



The considerable photostability improvement of photochromic terarylene by sulfone group

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ABSTRACT

Photochromic terarylene derivative **4** which has a sulfone group at the upper benzothiophene ring is readily synthesized using Suzuki coupling reaction. It exhibits good photochromic properties. Interestingly, the closed form of the compound **4** shows a good photostability as well as a thermal stability compared with its reduced analog **3**, that provides a method to enhance the photostability of versatile photochromic terarylenes under UV.

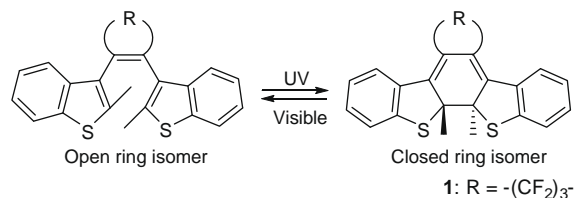
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Photochromic materials have attracted much attention as a key material for the erasable optical memory and optical switch device applications.¹ Diarylethene whose structure can be reversibly changed by light is the most promising candidate for such applications because the structural change of the diarylethene accompanies the change of various physical properties such as color, fluorescence, refractive index, and infrared absorption band that provides an efficient method to detect the ON/OFF state of the material (Scheme 1). Thus, a variety of diarylethenes have been prepared to optimize physical properties suitable for the photonic device applications.² Especially, photochromic terarylene derivatives containing a thiophene or thiazole unit caught our attention because the terarylene can be easily prepared in large quantity without much difficulty using Pd-catalyzed carbon–carbon bond forming reactions.³ Thus, these compounds may have a potential as materials for practical optoelectronic applications. However, physical properties such as fatigue and thermal properties of the terarylenes, which are critical for the practical applications, have received only limited scrutiny compared with the well-documented diarylethenes such as BTF6(**1**).

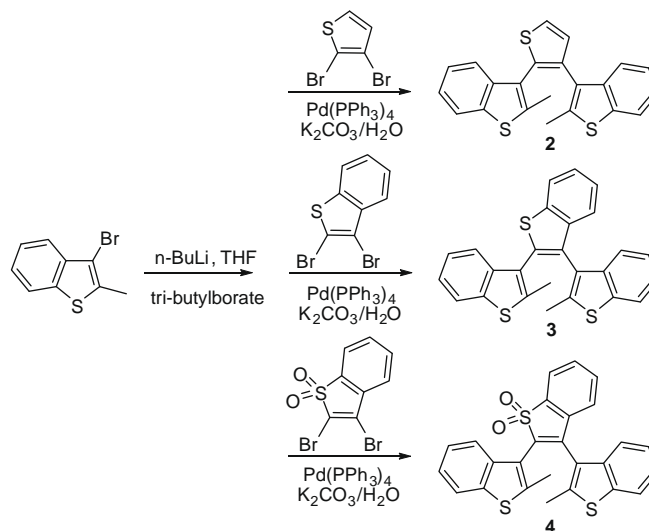
While we investigate the photochromic properties of terarylene **2–4**, we found that the fatigue and thermal properties of the terarylenes can be greatly improved by the oxidation of sulfide bond in the upper part of terarylenes such as **4**. Thus, here we report the detailed photochromic properties of terarylene **4** in comparison with its reduced analogs **2** and **3**, and their structure–property relationships.

Terarylenes **2**^{4a} **3**^{4b} and **4** were synthesized using Suzuki coupling reaction (Scheme 2) between dibutyl(2-methyl-benzo[*b*]thiophen-3-yl)borane and 2,3-dibromothiophene analogs such as 2,3-dibromothiophene, 2,3-dibromo-1-benzothiophene, and 2,3-dibromo-

1-benzothiophene-1,1-dioxide, respectively, in mild yield (45–50%).⁴ These structures were identified based on spectroscopic anal-



Scheme 1. Photochromic reaction of diarylethene.



Scheme 2. Preparation of terarylenes **2–4**.

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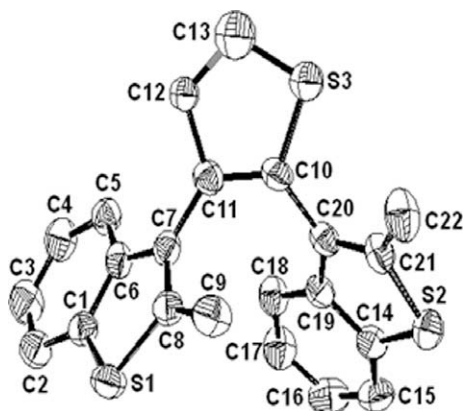


Figure 1. ORTEP drawings of terarylene **2** with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

Table 1
Photophysical properties of diarylethene

Compound	Ratio of p:ap ^a	Cyclization conversion ^{b,c}	λ_{\max} (nm)/ ϵ ($10^3 \text{ M}^{-1} \text{ cm}^{-1}$)	
			Open-ring isomer	Closed-ring isomer ^d
1 ^e	35:65	0.43	258/16.0	523/10.0
2	35:65	0.57	268/20.0	538/13.3
3	35:65	0.50	265/24.1	520/12.4
4	40:60	0.50	262/19.3	477/10.3

^a Observed in ¹H NMR spectra in CDCl₃.

^b For all compounds the conversion of the ring opening was 1.

^c Observed in HPLC (silica gel column, HIQ sil C-18, 1 mL/min, eluent; hexane for **2** and **3**, 15% ethyl acetate in hexane for **4**, monitored at their isosbestic point; 276 nm for **2**, 280 nm for **3**, 265 nm for **4**).

^d Absorption at visible region.

^e Taken from Ref. 6.

yses including NMR and mass spectroscopy. A single crystal of the open-ring isomer of terarylene **2** was obtained from the solution in ethyl acetate and hexane. Its structure was solved using X-ray single crystal diffractometer and was found to be in a photoinactive parallel conformation (Fig. 1).⁵ The ratios between parallel (p) and anti-

parallel (ap) conformation of open-ring isomers of **2–4** calculated from the ¹H NMR analyses (Table 1) were similar to that of **1**.⁶

The terarylenes **2–4** were cyclized upon UV irradiation accompanying absorption spectra changes. Figure 2 shows the absorption spectra of open-ring isomers (solid line) and at the photostationary states (dashed line) of (A) **1**, (B) **2**, (C) **3**, and (D) **4** in ethyl acetate ($1.0 \times 10^{-5} \text{ M}$) at room temperature.⁷ The absorption maxima (λ_{\max}) of the closed-ring isomers of **1–3** appeared in the region of 520–540 nm whereas λ_{\max} of terarylene **4** was greatly blue shifted to 477 nm. The large λ_{\max} shift of closed **4** may be due to the sulfonyl group in the structure as has been observed in the disulfone form of **1**.⁸ The cyclization conversions of terarylenes **2–4** which represent the fraction of closed form at the equilibrium state under UV were slightly increased compared with the diarylethene **1** (Table 1).

The fatigue property of terarylenes **2–4**, which is the main focus of this study, was investigated. Since terarylenes retain the equilibrium state between open and closed form under UV light, the photostability of these closed forms under UV is directly related to the fatigue resistance of photochromic terarylenes. Thus, we measured the absorption change at the λ_{\max} of the ring-closed form of terarylenes under UV light and plotted the absorption against the irradiation time as shown in Figure 3A.⁷ For comparison, the diarylethene **1** which exhibited a good fatigue resistance was also tested. The 1,2-dibenzothiophenyl-thiophene, **2**, showed a slightly poor fatigue property compared with **1**. The photostability of the closed-ring form of **3** under UV was far worse than **2**. However, the poor fatigue property of closed **3** was significantly improved by oxidizing the sulfide bond of middle benzothiophene subunit to sulfone such as **4**. We believe that the improvement in photostability of closed **4** is related with the electron withdrawing effect of the sulfone group, since it is well known that the middle cyclopentene ring with electron withdrawing groups such as perfluorocyclopentene in **1** leads to increase the fatigue resistance of diarylethenes compared with the normal cyclopentene analog.⁹

The thermal stability of the closed-ring isomer of photochromic materials **1–4** was also investigated. The solutions of **1–4** in xylene ($2.0 \times 10^{-5} \text{ M}$) at their photostationary state were kept at 80 °C in the dark. The absorbance changes of these solutions were monitored for 40 h (Fig. 3B). As shown in Figure 3B, the absorbance of closed **1** was consistent without a big change for 40 h as expected.⁹

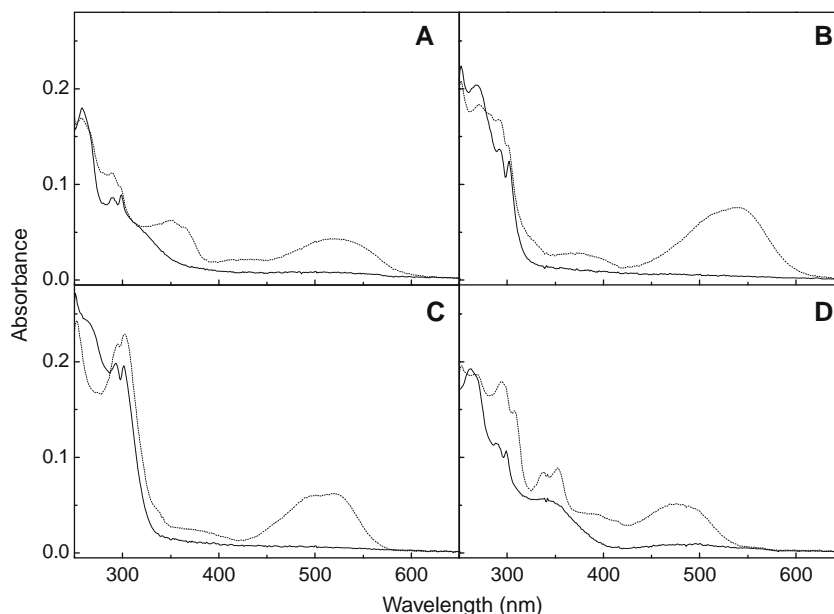


Figure 2. Absorption spectra of (A) **1**, (B) **2**, (C) **3**, and (D) **4** in ethyl acetate ($1.0 \times 10^{-5} \text{ M}$) at room temperature; open-ring isomer (solid line), at the photostationary state (dashed line).

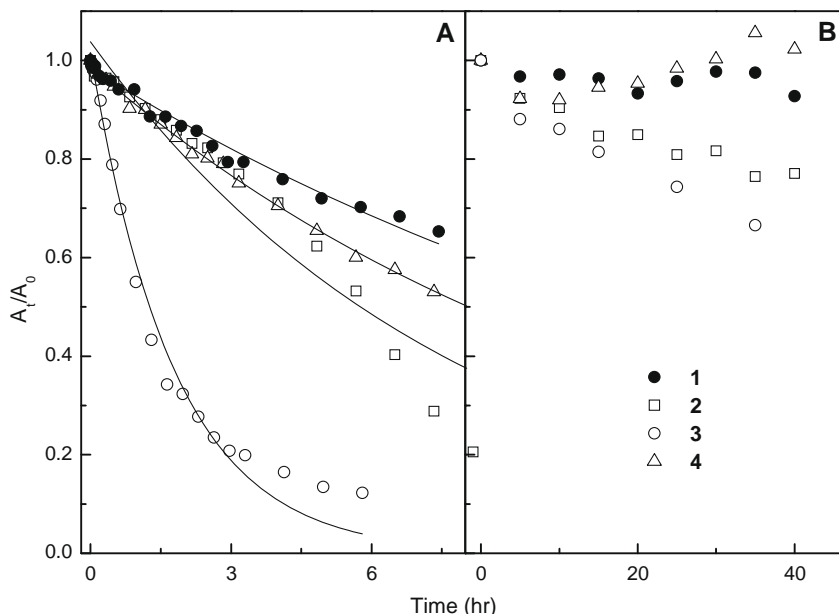


Figure 3. The absorbance changes of **1** (closed circle), **2** (open square), **3** (open circle), and **4** (open triangle) at absorption maximum of closed-ring isomer (A) as a function of UV illumination time in ethyl acetate (1.0×10^{-5} M) at room temperature and (B) kept in xylene at 80°C in the dark. The data are fitted with exponential decay (line) and the fitting data (photo-reaction time) represent the time to reach 37% of its initial absorbance following UV illumination.

However, closed **2** and closed **3** were slowly converted to their open-ring isomers with time. Interestingly, closed **4** was found to be stable similar to closed **1**. Thus, the electron withdrawing sulfone group in the middle benzothiophene subunit must have stabilized the closed-ring form of terarylene **4**. To explain the thermal stability property of closed **1–4**, we calculated the heat of formation of open- and closed-ring isomers of photochromic materials **1–4** by using an AM1 program of MOPAC pro Ver. 9.0 because the relative rate of the thermal ring opening reaction of closed-ring isomers is expected to depend on ground-state energy difference between the open- and closed-ring isomers.¹⁰ From the calculation, it was found that the energy difference between open- and closed-ring isomers of the oxidized terarylene **4** (11.55 kcal/mol) is similar to that of diarylethene **1** (11.64 kcal/mol). However, the energy difference of terarylenes **2** (27.53 kcal/mol) and **3** (18.12 kcal/mol) is much larger than that of **4** and **1**. These results imply that closed **2** and **3** are less stable compared with the closed **4** whose stability may be similar to closed **1**. These calculation data are well correlated with the experimental results.

In summary, we have synthesized terarylenes **2–4** using Suzuki coupling reaction and found that the oxidized terarylene **4** is a good fatigue resistant and thermally stable photochromic material. This study suggests a convenient method to improve the fatigue property of terarylenes.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2009.07.028.

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