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Control of the Photoreactivity of Diarylethene Derivatives by Quaternarization of the Pyridylethynyl Group

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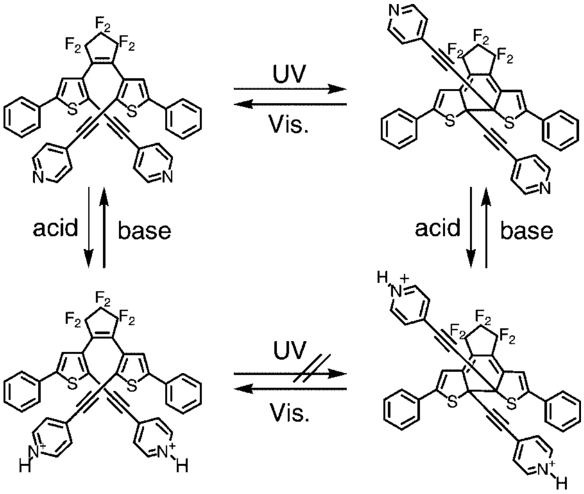
ABSTRACT



Photochromic behavior of diarylethene derivatives with (4-pyridyl)ethynyl group directly attached to the 6-π hexatriene moieties of the diarylethenes was investigated. Upon quaternarization of the pyridine moieties, the photoreactivity was strongly suppressed. On the other hand, diarylethene derivatives with nonconjugated (4-pyridyl)ethyl group exhibited the photochromic reactivity, regardless of whether pyridyl rings are quaternarized or not. In the case of the (4-pyridyl)ethynyl-substituted compounds, the photochromic reactivity was suppressed by the addition of trifluoroacetic acid and was restored by diethylamine.

For several decades, much attention has been focused on the compounds that undergo photoinduced switching of their properties, such as geometrical structure, redox potential, magnetic interaction, and electric conductivity.[1] Diarylethenes undergo reversible photoinduced cyclization/cycloreversion reactions upon irradiation with UV and visible light and have an advantage over other photochromic compounds in the sense of thermal stability and fatigue resistance.[2] The photochromic reactivity depends on several factors, such as

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conformation of the open-ring isomer, electron donor/acceptor substituents, and conjugation length of the heteroaryl groups.[3] Particularly, substituents on the reactive position greatly influence the photoreactivity. The introduction of methoxy groups to the reactive positions renders the ring-opening reaction quantum yield extraordinarily small.[4] It is worth noting that the orbital hybridization of the reactive carbon is interconverted from sp^2 to sp^3 accompanied by the photocyclization.[5]

When the nature of the substituents at the reactive positions is controlled by external stimulus, the photoreactivity is also anticipated to be controlled. The control of the photoreactivity by external stimuli such as pH or electric potential is important for the practical application of diarylethenes, because a controlled photoreactivity, namely a gated reactivity, can provide a nondestructive readout capability.[6] Pyridyl group is one of the external stimuli-responsive substituents that are quaternarized by alkylating reagent or protic acid. According to this idea, we have synthesized diarylethene derivatives having (4-pyridyl)ethynyl groups and (4-pyridyl)ethyl groups at the reactive positions and studied the control of the photochromic reactivity by the quaternarization of the nitrogen atoms on the pyridine rings.

We have synthesized dithienylethenes **1**−**4** with pyridyl or *N*-methylpyridinium substituents at the 2-positions of the thiophene rings (Figure 1). Diarylethene **1** and its *N*-methylated derivative **2** have an elongated π-electron system on the reactive position. Meanwhile, compounds **3** and **4** have no π-conjugation at the reactive position because of the single-bond linker.

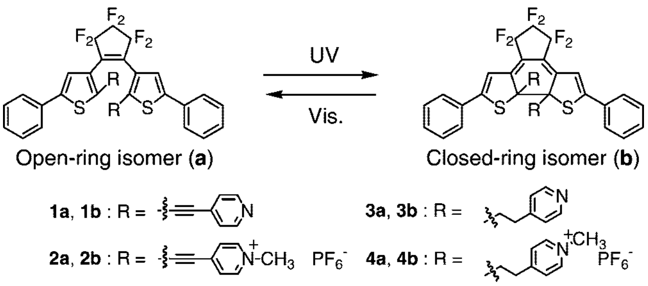

Figure 1. Diarylethenes with (4-pyridyl)ethynyl and (4-pyridyl)ethyl groups.

The synthesis was performed according to Scheme 1. 2,4-Dibromobenzene (**5**) was converted to 2,3-dibromo-5-phenylthiophene (**7**) by the literature method.[7] Introduction of (4-pyridyl)ethynyl group was carried out with Sonogashira-Hagihara coupling to give **8**, which is then converted to diarylethene **1**. Pd/C-catalyzed hydrogenation of diarylethene **1** was performed to give (4-pyridyl)ethyl derivative **3**. The preparation of quaternarized derivatives **2a** and **4a** was conducted by *N*-methylation of **1a** and **3a** with iodomethane and subsequent counterion exchange from I$^-$ to PF$_6^-$. The structures of the compounds were confirmed by NMR and mass spectroscopies and elemental analysis. X-ray crystallographic analysis of **1a**, **2a**, and **4a** were also carried out.[8]

Scheme 1. Synthesis of Diarylethenes **1a**−**4a**

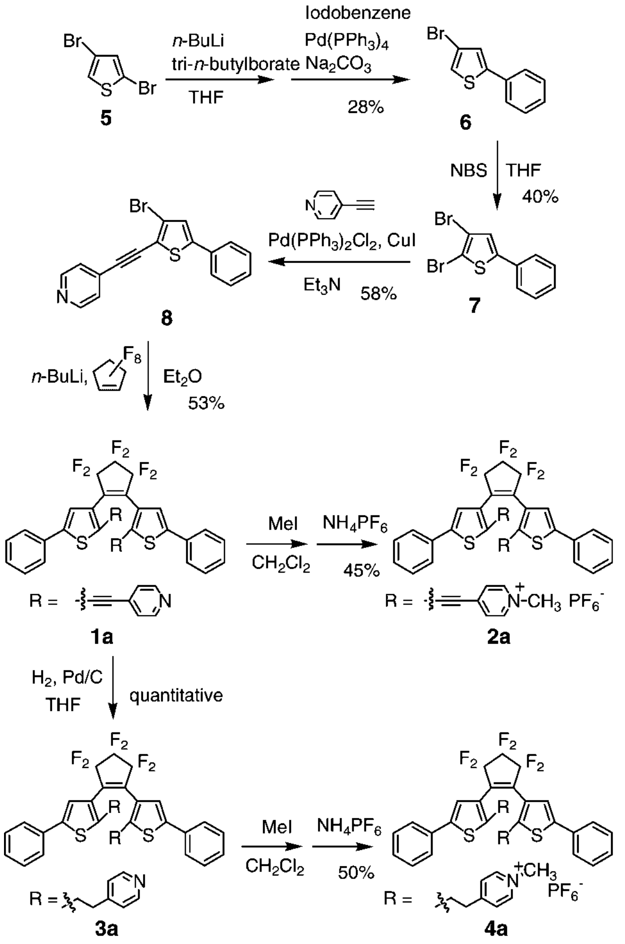

Figure 2 shows the photochromic absorption spectral change of compound **1** in dichloromethane. Upon irradiation with 313 nm light, a new band appeared in the visible region. The solution turned blue, which suggests the formation of the closed-ring isomer **1b**. The absorption maximum of **1b**

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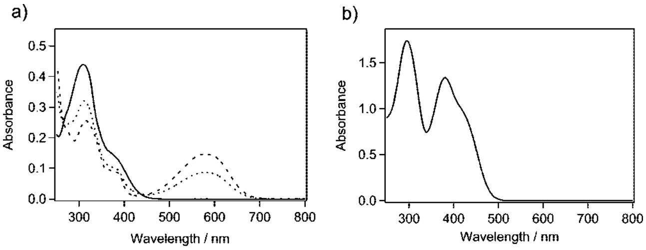

Figure 2. (a) Photochromic spectral change of **1** in CH_2Cl_2. Solid line: open-ring isomer **1a**; dashed line: closed ring isomer **1b**; dotted line: in the photostationary state under irradiation with 313 nm light. (b) Absorption spectrum of **2a** in CH_3CN. **2a** is photoinactive.

was observed at 581 nm. The cycloreversion of **1b** back to the open-ring isomer occurred by irradiation with visible light ($\lambda > 480$ nm).

However, cationic species **2a** did not show any spectral change upon irradiation in any solvent. It is worth noting that dithienylethene derivative containing *N*-methylpyridinium substituents at 5-positions of the thiophene rings, is reported to show reversible cyclization/cycloreversion.[9] The electron-withdrawing nature of the *N*-methylpyridinium cation at the reactive position is considered to affect the 6-π electron system through π-conjugation and to suppress the photoreactivity.

To confirm the electronic effect of the pyridinium cation, photochromic performance of **3** and **4**, which have single-bond linker between the pyridine ring and the hexatriene moiety, was examined. The absorption spectral changes are shown in Figure 3. Both **3** and **4** showed reversible photochromism by irradiation with UV and visible light. The spectra of both compounds are found to be very similar. The absorption maxima of the closed-ring isomers **3b** and **4b** are red-shifted more than 30 nm in comparison with **1b**. When the linker is a conjugated triple bond, the photoreactivity is suppressed by *N*-methylation of the nitrogen atoms on the pyridine rings, but when the linker is a nonconjugated single bond, the compounds show the photochromic reactivity regardless of whether the pyridine rings are quaternarized or not.

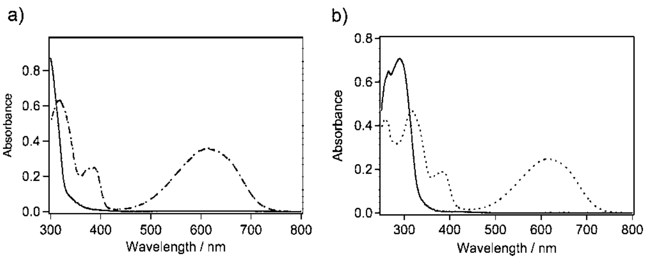

Figure 3. Photochromic spectral change of (a) **3a** in CH_2Cl_2 and (b) **4a** in CH_3CN. Solid line: open-ring isomers **3a** and **4a**; dashed line: closed ring isomer **3b**; dotted line: in the photostationary state under irradiation with 313 nm light. **4b** could not be isolated.

Table 1. Absorption Characteristics and Photoreactivity of **1** and **3** in CH_2Cl_2, **2** and **4** in CH_3CN, and **9** in Hexane

compd	ϵ_{open} /$M^{-1}cm^{-1}$	ϵ_{closed} /$M^{-1}cm^{-1}$	Φ_{OC}[a]	Φ_{CO}[b]	convn /%[c]
1	44400 (309 nm)	15300 (581 nm)	0.14	0.27	58
2	40800 (295 nm)	N/A	N/A	N/A	0
3	37200 (289 nm)	14300 (613 nm)	0.45	0.050	>99
4	35700 (289 nm)	12500 (614 nm)	0.47	0.082	>99
9[12]	35600 (280 nm)	15600 (575 nm)	0.59	0.013	97

[a] Cyclization quantum yields were measured using 313 nm light. [b] Cycloreversion quantum yields were measured using 517 nm light. [c] Conversion under irradiation with 313 nm light.

The quantum yields were measured in CH_2Cl_2 for **1** and **3** and in CH_3CN for **4**.[10] As references, furylfulgide and 1,2-bis(2-methylbenzothiophen-3-yl)perfluorocyclopentene were used for the cyclization and the cycloreversion reactions, respectively.[11] The measured quantum yields are summarized in Table 1. The cyclization quantum yields of diarylethenes **3** and **4**, which have single-bond linker, are more than 3 times larger than that of diarylethene **1**, which has triple-bond linker. The cycloreversion quantum yields of **3** and **4** are much smaller than that of **1**. As a consequence of the change in the quantum yields, high conversion from the open- to the closed-ring isomer under irradiation with UV light is achieved for the diarylethenes **3** and **4**. There is almost no difference in photochromic properties between **3** and **4**. Both the cyclization and cycloreversion quantum yields of **3** and **4** are similar with the quantum yield of the parent compound 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene (**9**).[12] The *N*-methylpyridinium cation substituent at the reactive position strongly perturbs the 6-π hexatriene conjugation through the triple-bond linker, but the electronic nature of the substituents is not transmitted through the single-bond linker.

By adding protic acid, quaternarization of the nitrogen of the pyridine ring can also be accomplished. Because the photoreactivity of diarylethene **1** was effectively changed by the quaternarization of the pyridine ring, the reactivity is also anticipated to be controlled by the addition of acid and base. Figure 4 shows the photochromic behavior of dichloromethane solution of **1a** after the addition of trifluoroacetic acid (TFA) and diethylamine. After the addition of TFA, the absorption edge of diarylethene **1a** showed a bathochromic shift, which is also observed for **2** (Figure 4b). As expected, after addition of an excess amount of TFA a new band did not appear in the visible region upon 313 nm light

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(10) In spite of our best efforts, we could not isolate closed-ring isomer **4b**. However, we estimated conversion to be >99% by using ^1H NMR. ^1H NMR change is shown in the Supporting Information.

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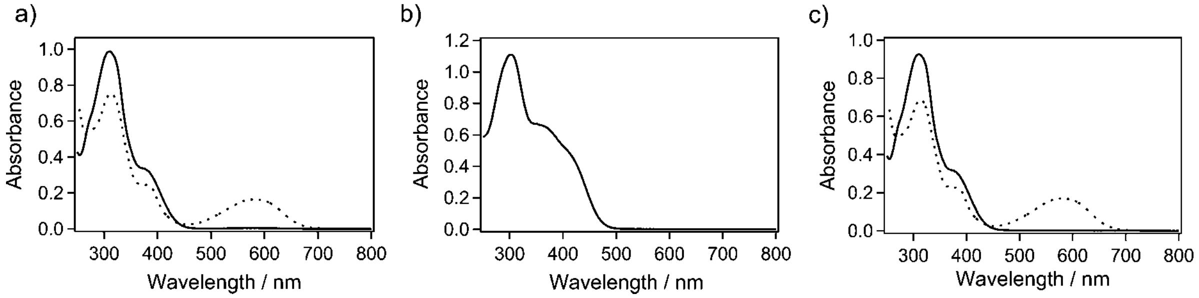
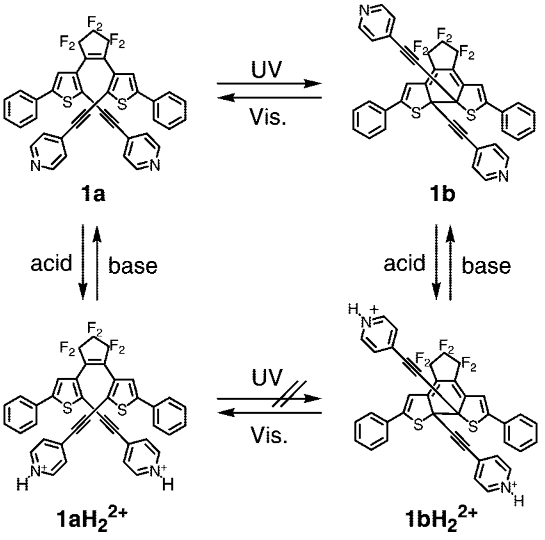


Figure 4. Control of the photochromic reactivity of **1a** by the addition of acid and base in CH_2Cl_2. Solid line: open-ring isomer; dotted line: in the photostationary state under irradiation with 313 nm light. (a) In CH_2Cl_2; (b) in CH_2Cl_2 in the presence of 10 equivalents of trifluoroacetic acid; (c) after addition of 10 equivalents of diethylamine to (b).

irradiation. The generated quaternary cation species **1aH$_2$$^{2+}$** did not undergo cyclization reaction. Then the sample was neutralized by the addition of diethylamine. The spectral shape became almost identical with original form **1a**. After the addition of base, the photochromic reactivity was restored as shown in Figure 4c. The protonated closed-ring isomer **1bH$_2$$^{2+}$** could be generated by adding acid to a solution of isolated **1b**.[13] The absorption maximum did not shift upon addition of acid, which is attributed to the fact that the cation is isolated from the chromophore by sp^3 carbon at the reactive position. Protonated **1bH$_2$$^{2+}$** was thermally stable and converted to **1aH$_2$$^{2+}$** by irradiation with visible light. The addition of acid and base enabled switching the photoactive and the photoinactive states, affording gated reactivity (Scheme 2).

Scheme 2. Schematic Representation of the Control of the Photoreactivity by the Addition of Acid and Base



In conclusion, a series of diarylethene derivatives with pyridyl rings at reactive positions of thiophene rings were synthesized. Although the photoreactivity was strongly suppressed upon quaternarization of the nitrogen atoms of (4-pyridyl)ethynyl groups, the derivative with (4-pyridyl)-ethyl groups showed photochromic reactivity regardless of whether pyridyl rings are quaternarized or not. The photochromic reactivity depends on the π-conjugation between pyridinium cation and the 6-π hexatriene conjugation.

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Supporting Information Available: Experimental methods, ^1H NMR spectra of synthesized compounds, photochromic NMR spectral change of **4**, absorption spectral change of **1b** upon addition of acid, and X-ray crystallographic analysis. CIF files of **1a**, **2a**, and **4a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) See Supporting Information. λ_{max}: **1aH$_2$$^{2+}$**, 304 nm; **1bH$_2$$^{2+}$**, 580 nm.