Chemical control of the photochromic reactivity of diarylethene derivatives†

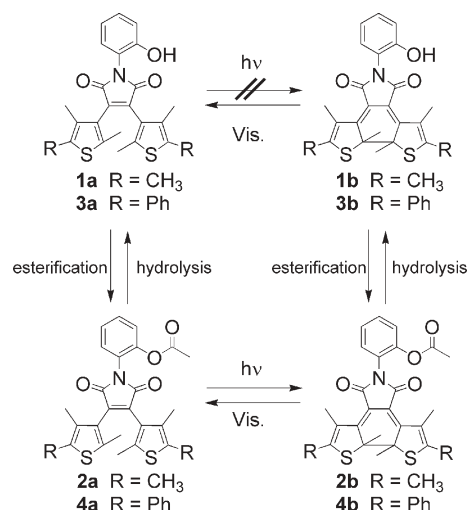**Masato Ohsumi, Tuyoshi Fukaminato and Masahiro Irie***

**Photochemically inactive diarylethene derivatives having a
N-(*O*-hydroxyphenyl) group underwent photochromic reaction
when they were esterified by the addition of acetic anhydride.**

Although photochromic performance of a certain type of
compounds has been remarkably improved,[1–4] several problems
still remain for practical applications. A property that is strongly
desired but is still inadequate is gated photochromic reactivity.
Gated reactivity is the property whereby irradiation with any given
wavelength of light alone causes no color change, while a color
change is induced when another external stimulus, such as
additional photons of different wavelength,[5,6] chemicals,[7–10] or
heat,[11] is present. Such threshold reactivity is indispensable for
application to display and memory technologies.

Several attempts to provide gated photochromic reactivity have
been reported.[5–12] One of the chemical approaches is to use
protons to control the photochromic reactivity. The ring-opening
quantum yield of an indole fulgide derivative with a dimethyl-
amino substituent at the 5-position of the indole ring was found to
change by the addition of acid.[7] Another approach is to use
intramolecular hydrogen bonds. When a diarylethene molecule is
interlocked by the hydrogen bonds, the molecule is photochemi-
cally inactive, while the molecule undergoes a photochromic
reaction when the bonds are unclasped by the addition of
hydrogen bond breaking agents, such as ethanol.[10]

We herein report on the design and synthesis of chemically
gated diarylethene derivatives having a *N*-(*O*-hydroxyphenyl)
group (Scheme 1). The excited states of the molecule are efficiently
quenched by the intramolecular proton transfer.[13,14] Therefore,
they are not photochromic. On the other hand, when the hydroxyl
group is protected by esterification, the esterified diarylethenes are
expected to undergo typical photochromic reactions.

1a was prepared from 2,3-bis(2,4,5-trimethyl-3-thienyl)maleic
anhydride[15] by a conventional thermal imidization with *o*-amino-
phenol in toluene. The structure was identified by ^{1}H NMR, mass
spectroscopy, and elemental analysis‡ (synthetic procedures and
analysis data for **1** are described in the Electronic Supplementary
Information†). For all measurements, non-polar cyclohexane was
used as the solvent because the photocyclization reactions of the
diarylethene derivatives are suppressed in polar solvents due to the
contribution of twisted intramolecular charge transfer.[16]

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† Electronic supplementary information (ESI) available: synthetic proce-
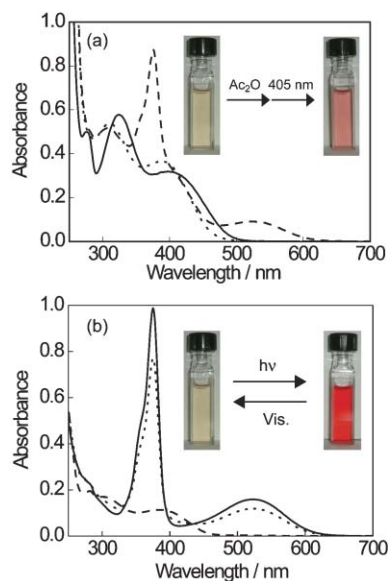dures and analytical data. See http://dx.doi.org/10.1039/b506801k

Scheme 1

The absorption spectrum of **1a** in cyclohexane solution at room
temperature is shown in Fig. 1a. **1a** does not exhibit any
photochromic reaction in cyclohexane upon irradiation with
405 nm light, indicating that the photochromic reactivity is
strongly suppressed by the intramolecular proton transfer. The
formation of the intramolecular hydrogen bonding in the ground
state between the hydrogen atom in the phenol group and the
oxygen atom in the imide carbonyl group was confirmed by
^{1}H NMR measurements as well as by molecular geometry
calculations (see ESI†). The hydrogen bonding induces quenching
of the excited state due to proton transfer.

When acetic anhydride was added during irradiation with
405 nm light, the pale yellow color solution turned to pale red and
the color intensity increased with time (Fig. 1a; inset). The color
change is considered to be due to the esterification of the hydroxyl
group of **1a**. In order to confirm the esterification, the colored
product was isolated by silica gel column chromatography and
HPLC. The colored product was identified as **2b** by ^{1}H NMR,
mass spectroscopy, and elemental analysis.‡ **2b** converted to **2a**
upon irradiation with visible (λ > 550 nm) light (synthetic
procedures and analysis data for **2** are described in the ESI†).

As expected, **2a** exhibits a typical photochromic response in
cyclohexane solution. Fig. 1b shows the absorption spectral
changes of **2** in cyclohexane solution at room temperature. **2a**
has a broad absorption band around 400 nm and the solution
color is pale yellow. Upon irradiation with 405 nm light, the pale
yellow color solution of **2a** turns red (Fig. 1b; inset), and
absorption maxima were observed at 524 nm, and 375 nm. The

Fig. 1 (a) Absorption spectral changes of **1** in cyclohexane solution; (——) open-ring isomer (**1a**), (······) after adding acetic anhydride, and (- - -) after irradiating a solution of **1** containing acetic anhydride with 405 nm light. Inset: Photograph of the color change of **1** upon irradiation with 405 nm light in the presence of acetic anhydride. (b) Absorption spectral changes of **2** in cyclohexane solution; (- - -) open-ring isomer, (······) photostationary state under irradiation with 405 nm light, and (——) closed-ring isomer. Inset: Photograph of the color change of **2** caused by photoirradiation.

color disappeared on irradiation with visible light ($\lambda > 550$ nm) and the absorption spectrum returned to that of **2a**. The colored product **2b** was isolated with HPLC and the absorption spectrum is shown in Fig. 1b. In the photostationary state in cyclohexane under irradiation with 405 nm light, 75% of **2a** converted to **2b**. The quantum yield yields of the cyclization ($\Phi_{a \to b}$) and cycloreversion ($\Phi_{b \to a}$) reactions of **2** in cyclohexane were measured by the standard procedure using furylfulgide as a reference.[17] The results are summarized in Table 1.

2a returned to the photo-inactive state upon addition of hydrochloric acid, indicating that **2a** is hydrolyzed by the addition of the acid. The esterification–hydrolysis processes can be repeated many times. It is concluded that the photochromic reaction is efficiently suppressed by the intramolecular proton transfer and the protection of a hydroxyl group with an ester group provides

Table 1 Absorption maxima and absorption coefficients of the open- and closed-ring isomers of diarylethenes, and the photochromic quantum yields in cyclohexane

	λ_{max}/nm (ε/M^{-1}cm^{-1})	$\Phi_{a \to b}{}^a$		λ_{max}/nm (ε/M^{-1}cm^{-1})	$\Phi_{b \to a}{}^b$
1a	324 (5700)	0	**1b**	385 (40000) 533 (5800)	0.11 (533 nm)
2a	306 (5200)	0.22 (405 nm)	**2b**	375 (30000) 524 (4900)	0.18 (524 nm)
3a	408 (3500)	0	**3b**	400 (36000) 563 (8700)	0.044 (563 nm)
4a	395 (3800)	0.30 (430 nm)	**4b**	391 (31000) 557 (8800)	0.056 (557 nm)

^{a} Photocyclization quantum yield. ^{b} Photocycloreversion quantum yield.

the photochromic reactivity. The esterification and hydrolysis reactions can be induced even in polymer matrices.[14] It is worth noting that the red color of **2b** disappeared upon irradiation visible light (>550 nm) even in the presence of hydrochloric acid. This means that the intramolecular proton transfer does not suppress the cycloreversion reaction.

Similar experiments were performed for **3** and **4** (synthetic procedures and analysis data of compounds **3** and **4** are described in ESI†). **3a** did not exhibit any photochromic reaction on photoirradiation. On the other hand, typical photochromic behavior was observed for **4a**. The optical and photochromic properties for **3** and **4** are also summarized in Table 1.

In summary, we have demonstrated that the photochromic reaction of diarylethene derivatives can be controlled by the addition of acid. Such chemically gated systems can be applied to display materials, memory media, as well as molecular logic gates.

Notes and references

‡ *Analytical Data for* **1a**: mp 224–225 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.76 (s, 3H), 1.92 (s, 3H), 1.94 (s, 3H), 2.08 (s, 3H), 2.27 (s, 3H), 2.29 (s, 3H), 6.09 (s, 1H), 7.05–7.38 (m, 4H); HRMS (FAB$^+$): m/z = 437.1111 [M]$^+$ (calcd. for C$_{24}$H$_{23}$NO$_3$S$_2$: 437.1119); Anal. calcd. for C$_{24}$H$_{23}$NO$_3$S$_2$: C, 65.88; H, 5.30; N, 3.20. Found: C, 66.08; H, 5.31; N, 3.15.

Analytical Data for **1b**: ^{1}H NMR (400 MHz, CDCl$_3$): δ = 2.04 (s, 6H), 2.16 (s, 6H), 2.28 (s, 6H), 6.49 (s, 1H), 7.00–7.15 (m, 2H), 7.26–7.35 (m, 2H); HRMS (FAB$^+$): m/z = 437.1121 [M]$^+$ (calcd. for C$_{24}$H$_{23}$NO$_3$S$_2$: 437.1119); Anal. calcd. for C$_{24}$H$_{23}$NO$_3$S$_2$: C, 65.88; H, 5.30; N, 3.20. Found: C, 65.97; H, 5.33; N, 3.18.

Analytical Data for **2a**: mp 156–157 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.79 (s, 3H), 1.95 (s, 3H), 1.97 (s, 3H), 2.11 (s, 3H), 2.19 (s, 3H), 2.25 (s, 3H), 2.28 (s, 3H), 7.31–7.54 (m, 4H); HRMS (FAB$^+$): m/z = 479.1228 [M]$^+$ (calcd. for C$_{26}$H$_{25}$NO$_4$S$_2$: 479.1225); Anal. calcd. for C$_{26}$H$_{25}$NO$_4$S$_2$: C, 65.11; H, 5.25; N, 2.92. Found: C, 65.07; H, 5.31; N, 2.96.

Analytical Data for **3a**: mp 143–145 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.99 (s, 3H), 2.11 (s, 3H), 2.13 (s, 3H), 2.25 (s, 3H), 5.59 (s, 1H), 7.11–7.49 (m, 14H); HRMS (FAB$^+$): m/z = 561.1422 [M]$^+$ (calcd. for C$_{34}$H$_{27}$NO$_3$S$_2$: 561.1432); Anal. calcd. for C$_{34}$H$_{27}$NO$_3$S$_2$: C, 72.70; H, 4.84; N, 2.49. Found: C, 72.12; H, 4.91; N, 2.52.

Analytical Data for **4a**: mp 124–125 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.99 (s, 3H), 2.11 (s, 3H), 2.12 (s, 3H), 2.21 (s, 3H), 2.25 (s, 3H), 7.33–7.52 (m, 14H); HRMS (FAB$^+$): m/z = 603.1527 [M]$^+$ (calcd. for C$_{36}$H$_{29}$NO$_4$S$_2$: 603.1538); Anal. calcd. for C$_{36}$H$_{29}$NO$_4$S$_2$: C, 71.62; H, 4.84; N, 2.32. Found: C, 71.57; H, 5.14; N, 2.21.

Analytical Data for N-(3-hydroxyphenyl)-2,3-bis(2,4,5-trimethyl-3-thienyl)maleimide (reference molecule): mp 109–110 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.78 (s, 3H), 1.94 (s, 3H), 1.95 (s, 3H), 2.10 (s, 3H), 2.26 (s, 3H), 2.28 (s, 3H), 4.89 (s, 1H), 6.84 (dd, 1H, J = 8.4 Hz, 2.4 Hz), 7.01–7.02 (m, 1H), 7.09 (d, 1H, J = 8 Hz), 7.35 (t, 1H, J = 8 Hz); HRMS (FAB$^+$): m/z = 437.1113 [M]$^+$ (calcd. for C$_{24}$H$_{23}$NO$_3$S$_2$: 437.1119); Anal. calcd. for C$_{24}$H$_{23}$NO$_3$S$_2$: C, 65.88; H, 5.30; N, 3.20. Found: C, 65.98; H, 5.32; N, 3.18.

1 G. H. Brown, *Photochromism*, Wiley-Interscience, New York, 1971; H. Dürr and H. Bouas-Laurent, *Photochromism: Molecules and Systems*, Elsevier, Amsterdam, 1990; H. Bouas-Laurent and H. Dürr, *Pure Appl. Chem.*, 2001, **73**, 639.
2 K. Uchida and M. Irie, *Bull. Chem. Soc. Jpn.*, 1998, **71**, 985; M. Irie, *Chem. Rev.*, 2000, **100**, 1685; H. Tian and S. Yang, *Chem. Soc. Rev.*, 2004, **33**, 85.
3 H. Hanazawa, R. Sumiya, Y. Horikawa and M. Irie, *J. Chem. Soc., Chem. Commun.*, 1992, 206; M. Irie, T. Lifka, S. Kobatake and N. Kato, *J. Am. Chem. Soc.*, 2000, **122**, 4871.

4 M. Irie, S. Kobatake and M. Horichi, *Science*, 2001, **291**, 1769; M. Irie, T. Fukaminato, T. Sasaki, N. Tamai and T. Kawai, *Nature*, 2002, **420**, 759; D. Dulić, S. J. van der Molen, T. Kudernac, H. T. Jonkman, J. J. D. de Jong, T. N. Bowden, J. van Esch, B. L. Feringa and B. J. van Wees, *Phys. Rev. Lett.*, 2003, **91**, 207402; K. Matsuda and M. Irie, *J. Photochem. Photobiol. C*, 2004, **5**, 169; D. Sud, T. B. Norsten and N. R. Branda, *Angew. Chem., Int. Ed.*, 2005, **44**, 1059.
5 M. Uchida and M. Irie, *J. Am. Chem. Soc.*, 1993, **115**, 6442.
6 M. Murakami, H. Miyasaka, T. Okada, S. Kobatake and M. Irie, *J. Am. Chem. Soc.*, 2004, **126**, 14764.
7 F. Matsui, H. Taniguchi, Y. Yokoyama, K. Sugiyama and Y. Kurita, *Chem. Lett.*, 1994, 1869.
8 S. H. Kawai, S. L. Gilat and J.-M. Lehn, *Eur. J. Org. Chem.*, 1999, 2359.
9 N. P. M. Huck and B. L. Feringa, *J. Chem. Soc., Chem. Commun.*, 1995, 1095.
10 M. Irie, O. Miyatake, K. Uchida and T. Eriguchi, *J. Am. Chem. Soc.*, 1994, **116**, 9894.
11 M. Irie, T. Eriguchi, T. Takata and K. Uchida, *Tetrahedron*, 1997, **53**, 12263.
12 I. Willner, A. Doron and E. Katz, *J. Phys. Org. Chem.*, 1998, **11**, 546.
13 W. Klöpffer, *Adv. Photochem.*, 1977, **10**, 311.
14 N. C. Yang, H. W. Choi, J. K. Lee, J. Il Hwang and D. H. Shu, *Chem. Lett.*, 2002, 824.
15 M. Irie and M. Mohri, *J. Org. Chem.*, 1988, **53**, 803.
16 M. Irie and K. Sayo, *J. Phys. Chem.*, 1992, **96**, 7671; T. Yamaguchi, K. Uchida and M. Irie, *J. Am. Chem. Soc.*, 1997, **119**, 6066.
17 Y. Yokoyama and Y. Kurita, *J. Synth. Org. Chem. Jpn.*, 1991, **49**, 364; H. G. Heller and J. R. Langan, *J. Chem. Soc., Perkin Trans. 2*, 1981, 341.