Synthesis and Photochromism of Diarylethenes with Isopropyl Groups at the Reactive Carbons and Long π-Conjugated Heteroaryl Groups

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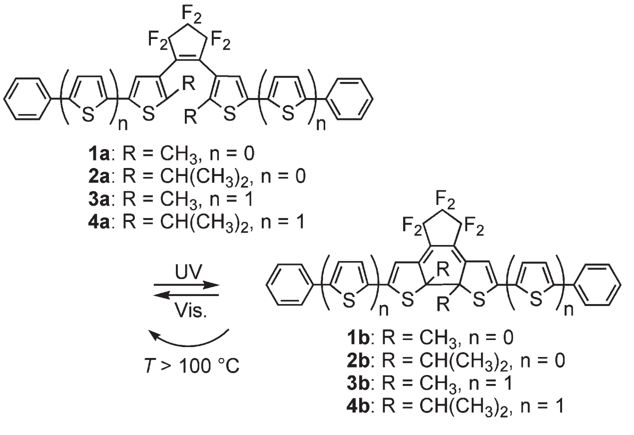
Diarylethenes with long π-conjugated heteroaryl groups were synthesized and their absorption spectra, photocyclization and cycloreversion quantum yields, and thermal stability were examined. The diarylethene with isopropyl groups at the reactive carbons was found to have a low decoloration quantum yield and thermal reversibility at high temperature above 100 °C.

Photochromic diarylethenes undergo reversible photoisomerization between two isomers with different absorption spectra upon irradiation with light of appropriate wavelength.[1–3] Diarylethenes with heteroaryl groups are the most promising candidates for practical applications to optical memory media and switching devices because of their thermal stability and fatigue resistance.[4,5] In order to apply the photochromic compounds to recording materials, it is desired to decrease the photodecoloration quantum yields to avoid the bleaching under room light. If the colored isomers return to the initial colorless isomers thermally at high temperature above 100 °C, it can be potentially used for reusable recording materials.

One of the approaches is to introduce alkoxy groups at the reactive carbons of diarylethenes.[6] The introduction of cyclohexyloxy groups decreased the photodecoloration quantum yields and increased the thermal decoloration rate at high temperature above 100 °C. The colored isomers can return to the colorless isomers thermally at the high temperature. Another strategy to decrease the decoloration quantum yields of diarylethenes is to introduce long π-conjugation to the diarylethenes. Here we report on synthesis of diarylethene derivatives (Scheme 1) which have both low decoloration quantum yields and thermal reversibility at high temperature.

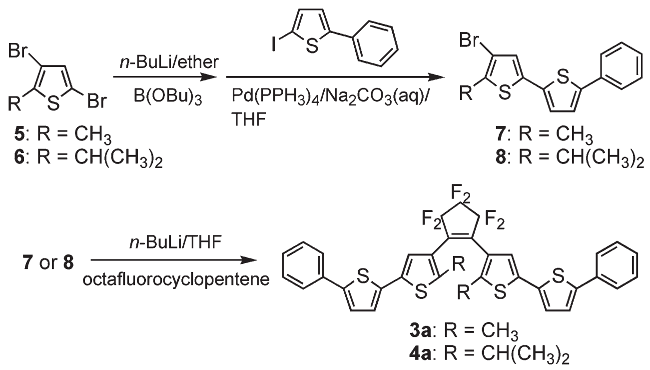
Synthetic procedures of diarylethenes **1a** and **2a** were described before.[7,8] Diarylethenes **3a** and **4a** were synthesized according to Scheme 2 and were identified by ^{1}H NMR spectrum, mass spectrum, and elemental analysis.[9,10]



1a: R = CH_3, n = 0
2a: R = $CH(CH_3)_2$, n = 0
3a: R = CH_3, n = 1
4a: R = $CH(CH_3)_2$, n = 1

1b: R = CH_3, n = 0
2b: R = $CH(CH_3)_2$, n = 0
3b: R = CH_3, n = 1
4b: R = $CH(CH_3)_2$, n = 1

Scheme 1. Photochromic reactions of diarylethene derivatives.



5: R = CH_3
6: R = $CH(CH_3)_2$

7: R = CH_3
8: R = $CH(CH_3)_2$

3a: R = CH_3
4a: R = $CH(CH_3)_2$

Scheme 2. Synthetic route of diarylethene derivatives.

Figure 1a shows the absorption spectrum of **3a** in toluene at room temperature. Compound **3a** has an absorption maximum at 350 nm in toluene. Upon irradiation with 350-nm light, the colorless solution of **3a** turned blue, in which the visible absorption maximum was observed at 640 nm. The color is due to the photogenerated closed-ring isomer **3b**. The colored product was isolated by HPLC (silica gel; hexane as the eluent). It was confirmed that the spectrum of **3b** was the same as that in the photostationary state upon irradiation with 350-nm light, indicating that the conversion from **3a** to **3b** is 100%. The blue color

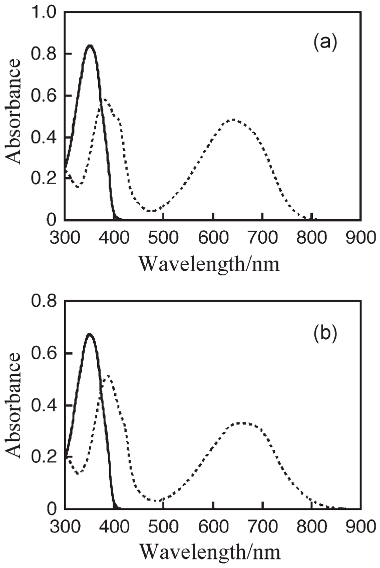


Figure 1. Absorption spectra of **3a** (—) and **3b** (- - - -) (a) and **4a** (—) and **4b** (- - - -) (b) in toluene at room temperature.

Table 1. Absorption data and photochromic property of **1a**–**4a**[a]

	$\lambda_{\max}$	ε/mol^{-1} dm^3 cm^{-1}	$\phi_{a\to b}$		$\lambda_{\max}$	ε/mol^{-1} dm^3 cm^{-1}	$\phi_{b\to a}$
1a[7]	280	35600	0.59	**1b**[7]	575	15600	0.013
2a	290	34900	0.50	**2b**	600	14800	0.026
3a	350	51600	0.47	**3b**	640	29800	0.00014
4a	350	43800	0.47	**4b**	655	22600	0.0024

[a] **1** and **2** were determined in hexane, and **3** and **4** were in toluene.

disappeared by irradiation with visible light ($\lambda > 500$ nm), and the absorption spectrum returned to that of **3a**. Diarylethene **4a** showed the similar behavior (Figure 1b). The open-ring isomers, **3a** and **4a**, have the same absorption maxima, but the absorption maxima in the closed-ring isomers showed a bathochromic shift by the introduction of the isopropyl groups. This is ascribed to the bulky substituents at 2- and 2′-positions of the thiophene rings.[6,11]

The quantum yields of cyclization ($\phi_{a\to b}$) and cycloreversion reactions ($\phi_{b\to a}$) were measured in toluene at room temperature. The results are summarized in Table 1. The photocyclization quantum yields of **3a** and **4a** were similar to those of **1a** and **2a**. The π-conjugation length and the introduction of isopropyl groups scarcely affected the quantum yields. However, the photocycloreversion quantum yields were found to depend on the π-conjugation length of the aryl groups. The cycloreversion quantum yield of **3b** was much smaller than that of **1b** by a factor of 100. The quantum yield of **4b** was also smaller than that of **2b** by a factor of 11. The quantum yield of **4b** was larger than that of **3b** by a factor of 17. The bulky isopropyl substituents increased the photocycloreversion quantum yield.

Diarylethenes **1a**–**4a** showed thermally irreversible photochromism at room temperature.[7,8] However, **2b** returned to the open-ring isomer **2a** upon heating above 100 °C.[8] The thermal cycloreversion reaction of **4b** at high temperature was examined in decalin. Figure 2a shows the decay curves of the absorbance of the closed-ring isomer **4b** at several temperatures. The decay curves followed the first-order kinetics. The rate constants (k) of the thermal cycloreversion reaction were estimated from the slope of the first-order kinetic plots. The temperature dependence of k is plotted in Figure 2b. The activation energy (E_a) and frequency factor (A) of the cycloreversion were determined from the linear relation. The values are summarized in Table 2. Extrapolation of the temperature dependence indicates that the half-life time of the closed-ring isomer **4b** is 36 days at 30 °C and 5 sec at 160 °C. The bulky substituents at 2- and 2′-positions of the thiophene rings are considered to destabilize the cyclohexadiene ring structure. It is concluded that introduction of the bulky isopropyl substituents and long π-conjugated heteroaryl groups resulted in the low decoloration quantum yield and the fast thermal reversion at high temperature above 100 °C.

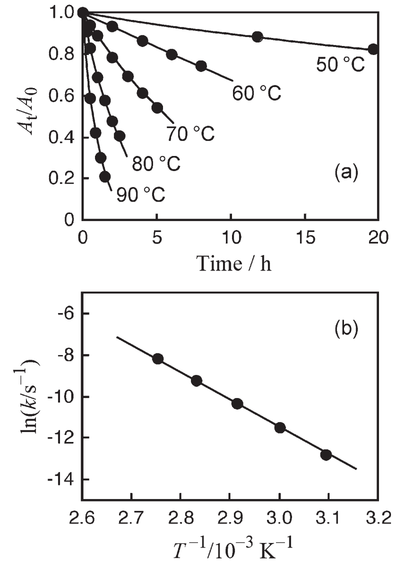


Figure 2. Decay curves (a) and temperature dependence (b) of thermal cycloreversion reactions of **4b** in decalin.

Table 2. Activation energy (E_a) and frequency factor (A) of the thermal cycloreversion reactions of **1b**–**4b**

	E_a/kJ mol^{-1}	A/s^{-1}
1b[7]	139	1.0×10^{13}
2b[8]	118	1.9×10^{13}
3b	131	2.0×10^{12}
4b	112	4.4×10^{12}

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9 **3a**: mp = 160–161 °C. ^{1}H NMR (CDCl$_3$, 200 MHz): $\delta = 1.98$ (s, 6H), 7.11 (d, 2H), 7.15 (s, 2H), 7.23 (d, 2H), 7.25–7.45 (m, 6H), 7.60 (d, 4H). MS $m/z = 684$ (M$^+$). Anal. Calcd for $C_{35}H_{22}F_6S_4$: C, 61.39%; H, 3.24%. Found: C, 61.75; H, 3.43%.
10 **4a**: mp = 205–206 °C. ^{1}H NMR (CDCl$_3$, 200 MHz): $\delta = 0.98$ (d, 12H), 2.80 (sept, 2H), 7.06 (s, 2H), 7.11 (d, 2H), 7.23 (d, 2H), 7.25–7.45 (m, 6H), 7.60 (d, 4H). MS $m/z = 740$ (M$^+$). Anal. Calcd for $C_{39}H_{30}F_6S_4$: C, 63.22; H, 4.08%. Found: C, 63.29; H, 4.12%.
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