Photocyclization reaction of a diarylmaleimide derivative in polar solvents†

Masato Ohsumi,[a] Masaki Hazama,[a] Tuyoshi Fukaminato*[a] and Masahiro Irie*[b]

Received (in Cambridge, UK) 19th February 2008, Accepted 21st April 2008
First published as an Advance Article on the web 19th May 2008
DOI: 10.1039/b802780c

Photochromism of a symmetric diarylmaleimide derivative, having two thiophene rings (1), and a non-symmetric derivative having a *S*,*S*-dioxide thiophene ring and a thiophene ring (2) as the aryl moieties, was studied in various solvents. The photocyclization quantum yield of 1 gradually decreased with increasing the solvent polarity and the reaction was not observed in polar solvents, such as ethanol and acetonitrile; on the other hand, such a strong solvent dependence of the photocyclization reaction was not observed for 2; the different behavior is attributed to the weaker electron donating ability of the *S*,*S*-dioxide thiophene ring.

Recently, photochromic compounds have attracted considerable attention as molecular switches to control various functions.[1] Among many photochromic compounds, diarylethene derivatives are the most promising for practical applications because of their thermal stability and fatigue resistance.[2,3] One of potential applications of the photochromic compounds is as a biological probe.[4] Photochromic chromophores can be used as an energy acceptor or donor group in FRET, which provides a tool for resolving molecular interactions in biological systems. Photochromic FRET is advantageous for the quantitative determination of FRET parameters.[5] In addition, photochromic biological probes are also useful as a super-resolution biological imaging technique.[6] For useful application, the photochromic compound should undergo photoreaction even in polar solvents. In addition, the photoreaction should be induced by irradiation with visible light, because in biological systems UV light is absorbed by proteins, such as indole residues. Diarylmaleimides[7] as well as diarylmaleic anhydrides[8,9] are possible candidates for this application, since these compounds undergo reversible photochromic reactions upon irradiation with visible light. One of the drawbacks of these derivatives is that the photochromic reactions are strongly suppressed in polar solvents.[8] It is strongly desired to develop a novel diarylethene derivative, in which both cyclization and cycloreversion reactions take place upon irradiation with light in the visible region even in polar solvents. Here, we report on a diarylmaleimide derivative, which exhibits reversible photochromism in polar solvents.

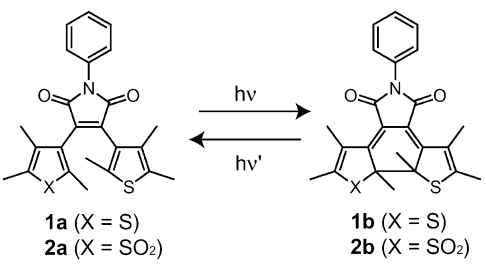
[a] *Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, Motooka 744, Nishi-ku, Fukuoka, 819-0395, Japan. E-mail: tuyoshi@cstf.kyushu-u.ac.jp; Fax: +81-92-802-2873; Tel: +81-92-802-2873*
[b] *Department of Chemistry, Rikkyo University, Nishi-Ikebukuro 3-34-1, Toshima-ku, Tokyo, 171-8501, Japan. E-mail: iriem@rikkyo.ac.jp; Fax: +81-3-3985-2397; Tel: +81-3-3985-2397*

† Electronic supplementary information (ESI) available: Details of synthesis of **1** and **2**. See DOI: 10.1039/b802780c

A symmetric diarylmaleimide derivative, having thiophene rings (**1**), and a non-symmetric derivative having a *S*,*S*-dioxide thiophene ring and a thiophene ring (**2**) as the aryl moieties (Scheme 1), were synthesized and their photochromic properties in various solvents were studied. Detailed synthetic procedures are described in the ESI.† Compound **1** was obtained by a typical condensation procedure in high yield. Compound **2** was prepared by the oxidation of **1** using 3-chloroperoxybenzoic acid (*m*-CPBA)[10] in 67% yield. The structures were identified with ^{1}H NMR, MS spectra and elemental analysis‡ (also see ESI†).

Fig. 1(a) shows the absorption spectral change along with the photochromic reaction of **1** in cyclohexane solution. Upon irradiation with 405 nm light, the yellow color solution turned to red–purple, and new absorption bands appeared at 526 and 377 nm. The color change is attributed to the photocyclization reaction from the open-ring isomer (**1a**) to closed-ring isomer (**1b**). Upon irradiation with visible light ($\lambda > 500$ nm), the peaks at 526 and 337 nm gradually decreased and finally disappeared (*i.e.* the red–purple solution returned to a yellow solution).

Remarkable solvent dependence was observed for the photochromic reaction of **1**. The conversion from the open- to the closed-ring isomer in the photostationary state under irradiation with 405 nm light decreased with increasing solvent polarity. The conversion of 54% in cyclohexane decreased to 42% in toluene, 27% in THF, 7% in ethanol, and 4% in acetonitrile, respectively (Fig. 1(b) and Fig. S1 in ESI†). In ethanol and acetonitrile solutions, no appreciable color change was observed upon irradiation with 405 nm light, as shown in Fig. 1(c). Table 1 summarizes the quantum yields of **1** in various solvents. The strong solvent dependence was observed only in the cyclization reaction. The cyclization quantum yield of **1a** decreases with increasing solvent polarity. The cyclization quantum yield decreases to 0.097 in THF, 0.029 in ethanol and 0.013 in acetonitrile, respectively. On the other hand, the photocycloreversion



Scheme 1 Photochromism of diarylmaleimide derivatives.

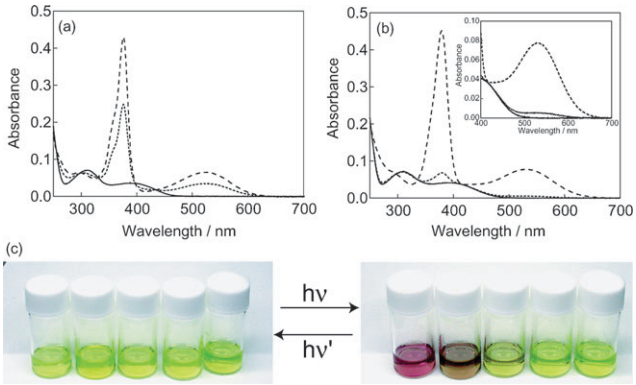


Fig. 1 Absorption spectra of **1** (a) in cyclohexane, (b) in ethanol; the open-ring isomer (solid line), the photostationary state under irradiation with 405 nm light (dashed line), and the closed-ring isomer (broken line). The inset in Fig. 1(b) shows the absorption spectra between 400 and 700 nm. (c) Photographs of color changes of **1** upon irradiation with 405 nm light in various solvents (from left to right: cyclohexane, toluene, THF, ethanol, acetonitrile): Left: before photoirradiation, right: after photoirradiation.

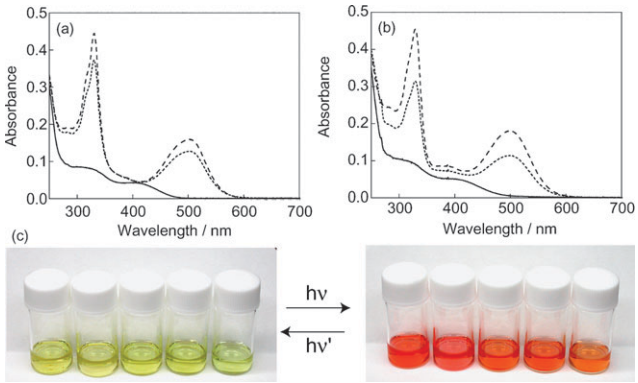


Fig. 2 Absorption spectra of **2** (a) in cyclohexane, (b) in ethanol; the open-ring isomer (solid line), the photostationary state under irradiation with 405 nm light (dashed line), and the closed-ring isomer (broken line). (c) Photographs of color changes of **2** upon irradiation with 405 nm light in various solvents (from left to right: cyclohexane, toluene, THF, ethanol, acetonitrile): Left: before photoirradiation, right: after photoirradiation.

quantum yields are almost the same in cyclohexane, toluene, THF, ethanol and acetonitrile. These results are similar to the behavior of diarylmaleic anhydride derivatives previously reported.[8]

Fig. 2(a) shows the absorption spectral change along with photochromic reaction of **2** in cyclohexane solution. Upon irradiation with 405 nm light, the yellow color solution turned to red, and new absorption bands appeared at 498 and 331 nm. The color change is attributed to the photocyclization reaction from the open-ring isomer (**2a**) to the closed-ring isomer (**2b**). Upon irradiation with visible light ($\lambda > 500$ nm), the peaks at 498 and 331 nm gradually decreased and finally disappeared (*i.e.* the red color solution returned to a yellow solution). The conversion from **2a** to **2b** in cyclohexane was 80%, which is much higher than that of **1a** in the same solvent. **2a** was efficiently converted to **2b** even in polar solvents such as ethanol and acetonitrile (Fig. 2(b) and Fig. S2 in ESI†). The color change along with photochromic reaction was clearly observed even in polar acetonitrile (Fig. 2(c)). These results suggest that the solvent polarity scarcely affects the photoreaction. The cyclization quantum yields were measured in various solvents and are summarized in Table 2. As expected, the cyclization quantum yield of **2a** is still high even in acetonitrile.

Table 1 Absorption maxima, quantum yields and conversion ratios from the open- to the closed-ring isomers upon irradiation with 405 nm light of **1** in various solvents

	λ_{max}/nm		Quantum yield		
Solvent	**1a**	**1b**	**1a** → **1b**[a]	**1b** → **1a**[b]	Conversion (%)
Cyclohexane	392	526	0.22	0.16	54
Toluene	398	527	0.13	0.14	42
THF	393	526	0.097	0.12	27
Ethanol	396	528	0.029	0.13	7
Acetonitrile	388	525	0.013	0.14	4

[a] Irradiation with 405 nm light. [b] Irradiation with 516 nm light.

Table 2 Absorption maxima, quantum yields and conversion ratios from the open- to the closed-ring isomers upon irradiation with 405 nm light of **2** in various solvents

	λ_{max}/nm		Quantum yield		
Solvent	**2a**	**2b**	**2a** → **2b**[a]	**2b** → **2a**[b]	Conversion (%)
Cyclohexane	401	502	0.30	0.031	80
Toluene	400	505	0.24	0.022	65
THF	401	498	0.22	0.024	70
Ethanol	405	500	0.17	0.030	63
Acetonitrile	400	494	0.11	0.038	40

[a] Irradiation with 405 nm light. [b] Irradiation with 494 nm light.

In a previous paper,[8] the solvent dependence of analogous compounds, 1,2-bis(2,4,5-trimethylthiophene-3-yl)maleic anhydride and 1,2-bis(2-methylbenzothiophen-3-yl)maleic anhydride was attributed to the contribution of a twisted intramolecular charge transfer interaction (TICT).[11] The donor–acceptor interaction between the thiophene and maleic anhydride moieties play a role to control the reactivity. The weak solvent dependence observed in **2a** can be attributed to the weak electron donating ability of the *S*,*S*-dioxide thiophene ring.

In conclusion, a non-symmetric derivative having a *S*,*S*-dioxide thiophene ring and a thiophene ring as the aryl moieties was synthesized and showed high photochromic reactivity even in polar solvents such as acetonitrile. The weak electron donating ability of the *S*,*S*-dioxide moiety favored the cyclization reaction even in polar solvents.

This work was partly supported by Grant-In-Aid for Fundamental Research Program (S) (No. 15105006), Grant-in-Aids for Young Scientist (B) (No. 18750119), Grant-in-Aids for Scientific Research on Priority Areas (471) (No. 19050009) from the Ministry of Education, Culture, Sports, Science, and Technology (MEXT) of Japanese Government and also by Grant-in-Aid for The Global COE Program, "Future Molecular Systems" from the Ministry of Education, Culture, Science, Sports and Technology of Japan.

Notes and references

‡ *Analytical data for* **1a**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.79 (s, 3H), 1.95–1.96 (m, 6H), 2.11 (s, 3H), 2.26–2.28 (m, 6H), 7.33–7.40 (m, 1H), 7.45–7.54 (m, 4H); MS (FAB$^+$): m/z 422 $[M + H]^+$; Anal. Calc. for $C_{24}H_{23}NO_2S_2$: C, 68.38; H, 5.50; N, 3.32. Found: C, 68.32; H, 5.59; N, 3.32%.

Analytical data for **2b**:[12] ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.54 (s, 3H), 1.82 (s, 3H), 2.23 (d, 3H, J = 0.8 Hz), 2.32 (s, 3H), 2.41 (s, 3H), 2.48 (d, 3H, J = 0.8 Hz), 7.35–7.43 (m, 3H), 7.48–7.52 (m, 2H); MS (FAB$^+$): m/z 454 $[M + H]^+$; Anal. Calc. for $C_{24}H_{23}NO_4S_2$: C, 63.55; H, 5.11; N, 3.09. Found: C, 63.21; H, 5.32; N, 2.97%.

1. H. Bouas-Laurent and H. Dürr, *Pure Appl. Chem*., 2001, **73**, 639; F. M. Raymo and M. Tomasulo, *Chem. Soc. Rev*., 2005, **34**, 327; D. Gust, T. A. Moore and A. L. Moore, *Chem. Commun*., 2006, 1169; W. R. Browne and B. L. Feringa, *Nat. Nanotechnol*., 2006, **1**, 25; N. Katsonis, M. Lubomska, M. M. Pollard, B. L. Feringa and P. Rudolf, *Prog. Surf. Sci*., 2007, **82**, 407.
2. M. Irie, *Chem. Rev*., 2000, **100**, 1685; M. Irie and K. Uchida, *Bull. Chem. Soc. Jpn*., 1998, **71**, 985; H. Tian and S. Yang, *Chem. Soc. Rev*., 2004, **33**, 85; K. Matsuda and M. Irie, *J. Photochem. Photobiol., C*, 2004, **5**, 169.
3. M. Hanazawa, R. Sumiya, Y. Horikawa and M. Irie, *J. Chem. Soc., Chem. Commun*., 1992, 206; M. Irie, T. Lifka, K. Uchida, S. Kobatake and Y. Shindo, *Chem. Commun*., 1999, 747; S. Takami, S. Kobatake, T. Kawai and M. Irie, *Chem. Lett*., 2003, **32**, 892.
4. R. Ando, H. Mizuno and A. Miyawaki, *Science*, 2004, **306**, 1370; N. Soh, K. Yoshida, H. Nakajima, K. Nakano, T. Imato, T. Fukaminato and M. Irie, *Chem. Commun*., 2007, 5206.
5. L. Giordano, T. M. Jovin, M. Irie and E. Jares-Erijiman, *J. Am. Chem. Soc*., 2002, **124**, 7481; E. Jares-Erijiman and T. M. Jovin, *Nat. Biotechnol*., 2003, **21**, 1387.
6. S. W. Hell, S. Jakobs and L. Kastrup, *Appl. Phys. A*, 2003, **77**, 859; S. W. Hell, *Science*, 2007, **316**, 1153; P. Dedecker, C. Flors, J. Hotta, H. Uji-i and J. Hofkens, *Angew. Chem., Int. Ed*., 2007, **46**, 8330.
7. K. Uchida and M. Irie, *Bull. Chem. Soc. Jpn*., 1998, **71**, 1101; T. Yamaguchi and M. Irie, *Chem. Lett*., 2004, **33**, 1398.
8. M. Irie and K. Sayo, *J. Phys. Chem*., 1992, **96**, 7671.
9. H. Miyasaka, T. Nobuto, M. Murakami, A. Itaya, N. Tamai and M. Irie, *J. Phys. Chem. A*, 2002, **106**, 8096.
10. Y.-C. Jeong, D. G. Park, E. Kim, K. Ahn and S. I. Yang, *Chem. Commun*., 2005, 2503.
11. N. Mataga, Y. Kaifu and M. Koizumi, *Bull. Chem. Soc. Jpn*., 1956, **29**, 465; Z. Grabowski, K. Rotkiewicz and W. Rettig, *Chem. Rev*., 2003, **103**, 3899.
12. The identification of the molecular structure of compound **2** was carried out by using the closed-ring isomer (**2b**), since the ^{1}H NMR signal of the open-ring isomer (**2a**) was very complex due to the non-symmetric molecular structure and the existence of parallel and anti-parallel conformers.