Thiophene-S,S-dioxidized diarylethenes for light-starting irreversible thermosensors that can detect a rise in heat at low temperature

メタデータ	言語: English 出版者: Royal Society of Chemistry 公開日: 2018-08-29 キーワード (Ja): キーワード (En): 作成者: 北川, 大地, 田中, 浩貴, 小畠, 誠也 メールアドレス: 所属: Osaka City University, Osaka City University, Osaka City University
URL	https://ocu-omu.repo.nii.ac.jp/records/2019999

Thiophene-*S,S*-dioxidized diarylethenes for light-starting irreversible thermosensors that can detect a rise in heat at low temperature

Daichi Kitagawa, Koki Tanaka, Seiya Kobatake

Citation	Journal of Materials Chemistry C, 5(25); 6210-6215
Issue Date	2017-05-18
Type	Journal Article
Textversion	author
Supplementary files	Supplementary information is available at https://doi.org/10.1039/C7TC01261F.
Rights	This is the peer reviewed version of the following article: KITAGAWA D., TANAKA K., & KOBATAKE S. (2017). Thiophene-S, S -dioxidized diarylethenes for light-starting irreversible thermosensors that can detect a rise in heat at low temperature. Journal of Materials Chemistry C. 5, 6210-6215., which has been published in final form at https://doi.org/10.1039/C7TC01261F . This is the accept manuscript version. Please cite only the published version.
DOI	10.1039/C7TC01261F

KITAGAWA D., TANAKA K., & KOBATAKE S. (2017). Thiophene-S, S -dioxidized diarylethenes for light-starting irreversible thermosensors that can detect a rise in heat at low temperature. *Journal of Materials Chemistry C.* 5, 6210-6215.

Journal of Materials Chemistry C

ARTICLE

Thiophene-*S*,*S*-dioxidized diarylethenes for light-starting irreversible thermosensors that can detect a rise in heat at low temperature

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Daichi Kitagawa, Koki Tanaka and Seiya Kobatake*

Diarylethenes having trimethylsilyl and triethylsilyl groups at the reactive positions and their *S*,*S*-dioxidized diarylethenes were synthesized and their optical and thermal properties were investigated. Upon irradiation with ultraviolet light, the diarylethenes and thiophene-*S*,*S*-dioxidized diarylethenes underwent photochromic reactions from the colourless open-ring isomer to the coloured closed-ring isomer. The photogenerated closed-ring isomers were found to undergo thermal bleaching reactions to produce colourless byproducts. Especially, the thiophene-*S*,*S*-dioxidized diarylethene having triethylsilyl group at the reactive positions underwent the thermal bleaching reaction even at −40 **°**C. Such materials could be used as light-starting irreversible thermosensors that can detect a rise in heat at low temperature.

Introduction

Materials that work as a sensor in response to a change in conditions such as heat,[1–3] viscosity,[4–6] pH[7–9] and other external stimuli have attracted much attention in practical applications. Especially, sensors that can be detected as a change in colour have an advantage that it can be easily detected with naked eyes. Among various sensors, a sensor that can detect a rise in heat at low temperature, i.e., below room temperature is required as time-temperature indicators to indicate exposure to excessive temperatures in food, pharmaceutical and medical products.[10] However, such a thermosensor that works below room temperature has a drawback that it has to be stored at low temperature before use, which limits the possibilities for many applications. In order to overcome this point, a thermosensor that starts with an external stimulus as a trigger is indispensable.

Diarylethene is one of the photochromic compounds that change not only in colours but also in geometrical structures and physicochemical properties such as conductivity, dielectric constant, refractive index and fluorescence upon photoirradiation.[11] In addition, diarylethene derivatives undergo photoreversible isomerizations between the colourless open-ring isomer and the coloured closed-ring isomer upon alternating irradiation with ultraviolet (UV) and visible light even in solid states. Therefore, diarylethenes are expected to be applicable in optical memories,[12] photooptical switches,[13] displays,[14] nonlinear optics[15] and photoresponsive actuators.[16] Furthermore, in recent studies, we have reported the concept of light-starting irreversible thermosensors using diarylethenes as shown in Fig. 1.[17,18] When diarylethenes can undergo irreversible thermal bleaching reactions to produce colourless byproducts, light-starting irreversible thermosensors that can detect a rise in heat at low temperatures could be created by combining the following conditions: (i) fast colouration upon irradiation with UV light, (ii) a photostability of the coloured state, (iii) thermal bleaching at an appropriate temperature and (iv) a photostability of the thermal bleaching state. From this point of view, thiophene-*S*,*S*-dioxidized diarylethenes having secondary alkyl groups at the reactive positions were synthesized and their thermal bleaching reactions were investigated.[17,18] Thiophene-*S*,*S*-dioxidized diarylethenes having secondary alkyl groups at the reactive positions exhibit efficient photocyclization ($\Phi_{o\to c} > 0.2$) and very slow photocycloreversion ($\Phi_{c\to o} < 10^{-4}$). Moreover, the coloured closed-ring isomers undergo irreversible thermal bleaching reactions to produce photostable byproducts at room temperature. Thus, thiophene-*S*,*S*-dioxidized diarylethenes having secondary alkyl groups at the reactive positions meet above mentioned conditions and can be used for light-starting irreversible thermosensors. However, for practical use, the light-starting thermosensor should be usable at low temperature below 0 °C.

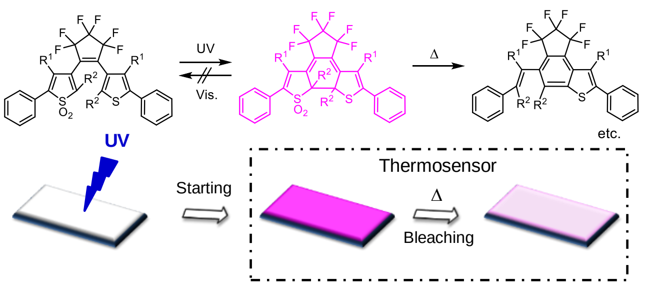
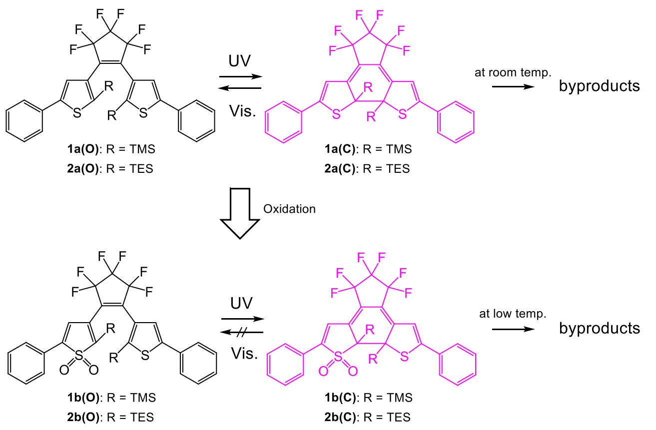


Fig. 1 Concept of light-starting irreversible thermosensors using thiophene-*S*,*S*-dioxidized diarylethenes

---

Department of Applied Chemistry, Graduate School of Engineering, Osaka City University, 3-3-138 Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan.
E-mail: kobatake@a-chem.eng.osaka-cu.ac.jp; Fax: +81 6 6605 2797;
Tel: +81 6 6605 2797;

† Electronic supplementary information (ESI) available: The molecular structure of diarylethenes and thiophene-*S*,*S*-dioxidized diarylethenes and their ε_o and ε_c values. See DOI: 10.1039/c000000x/



Scheme 1. Diarylethenes and thiophene-*S*,*S*-dioxidized diarylethenes used in this work.

To realize the light-starting irreversible thermosensor that works at low temperature, we have focused on diarylethene having trimethylsilyl (TMS) group at the reactive positions (**1a**). In our previous work, we reported that the closed-ring isomer of diarylethene **1a** exhibits a thermal irreversible bleaching reaction to produce a colourless byproduct even at 30 °C although it has no photostability.[19] If a photostability of the coloured state and a decrease of temperature undergoing thermal bleaching reaction are added to diarylethene **1a**, the light-starting irreversible thermosensor that works at low temperature can be achieved. From such a point of view, in this work, we have designed and synthesized thiophene-*S*,*S*-dioxidized diarylethenes having TMS and triethylsilyl (TES) groups at the reactive positions (**1b** and **2b**) which can suppress the photocycloreversion reaction and exhibit the thermal irreversible bleaching reaction at low temperature below 0 °C (Scheme 1). The photochromic reactivity and thermal bleaching reactivity of the closed-ring isomers are discussed in this paper.

Experimental

General

Solvents used were of spectroscopic grade and purified by distillation before use. ^{1}H NMR (300 MHz) spectra were recorded on a Bruker AV-300N spectrometer with tetramethylsilane as the internal standard. High resolution mass spectra (HRMS) were obtained on a Bruker FT-ICR/solariX mass spectrometer. The matrix-assisted laser desorption/ionization (MALDI) was used as an ionization technique. UV-Vis absorption spectra were measured using a JASCO V-560 absorption spectrophotometer. High performance liquid chromatography (HPLC) was carried out using a HITACHI L-7150 pump/L-2400 detector/D-2500 Integrator and a Kanto Chemical Mightysil Si 60 column.

Materials

Diarylethene **1a(O)** and its precursors were synthesized according to the synthetic route described in the literature.[19] Diarylethene **2a(O)** and its precursors were synthesized according to the synthetic route shown in Scheme 2.

1-(1,1-Dioxide-5-phenyl-2-trimethylsilyl-3-thienyl)-2-(2-trimethylsilyl-5-phenyl-3-thienyl)perfluorocyclopentene (1b(O))

m-Chloroperbenzoic acid (*m*CPBA) (70 wt%, 130 mg, 0.52 mmol) was added to a stirred dichloromethane solution (5.0 mL) containing **1a(O)** (130 mg, 0.21 mmol). The reaction mixture was stirred overnight in the dark at room temperature. The reaction mixture was extracted with dichloromethane. The organic phase was dried over $MgSO_4$, filtered and evaporated. The crude product was purified by column chromatography on silica gel (*n*-hexane/ethyl acetate = 85:15) and by HPLC (*n*-hexane/ethyl acetate = 95:5) to give 34 mg of **1b(O)** in 24% yield as a pale yellow crystal. ^{1}H NMR (300 MHz, $CDCl_3$, tetramethylsilane) δ = 0.25 (s, 9H, CH_3), 0.34 (s, 9H, CH_3), 6.72 (s, 1H, Aromatic H), 7.25 (s, 1H, Aromatic H), 7.32-7.54 (m, 8H, Aromatic H), 7.68-7.71 (m, 2H, Aromatic H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = −1.24, 0.98, 121.48, 126.40, 126.47, 126.54, 127.10, 128.69, 129.25, 129.49, 131.16, 131.71, 132.90, 136.07, 143.25, 145.44, 147.70, 150.74. HRMS (MALDI) m/z = 668.1127 (M^+). Calcd for $C_{31}H_{30}F_6O_2S_2Si_2^+$ = 668.1124.

3-Bromo-5-phenyl-2-triethylsilylthiophene (5)

Into a flask containing diisopropylamine (2.8 mL, 20 mmol) in dry THF (100 mL) was added dropwise a 1.6 M *n*-BuLi (1.6 M solution in *n*-hexane) (9.8 mL, 16 mmol) at −30 °C under an argon atmosphere. The solution was stirred for 1 h at this temperature. To the reaction mixture was added a dry THF solution of 2-bromo-5-phenylthiophene (**4**) (3.0 g, 13 mmol) at −78 °C in one batch. The reaction mixture was stirred for 2 h at this temperature. A dry THF solution containing triethylsilyl chloride (2.7 mL, 16 mmol) was added to the reaction mixture, and it was stirred for 30 min. The reaction mixture was then washed with water, extracted with ether and the organic layer dried over $MgSO_4$. The filtrate was concentrated and purified by column chromatography on silica gel (*n*-hexane) to give 4.1 g of **5** in 93% yield as a colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$, tetramethylsilane) δ = 0.92-1.05 (m, 15H, CH_2CH_3), 7.30-7.40 (m, 4H, Aromatic H), 7.55-7.59 (m, 2H, Aromatic H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 3.91, 7.55, 117.96, 125.83, 128.23, 128.41, 129.08, 131.56, 133.35, 149.63. HRMS (MALDI) m/z = 352.0311 (M^+). Calcd for $C_{16}H_{21}BrSSi^+$ = 352.0311.

1-(5-Phenyl-2-triethylsilyl-3-thienyl)heptafluorocyclopentene (6)

n-BuLi (1.6 M solution in *n*-hexane) (6.6 mL, 11 mmol) was slowly added to a stirred dry ether solution (30 mL) containing compound **5** (3.4 g, 9.6 mmol) at −78 °C under argon atmosphere. After 1.5 h, octafluorocyclopentene (1.9 mL, 14 mmol) in dry ether was added quickly to the reaction mixture and kept stirring for 2 h at −78 °C under argon atmosphere. The reaction was quenched by the addition of water. The reaction mixture was extracted with diethyl ether. The organic layer was dried over $MgSO_4$, filtered and concentrated. The residue was purified by column chromatography on silica gel (*n*-hexane) to give 3.0 g of **6** in 67% yield as a colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$, tetramethylsilane) δ = 0.82 (q, J = 7.6 Hz, 6H, CH_2), 0.98 (t, J = 7.6 Hz, 9H, CH_3), 7.30-7.43 (m, 4H, Aromatic H), 7.61-7.63 (m, 2H, Aromatic H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 4.09, 7.25, 125.05, 126.22, 128.49, 128.68, 129.19, 133.15, 140.56, 150.91. HRMS (MALDI) m/z = 466.1018 (M^+). Calcd for $C_{21}H_{21}F_7SSi^+$ = 466.1016.

1,2-Bis(5-phenyl-2-triethylsilyl-3-thienyl)perfluorocyclopentene (2a(O))

n-BuLi (1.6 M solution in *n*-hexane) (1.9 mL, 3.1 mmol) was slowly added to a stirred dry ether solution (10 mL) containing compound **5** (980 mg, 2.8 mmol) at −78 °C under argon atmosphere. After the mixture was stirred for 2 h, compound **6** (1.3 g, 2.8 mmol) in dry ether was added to the mixture. The reaction was further stirred for 2 h at −78 °C and the reaction was allowed to slowly warm up to room temperature. The reaction was quenched by the addition of water. The product was extracted with diethyl ether. The organic layer was dried over $MgSO_4$, filtered and concentrated. The crude product was purified by column chromatography on silica gel (*n*-hexane) and by recrystallization from *n*-hexane to give 380 mg of **2a(O)** in 19% yield as a colourless crystal. ^1H NMR (300 MHz, $CDCl_3$, tetramethylsilane) δ = 0.53 (q, *J* = 7.8 Hz, 12H, CH_2), 0.82 (t, *J* = 7.8 Hz, 18H, CH_3), 7.29-7.43 (m, 8H, Aromatic H), 7.56-7.59 (m, 4H, Aromatic H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 3.85, 7.35, 126.16, 126.89, 128.30, 129.15, 133.42, 134.03, 139.53, 150.20. HRMS (MALDI) *m*/*z* = 720.2168 (M^+). Calcd for $C_{37}H_{42}F_6S_2Si_2^+$ = 720.2165.

1-(1,1-dioxide-5-phenyl-2-triethylsilyl-3-thienyl)-2-(5-phenyl-2-triethylsilyl-3-thienyl)perfluorocyclopentene (2b(O))

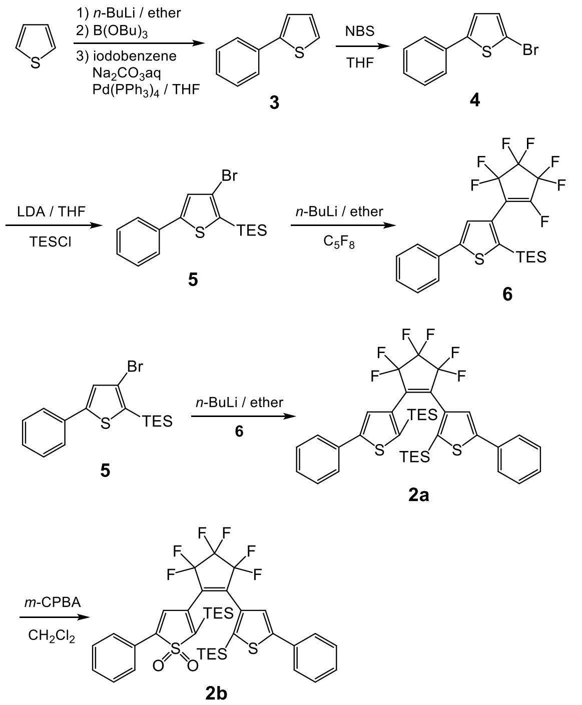
*m*CPBA (70 wt%, 300 mg, 1.2 mmol) was added to a stirred dichloromethane solution (3.0 mL) containing **2a(O)** (350 mg, 0.49 mmol). The reaction mixture was stirred overnight in the dark at room temperature. The reaction mixture was extracted with dichloromethane. The organic phase was dried over $MgSO_4$, filtered and evaporated. The crude product was purified by column chromatography on silica gel (*n*-hexane/ethyl acetate = 9:1) and by HPLC (*n*-hexane/ethyl acetate = 98:2) to give 170 mg of **2b(O)** in 48% yield as a pale yellow crystal. ^1H NMR (300 MHz, $CDCl_3$, tetramethylsilane) δ = 0.67-0.98 (m, 30H, CH_2CH_3), 6.76 (s, 1H, Aromatic H), 7.31-7.41 (m, 4H, Aromatic H), 7.44-7.46 (m, 3H, Aromatic H), 7.53-7.57 (m, 2H, Aromatic H), 7.70-7.73 (m, 2H, Aromatic H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 2.77, 4.58, 7.08, 7.39, 121.65, 126.28, 126.58, 126.64, 127.07, 128.64, 129.23, 129.46, 131.10, 132.37, 132.88, 137.09, 140.24, 145.12, 147.40, 151.09. HRMS (MALDI) *m*/*z* = 752.2065 (M^+). Calcd for $C_{37}H_{42}F_6O_2S_2Si_2^+$ = 752.2063.

Photochemical reaction

Photoirradiation was carried out using a 300 W xenon lamp (Asahi Spectra MAX-301) as a light source. Monochromatic light was obtained by passing the light through a band-pass filter and monochromator (Jobin Yvon H10-UV). The photocyclization and photocycloreversion reactions were followed by absorption spectra. The samples were not degassed. The optical quartz cell containing samples was placed in a cryostat for spectroscopy (UNISOKU CoolSpek UV/CD) during the photochemical reaction.

Thermal bleaching reaction

The thermal bleaching reaction of diarylethene closed-ring isomers was carried out in *n*-hexane as follows. The diarylethene open-ring isomer was put in an optical quartz cell. The solution in the cell was irradiated with 313 nm light to give the closed-ring isomer at the measurement temperature. The cell was placed in a cell temperature controller unit (JASCO ETC-505S/ETC-505T) or a cryostat for spectroscopy (UNISOKU CoolSpek UV/CD) during the thermal bleaching reaction. The reaction yields were periodically determined by absorption spectroscopic analysis.



Scheme 2 Synthetic route for diarylethene **2a** and thiophene-*S,S*-dioxidized diarylethene **2b**.

Results and discussion

Photochromic reaction behavior

Diarylethenes **1a**−**2a** and thiophene-*S,S*-dioxidized diarylethenes **1b**−**2b** exhibited photoisomerization from the colourless open-ring isomers to the coloured closed-ring isomers upon irradiation with UV light. The photogenerated closed-ring isomers were thermally unstable at room temperature and underwent thermal bleaching reactions. To investigate the photochromic reactivity, we performed absorption spectroscopic measurements at −60 °C. Fig. 2 shows absorption spectral changes of diarylethenes **1a**−**2a** and thiophene-*S,S*-dioxidized diarylethenes **1b**−**2b** in *n*-hexane at −60 °C. **1a(O)**−**2a(O)** and **1b(O)**−**2b(O)** have absorption maxima (λ_{max}) at 278, 280, 281 and 283 nm, respectively. Upon irradiation with UV light, the colourless solution of **1a(O)**−**2a(O)** and **1b(O)**−**2b(O)** turned blue, in which visible light absorption maxima were 615, 617, 590 and 600 nm, respectively. This absorption spectral change is ascribed to the photoisomerizations from the open-ring isomers to the closed-ring isomers. The absorption maxima of the open-ring isomers scarcely changed by oxidation. On the other hand, the closed-ring isomers having a thiophene-*S,S*-dioxidized ring were blue-shifted for the absorption band in the visible region in comparison with those having a thiophene ring. This feature is similar to thiophene-*S,S*-dioxidized diarylethenes reported previously.[17,18]

The molar absorption coefficient of the open-ring isomer (ε_o) at −60 °C was determined to be 43000 M^{-1} cm^{-1} for **1a(O)**, 49400 M^{-1} cm^{-1} for **2a(O)**, 29300 M^{-1} cm^{-1} for **1b(O)** and 31500 M^{-1} cm^{-1} for **2b(O)**. On the other hand, it is difficult to determine the molar absorption coefficient of the closed-ring isomer (ε_c) because the closed-ring isomer cannot be isolated due to the thermal unstability at room temperature. To estimate the ε_c values at −60 °C, we focused on the relationship between ε_o and ε_c for diarylethenes and thiophene-*S*,*S*-dioxidized diarylethenes reported previously.[18,20] The molecular structure of diarylethenes and thiophene-*S*,*S*-dioxidized diarylethenes reported previously was depicted in Scheme S1 and ε_o and ε_c values are summarized in Table S1. Fig. 3 shows the plots of ε_c relative to ε_o for diarylethenes and thiophene-*S*,*S*-dioxidized diarylethenes reported previously. There is a roughly liner relationship between ε_o and ε_c values for diarylethenes and thiophene-*S*,*S*-dioxidized diarylethenes. The relationships are expressed as follows:

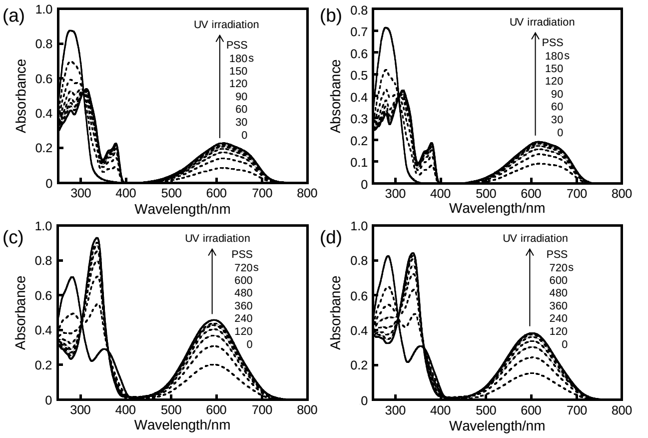


Fig. 2 Absorption spectral changes of (a) **1a**, (b) **2a**, (c) **1b** and (d) **2b** in *n*-hexane upon irradiation with 313 nm light at −60 °C: [**1a**] = 2.03×10^{-5} M, [**2a**] = 1.44×10^{-5} M, [**1b**] = 2.40×10^{-5} M and [**2b**] = 2.62×10^{-5} M, respectively.

In the case of diarylethenes:

$$\varepsilon_c/\mathrm{M^{-1}\,cm^{-1}} = 0.469 \times (\varepsilon_o/\mathrm{M^{-1}\,cm^{-1}}) - 2970$$

In the case of thiophene-*S*,*S*-dioxidized diarylethenes:

$$\varepsilon_c/\mathrm{M^{-1}\,cm^{-1}} = 0.323 \times (\varepsilon_o/\mathrm{M^{-1}\,cm^{-1}}) + 9200$$

From these equations, ε_c value was estimated to be 17200 M^{-1} cm^{-1} for **1a(C)**, 20200 M^{-1} cm^{-1} for **2a(C)**, 18700 M^{-1} cm^{-1} for **1b(C)** and 19400 M^{-1} cm^{-1} for **2b(C)**. By using these values, the photocyclization quantum yield ($\Phi_{o\to c}$) and the photocycloreversion quantum yield ($\Phi_{c\to o}$) at −60 °C were calculated as shown in Table 1. The photocycloreversion quantum yields decreased by a factor of 10–10^2 upon oxidation, whereas the photocyclization quantum yields were maintained. These phenomena are also similar to those of thiophene-*S*,*S*-dioxidized diarylethenes reported previously.[17,18]

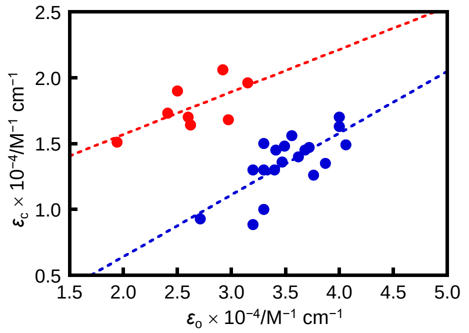


Fig. 3 Relationship between the molar absorption coefficients of the open-ring isomer (ε_o) and the closed-ring isomer (ε_c) for diarylethenes (●: R^2 = 0.517) and thiophene-*S*,*S*-dioxidized diarylethenes (●: R^2 = 0.447) reported previously.[18,20]

Table 1 Optical properties for diarylethenes **1a**–**2a** and thiophene-*S*,*S*-dioxidized diarylethenes **1b**–**2b**

	open-ring isomer		closed-ring isomer		$\Phi_{o\to c}$[a]	$\Phi_{c\to o}$[b]
	λ_{max}/nm	ε_o/M^{-1}cm^{-1}	λ_{max}/nm	ε_c/M^{-1}cm^{-1}		
1a	278	43000[c]	615	17200[d]	0.56[c]	2.3 × 10^{-4} [c]
2a	280	49400[c]	617	20200[d]	0.46[c]	3.7 × 10^{-4} [c]
1b	281	29300[c]	590	18700[d]	0.15[c]	7.6 × 10^{-6} [c]
2b	283	31500[c]	600	19400[d]	0.12[c]	4.5 × 10^{-5} [c]

[a] Irradiation with 313 nm light. [b] Irradiation with 590 nm light. [c] Measured at −60 °C. [d] Calculated from the equation of molar absorption coefficient.

Thermal bleaching behavior

Thermal reaction behavior of the closed-ring isomers **2a(C)**, **1b(C)** and **2b(C)** was investigated. The blue-coloured solutions, produced by irradiation with UV light, were gradually bleached to colourless even at low temperature. The colourless solutions did not change their colour upon irradiation with UV and visible light. This result indicates that the coloured closed-ring isomers were thermally converted to the colourless byproducts. Fig. 4a-c shows the absorbance changes of the coloured solutions of **2a(C)**, **1b(C)** and **2b(C)** in *n*-hexane. The decay curves obey the first-order kinetic plots. The rate constant (k) of the thermal reaction can be determined from the slope of the linear relationship in the first-order kinetic plots. Fig. 4d-f also exhibits temperature dependence of the rate constants of the thermal reactions. The k value of the thermal bleaching reaction increased as the measuring temperature increased. Activation energy (E_a) and frequency factor (A) of the thermal bleaching reactions can be determined from the slope and intercept of the linear relationship shown in Fig. 4d-f. Table 2 summarizes the kinetic parameters. For comparison, the kinetic parameters of **1a** are also shown in Table 2.[19] The E_a and A values were estimated to be 95 kJ mol^{-1} and 6.0 × 10^{13} s^{-1} for **2a**, 78 kJ mol^{-1} and 2.8 × 10^{12} s^{-1} for **1b** and 92 kJ mol^{-1} and 3.3 × 10^{16} s^{-1} for **2b**, respectively. The k value and half-life time ($t_{1/2}$) of **1a**, **2a**, **1b** and **2b** at 0 °C were also calculated as shown in Table 2. It is revealed that the thermal bleaching reaction was accelerated by oxidation of thiophene ring and introduction of bulky substituents at the reactive positions. These thermal bleaching reactions could be observed even in a filter paper (Fig. S1).

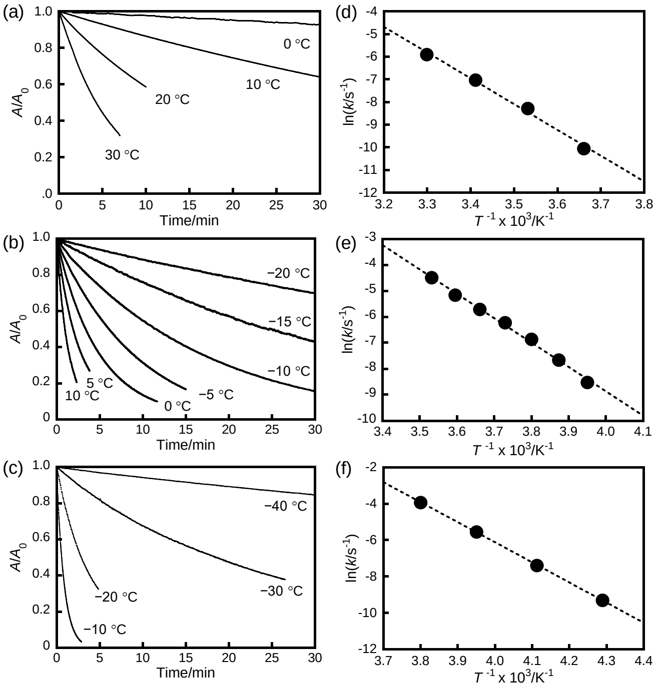


Fig. 4 Absorption decay curves of (a) **2a(C)**, (b) **1b(C)** and (c) **2b(C)** in *n*-hexane and temperature dependence of the rate constants for the thermal bleaching reaction of (d) **2a(C)**, (e) **1b(C)** and (f) **2b(C)** in *n*-hexane.

To confirm the formation of the colourless byproducts by the thermal bleaching reaction, re-colouration examination was performed. Fig. 5 shows absorption spectra of the photostationary solution of **2b** upon irradiation with UV light, the solution after the thermal bleaching reaction and the UV irradiated solution after the thermal bleaching reaction. After the thermal bleaching reaction, absorption band appeared in only UV region, which results in the colourless solution. Upon irradiation with UV light to the solution after the thermal bleaching reaction, no change in absorption spectrum in visible region was observed. This result indicates that the closed-ring isomer **2b(C)** was irreversibly converted to colourless byproducts. Moreover, thermal reaction products of **2b(C)** were analysed by HPLC with a normal phase silica gel column using a *n*-hexane/ethyl acetate (98:2) mixture as the eluent. Fig. 6 shows chromatographs of the open-ring isomer **2b(O)** and the colourless solution after the thermal bleaching reaction of a PSS solution of **2b**. **2b(O)** was eluted at 29 min. After the thermal bleaching reaction, the new peaks appeared mainly at 17 and 19 min, which are different from the open-ring isomer **2b(O)**. Unfortunately, the molecular structure of byproducts could not completely determined because there are many kinds of byproducts that are too little to isolate. However, these results clearly indicate that the closed-ring isomer **2b(C)** gave the byproducts.

Table 2 Arrhenius parameters for thermal bleaching of the closed-ring isomers

	E_a/kJ mol^{-1}	A/s^{-1}	k/s^{-1} at 0 °C	$t_{1/2}$/s at 0 °C	T ($t_{1/2}$ = 30 min) /°C
1a[a]	103	3.3×10^{13}	6.5×10^{-7}	1.1×10^{6}	45
2a	95	6.0×10^{13}	4.0×10^{-5}	1.7×10^{4}	16
1b	78	2.8×10^{12}	0.0033	2.1×10^{2}	−16
2b	92	3.3×10^{16}	0.082	8.4	−32

[a] Ref. 19.

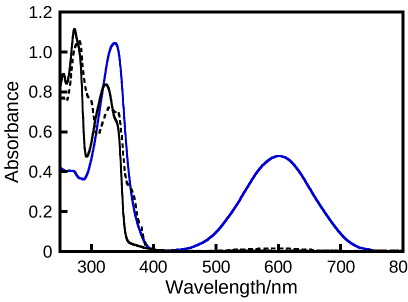


Fig. 5 Absorption spectra of the photostationary solution of **2b** at −60 °C (blue solid line), the solution after the thermal bleaching reaction (black solid line) and the UV irradiated solution after the thermal bleaching reaction (black dashed line).

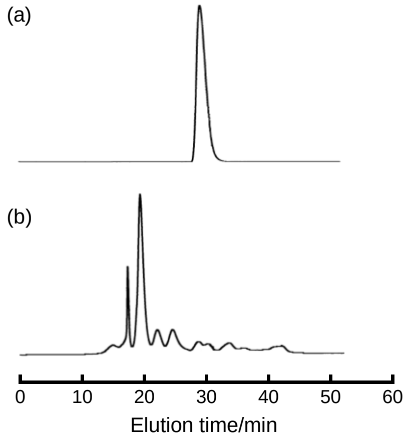


Fig.6 HPLC charts of (a) **2b(O)** and (b) the colourless solution after the thermal bleaching reaction of a photostationary solution of **2b** upon irradiation with UV light at −60 °C. The peak intensity was detected by absorbance at 254 nm in hexane/ethyl acetate (98:2).

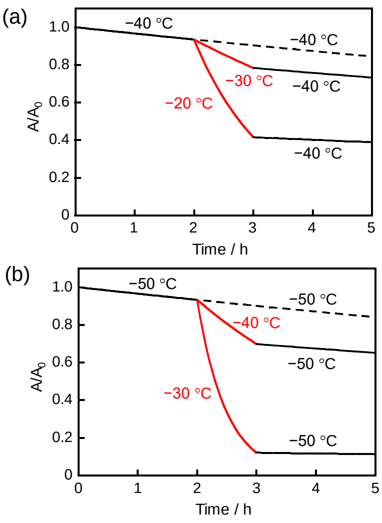


Fig. 7 Calculated absorbance changes of (a) **1b(C)** and (b) **2b(C)** in *n*-hexane stored for 5 h at −40 or −50 °C (- - -) and heated up for 1 h on the way (———).

To confirm which thiophene-*S*,*S*-dioxidized diarylethenes **1b** and **2b** function as light-starting irreversible thermosensors that can detect a rise in heat at low temperature, we have calculated a thermal bleaching behaviour from Arrhenius parameters. Fig. 7 shows the calculated absorbance changes of **1b(C)** and **2b(C)** stored for 5 h at −40 or −50 °C and heated up for 1 h on the way. Although the absorbance gradually decreased at −40 °C for **1b(C)** and −50 °C for **2b(C)**, it decreased drastically at −30 °C for **1b(C)** and −40 °C for **2b(C)**. After 5 h, there is a clear difference in the absorbance between the solution stored for 5 h at that low temperature and the solution heated up for 1 h on the way. This result indicates that thiophene-*S*,*S*-dioxidized diarylethenes **1b** and **2b** can detect a rise of a temperature differential of 10 °C for 1 h. Thus, it has potential application for light-starting irreversible thermosensors that can detect a rise in heat at low temperature.

Conclusions

We have synthesized diarylethenes and thiophene-*S*,*S*-dioxidized diarylethenes having TMS and TES groups at the reactive positions and investigated their optical properties and thermal stability. Diarylethenes and thiophene-*S*,*S*-dioxidized diarylethenes showed photochromic reactions from the colourless open-ring isomers to the coloured closed-ring isomers upon irradiation with UV light. The closed-ring isomer of thiophene-*S*,*S*-dioxidized diarylethenes was stable under visible light. Moreover, the photogenerated closed-ring isomer was found to undergo a thermal bleaching reaction to produce byproducts below room temperature. In particular, the thiophene-*S*,*S*-dioxidized diarylethene having TES group at the reactive positions exhibited the thermal bleaching reaction even at −40 °C. These photochromic compounds could be used in applications as light-starting irreversible thermosensors that can detect a rise in heat at low temperature.

Acknowledgements

This work was partly supported by a Matching Planner Program (No. MP27115663071) from Japan Science and Technology Agency (JST), JSPS KAKENHI Grant Number JP26107013 in Scientific Research on Innovative Areas "Photosynergetics", JSPS KAKENHI Grant Number JP16K17896 in Scientific Research for Young Scientists (B) and The Murata Science Foundation. The authors also thank Nippon Zeon Co., Ltd. for providing octafluorocyclopentene.

References

1. A. Narayan, L. A. Campos, S. Bhatia, D. Fushman and A. N. Naganathan, *J. Am. Chem. Soc*., 2017, **139**, 792.
2. Ferdinandus, S. Arai, S. Takeoka, S. Ishiwata, M. Suzuki and H. Sato, *ACS Sens*., 2016, **1**, 1222.
3. G. Kwak, S. Fukao, M. Fujiki, T. Sakaguchi and T. Masuda, *Chem. Mater*., 2006, **18**, 2081.
4. C. Zhou, L. Yuan, Z. Yuan, N. K. Doyle, T. Dilbeck, D. Bahadur, S. Ramakrishnan, A. Dearden, C. Huang and B. Ma, *Inorg. Chem.*, 2016, **55**, 8564.
5. Z. Yang, Y. He, J. Lee, N. Park, M. Suh, W. Chae, J. Cao, X. Peng, H. Jung, C. Kang and J. S. Kim, *J. Am. Chem. Soc*., 2013, **135**, 9181.
6. M. A. Haidekker, T. P. Brady, D. Lichlyter and E. A. Theodorakis, *J. Am. Chem. Soc*., 2006, **128**, 398.
7. S. Kobatake and Y. Terakawa, *Chem. Commun*., 2007, 1698.
8. K. Paek, H. Yang, J. Lee, J. Park and B. J. Kim, *ACS Nano.*, 2014, **8**, 2848.
9. Z. Bai, R. Chen, P. Si, Y. Huang, H. Sun and D. Kim, *ACS Appl. Mater. Interfaces.*, 2013, **5**, 5856.
10. (a) G. L. Robertson, *Food Packaging*: *Principles and Practice*, Marcel Dekker, New York, 1993. (b) T. I. Lucas, R. H. Bishara and R. H. Seevers, *Pharm. Technol.*, 2004, **28**, 68. (c) J. Taylor, *Pharm. J.*, 2001, **267**, 128-131.
11. M. Irie, K. Matsuda, In *Electron Transfer in Chemistry*; V. Balzani, Ed.; Wiley-VCH, Weinheim: 2001, 215.
12. M. Irie, *Chem. Rev*., 2000, 100, 1685.
13. M. Irie, In *Molecular Switchings*; B. L. Feringa, Ed.; Wiley-VCH, Weinheim: 2001, 37.
14. J. A. Delaire and K. Nakatani, *Chem. Rev.*, 2000, **100**, 1817.
15. (a) C. Bechinger, S. Ferrere, A. Zaban, J. Sprague and B. A. Gregg, *Nature*, 1996, **383**, 608. (b) K. J. Chen, A. D. Laurent and D. Jacquemin, *J. Phys. Chem. C*, 2014, **118**, 4334.
16. (a) S. Kobatake, S. Takami, H. Muto, T. Ishikawa and M. Irie, *Nature*, 2007, **446**, 778. (b) M. Irie, T. Fukaminato, K. Matsuda and S. Kobatake, *Chem. Rev.*, 2014, **114**, 12174.
17. H. Shoji and S. Kobatake, *Chem. Commun*., 2013, **49**, 2362.
18. H. Shoji, D. Kitagawa and S. Kobatake, *New J. Chem*., 2014, **38**, 933.
19. S. Kobatake, H. Imagawa, H. Nakatani and S. Nakashima, *New J. Chem*., 2009, **33**, 1362.
20. D. Kitagawa and S. Kobatake, *Chem. Rec.*, 2016, **16**, 2005.