as the hyper-fine interaction by inserting the *p*-phenylene group spacer, therefore photo-switching of the exchange interaction can be observed by ESR.

Figure 20. Temperature dependence of the magnetic susceptibility of biradical **17a** (O) of **17b** ($\triangle$) (*xT-T* plot).

Figure 21. Diarylethene **18**.

4.3. Detection by ESR

The open-ring isomer **17a** and the closed-ring isomer **17b** displayed 9 lines in their ESR spectra at room temperature, with equivalent four nitrogen hyper-fine coupling in benzene solution. This result indicates that in the open-ring isomer **17a**, the exchange interaction is much larger than the hyperfine coupling constant. The value of the exchange interaction becomes smaller with increased distance between two spins. In order to promptly detect the change in the exchange interaction by ESR at room temperature, an appropriate length of a spacer should be introduced. Therefore, we have introduced a *p*-phenylene group into **17a** to synthesize **18a** and studied its behavior (Figure 21).[22]

18a (n = 1, 2) exhibited reversible photochromism. The open-ring isomer **18a** (n = 1) in benzene solution was irradiated in the ESR cavity and we observed changes in the ESR spectrum (Figure 22). The open-ring isomer **18a** (n =1) exhibited a complicated 15 lines, indicating that the exchange interaction is of the same level as the hyper-fine coupling constant.[23] On the other hand, the ESR spectrum of the closed-ring isomer **18b** (n = 1) consists of 9 lines, which indicates that the value of the exchange interaction is significantly larger than the hyper-fine coupling constant. The exchange interaction was smaller
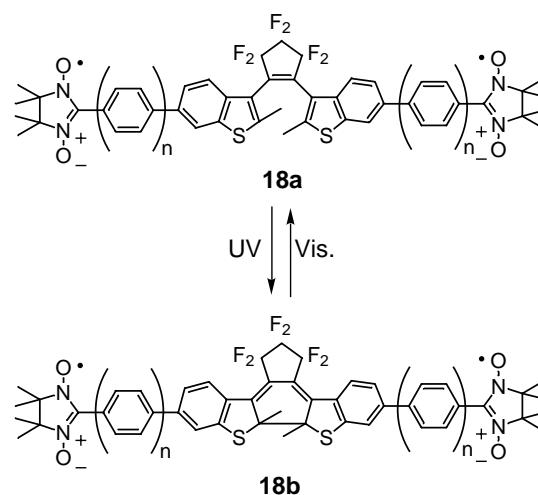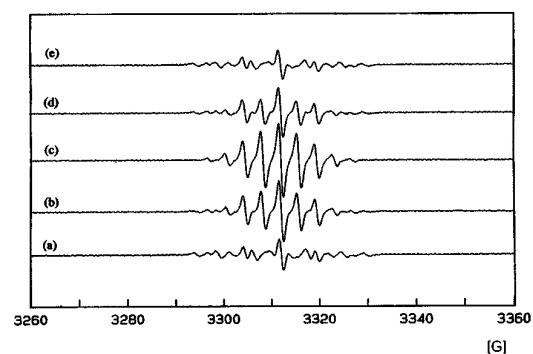

Figure 22. Changes in the spectrum along with the photochromic reaction of **18** (n = 1). (Benzene solution, 1.1×10^{-4} M) a) open-ring isomer, b) irradiated with 366 nm light for one minutes c) irradiated for 4 minutes d) irradiated >520 nm light for 20 minutes e) irradiated for 50 minutes.

Oligothiophene has been attracting much attention as a material for conductive molecular wires.[24] The thiophene-2,5-diyl group has been used as a molecular wire unit for energy and electron transfer. It also serves as a strong magnetic coupler. Based on the idea, the diarylethene biradical, **19a** was synthesized (n = 1, 2) with an oligo-thiophene spacer unit (Figure 23).[25] **19** (n = 1, 2) could be reversibly photo-isomerized with UV and visible light.
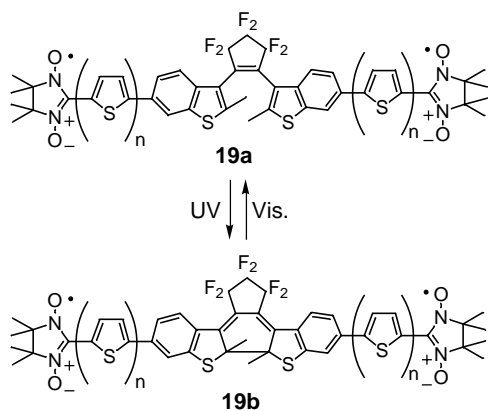

Figure 23. Diarylethene **19**.

Table 1 lists all of the photo-switching molecules that we have discussed in terms of the intensity of magnetic interactions in both the open- and closed-ring isomers. In all of the molecules, the closed-ring isomer exhibited a stronger exchange interaction than the open-ring isomer. Interactions through the oligothiophene spacer showed larger value than that through oligophenylene. The result can be attributed to the effective π-conjugation chain of the thiophene ring. In the bithiophene spacer molecule **19** (n = 2), the difference in the exchange interaction between the open- and the closed-ring isomers was more than 150-fold.

Table 1. Exchange interaction of spins between the open-ring isomer and the closed-ring isomer of biradicals **17**, **18** and **19**.

	open-ring form isomer		closed-ring form isomer	
	ESR line shape	$\mid 2J/k_B \text{ K} \mid$	ESR line shape	$\mid 2J/k_B \text{ K} \mid$
17	9 lines	2.2	9 lines	11.6
18(n=1)	15 lines	$\begin{cases} 1.2 \times 10^{-3} \\ < 3 \times 10^{-4} \end{cases}$	9 lines	> 0.04
18(n=2)	5 lines	$< 3 \times 10^{-4}$	distorted 9 lines	0.010
19(n=1)	13 lines	$\begin{cases} 5.6 \times 10^{-3} \\ < 3 \times 10^{-4} \end{cases}$	9 lines	> 0.04
19(n=2)	5 lines	$< 3 \times 10^{-4}$	9 lines	> 0.04

4.4. Reversed Photo-Switching of a Compound with a Reversed Thiophene Ring

We studied the photo-switching of diarylethene using a reversed thiophene ring, 2-thienyl ring.[26] We investigated molecule **20a** (Figure 24). Here the open-ring isomers have a bond-alternative π-conjugation system and a strong interaction can be assumed. However, in the closed-ring isomers, the π-conjugation is disrupted by the sp[3] carbon. Therefore, the exchange interaction could be weaker. The synthesized **20a** did not undergo photochromism, but the isomers of the precursors exhibited photochromism. We obtained **20b** by making it the closed-ring isomer at the precursor stage, then transforming it to radicals. The ESR spectrum of **20b** exhibited 5 lines, while **20a** showed 9 cor-rupted lines. It was revealed that reverse photo-switching, in which the interaction becomes weaker in the closed-ring isomer, could be realized by using diarylethene with a 2-thienyl ring.
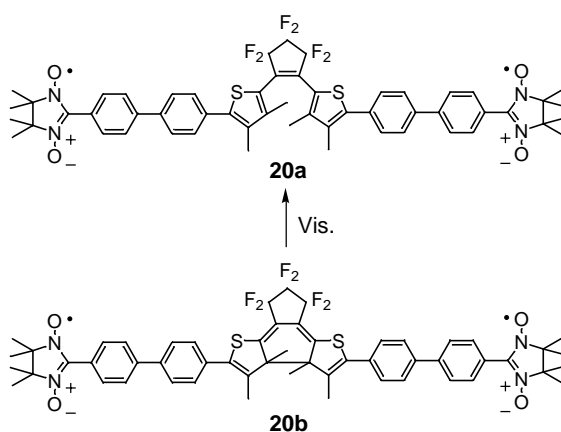

Figure 24. Diarylethene **20**.

4.5. Photo-Switching with Two Switches Connected in Series

Since it was revealed from the above study that the switches perform independently, we tested two photo-switches connected in series (Figure 25).[27] Since the two switches are in series, the total system will only be ON when both switches are in the ON state. The diarylethene dimer **21(OO)** was designed. When **21(OO)** was irradiated with UV light, one closed-ring isomer **21(CO)** was initially generated, with a conversion rate of 78%. Then the second stage reaction proceeded. In the photostationary state, the ratio of **21(OO)** : **21(CO)** : **21(CC)** was 0 : 23 : 77. The ESR spectra for both **21(OO)** and **21(CO)** showed five lines, while **21(CC)** showed 9 lines. These results indicate that only when both switches are closed does the exchange interaction become strong (Figure 26). This means that an intramolecular magnetic switching system made from diarylethene performs as an analogue of an electrical circuit, and consequently it could in theory be expanded into an arithmetic circuit.
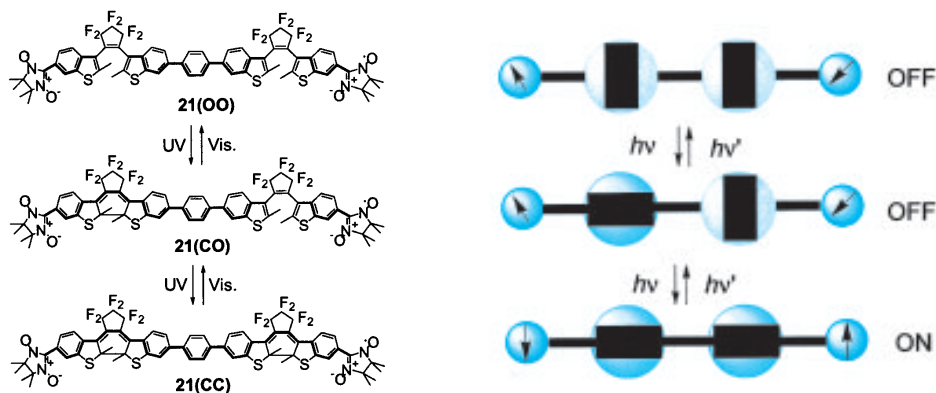
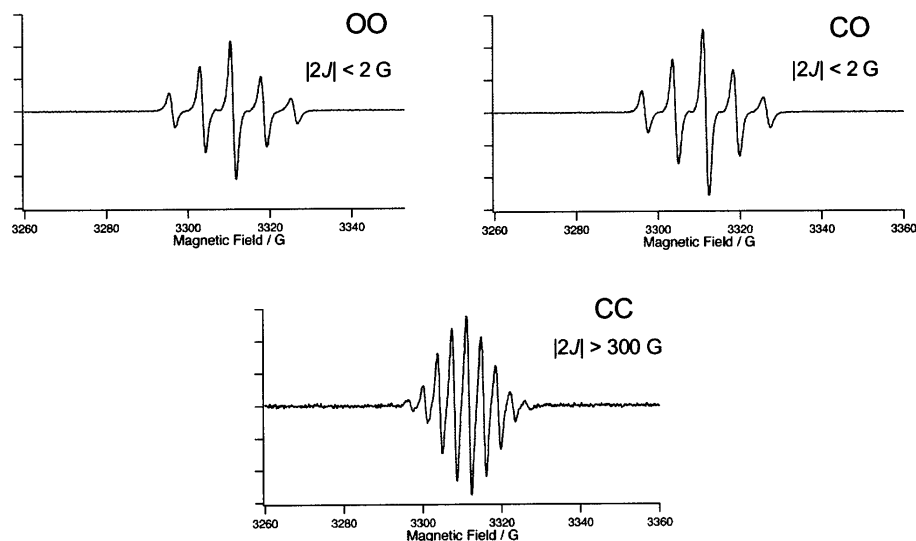**Figure 25.** Molecule **21** designed by connecting two diarylethene groups and its conceptual diagram.

Figure 26. ESR spectrum of Molecule **21**.

5. Conclusion

A study named "molecular electronics", which has the aim of fabricating molecular-scale computers using each individual molecule as a logic device, is in its infancy. Toward this end, various suggestions have been put forward from a wide range of scientific fields.[28] The fluorescent, conductive and magnetic photo-switching molecules that we mention in this report are distinctive enough to cause great interest. We expect that innovative developments will be made in this new field.

References

1) a) B. L. Feringa Ed., *Molecular Switches*, Wiley-VCH, Weinheim, 2001. b) G. H. Brown, *Photochromism*, Wiley-Interscience, New York, 1971. c) H. Dürr, H. Bouas-Laurent, *Photochromism: Molecules and Systems*, Elsevier, Amsterdam, 1990.
2) a) M. Irie, *Chem. Rev.* **2000**, *100*, 1685. b) M. Irie, K. Uchida, *Bull. Chem. Soc. Jpn.* **1998**, *71*, 985.
3) a) K. Uchida, Y. Nakayama, M. Irie, *Bull. Chem. Soc. Jpn.* **1990**, *63*, 1311.
4) a) T. Kawai, N. Fukuda, D. Dröschl, S. Kobatake, M. Irie, *Jpn. J. Appl. Phys.* **1999**, *38*, L1194. b) J. Chauvin, T. Kawai, M. Irie, *Jpn. J. Appl. Phys.* **2001**, *40*, 2518.
5) M. Irie, H. Ishida, T. Tsujioka, *Jpn. J. Appl. Phys.* **1999**, *38*, 6114.
6) a) G. M. Tsivgoulis, J.-M. Lehn, *Angew. Chem. Int. Ed.* **1995**, *34*, 1119. b) G. M. Tsivgoulis, J.-M. Lehn, *Chem. Eur. J.* **1996**, *2*, 1399.

7) M. Takeshita, M. Irie, *Chem. Lett.* **1998**, 1123.

8) K. Yagi, C. F. Soong, M. Irie, *J. Org. Chem.* **2001**, *66*, 5419.

9) A. Osuka, D. Fujikane, H. Shinmori, S. Kobatake, M. Irie, *J. Org. Chem.* **2001**, *66*, 3913.

10) T. Kawai, T. Sasaki, M. Irie, *Chem. Commun.* **2001**, 711.

11) T. B. Norsten, N. R. Branda, *Adv. Mater.* **2001**, *13*, 347.

12) A. Fernández-Acebes, J.-M. Lehn, *Chem. Eur. J.* **1999**, *5*, 3285.

13) M.-S. Kim, T. Kawai, M. Irie, *Chem. Lett.* **2001**, 702.

14) M. Irie, T. Fukaminato, T. Sasaki, N. Tamai, T. Kawai, *Nature* **2002**, *420*, 759.

15) a) S. L. Gilat, S. H. Kawai, J.-M. Lehn, *Chem. Eur. J.* **1995**, *1*, 275. b) S. L. Gilat, S. H. Kawai, J.-M. Lehn, *Chem. Commun.* **1993**, 1439.

16) T. Kawai, T. Kunitake, M. Irie, *Chem. Lett.* **1999**, 905.

17) O. Kahn, *Molecular Magnetism*, VCH, New York, 1993.

18) W. T. Borden, E. R. Davidson, *J. Am. Chem. Soc.* **1977**, *99*, 4587.

19) K. Matsuda, H. Iwamura, *J. Am. Chem. Soc.* **1997**, *119*, 7412.

20) a) K. Matsuda, M. Irie, *Chem. Lett.* **2000**, 16. b) K. Matsuda, M. Irie, *J. Am. Chem. Soc.* **2000**, *122*, 7195.

21) K. Matsuda, M. Irie, *Tetrahedron Lett.* **2000**, *41*, 2577.

22) a) K. Matsuda, M. Irie, *J. Am. Chem. Soc.* **2000**, *122*, 8309. b) K. Matsuda, M. Irie, *Chem. Eur. J.* **2001**, *7*, 3466.

23) a) R. Briére, R.-M. Dupeyre, H. Lemaire, C. Morat, A. Rassat, P. Rey, *Bull. Soc. Chim. France* **1965**, *11*, 3290. b) S. H. Glarum, J. H. Marshall, *J. Chem. Phys.* **1967**, *47*, 1374.

24) a) J. M. Tour, *Acc. Chem. Res.* **2000**, *33*, 791. b) J. M. Tour, *Chem. Rev.* **1996**, *96*, 537. c) T. Mitsumori, K. Inoue, N. Koga, H. Iwamura, *J. Am. Chem. Soc.* **1995**, *117*, 2467.

25) a) K. Matsuda, M. Matsuo, M. Irie, *Chem. Lett.* **2001**, 436. b) K. Matsuda, M. Matsuo, M. Irie, *J. Org. Chem.* **2001**, *66*, 8799.

26) K. Matsuda, M. Matsuo, S. Mizoguti, K. Higashiguchi, M. Irie, *J. Phys. Chem. B* **2002**, *106*, 11218.

27) K. Matsuda, M. Irie, *J. Am. Chem. Soc.* **2001**, *123*, 9896.

28) a) C. Joachim, J. K. Gimzewski, A. Aviram, *Nature* **2000**, *408*, 541. b) T. Nakamura, T. Matsumoto, H. Tada, K.-I. Sugiura Eds. *Chemistry of Nanomolecular Systems: Towards the Realization of Nanomolecular Devices*, Springer, Heidelberg, 2003.

Introduction of the authors:

Kenji Matsuda received his B.S.(1992) and M.S.(1994) degrees from the University of Tokyo and his Ph.D. from the University of Tokyo in 1997. After engaging in research work at the Graduate School of Engineering, the University of Tokyo, he joined the Institute for Fundamental study of Organic Chemistry, Kyushu University, as a research associate in 1995. Currently, Dr. Matsuda is engaging in research work at the Department of Chemistry and Biochemistry, the Graduate School of Engineering, Kyushu University. He also held the post of Postdoctral Fellowship for Research Abroad, Japan Society for the Promotion of Science, for a period from 2001 through to 2002.
He has particular expertise in Physical Organic Chemistry and Organic Material Chemistry.

Masahiro Irie received his B.S. (1966) and M.S. (1968) degrees from Kyoto University, and his Ph.D. (1973) in radiation chemistry from Osaka University. In 1968 he joined the Faculty of Engineering, Hokkaido University as a research associate, and started his research on photochemistry. He moved to Osaka University and was promoted to Associate Professor at the Institute of Scientific and Industrial Research in 1978. In 1988 he was appointed to Professor at the Institute of Scientific Material Study, Kyushu University, and in 1996 he was reappointed to Professor of Chemistry at the Graduate School of Engineering. He was the CREST project leader of the "Development of Photochromic Systems with Perfect Performance" sponsored by the Japan Science and Technology Corporation during the period from 1997-2002.
He received awards from the Japan Society of Polymer Science in 1988, from the Photochemistry Association in 1993 and Vinci d'Excellence (LVMH, France) Award in 1995. He also received Docteur Honoris Causa of University of Bordeaux 1 in 2003.