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Thermal bleaching reactions of photochromic diarylethenes with thiophene-*S*,*S*-dioxide for a light-starting irreversible thermosensor†

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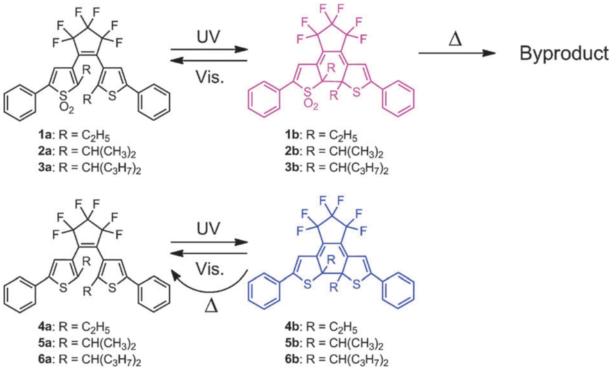
Thiophene-*S*,*S*-dioxidized diarylethenes introducing bulky substituents at the reactive positions were newly synthesized. The diarylethenes showed reversible photochromism, whereas the photocycloreversion reaction was suppressed by thiophene-oxidation. The diarylethene closed-ring isomers having secondary alkyl groups at the reactive positions were found to undergo thermal bleaching reactions which produce at least three types of byproducts. Such materials could find application as light-starting irreversible thermosensors.

Photochromic compounds can exhibit interconversion between two isomers upon irradiation at an appropriate wavelength of light.[1,2] The photoisomerizations of these compounds produce changes in chemical and physical properties, such as molecular structures, absorption spectra, refractive indices, dielectric constants, and oxidation–reduction potentials. Photochromic compounds are categorized into two types, T-type and P-type.[1,3] T-type photochromic compounds provide thermally unstable isomers by photoirradiation. Azobenzene, spiropyran, and spirooxazine are well known as representative T-type photochromic compounds. In contrast, P-type photochromic compounds are thermally stable for both isomers at room temperature. Furylfulgide and diarylethene are well known as representative P-type photochromic compounds. Among these compounds, diarylethenes have attracted much attention due to their excellent fatigue resistance.[4–8]

We have recently designed and synthesized diarylethenes with novel functions. Photochromic diarylethenes can change their properties such as thermal and photochemical reactivities by introducing substituents at the aryl groups and the reactive positions. The thermal cycloreversion reactivity can be promoted by introduction of bulky substituents at the reactive positions.[9–11] However, when a trimethylsilyl or methoxymethyl group was introduced at the reactive positions, thermal bleaching reactions which produce colorless byproducts were observed.[12,13] If diarylethenes have a photostability of the closed-ring isomers in addition to the formation of colorless byproducts, a light-starting irreversible thermosensor can be created by combining the following conditions: (1) fast coloration upon irradiation with UV light, (2) a photostability of the colored state, (3) thermal bleaching at an appropriate temperature, and (4) a photostability of the thermal bleaching state. The light-starting irreversible thermosensor can be used as a sensor which can detect a rise in heat at low temperature below room temperature. Such a thermosensor has an advantage that it can be stored at room temperature before use.



It has been recently reported that thiophene-*S*,*S*-dioxidized diarylethenes can suppress the photocycloreversion reaction.[14–16] This finding can encourage us to make the light-starting irreversible thermosensor. Here, we have designed and synthesized thiophene-*S*,*S*-dioxidized diarylethenes (**1a–3a**) which can suppress the photocycloreversion reaction and produce colorless byproducts upon heating.

Thiophene-*S*,*S*-dioxidized diarylethenes **1a–3a** were prepared by oxidation of the precursor compounds, 1,2-bis(2-alkyl-5-phenyl-3-thienyl)perfluorocyclopentenes (**4a–6a**) using 3-chloroperoxybenzoic acid (*m*-CPBA) (see Table S1, ESI†). The oxidation reaction proceeded at only one side of the thiophene rings.

Diarylethenes **1a–3a** showed photochromism upon alternating irradiation with UV and visible light. Fig. 1 shows absorption

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† Electronic supplementary information (ESI) available: Synthesis of **1a–3a**, HPLC chart after the thermal reaction at 100 °C, ^{1}H NMR spectra, mass spectra, and X-ray crystallographic data of **2c–2e**, and the reaction mechanism of the formation of the byproducts. CCDC 917414–917416. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3cc00053b

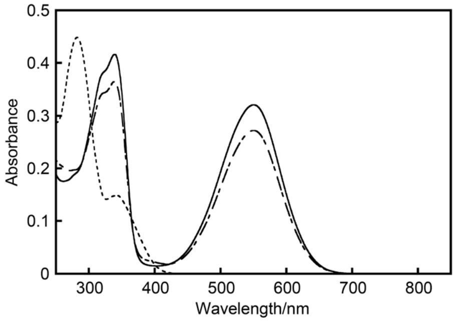

Fig. 1 Absorption spectra of **2a** (1.9×10^{-5} M) (---), **2b** (—), and the photostationary solution (-·-) upon irradiation with 313 nm light in hexane.

Table 1 Optical properties of diarylethenes having thiophene or thiophene-*S*,*S*-dioxide substituent in hexane

Diarylethene	R	Open-ring isomer λ_{max}/nm	Open-ring isomer ε/M^{-1} cm^{-1}	Closed-ring isomer λ_{max}/nm	Closed-ring isomer ε/M^{-1} cm^{-1}	Quantum yields $\Phi_{o\rightarrow c}$	Quantum yields $\Phi_{c\rightarrow o}$
1a	CH_2CH_3	284	29 200	556	20 600	0.49	2.1×10^{-4}
2a	$CH(CH_3)_2$	282	24 100	550	17 300	0.36	2.8×10^{-5}
3a	$CH(C_3H_7)_2$	286	29 500	580	—[a]	—[a]	—[a]
4a[b]	CH_2CH_3	286	40 000	600	17 000	0.52	0.0081
5a[c]	$CH(CH_3)_2$	290	34 900	600	14 800	0.50	0.026
6a	$CH(C_3H_7)_2$	296	37 600	602	12 600	0.48	0.074

[a] Not determined due to less thermal stability for the closed-ring isomer. [b] Ref. 9. [c] Ref. 17.

spectral changes of **2a** upon irradiation with UV light. Upon irradiation with 313 nm light, the new absorption band of the closed-ring isomer **2b** appeared at 550 nm. The violet-colored solution gradually returned to colorless at a considerably slow rate upon irradiation with visible light ($\lambda > 500$ nm).

Photocyclization and photocycloreversion quantum yields were examined in hexane. Table 1 shows the optical properties of the diarylethenes before and after the oxidation reaction. The molar absorption coefficient (ε) and the photocyclization quantum yield ($\Phi_{o\rightarrow c}$) of each compound are similar before and after the oxidation reaction. However, the absorption maximum wavelength (λ_{max}) of the closed-ring isomers **1b**–**3b** in the visible range is shifted to 20–50 nm shorter than those of the closed-ring isomers **4b**–**6b**. The photocycloreversion quantum yields of **1b**–**2b** are lower than those of the closed-ring isomers **4b**–**6b** by a factor of 10^2–10^3. It is concluded that shorter wavelength shift of λ_{max} and the suppression of the photocycloreversion reaction are due to the influence of the thiophene-*S*,*S*-dioxide ring. The energy level of the closed-ring isomer at the ground state is considered to become lower with the thiophene-*S*,*S*-oxidation.

Thermal stability of the closed-ring isomers **1b**–**3b** was examined in toluene. Fig. 2 shows decay curves of absorbance at λ_{max} in the closed-ring isomers at various temperatures. The closed-ring isomer having ethyl substituents (**1b**) is thermally stable at 120 °C; whereas **4b** returns to **4a** in 68% yield for 10 h at 120 °C.[9] In contrast, the thermal bleaching reactivities of the closed-ring isomers having $CH(CH_3)_2$ and $CH(CH_2CH_2CH_3)_2$ substituents (**2b** and **3b**) are quite different from **1b**. The reaction rates were accelerated by an increase of temperature. The thermal bleaching reaction of **3b** proceeded even at 20 °C, and the half-life time was estimated to be 4.4 h at that temperature.

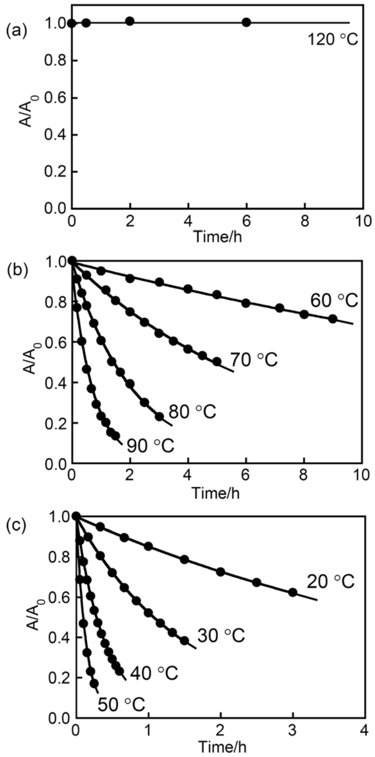

Fig. 2 Decay curves of **1b** (a), **2b** (b), and **3b** (c) in toluene.

The reaction obeyed the first-order kinetics; thus, the rate constant (k) was determined from the slope of the linear relationship of the first-order plots. Fig. 3 shows the k value of the bleaching reaction depending on the temperature. Activation energy (E_a) and frequency factor (A) can be estimated from Arrhenius equation using the plots in Fig. 3. The E_a and A values for **2b** were estimated to be 121 kJ mol^{-1} and 9.7×10^{13} s^{-1}, respectively. Those of **3b** were 101 kJ mol^{-1} and 5.3×10^{13} s^{-1}. The k value and half-life time ($t_{1/2}$) of **2b** at 100 °C were calculated to be 1.2×10^{-3} s^{-1} and 10 min, respectively. Those of **3b** were 3.6×10^{-1} s^{-1} and 1.9 s, respectively. It is revealed that the more bulky substituents are introduced, the more the thermal bleaching reaction is promoted. The half-life time of diarylethenes **5b** and **6b** before oxidation was estimated to be 20 min and 72 s at 100 °C, respectively. Thus, the thermal bleaching reaction was accelerated by oxidation of the thiophene ring. The E_a values did not change before and after oxidation. However, the A values of **2b** and **3b** are much larger than

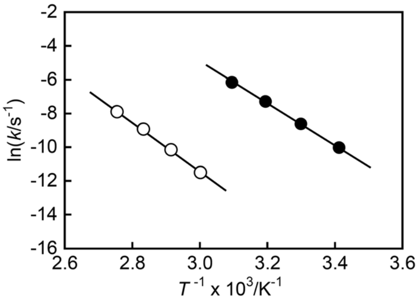

Fig. 3 Temperature dependence of the rate constant for the thermal bleaching reaction of **2b** (○) and **3b** (●) in toluene.

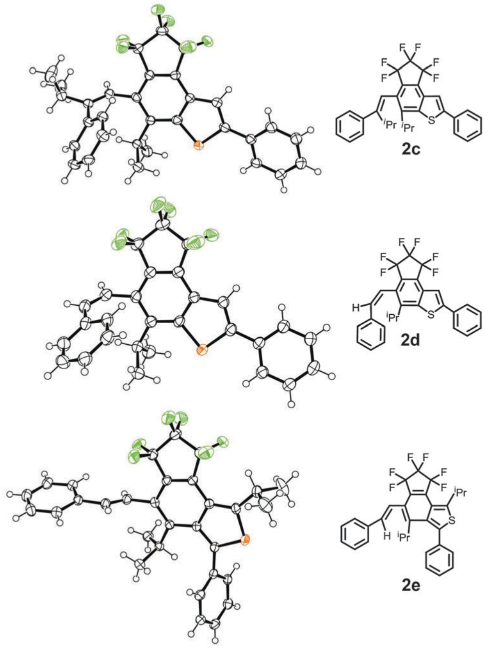

Fig. 4 ORTEP drawings of byproducts **2c–2e** showing 50% probability displacement ellipsoids.

those of **5b** and **6b**. The large *A* value contributes to a bond cleavage in the bleaching reaction.

In order to confirm the structure of thermal bleaching products of thiophene-*S*,*S*-dioxidized diarylethenes, thermal reaction products of **2a** and **2b** were analyzed by high performance liquid chromatography (HPLC). The open-ring isomer **2a** was confirmed to have thermal stability even at 100 °C. Fig. S1 (ESI†) exhibits chromatographs (hexane : ethyl acetate = 95 : 5) after thermal reaction of **2b** for 15 min at 100 °C. Judging from the HPLC chart, the closed-ring isomer does not return to the open-ring isomer in the thermal reaction, but other products were formed. At least five byproducts can be seen from the HPLC profile. Among them, we could isolate three byproducts. Byproducts **2c**, **2d**, and **2e** were eluted at 13, 15, and 16 min, respectively, and isolated by HPLC (hexane : ethyl acetate = 99 : 1). Their products were purified and recrystallized from hexane. The structures of **2c–2e** were identified by ^{1}H NMR, mass spectroscopy, and X-ray crystallographic analysis. The presence of isopropyl groups was confirmed by ^{1}H NMR spectroscopy (see Fig. S2, ESI†). Byproducts **2c** and **2e** have two different types of isopropyl groups. In contrast, byproduct **2d** has only one type of isopropyl group; thus, one of the two isopropyl groups was eliminated by the formation of the byproduct. The molecular weights of the byproducts were determined by mass spectroscopy (see Fig. S3, ESI†). The molecular mass of **2c** and **2e** was 544 g mol^{-1}, which is 64 g mol^{-1} smaller than that of **2b**; thus, it indicates that the sulfonyl group is eliminated from **2b**. The molecular mass of **2d** was 502 g mol^{-1}, which is 106 g mol^{-1} smaller than that of **2b**. This indicates that sulfonyl and isopropyl groups are eliminated from **2b**.

The complete molecular structures of **2c–2e** were determined by X-ray crystallographic analysis (see Table S2, ESI†). Fig. 4 shows ORTEP drawings of **2c–2e**. Byproducts **2c–2e** confirmed that the sulfonyl group is eliminated from the diarylethenes. **2c** and **2d** were produced by rearrangement and elimination of the isopropyl group, respectively. **2e** was produced by inversion of the thienyl group. Thus, **2c–2e** were confirmed to be produced by cleavage of the C–S bond. Bulky secondary alkyl substituents have a critical role in generation of the thermal reaction.

Thiophene-*S*,*S*-dioxidized diarylethenes introducing primary alkyl substituents at the reactive positions do not exhibit any thermal reaction; thus, **1b** is thermally more stable than **4b**.[9] This indicates that the thermal cycloreversion reaction is suppressed by oxidation of thiophene. In contrast, thiophene-*S*,*S*-dioxidized diarylethenes introducing secondary alkyl groups at the reactive positions show no thermal cycloreversion reaction but show the formation of the colorless byproducts by the thermal process. The thermal cycloreversion reaction and the thermal formation of the byproducts are considered to take place through different reaction paths. The reaction mechanism proposed is depicted in Fig. S4 (ESI†). First, a sulfonyl radical is formed by homolysis of a C–S bond, and SO_2 is eliminated. Second, intermediates are produced by radical migration, and three byproducts are produced.

In conclusion, we succeeded in designing diarylethenes with suppression of photocycloreversion reactivity and thermal formation of colorless byproducts by introduction of thiophene-*S*,*S*-dioxide and secondary alkyl substituents at the reactive positions. The structures of thermal bleaching byproducts were confirmed by X-ray crystallographic analysis. **3b** showed the half-life time of 1 h at 30 °C. These compounds have the potential for applications such as the light-starting irreversible thermosensor.

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