Invisible photochromism of diarylethene derivatives†

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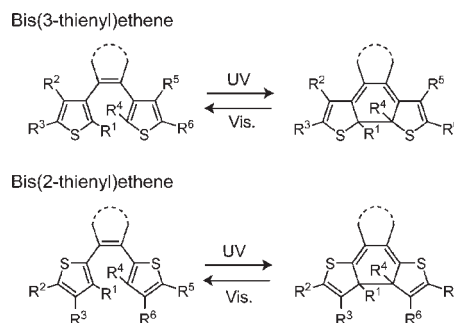
Diarylethene derivatives with oxidized thiophene rings shift their absorption band to a shorter wavelength in the UV region upon photocyclization; no color change was observed during the photochromic reaction, and the invisible photochromism is advantageous for devices used under room light.

Photochromism is defined as "a reversible transformation of a chemical species induced in one or both directions by absorption of light between two forms, A (before) and B (after), having different absorption spectra".[1]

$$A \underset{h\nu',\Delta}{\overset{h\nu}{\rightleftarrows}} B$$
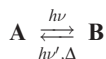
In general, photochromic molecules are initially in a colorless or pale yellow form (A) and convert to a colored form (B) upon photoirradiation. Although the color changes are the most eminent performance of photochromic molecules, the molecules can modulate or switch not only the color but also other properties, such as π-conjugation length,[2] refractive indices,[3] geometrical structures,[4] chiral properties,[5] and solubility.[6] These property changes are applied to photo-switches of conductance and magnetic interactions,[7] light-driven actuators,[8] photoresponsive liquid crystals[9,10] and others. For such applications, the color changes are not necessary conditions and perturb the performance in some cases. Therefore, the development of photochromic systems, in which both isomers are colorless, is of significance.[11] The insensitivity to visible light is also advantageous for devices used under room light. To realize such invisible photochromic systems, both the A and B isomers should have their longest absorption bands in the UV region, and A and B should be exchanged repeatedly by UV light irradiation with different wavelengths.

Diarylethenes undergo thermally irreversible and fatigue resistant photochromic reactions.[12] There exist two types of diarylethene derivatives, 3- and 2-thienylethene derivatives, as shown in Scheme 1. The color change in diarylethene derivatives is based on the change in the π-conjugation length along with the photocyclization/photocycloreversion reactions. As
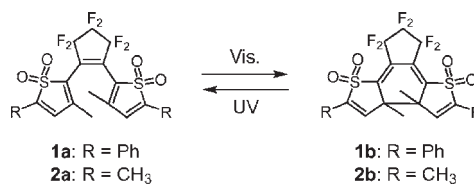
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Scheme 1 Photochromism of bis(3-thienyl)ethene and bis(2-thienyl)-ethene derivatives.

the π-conjugation length becomes longer, the absorption maximum shifts to a longer wavelength. Therefore, it is anticipated that the absorption band of 3-thienylethene derivatives shifts to a longer wavelength upon photocyclization, while the band of 2-thienylethene derivatives shifts to a shorter wavelength. Predictions based on the chemical structure changes are not always correct. All photochromic 2-thienylethene derivatives so far reported showed bathchromic shifts upon UV irradiation (see Table S1, ESI†).[13]

Here we report on unusual photochromic diarylethene derivatives, which shift the absorption band to a shorter wavelength in the UV region upon photocyclization. We have synthesized diarylethene derivatives, in which oxidized thiophene rings are attached to the ethene moiety through the 2-positions (1 and 2) (Scheme 2), and have examined the photochromic behavior in detail.

Compounds 1 and 2 were prepared by oxidation of 1,2-bis-(3-methyl-5-phenyl-2-thienyl)perfluorocyclopentene and 1,2-bis-(3,5-dimethyl-2-thienyl)perfluorocyclopentene using 3-chloroperoxybenzoic acid (m-CPBA) in 85% and 79% yields, respectively.[14] The structures were identified by ^{1}H NMR spectroscopy, MS spectra, elemental analysis, and X-ray crystallographic analysis (see ESI†).

Fig. 1 shows the absorption spectral change of 1 in 1,4-dioxane solution upon irradiation with visible (λ > 430 nm) and UV light. Before photoirradiation, the absorption

1a: R = Ph
2a: R = CH₃

1b: R = Ph
2b: R = CH₃

Scheme 2 Molecular structures and photochromism of the oxidized bis(2-thienyl)ethene derivatives (1 and 2).
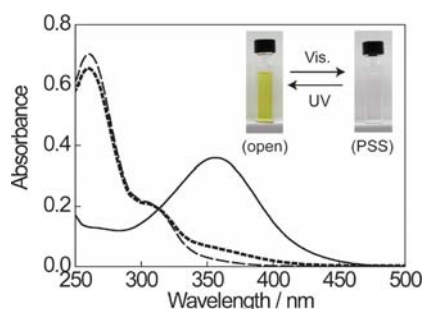
Fig. 1 Absorption spectra of the open-ring isomer (solid line), the photostationary state under irradiation with 430 nm light (dashed line), and the closed-ring isomer (broken line) of **1** in 1,4-dioxane solutions (2.4×10^{-5} M) at room temperature. The conversion from the open- to the closed-ring isomer under irradiation with 430 nm light was estimated to be 92%. Inset: photographs of the solution of **1a** and the photostationary state upon irradiation with 430 nm light.

maximum was observed at 356 nm ($\varepsilon = 1.5 \times 10^4$ M^{-1} cm^{-1}) and the solution was pale yellow as shown in the inset of Fig. 1. Upon irradiation with visible light ($\lambda > 430$ nm), the pale yellow color disappeared and a new absorption band grew up in the UV region at 260 nm. Upon irradiation with UV (313 nm) light, the colorless solution returned to yellow and the absorption band at 356 nm was restored. The photo-generated isomer was stable even at 80 °C and the spectral change could be repeated for more than 100 times.

The molecular structures of both isomers were determined using X-ray crystallographic analysis. The yellow colored isomer (*i.e.* before visible light irradiation) and the photogenerated colorless isomer were isolated by HPLC and their respective single crystals were obtained by recrystallization from methanol. Fig. 2a shows ORTEP drawings for the yellow colored isomer. There exist two conformers and both isomers
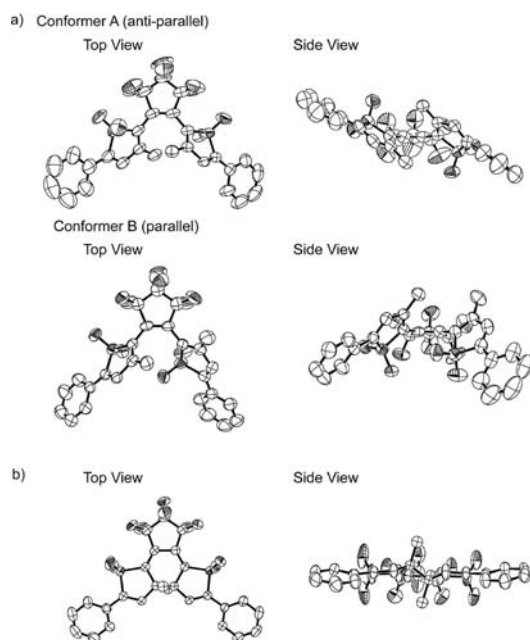

Fig. 2 ORTEP drawings of (a) **1a**, conformer A (anti-parallel) and B (parallel) and (b) **1b** showing 50% probability displacement ellipsoids. Hydrogen atoms and minor structures have been omitted for clarity.

are the open-ring isomer (**1a**). Fig. 2b shows the ORTEP drawings of the photogenerated isomer. The photogenerated isomer is the closed-ring isomer (**1b**). The result clearly indicates that **1a** undergoes a photocyclization reaction to give the closed-ring isomer (**1b**), which has an absorption band at a shorter wavelength compared to that of the open-ring isomer (**1a**).

Similar and more marked absorption change was observed for compound **2** in 1,4-dioxane, as shown in Fig. 3. Before photoirradiation, the absorption maximum was observed at 317 nm ($\varepsilon = 5 \times 10^3$ M^{-1} cm^{-1}) and the solution was colorless. Upon irradiation with 390 nm light, the absorption at 317 nm gradually decreased and a new absorption appeared at 284 nm. Upon UV light (284 nm) irradiation, the initial absorption band was restored. The spectral changes could be repeated more than 100 times. In compound **2**, no color change was observed along with the photocyclization and photocycloreversion reactions. The photochromic behaviour can be termed as "*invisible photochromism*".

The molecular structures of both isomers of **2** were also determined from X-ray crystallographic analysis. The single crystals of both isomers were obtained by recrystallization from a methanol solution. Fig. 4 shows ORTEP drawings of both isomers of **2**. The analysis confirmed that the initial isomer with the absorption band at 317 nm is the open-ring isomer and the photogenerated isomer is the closed-ring isomer.

The photocyclization and photocycloreversion quantum yields were determined by applying the standard procedure.[15] The results are summarized, along with the absorption characteristics of both open- and closed-ring isomers, in Table 1. Although the quantum yield of the cyclization reaction of **1a** is quite low, the value of **2a** is moderate. The low yield of **1a** is attributed to the extended π-conjugation in the open-ring isomer.[2]

In conclusion, we have prepared diarylethene derivatives (**1** and **2**), which exhibit thermally irreversible inverse photochromic reactions. The absorption maxima shift to shorter wavelengths with the photocyclization reactions. In compound **2**, no color change was observed during the photochromic reaction. This photochromic performance is termed "invisible
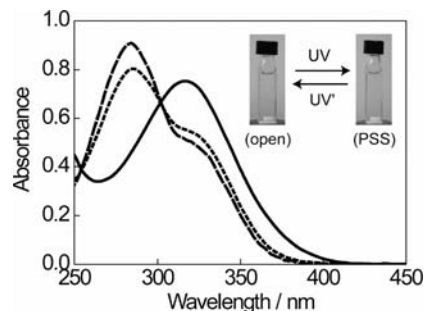

Fig. 3 Absorption spectra of the open-ring isomer (solid line), the photostationary state under irradiation with 390 nm light (dashed line), and the closed-ring isomer (broken line) of **2** in 1,4-dioxane solutions (1.5×10^{-4} M) at room temperature. The conversion from the open- to the closed-ring isomer under irradiation with 390 nm light was estimated to be 83%. Inset: photographs of the solution of **2a** and the photostationary state upon irradiation with 390 nm light.
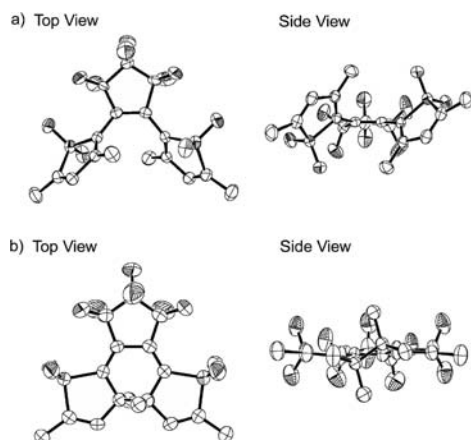
Fig. 4 ORTEP drawings of (a) **2a** and (b) **2b** showing 50% probability displacement ellipsoids. Only one half of **2a** is independent. The CF$_2$ groups in the cyclopentene ring of **2a** and the reaction center of **2b** were disordered. Hydrogen atoms and minor structures have been omitted for clarity.

Table 1 Absorption coefficients (ε) at absorption maxima and the quantum yields of photocyclization and photocycloreversion of **1** and **2** in 1,4-dioxane

	$\varepsilon/10^{-4}$ M^{-1} cm^{-1a}		Quantum yields	
	a	**b**	Cyclization	Cycloreversion
1	1.5 (356 nm)	2.9 (260 nm)	1.9×10^{-4b}	0.55^c
2	0.5 (317 nm)	0.6 (284 nm)	0.01^d	0.19^e

^{a} Absorption coefficient. ^{b} Quantum yield was measured at 356 nm. ^{c} Quantum yield was measured at 313 nm. ^{d} Quantum yield was measured at 366 nm. ^{e} Quantum yield was measured at 284 nm.

photochromism". The invisible photochromism is advantageous for opto- and electromolecular devices used under room light.

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