Highlight Review

Recent Development of 6π-Electrocyclic Photochromic Systems

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Abstract

Photochromic compounds are currently recognized as the promising candidates for future optoelectronic devices, such as memories and switches. Photochemical pericyclic reactions between 1,3,5-hexatriene and 1,3-cyclohexadiene have been used in several ways to construct versatile photochromic compounds. Recent development of the 6π-electrocyclic photochromic systems is overviewed.

◆ Introduction

Photochromic compounds interconvert between two isomers by irradiation with appropriate wavelength of light.[1,2] Among several kinds of photochromic compounds, there is a series of compounds which use photochemical pericyclic reactions between 1,3,5-hexatriene and 1,3-cyclohexadiene. This 6π-electrocyclization/cycloreversion reaction proceeds according to the Woodward–Hoffmann rule (Figure 1). Many photochromic compounds based on this 1,6-electrocyclization have been synthesized. In general, irradiation with UV light to the colorless hexatriene derivatives gives colored cyclohexadiene derivatives and upon irradiation with visible light the cyclohexadiene derivatives return back to the original hexatriene derivatives.

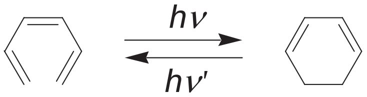

Figure 1. Photochemical isomerization between 1,3,5-hexatriene and 1,3-cyclohexadiene.

In the 6π-electrocyclization/cycloreversion, photochemical reactions proceed in conrotatory fashion, and the thermal reactions proceed in disrotatory fashion. From the simple Woodward–Hoffmann rule we can not anticipate thermal irreversible electrocyclic reactions. Based on detailed theoretical calculations and experiments it was proved that the 6π-electron systems having heteroaryl rings with low aromatic stabilization energy undergo thermally irreversible photochromic reactions.[3] Suitably designed 6π-electrocyclic photochromic compounds undergo photochemical conrotatory reactions and thermal reactions are strongly prohibited. The thermal stability is one of the features of the recently developed photochromic systems compared with other classic photochromic compounds such as azobenzene or spiropyran.

Fulgides[4–9] and diarylethenes[10–13] are well-known thermally stable photochromic compounds (Figure 2). Fulgides, which was developed by Heller and Yokoyama, has a core structure of bismethylenesuccinic anhydrides. When one of the four substituents at exomethylene moiety is furan or thiophene, the compounds show excellent photochromic reactivity. The reactive position in the furan or thiophene ring should be substituted to avoid further oxidation or rearrangement.

Diarylethenes have a basic structure with two heterocyclic five-membered rings and a cyclic ethene moiety. Diarylethenes show not only thermally irreversible photochromic reactivity but also fatigue-resistant characteristics. Since the discovery of the diarylethene derivatives, extremely rich chemistry of diarylethenes has been explored. The recent intensive studies by our group and others extend over many fields, such as crystalline-state photochromism,[14–17] enantio- or diastereoselective cyclization,[18–20] effective switching of π-conjugation,[21–25] very fast reaction dynamics,[26,27] formation of supramolecular assembly,[28–30] and observation of photoswitch at single-molecule level.[31,32] Recent studies on fulgides and diarylethenes have been reviewed already.[4,10]

Because the photochromic compounds are currently recognized as the promising candidates for the future optoelectronic devices, such as memories and switches, the interests on the photochromic compounds have been increasing. Among diverse studies on photochromism, many new structures utilizing 6π-electron systems have been reported. In this review, the new design, synthesis and properties of these compounds will be focused.

◆ Dihydropyrene and [2,n]Metacyclophan-1-ene

Dihydropyrene[33] and [2,*n*]metacyclophan-1-ene[34] were originally developed by Boekelheide (Figure 3). The thermally stable form for the dihydropyrene system is the cyclohexadiene closed-ring isomer, but to the contrary the hexatriene open-ring isomer is more stable for the [2,*n*]metacyclophan-1-ene system. For both dihydropyrene and [2,*n*]metacyclophan-1-ene, the photogenerated metastable form converts back to the stable form in the dark. The thermal back reaction of [2,*n*]metacyclophan-1-ene is strongly affected by the length of the bridging chain.[35] For instance, [2,3]metacyclophan-1-ene showed much faster decoloration reaction than [2,2]metacyclophan-1-ene. The decoloration rate of [2,2]metacyclophan-1-ene was the slowest due to the steric hindrance of the hexatriene open-ring isomer. In general the thermal ring-opening reaction of [2,*n*]metacyclophan-1-ene readily takes place because the open-ring isomer gains the aromatic stabilization. In the case of [2,2]metacyclo-

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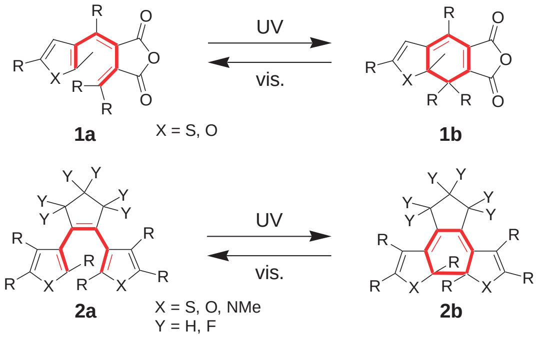

Figure 2. Photochromic reactions of fulgides and diarylethenes.

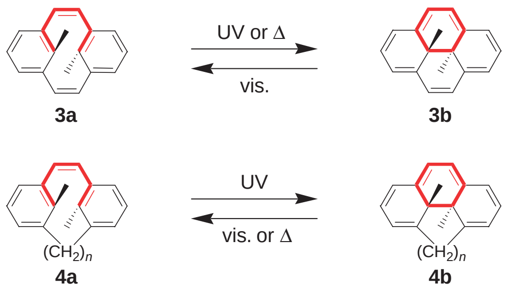

Figure 3. Photochromic reactions of dihydropyrene and [2,*n*]metacyclophan-1-ene.

phan-1-ene, the instability of the open-ring isomer gives rise to the large activation energy to supress the thermal ring-opening reaction.

Mitchell et al. reported that benzo-annelated dihydropyrene **5b** is a stable form, while the open-ring isomer **6a** becomes stable when two phenyl rings are introduced to the parent dihydropyrene (Figure 4).[36] Photogenerated green-colored isomer **6b** returned back to the colorless isomer **6a** rapidly.

By combining mono-benzo-annelated dihydropyrene and bis-benzo-annelated dihydropyrene, the multi-state photochromic compound **7a** was designed and synthesized (Figure 5). In this system, the thermally stable form is **7b**, in which one of the dihydropyrene rings is open and the other is closed. Although the lifetime of bis-closed **7c** was very short and could be detected only by flash photolysis, three-state photochromic reaction was confirmed.[37]

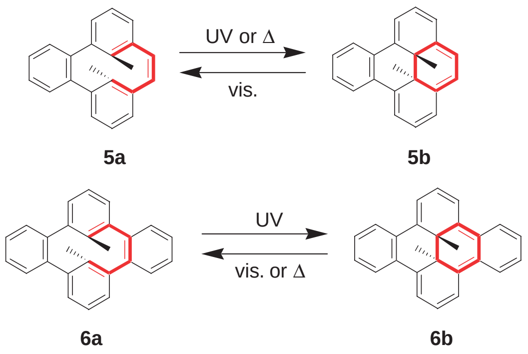

Figure 4. Photochromic reactions of benzo-annelated dihydropyrenes.

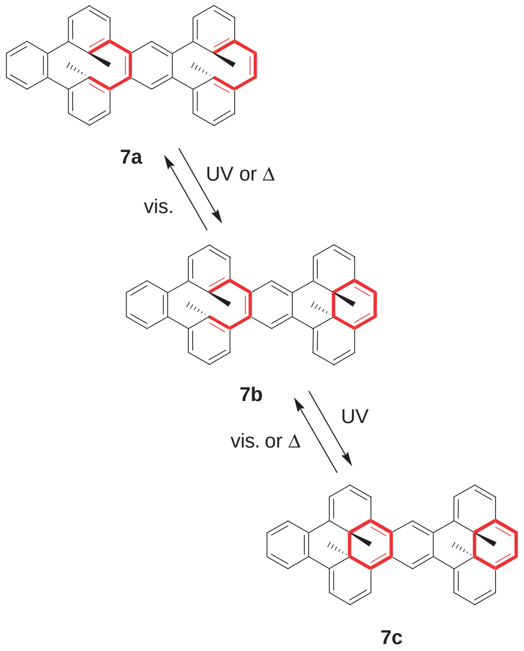

Figure 5. Three-state photochromic reactions of a dihydropyrene dimer.

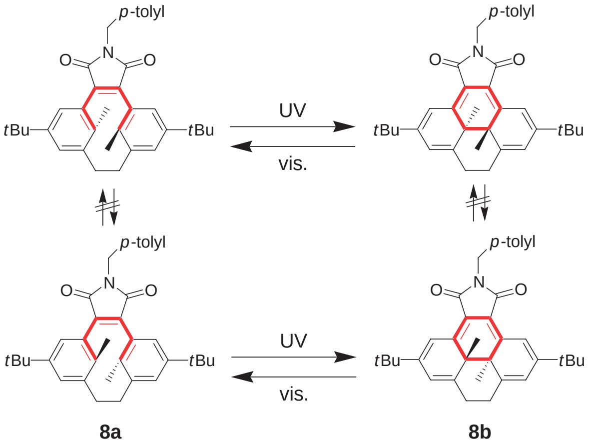

Figure 6. Photochromic reaction of [2,2]metacyclophan-1-ene with fixed conformation.

Takeshita and Yamato applied the fixed conformation of [2,2]metacyclophan-1-ene to the enatioselective photocyclization reaction (Figure 6).[38] Two chiral open-ring isomers of **8a** could be separated and photocyclized to two enantiomeric closed-ring isomers. The closed-ring isomers showed distinct CD signals and the cyclization reactions could be detected by CD spectra.

◆ Modification at Ethene Moiety

The cyclic ethene moiety of diarylethenes can be modified to endow the unique reactivity to diarylethenes (Figure 7).[39–43] Triangle-shaped terthiophene derivative **9a** showed photochromic reactivity which can be used as re-router of the π-conjugation pathway.[39]

Yam et al. used phenanthroline as the ethene moiety.[40] Rhenium complex **10a** showed luminescence switching. In the

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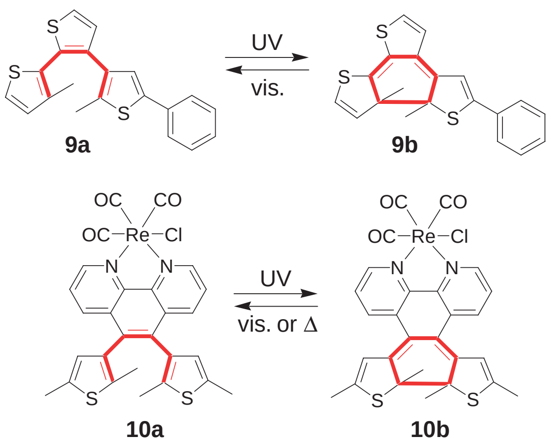


Figure 7. Diarylethenes modified at ethene moiety.

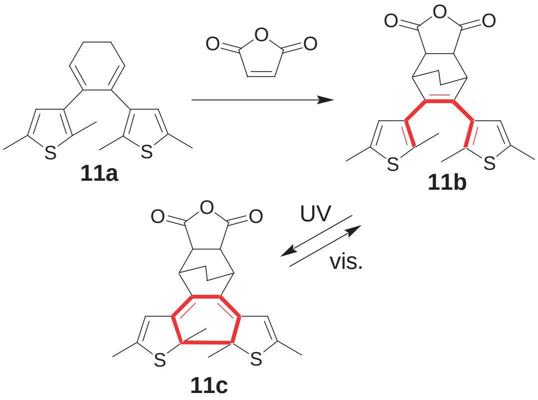


Figure 8. Tuning of the photochromic reactivity by Diels–Alder reaction at cyclic ethene moiety of a diarylethene.

open-ring isomer, the emission from MLCT (metal-to-ligand charge transfer) state is predominant, but in the closed-ring isomer the emission from IL (intraligand) state was observed. A slow thermal back reaction of **10b** to **10a** was also detected.

Branda and Lemieux replaced the cyclic ethene moiety with cyclohexadiene (Figure 8).[41] The synthesized molecule **11a**, which does not have a double-bond at the central position, did not show any photochromic reactivity, but after the Diels–Alder reaction with maleic anhydride, the product **11b**, which has a [2.2.2]bicyclooctene moiety, gained the photochromic reactivity to the corresponding closed-ring isomer **11c**. The closed-ring isomer **11c** was reported to be thermally stable.

Modification at Aryl Groups

The aryl groups of diarylethenes are not necessarily heteroaryl rings. Yokoyama et al. and Branda et al. independently reported that the simple olefins can be replaced with the heteroaryl rings of diarylethenes (Figure 9).[44–49] The absorption band of the closed-ring isomer was observed at shorter wavelength region than those of the conventional diarylethenes. For example, the closed-ring isomer **12b** and **13b** showed absorption maxima at 450 nm for both compounds. In these systems, the closed-ring isomers are thermally stable. The interconversion was not observed without irradiation of light.

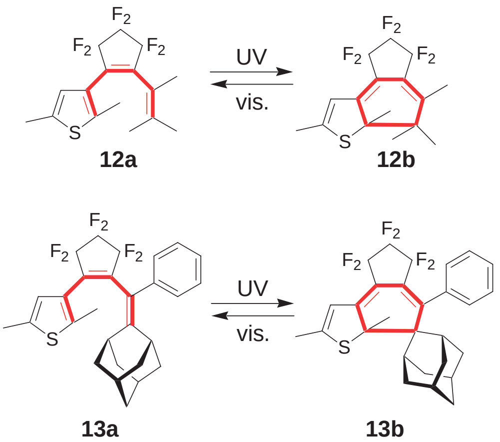


Figure 9. Diarylethene derivatives modified at aryl groups.

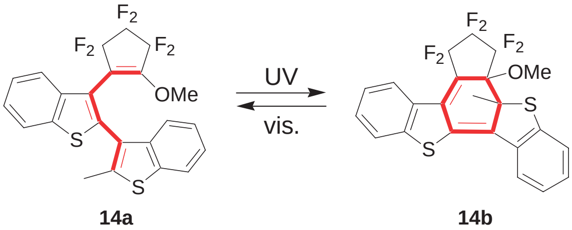


Figure 10. A diarylethene derivative modified at aryl groups.

Compound **14a** has a similar structure of conventional diarylethenes but the reaction manner is totally different (Figure 10).[47] In this case, the roles of perfluorocyclopentene ring and benzothiophene ring are opposite. The color of the closed-ring isomer **14b** was red. The closed-ring isomer was fairly thermally stable. The color persists for more than 1 week in toluene at 70 °C.

The photochromic reactions of these compounds showed the generality of the photochemical 6π pericyclic reactions. Although the modification of the parent diarylethene skeleton was anticipated to cause the thermal instability of the closed-ring isomer, most of the synthesized compounds showed good thermal stability.

Fused Diarylethenes

Recently, fused diarylethenes, in which multiple diarylethene chromophores are integrated by sharing the same thiophene ring, have been developed.[50–52] This design enables multimode photochromism. Some advantages of the one-molecule system over mixed systems for multimode photochromism include the high resolution available arising from local homogeneity, long-term storage stability, and applications to multifrequency single-molecular memories.

The colorless open-ring isomer **15a** showed multimode photochromism (Figure 11).[51] A solution of **15a** in hexane turned yellow then green upon irradiation with light of 365 nm. Upon further irradiation with light of 313 nm, the solution turned black. When the solution was exposed simultaneously to UV (313 nm) and blue (436 nm) light, it turned blue. The solution turned yellow, when it was irradiated with UV (313 nm) and yellow ($\lambda > 500$ nm) light. Different colors can

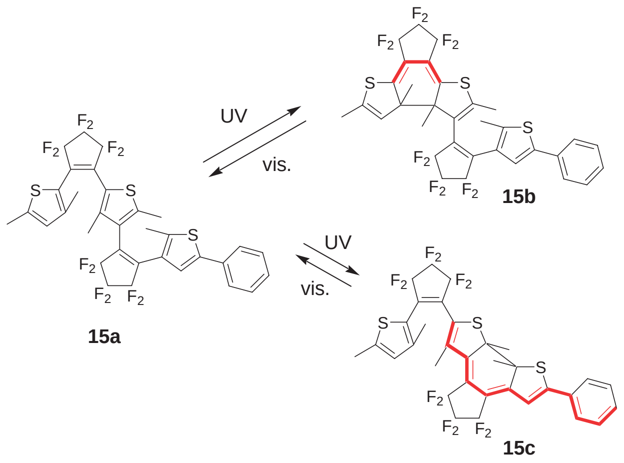


Figure 11. Photochromism of a fused diarylethene dimer.

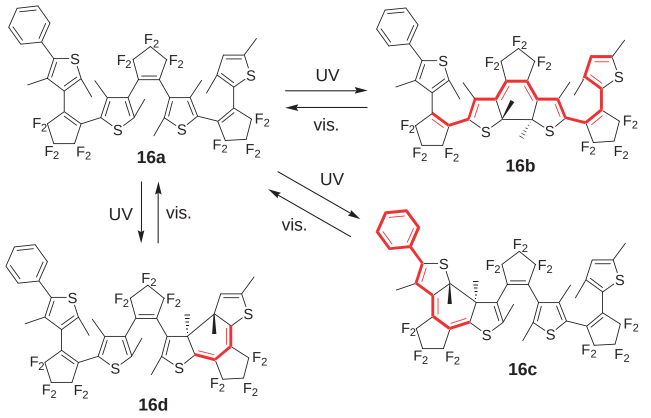


Figure 12. Photochromism of fused diarylethene trimer.

be obtained by irradiation with different wavelengths of light and for different periods of time. This phenomenon is characteristic of fused diarylethenes.

Figure 12 shows full color photochromism of a fused diarylethene trimer.[52] Three kinds of the closed-ring isomer **16b**, **16c**, and **16d** showed blue, red, and yellow colors, respectively (Figure 13). Full color property is a necessary condition for the application to the display materials.

◆ Switching on Aryl Group

One of the interesting properties of 6π-electrocyclic systems is a photoswitching behavior. For the conventional diarylethenes, the most distinctive feature is the difference in π-conjugation. In the open-ring isomer, the π-conjugation is separated at each side of the aryl group but the π-conjugation is connected throughout the molecule in the closed-ring isomer. This difference in the π-conjugation gives rise to the switching of the exchange interaction between two organic radicals.[20–24]

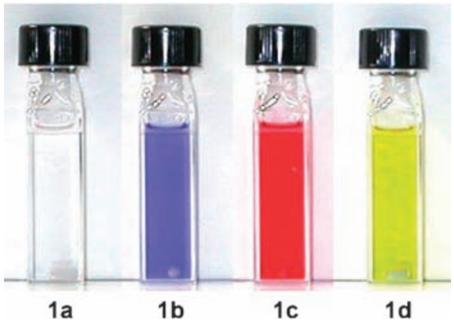


Figure 13. Colors of the open-ring isomer **16a** and the isolated closed-ring isomers **16b**–**16d** in hexane solution. (Reprinted by permission from *J. Am. Chem. Soc.*, **2005**, *127*, 8922. Copyright American Chemical Society.)

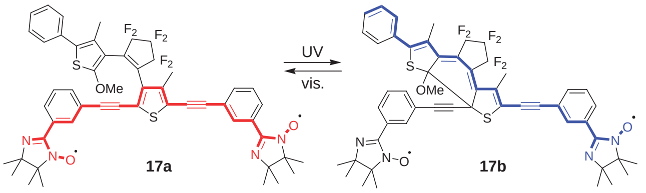


Figure 14. Photochromism of diarylethene having 2,5-arylethynyl-3-thienyl unit.

Recently, another strategy of the switching has been developed.[53–55] The photocyclization reaction of the diarylethene unit breaks the π-conjugation in 2,5-bis(arylethynyl)-3-thienyl unit due to the change of the orbital hybridization from sp^2 to sp^3 at the 2-position of the thiophene ring. Branda et al. also used the switching of the orbital hybridization for the control of absorption spectrum.[56] Imino nitroxide radicals are introduced at both ends of the 2,5-bis(arylethynyl)thiophene π-conjugated chain to give **17a** (Figure 14).[53] The magnetic interaction between the two radicals via the π-conjugated chain could be altered by the photocyclization. The open-ring isomer represents "ON" state because π-conjugated system is delocalized between two radicals, while the closed-ring isomer represents "OFF" state because π-conjugated system is disconnected at 2-position of the thiophene ring. The switching is opposite direction to the conventional diarylethenes.

Figure 15 shows ESR spectral change along with the photochromic reaction of biradical **17**. In the open-ring isomer the spectrum is 13 lines, which indicates the exchange interaction takes place between the two radicals ($|2J/k_B| > 0.04$ K). The photogenerated closed-ring isomer showed 7 lines, which is a spectrum of an isolated imino nitroxide ($|2J/k_B| < 3 \times 10^{-4}$ K).

This switching strategy has been applied to oligothiophene.[54] Figure 16 shows the switching behavior of photochromic oligothiophene **18a**. The closed-ring isomer has the different π-conjugation pathway from the open-ring isomer.

Figure 17 shows the photochemical control of pK_a by changing the π-conjugation pathway from π-donor to π-acceptor.[55] The open-ring isomer **19a** has a π-conjugation between methoxy group and phenol group, though the closed-ring isomer **19b** has a π-conjugation between pyridinium group and phenol group. Thus, the effect on the phenol group changed from donor to acceptor. Therefore, the pK_a value decreased from 10.2 to 9.0 as the cyclization reaction proceeds.

◆ Summary and Future Outlook

As overviewed in this review, the 6π-electrocyclic system is a robust core which is suitable for the photochromic compounds. Thermal irreversibility and fatigue resistance of the photochro-

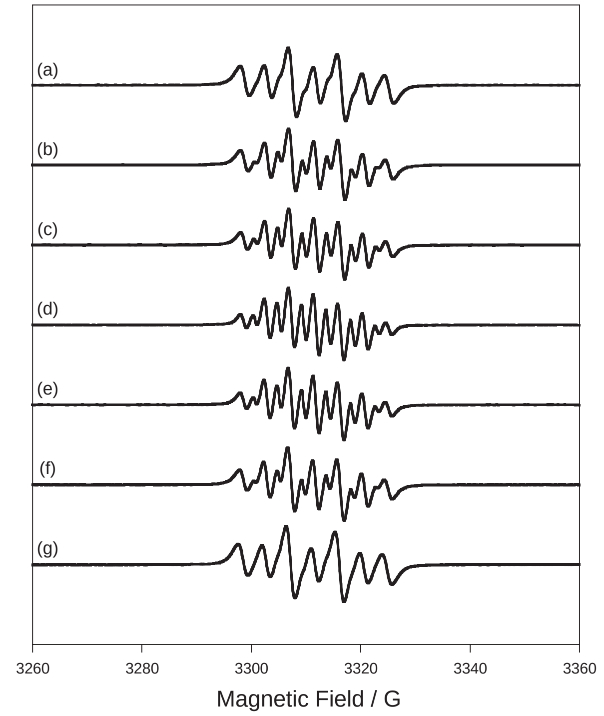
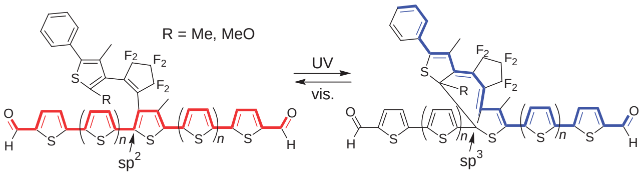
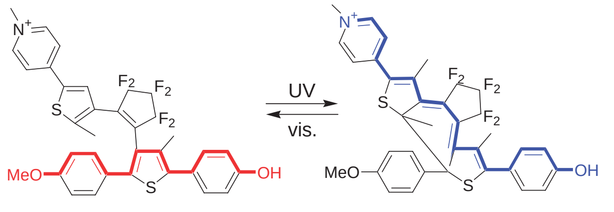


Figure 15. ESR spectra of biradical **17** along with photochromic reaction measured in toluene at room temperature (9.32 GHz): (a) the closed-ring isomer **17b**; (b) after irradiation with 578 nm light for 5 min; (c) for 7 min; (d) for 10 min, which is identical with the spectrum of **17a**; (e) after irradiation with 365 nm light for 1 min; (f) for 3 min; (g) for 5 min, which is identical with the spectrum of **17b**. (Reprinted by permission from *J. Am. Chem. Soc.*, **2005**, *127*, 13344. Copyright American Chemical Society.)



18a **18b**

Figure 16. Photochromic oligothiophenes.



19a **19b**

Figure 17. Photochromic control of pK_a by changing the π-conjugation pathway from π-donor to π-acceptor.

mic diarylethene systems are the advantages over other photochromic compounds. These features are the suitable for the applications to optoelectronic devices. The photochemical pericyclic reaction of 6π-electron systems inherently has a switching property of the π-conjugation. This switching can be used in the future optoelectronic devices such as memories and switches.

References

1 *Molecular Switches*, ed. by B. L. Feringa, Wiley-VCH, Weinheim, **2001**.
2 *Photochromism: Molecules and Systems*, ed. by H. Dürr, H. Bouas-Laurent, Elsevier, Amsterdam, **2003**.
3 S. Nakamura, M. Irie, *J. Org. Chem.* **1988**, *53*, 6136.
4 Y. Yokoyama, *Chem. Rev.* **2000**, *100*, 1717.
5 H. G. Heller, S. Oliver, *J. Chem. Soc., Perkin Trans. 1* **1981**, 197.
6 P. J. Darcy, H. G. Heller, P. J. Strydom, J. Whittall, *J. Chem. Soc., Perkin Trans. 1* **1981**, 202.
7 H. G. Heller, J. R. Langan, *J. Chem. Soc., Perkin Trans. 2* **1981**, 341.
8 A. P. Glaze, S. A. Harris, H. G. Heller, W. Johncock, S. N. Oliver, P. J. Strydom, J. Whittall, *J. Chem. Soc., Perkin Trans. 2* **1985**, 957.
9 Y. Yokoyama, T. Goto, T. Inoue, M. Yokoyama, Y. Kurita, *Chem. Lett.* **1988**, 1049.
10 M. Irie, *Chem. Rev.* **2000**, *100*, 1685.
11 M. Irie, M. Mohri, *J. Org. Chem.* **1988**, *53*, 803.
12 M. Irie, K. Uchida, *Bull. Chem. Soc. Jpn.* **1998**, *71*, 985.
13 K. Matsuda, M. Irie, *J. Photochem. Photobiol., C* **2004**, *5*, 169.
14 S. Kobatake, T. Yamada, K. Uchida, N. Kato, M. Irie, *J. Am. Chem. Soc.* **1999**, *121*, 2380.
15 S. Kobatake, M. Yamada, T. Yamada, M. Irie, *J. Am. Chem. Soc.* **1999**, *121*, 8450.
16 T. Yamada, S. Kobatake, K. Muto, M. Irie, *J. Am. Chem. Soc.* **2000**, *122*, 1589.
17 M. Irie, T. Lifka, S. Kobatake, N. Kato, *J. Am. Chem. Soc.* **2000**, *122*, 4871.
18 T. Yamaguchi, K. Uchida, M. Irie, *J. Am. Chem. Soc.* **1997**, *119*, 6066.
19 T. Kodani, K. Matsuda, T. Yamada, S. Kobatake, M. Irie, *J. Am. Chem. Soc.* **2000**, *122*, 9631.
20 S. Yamamoto, K. Matsuda, M. Irie, *Angew. Chem., Int. Ed.* **2003**, *42*, 1636.
21 K. Matsuda, M. Irie, *J. Am. Chem. Soc.* **2000**, *122*, 7195.
22 K. Matsuda, M. Irie, *J. Am. Chem. Soc.* **2000**, *122*, 8309.
23 K. Matsuda, M. Irie, *Chem.—Eur. J.* **2001**, *7*, 3466.
24 K. Matsuda, M. Irie, *J. Am. Chem. Soc.* **2001**, *123*, 9896.
25 K. Takayama, K. Matsuda, M. Irie, *Chem.—Eur. J.* **2003**, *9*, 5605.
26 C. Okabe, T. Nakabayashi, N. Nishi, T. Fukaminato, T. Kawai, M. Irie, H. Sekiya, *J. Phys. Chem. A* **2003**, *107*, 5384.
27 M. Murakami, H. Miyasaka, T. Okada, S. Kobatake, M. Irie, *J. Am. Chem. Soc.* **2004**, *126*, 14764.
28 K. Matsuda, K. Takayama, M. Irie, *Inorg. Chem.* **2004**, *43*, 482.
29 S. Yamamoto, K. Matsuda, M. Irie, *Chem.—Eur. J.* **2003**, *9*, 4878.
30 T. Hirose, K. Matsuda, M. Irie, *J. Org. Chem.*, in press.
31 M. Irie, T. Fukaminato, T. Sasaki, N. Tamai, T. Kawai, *Nature* **2002**, *420*, 759.
32 T. Fukaminato, T. Sasaki, T. Kawai, N. Tamai, M. Irie, *J. Am. Chem. Soc.* **2004**, *126*, 14843.

33 H.-R. Blattmann, D. Meuche, E. Heilbronner, R. J. Molyneux, V. Boekelheide, *J. Am. Chem. Soc.* **1965**, *87*, 130.
34 C. E. Ramey, V. Boekelheide, *J. Am. Chem. Soc.* **1970**, *92*, 3681.
35 S.-i. Murakami, T. Tsutsui, S. Saito, A. Miyazawa, T. Yamato, M. Tashiro, *Chem. Lett.* **1988**, 5.
36 R. H. Mitchell, T. R. Ward, Y. Chen, Y. Wang, S. A. Weerawarna, P. W. Dibble, M. J. Marsella, A. Almutairi, Z.-Q. Wang, *J. Am. Chem. Soc.* **2003**, *125*, 2974.
37 R. H. Mitchell, T. R. Ward, Y. Wang, P. W. Dibble, *J. Am. Chem. Soc.* **1999**, *121*, 2601.
38 M. Takeshita, T. Yamato, *Angew. Chem., Int. Ed.* **2002**, *41*, 2156.
39 T. Kawai, T. Iseda, M. Irie, *Chem. Commun.* **2004**, 72.
40 V. W.-W. Yam, C.-C. Ko, N. Zhu, *J. Am. Chem. Soc.* **2004**, *126*, 12734.
41 V. Lemieux, N. R. Branda, *Org. Lett.* **2005**, *7*, 2969.
42 L. Dinescu, Z. Y. Wang, *Chem. Commun.* **1999**, 2497.
43 X. Deng, L. S. Liebeskind, *J. Am. Chem. Soc.* **2001**, *123*, 7703.
44 S. M. Shrestha, H. Nagashima, Y. Yokoyama, Y. Yokoyama, *Bull. Chem. Soc. Jpn.* **2003**, *76*, 363.
45 A. Peters, C. Vitols, R. McDonald, N. R. Branda, *Org. Lett.* **2003**, *5*, 1183.
46 S. Takami, M. Irie, *Tetrahedron* **2004**, *60*, 6155.
47 T. Yamaguchi, Y. Fujita, M. Irie, *Chem. Commun.* **2004**, 1010.
48 Y. Yokoyama, H. Nagashima, S. M. Shrestha, Y. Yokoyama, K. Takada, *Bull. Chem. Soc. Jpn.* **2003**, *76*, 355.
49 B. Wüstenberg, N. R. Branda, *Adv. Mater.* **2005**, *17*, 2134.
50 K. Higashiguchi, K. Matsuda, M. Matsuo, T. Yamada, M. Irie, *J. Photochem. Photobiol., A* **2002**, *152*, 141.
51 K. Higashiguchi, K. Matsuda, M. Irie, *Angew. Chem., Int. Ed.* **2003**, *42*, 3537.
52 K. Higashiguchi, K. Matsuda, N. Tanifuji, M. Irie, *J. Am. Chem. Soc.* **2005**, *127*, 8922.
53 N. Tanifuji, M. Irie, K. Matsuda, *Chem. Lett.* **2005**, *34*, 1580.
54 N. Tanifuji, M. Irie, K. Matsuda, *J. Am. Chem. Soc.* **2005**, *127*, 13344.
55 Y. Odo, K. Matsuda, M. Irie, *Chem.—Eur. J.* **2006**, *12*, 4283.
56 A. Peters, R. McDonald, N. R. Branda, *Chem. Commun.* **2002**, 2274.