Acid-induced photochromic system switching of diarylethene derivatives between P- and T-types†

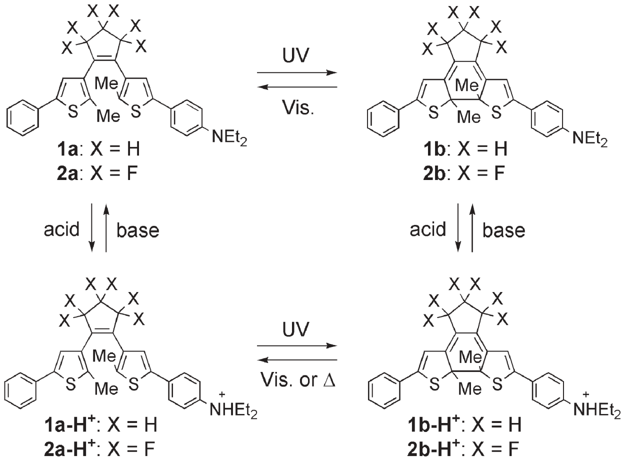
Seiya Kobatake* and Yuko Terakawa

Received (in Cambridge, UK) 5th January 2007, Accepted 23rd January 2007
First published as an Advance Article on the web 9th February 2007
DOI: 10.1039/b700177k

P-type photochromic diarylethenes having a diethylamino group can switch to T-type photochromic system by the addition of trifluoromethanesulfonic acid as external stimuli.

Photochromism has attracted particular attention because the chemical and physical properties can be changed by the external stimuli of light. Photochromic compounds are classified into two types, thermally unstable (T-type) and thermally stable (P-type) of the photogenerated isomers.[1] Azobenzene and spiropyran belong to T-type photochromic compounds. Diarylethene and furylfulgide can undergo thermally irreversible P-type photochromic reactions. Therefore, P-type photochromic compounds potentially can be used for sustainable application such as optical memory media, switching devices, and display materials.[2–7] If materials switch between P-type and T-type photochromism by other external stimuli, the photochromic materials can be developed as novel material applications such as rewritable papers of write-by-light/erase-by-heat systems.

Most of the diarylethenes having heterocyclic aryl groups belong to P-type photochromic compounds.[8] Even at 100 °C, the colored closed-ring isomers have a long-term stability.[2] However, some diarylethenes having electron-withdrawing substituents on the aryl group undergo a thermal cycloreversion reaction.[9] For example, the closed-ring isomer having 2,2-dicyanovinyl substituents at the end of diarylethene completely returned to the open-ring isomer within ten minutes at 60 °C.[9] If aryl groups of diarylethenes change from electron-donating to electron-withdrawing substituents by external stimulus, they have a possibility to switch between P-type and T-type photochromism. An acid–base-induced system as the external stimulus can easily exchange donor and acceptor of the substituents. The effect of the addition of an acid to a diarylethene having diethylamino groups has been reported so far.[10,11] However, the thermal stability has not been reported in the literature. We synthesized novel diethylamino-substituted diarylethenes (**1a** and **2a**),‡ and found that the protonated closed-ring isomers underwent thermal cycloreversion reaction even at room temperature. In this communication, we focus on photochromic system switching between P-type and T-type of **1a** and **2a** by the addition of an acid.



Diarylethenes **1a** and **2a** showed thermally irreversible photochromism in acetonitrile as well as in hexane, toluene, and other organic solvents. Fig. 1 shows the absorption spectral changes of **1a** in acetonitrile. Upon irradiation with ultraviolet light (UV), the acetonitrile solution of **1a** changed from colorless to violet. The absorption maximum of **1b** appeared at 540 nm. The colored solution was thermally stable and returned to the colorless one by irradiation with visible light. The closed-ring isomer **1b** was isolated by HPLC. The photocyclization conversion was determined by comparing the absorption spectra of **1b** with the photostationary solution. The conversion in acetonitrile was 100%

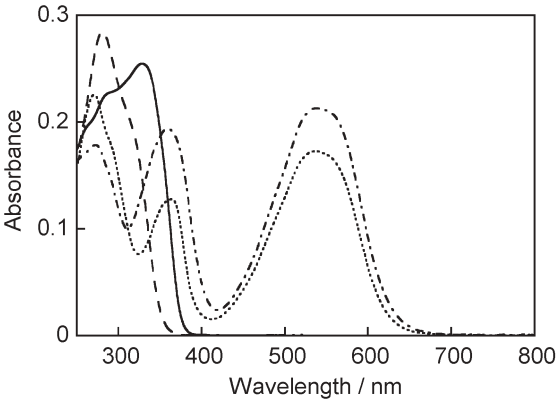


Fig. 1 Absorption spectra of **1a** (—), **1b** (-··-), **1a-H**$^+$ (– –), and **1b-H**$^+$ (···) in acetonitrile. 3 eq. of trifluoromethanesulfonic acid was used for formation of **1a-H**$^+$ and **1b-H**$^+$.

Department of Applied Chemistry, Graduate School of Engineering, Osaka City University and JST-PRESTO, 3-3-138 Sugimoto, Sumiyoshi-ku, Osaka, Japan. E-mail: kobatake@a-chem.eng.osaka-cu.ac.jp; Fax: +81-6-6605-2797; Tel: +81-6-6605-2797

† Electronic supplementary information (ESI) available: synthesis of **1a** and **2a**, and photochromic properties of **1a**, **2a**, and the related compounds. See DOI: 10.1039/b700177k

upon irradiation with 313 nm light. When trifluoromethanesulfonic acid (TFMSA) was added to **1b**, the absorption spectrum immediately showed hypochromic change to give **1b-H**$^+$, as shown in Fig. 1. The ε value decreased to 81% of **1b**. The absorption coefficient of **1b-H**$^+$ is almost the same as that of the unsubstituted compound, 1,2-bis(2-methyl-5-phenylthien-3-yl)cyclopentene.[12] When the diethylamino groups are protonated, the electron-donating property of the diethylamino group is lost. The absorption intensity was also recovered by the addition of triethylamine. The protonation and deprotonation can be reversibly carried out by the addition of an acid and a base, respectively.

The acetonitrile solution of **2a** also showed similar photochromic behavior (see ESI†). The photocyclization conversion from **2a** to **2b** was 66% in acetonitrile upon irradiation with 313 nm light. As summarized in Table 1, the absorption maximum of **2b** was shifted to short wavelength as long as 40 nm by protonation.

When the solution of the protonated compound **1b-H**$^+$ was kept in the dark at room temperature, the color of the solution was gradually bleached with a slow rate. Fig. 2 shows color changes in the absence and presence of 10 eq. of TFMSA in acetonitrile by UV irradiation and heating at 80 °C. Upon irradiation with UV light the color of the solutions turned to violet (**1b** and **1b-H**$^+$), green (**2b**), or blue (**2b-H**$^+$). After heating, the solutions in the presence of TFMSA returned to colorless, whereas non-protonated compounds were thermally stable. When the bleached solution was irradiated with UV light again, the solution turned to violet (**1b-H**$^+$) or blue (**2b-H**$^+$). These results indicate that **1b-H**$^+$ and **2b-H**$^+$ are thermally unstable and return to the colorless solutions. The thermal bleaching of **2b-H**$^+$ proceeded at a much slower rate than that of **1b-H**$^+$. The difference between diarylcyclopentene and diarylperfluorocyclopentene must be directly related to the different electron densities at the central single bond of the closed-ring forms because the perfluorocyclopentene ring has an electron-withdrawing character. This indicates that there is a significant intramolecular electronic interaction between the phenylthienyl moiety and perfluorocyclopentene ring in the closed-ring isomers.[13]

The effect of the protonation of **1a** and **2a** on the addition of TFMSA in acetonitrile was evaluated from changes in the absorption spectra. The absorption spectra changed on the addition of TFMSA, but no further changes were observed when more than 3 eq. of the acid were added to **1a**, **1b**, and **2a**. On the other hand, for **2b** changes in the absorption spectrum continued to be observed even with more than 3 eq. of acid added until finally the addition of a large amount of acid (>10 eq.) to the solution caused no further spectral change. The protonated species are in the fully protonated state in the presence of 10 eq. of TFMSA. From the titration by TFMSA, pK_a values of these protonated species in acetonitrile were determined to be 6.4 (**1a**, **1b**), 6.7 (**2a**), and 5.0 (**2b**) (see ESI†). This means that the pK_a of the protonated species of **2a**/**2b** in acetonitrile can change by photoisomerization. Some pK_a-switching systems of diarylethenes in water/methanol have been reported.[14,15] The pK_a value of a phenol group by the switching of a π-conjugated chain led to a large change (a 16-fold change in pK_a). In our systems, the electron-withdrawing perfluorocyclopentene ring plays an important role in decreasing the π-conjugated electron density of the diethylaminophenyl group in the closed-ring isomer, whereas in the open-ring isomer it does not. As a result, diarylcyclopentene did not change the pK_a between the open- and closed-ring isomers, whereas diarylperfluorocyclopentene led to a 50-fold change in pK_a between the open- and closed-ring isomers in acetonitrile.

Table 1 Absorption maxima and coefficients of the diarylethenes in the absence and presence of TFMSA in acetonitrile

	λ_{max}/nm	ε/M^{-1} cm^{-1}		λ_{max}/nm	ε/M^{-1} cm^{-1}
1a	329	26600	**1b**	540	22400
1a-H$^+$	280	29800	**1b-H**$^+$	534	16700
2a	335	32500	**2b**	630	28300
2a-H$^+$	293	37400	**2b-H**$^+$	590	15800

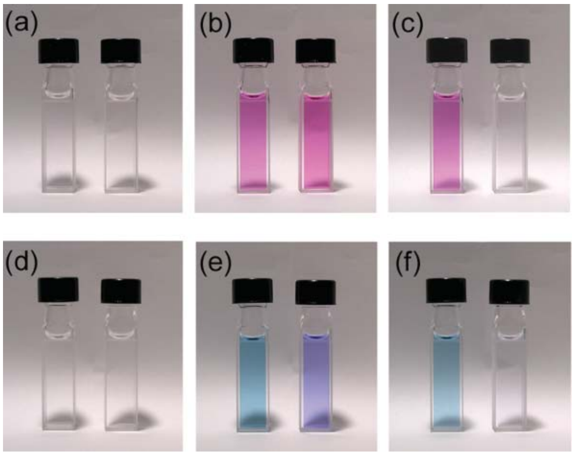


Fig. 2 Color changes of diarylethenes **1a** (top) and **2a** (bottom) in the absence (left) and presence (right) of 10 eq. of TFMSA in acetonitrile. (a) and (d): before photoirradiation. (b) and (e): after UV irradiation. (c): after heating for 30 min at 80 °C, (f) after heating for 5 h at 80 °C.

The thermal bleaching reactions of **1b-H**$^+$ and **2b-H**$^+$ in the degassed acetonitrile solution were followed by the decrease of the absorbance at 534 and 590 nm for **1b-H**$^+$ and **2b-H**$^+$, respectively, at different temperatures. The protonated compounds were prepared by the addition of 10 eq. of TFMSA. The thermal bleaching reaction proceeded to follow a first-order kinetics. The rate constants of the thermal cycloreversion reactions were determined from the slope of the first-order plots. Fig. 3 shows

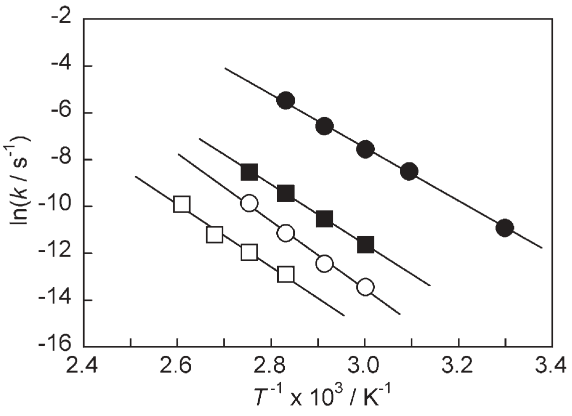


Fig. 3 Temperature dependence of rate constants of thermal cycloreversion reaction of **1b** (○), **1b-H**$^+$ (●), **2b** (□), and **2b-H**$^+$ (■) in acetonitrile.

Table 2 Activation energy and frequency factor of thermal cycloreversion reaction of the closed-ring isomers

	E_a/kJ mol^{-1}	A/s^{-1}	$t_{1/2}$ at 160 °C/s	$t_{1/2}$ at 25 °C/days
1b	121	1.3×10^{13}	21	980
1b-H$^+$	96	5.5×10^{11}	0.48	0.96
2b	109	3.5×10^{10}	280	2900
2b-H$^+$	104	2.1×10^{11}	11	64

a temperature dependence of the rate constants for the thermal cycloreversion reaction. The slope corresponds to the activation energy of the reaction. The kinetics parameters determined are summarized in Table 2. The thermal cycloreversion reactions of **1b** and **2b** were very slow. The thermal half-life times of the non-protonated closed-ring isomers were 2.7 and 7.9 years for **1b** and **2b**, respectively, at 25 °C. The colored states are thermally stable in the absence of acid. They return at a slow rate to the open-ring isomers at a high temperature such as 160 °C. On the other hand, the enhancement of the thermal cycloreversion reaction by protonation was observed. The thermal half-life times of **1b-H$^+$** and **2b-H$^+$** were 35 s and 5.5 min at 100 °C and 0.48 s and 11 s at 160 °C, respectively. These results indicate that **1b** is stable for a few years at room temperature, and the protonation led to the very rapid thermal cycloreversion reaction at 160 °C. **1b-H$^+$** was more effective than **2b-H$^+$** because of the smaller activation energy. As a result, the non-protonated diarylethenes underwent P-type photochromic reactions and protonated diarylethenes underwent T-type photochromic reactions.

In conclusion, we have demonstrated that diethylamino-substituted diarylethenes can switch photochromic systems between P-type and T-type photochromism. Non-protonated diarylethenes exhibit a thermally stable photochromic reaction, and the diarylethenes can change to a T-type system by the addition of TFMSA. Therefore, the protonated colored isomers return to open-ring isomers at a fast rate at elevated temperature such as 160 °C. The protonation and deprotonation of the open- and closed-ring isomers were reversible. Such photochromic materials could be useful for application as reversible switching materials in write-by-light/erase-by-heat systems.

This work was partly supported by PRESTO, JST and Grants-in-Aid for Scientific Research (No. 16685014) from MEXT, Japan.

Notes and references

‡ **1a**: ^{1}H-NMR (CDCl$_3$, 400 MHz, TMS): δ = 1.16 (t, J = 7.2 Hz, 6H), 1.95 (s, 3H), 1.98 (s, 3H), 2.05 (quintet, J = 7.6 Hz, 2H), 2.83 (t, J = 7.6 Hz, 4H), 3.35 (q, J = 7.2 Hz, 4H), 6.62 (d, J = 8.8 Hz, 2H), 6.85 (s, 1H), 7.05 (s, 1H), 7.2–7.6 (m, 7H); FAB-MS m/z = 483.2058 (M$^+$) (calc. 483.2054).

2a: ^{1}H-NMR (CDCl$_3$, 400 MHz, TMS): δ = 1.18 (t, J = 7.2 Hz, 6H), 1.92 (s, 3H), 1.95 (s, 3H), 3.37 (q, J = 7.2 Hz, 4H), 6.65 (d, J = 8.8 Hz, 2H), 7.08 (s, 1H), 7.29–7.40 (m, 6H), 7.54 (d, J = 7.2 Hz, 2H); FAB-MS m/z = 591.1483 (M$^+$) (calc. 591.1489).

1 H. Dürr and H. Bouas-Laurent, *Photochromism: Molecules and Systems*, Elsevier, Amsterdam, 1990.
2 M. Irie, *Chem. Rev.*, 2000, **100**, 1685.
3 Y. Yokoyama, *Chem. Rev.*, 2000, **100**, 1717.
4 S. Kawata and Y. Kawata, *Chem. Rev.*, 2000, **100**, 1777.
5 B. L. Feringa, *Molecular Switches*, Wiley-VCH, Weinheim, 2001.
6 M. Irie, T. Fukaminato, T. Sasaki, N. Tamai and T. Kawai, *Nature*, 2002, **420**, 759.
7 K. Matsuda and M. Irie, *J. Photochem. Photobiol., C*, 2004, **5**, 169.
8 M. Irie and K. Uchida, *Bull. Chem. Soc. Jpn.*, 1998, **71**, 985.
9 S. L. Gilat, S. H. Kawai and J.-M. Lehn, *Chem.–Eur. J.*, 1995, **1**, 275.
10 M. Irie, K. Sakemura, M. Okinaka and K. Uchida, *J. Org. Chem.*, 1995, **60**, 8305.
11 K. Uchida, T. Matsuoka, S. Kobatake, T. Yamaguchi and M. Irie, *Tetrahedron*, 2001, **57**, 4559.
12 L. N. Lucas, J. J. D. de Jong, J. H. van Esch, R. M. Kellogg and B. L. Feringa, *Eur. J. Org. Chem.*, 2003, 155.
13 A. Bianco, C. Bertarelli, J. F. Rabolt and G. Zerbi, *Chem. Mater.*, 2005, **17**, 869.
14 S. H. Kawai, S. L. Gilat and J.-M. Lehn, *Eur. J. Org. Chem.*, 1999, 2359.
15 Y. Odo, K. Matsuda and M. Irie, *Chem.–Eur. J.*, 2006, **12**, 4283.