Chemical control of the photochromic reactivity of diarylethene derivatives†

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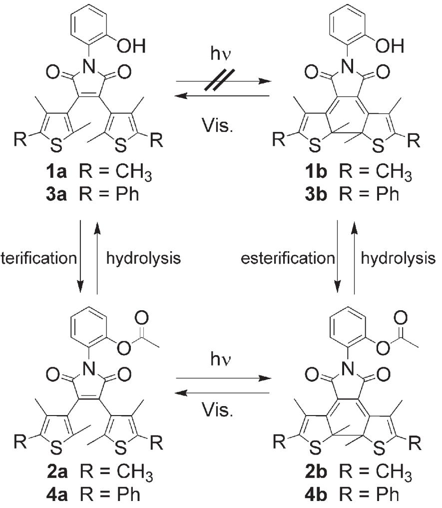
Photochemically inactive diarylethene derivatives having a *N*-(*O*-hydroxyphenyl) group underwent photochromic reaction when they were esterified by the addition of acetic anhydride.

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 dimethylamino 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 photochemically 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*-aminophenol 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]



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 ($\lambda > 550$ 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

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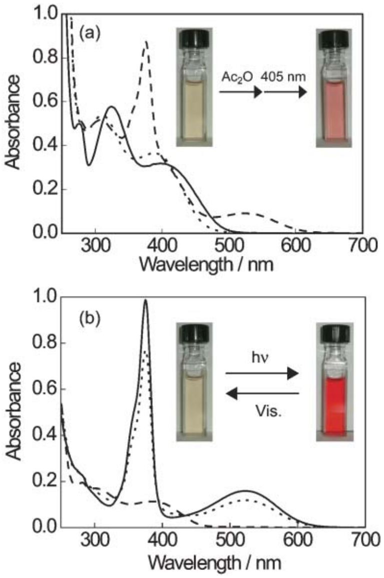

Fig. 1 (a) Absorption spectral changes of **1** in cyclohexane solution; (——) open-ring isomer (**1a**), (·······) after adding acetic anhydride, and (- - -) after irradiating a solution of **1** containing acetic anhydride with 405 nm light. Inset: Photograph of the color change of **1** upon irradiation 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 (λ > 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 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.

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.

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.

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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 $C_{24}H_{23}NO_3S_2$: 437.1119); Anal. calcd. for $C_{24}H_{23}NO_3S_2$: 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 $C_{24}H_{23}NO_3S_2$: 437.1119); Anal. calcd. for $C_{24}H_{23}NO_3S_2$: 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 $C_{26}H_{25}NO_4S_2$: 479.1225); Anal. calcd. for $C_{26}H_{25}NO_4S_2$: 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 $C_{34}H_{27}NO_3S_2$: 561.1432); Anal. calcd. for $C_{34}H_{27}NO_3S_2$: 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 $C_{36}H_{29}NO_4S_2$: 603.1538); Anal. calcd. for $C_{36}H_{29}NO_4S_2$: 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 $C_{24}H_{23}NO_3S_2$: 437.1119); Anal. calcd. for $C_{24}H_{23}NO_3S_2$: C, 65.88; H, 5.30; N, 3.20. Found: C, 65.98; H, 5.32; N, 3.18.

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