Very High Cyclization Quantum Yields of Diarylethene Having Two *N*-Methylpyridinium Ions

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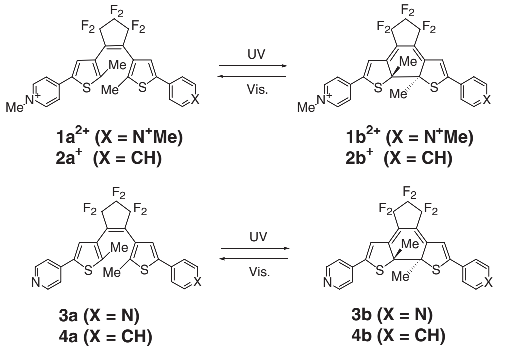
Dithienylethenes having a pyridinium cation at one and both thiophene rings were synthesized. The derivatives with two pyridinium cation showed the cyclization quantum yield as high as 0.71, which is much larger than the values of the monocation derivative and the neutral form. This can be explained by the conformation of the open-ring isomer of the diarylethenes.

Photochromic diarylethenes undergo reversible cyclization/cycloreversion photoreactions upon alternate irradiation with UV and visible light.[1] Diarylethenes are superior to other photochromic compounds in the sense of the thermal stability and fatigue resistance.[2] The cyclization quantum yields of diarylethenes are dependent on the conformations of the open-ring isomers. Several attempts, such as introducing bulky substituents,[3] encapsulation in cyclodextrin host,[4] or incorporating into the main chain of the polymer,[5] have been carried out to increase the photoactive anti-parallel conformation.[6] Ionic moieties are anticipated to affect the conformation of the molecules and to control the quantum yield when introduced into the diarylethene. Although some diarylethenes having ionic substituents are synthesized,[7] the photochromic reactivity has not yet been investigated. Herein we will describe the photochromism of diarylethenes which possess an *N*-methylpyridinium group in solution in terms of the cyclization quantum yields (Scheme 1).

We prepared diarylethenes **1**–**4**. The syntheses of $\mathbf{1a}^{2+}\cdot\mathbf{2I}^-$ and $\mathbf{2a}^{+}\cdot\mathbf{I}^-$ were performed by a similar procedure for $\mathbf{1a}^{2+}\cdot\mathbf{2TfO}^-$ by Lehn et al.[7a] Methylation of the pyridine ring was performed by treating with methyl iodide in dichloromethane. $\mathbf{1a}^{2+}\cdot\mathbf{2I}^-$ was purified effectively by filtration of the water solution and solvent evaporation of the filtrate. The structures of $\mathbf{1a}^{2+}\cdot\mathbf{2I}^-$ and $\mathbf{2a}^{+}\cdot\mathbf{I}^-$ were confirmed by NMR and elemental analysis.[8,9]

Figure 1 shows the photochromic reaction of $\mathbf{1a}^{2+}\cdot\mathbf{2I}^-$ in methanol. Upon irradiation with 365 nm light absorption at 655 nm increased and reached a photostationary state. The solution turned blue, which is the color of the closed-ring isomer $\mathbf{1b}^{2+}\cdot\mathbf{2I}^-$.[7] Upon irradiation with 578 nm light the closed-ring isomer $\mathbf{1b}^{2+}\cdot\mathbf{2I}^-$ was completely returned back to the open-ring isomer $\mathbf{1a}^{2+}\cdot\mathbf{2I}^-$.



Scheme 1. Photochromism of diarylethene $\mathbf{1}^{2+}$–**4**.

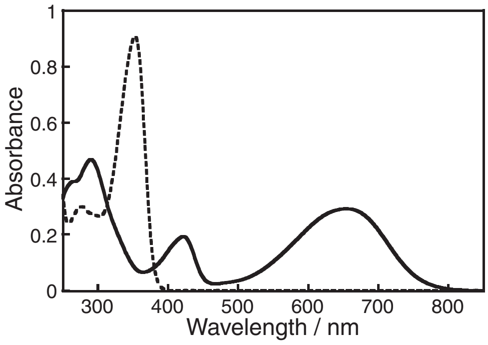


Figure 1. Absorption spectra of $\mathbf{1}^{2+}\cdot\mathbf{2I}^-$ in MeOH (1.8×10^{-5} M). The open-ring isomer (dotted line) and in the photostationary state (solid line).

The conversions of $\mathbf{1a}^{2+}\cdot\mathbf{2I}^-$ and $\mathbf{2a}^{+}\cdot\mathbf{I}^-$ from the open- to the closed-ring isomers in methanol in the photostationary state under irradiation with 365-nm light were close to 100%. The 100% conversions were confirmed by the ε values of the closed-ring isomers determined from the absorption spectra and the NMR integral value.

The quantum yields of these diarylethenes are measured using 1,2-bis(2-methylbenzothiophen-3-yl)perfluorocyclopentene as a reference.[10] The results are summarized in Table 1. The cyclization quantum yield of cation $\mathbf{1}^{2+}\cdot\mathbf{2I}^-$ was 0.71, which is much larger than that of the corresponding pyridyl derivatives **3**. This can be attributed to the preference of the photoreactive antiparallel conformation due to Coulombic repulsion of the plus-charged cation moieties. The quantum yield of 0.71 is the highest class of values so far reported for diarylethene derivatives in solution. Recrystallization of $\mathbf{1a}^{2+}\cdot\mathbf{2I}^-$ from methanol gave plate shaped yellow crystal. X-ray crystallographic analysis revealed that the diarylethene adopted antiparallel conformation in the crystal (Figure 2).[11] The crystal contained two methanol molecules per one diarylethene.

On the other hand the cyclization quantum yield of cation $\mathbf{2}^{+}\cdot\mathbf{I}^-$ was much smaller than that of **4**. The low cyclization

Table 1. Quantum yields of **1**–**4** in methanol

	$\Phi_{\text{(open}\rightarrow\text{closed)}}$	$\Phi_{\text{(closed}\rightarrow\text{open)}}$
$\mathbf{1}^{2+}\cdot\mathbf{2I}^-$	0.71 (280 nm)	—[a]
$\mathbf{2}^{+}\cdot\mathbf{I}^-$	0.20 (280 nm)	0.0068 (645 nm)
3	0.57 (280 nm)	0.014 (592 nm)
4	0.51 (280 nm)	0.015 (592 nm)

[a] Not measured due to the partial decomposition. Irradiated wavelengths were described in the parentheses.

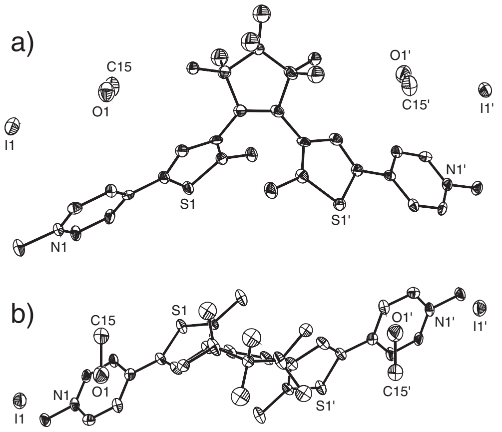


Figure 2. ORTEP drawing of $\mathbf{1}^{2+}\cdot\mathbf{2I}^-\cdot\mathbf{2}$(MeOH). (a) Top view (b) Side view. Hydrogen atoms are omitted for clarity. Hydrogen atoms on the water molecules are not assigned.

quantum yield suggests the preferred parallel conformation of the monocation $\mathbf{2a}^+\cdot\mathbf{I}^-$. Cation-$\pi$ interaction are reported to operate between phenyl ring and pyridinium ring.[12,13] This interaction may lead to the stabilization of the photo-inactive parallel conformation. The cycloreversion quantum yields of $\mathbf{2b}^+\cdot\mathbf{I}^-$ were twice smaller than that of the corresponding pyridyl derivatives **4b**. This is considered to originate from the electronic stabilization of the closed-ring isomers.

In conclusion we have found that the cyclization quantum yield of the dication derivative is much larger than that of the parent neutral pyridyl derivative, though the cyclization quantum yield of the monocation derivative is small. This can be explained by the conformation of the open-ring isomer of the diarylethenes.

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8 Analytical data for $\mathbf{1a}^{2+}\cdot\mathbf{2I}^-$: ^{1}H NMR (200 MHz, MeOH-d_4) δ 2.18 (s, 6H), 4.33 (s, 6H), 8.17 (s, 2H), 8.26 (d, $J = 8$ Hz, 4H), 8.78 (d, $J = 8$ Hz, 4H); UV–vis (MeOH) $\lambda_{\max}$ (ε) 353 (50500) nm. Anal. Found: C,39.43; H,2.95; N,3.36%. Calcd for $C_{27}H_{22}F_6N_2S_2I_2\cdot H_2O$: C,39.34; H,2.93; N,3.40%. Corresponding closed-ring isomer $\mathbf{1b}^{2+}\cdot\mathbf{2I}^-$: UV–vis (MeOH) $\lambda_{\max}$ (ε) 290 (26000), 421 (10700), 655 (16200) nm.

9 Analytical data for $\mathbf{2a}^+\cdot\mathbf{I}^-$: ^{1}H NMR (200 MHz, MeOH-d_4) δ 2.04 (s, 3H), 2.16 (s, 3H), 4.32 (s, 3H), 7.31–7.60 (m, 6H), 8.15 (s, 1H), 8.25 (d, $J = 8$ Hz, 2H), 8.76 (d, $J = 8$ Hz, 2H); UV–vis (MeOH) $\lambda_{\max}$ (ε) 349 (25300) nm. Anal. Found: C,47.84; H,3.25; N,2.06%. Calcd for $C_{27}H_{20}F_6NS_2I\cdot H_2O$: C,47.58; H,3.17; N,2.06%. Corresponding closed-ring isomer $\mathbf{2b}^+\cdot\mathbf{I}^-$: UV–vis (MeOH) $\lambda_{\max}$ (ε) 329 (14800), 407 (9900), 645 (16400) nm.

10 The cyclization and cycloreversion quantum yields of 1,2-bis(2-methylbenzothiophen-3-yl)perfluorocyclopentene were reported to be both 0.35 in Ref. 3.

11 Crystal data for $\mathbf{1a}^{2+}\cdot\mathbf{2I}^-\cdot\mathbf{2}$(MeOH): $C_{29}H_{30}F_6S_2N_2I_2O_2$, $M_r = 870.47$, Temperature = 127 K, monoclinic $C2/c$, $a = 22.612(14)$ Å, $b = 8.183(5)$ Å, $c = 18.206(11)$ Å, $\beta = 106.285(9)^\circ$, $V = 3234(3)$, $Z = 4$, R ($I > 2\sigma$) = 0.0606, wR_2 (all data) = 0.1729. Crystallographic data reported in this paper have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-219014. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk). Instruction for depositing the crystallographic data is available on the Web at http://www.ccdc.cam.ac.uk/conts/depositing.html.

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13 Although we measured NMR in methanol-d_4 for all four compounds, the spectral shift by the formation of the cation-π stacking was not discerned. This is probably due to the long distance between two rings even in the parallel conformation.

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