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# Photochromic and fluorescence switching properties of oxidized triangle terarylenes in solution and in amorphous solid states<sup>†</sup>

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Three hexatriene-type photochromic compounds 4,5-bis(2,4-dimethyl-5-phenylthiophene-*S*,*S*-dioxide-3-yl)-2-phenylthiazole, **1**, 4,5-bis(2-methylbenzo[*b*]thiophene-*S*,*S*-dioxide-3-yl)-2-phenylthiazole, **2**, and 1,2-bis(2,4-dimethyl-5-phenylthiophene-*S*,*S*-dioxide-3-yl)-3,3,4,4,5,5-hexafluorocyclopentene, **3**, are synthesized and their photochromic and fluorescence properties are studied, which are analogous to photochromic molecules of triangle terarylene and diarylethene with oxidized aryl units containing *S*,*S*-dioxide moieties. These compounds showed photochromic coloration reaction to form a ring-closed form isomer having a cyclohexadiene backbone. Compound **2** showed backward cycloreversion reaction with about 2.4% of photochemical quantum yield, whereas compounds **1** and **3** showed markedly low cycloreversion quantum yields less than 0.1%. Their colored isomers exhibited green or orange fluorescence with relatively high fluorescence quantum yields. Compound **1** also showed similar fluorescence switching nature and fluorescence pattern formation in a stable amorphous film. Intramolecular hydrogen bonding between *S*,*S*-dioxide units and methyl groups at photo-reactive carbon atoms is discussed on the basis of molecular structure determined by X-ray single analysis and quantum chemical calculation in the DFT method, which is regarded to contribute to the enhanced emission nature and suppressed cycloreversion photoreactivity of the ring-closed form isomers.

## Introduction

Photochromic molecules have recently been extensively studied as versatile photoswitching components for controlling various chemical,<sup>1</sup> electrical,<sup>2</sup> electrochemical,<sup>3</sup> biofunctional,<sup>4</sup> mechanical,<sup>5</sup> and optical properties of molecular-based materials.<sup>6</sup> Among various photochromic molecules, those based on hexatriene structures such as fluguides, diarylethenes and terarylenes have been attracting considerable interest since some of them exhibit kinetic persistency in the thermodynamically unstable cyclohexadiene state and can be potential candidates for an active material in future molecular memory systems.<sup>7–9</sup> Especially, photo-responsive modulation of fluorescence emission properties has been most extensively studied for developing active materials for future 3-D ultrahigh density optical recording and for ultra high resolution bio-imaging technology. While intrinsic emission properties of these photochromic compounds themselves have been studied,<sup>10</sup> external fluorophores have been combined with them for extensive emission properties, such as organic  $\pi$ -conjugated molecules,<sup>11</sup> metal complexes<sup>12</sup> and nanocrystals.<sup>13</sup> Such an external control of the fluorescence emission with the photochromic units is usually based on the photochromic modulation of electron or energy transfer in the excited states. Structural distortion<sup>14</sup> and molecular aggregation<sup>15</sup> upon the photochromic reactions have also been applied for external control of fluorescence emission properties. Recently, Prof. Kim and Prof. Ahn and their coworkers have proposed oxidized diarylethene derivatives having sulfone SO<sub>2</sub> units. The tetra-oxidation of benzothienyl units led to the enhancement of the fluorescent property in the ring-closed form<sup>16</sup> in comparison with that of non-oxidized dibenzothienylethene whose fluorescence is detectable only at low temperature (e.g. 77 K).<sup>10c</sup> Meanwhile, recent progress in highly sensitive photochromic terarylenes highlights the photonquantitative photocyclization reaction, which has motivated us to explore oxidized terarylenes with SO<sub>2</sub> unit.<sup>17</sup>

In the present paper, we report on the preparation and photochromic properties of S,S-dioxide derivatives of triangle terarylenes whose molecular structures are shown in Scheme 1. Two precursor terarylenes are oxidized to form tetra-oxidized terarylenes 1a and 2a and their photochromic and fluorescent properties are studied in solution and also in amorphous states. They exhibited relatively high fluorescence emission quantum

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Scheme 1 Oxidation of photochromic precursors of P1-P4 to form 1a-4a, respectively, and the photochromic reaction of 1a-4a.

yields in the ring-closed forms and significantly suppressed photo-cycloreversion reaction quantum yields compared to those of precursor terarylenes **P1** and **P2**, which provide turn-on type fluorescence switching nature of photochromic molecules without external fluorophores. Oxidized diarylethene **3** is also synthesized as a reference compound and its properties were compared with a previous molecule **4**.<sup>16a</sup>

## Experimental

## General

<sup>1</sup>H NMR (300 MHz) and <sup>13</sup>C NMR (75 MHz) spectra were recorded on a JEOL JNM-AL-300 spectrometer. Mass spectra were measured with mass spectrometers (for: JEOL JMS-700, JEOL AccuTOF JMS-T100LC and PE biosystems Voyage DE-STR, for FAB, ESI and MALDI-TOF MS, respectively). Elemental analyses were performed with an elemental analyzer (Perkin Elmer, 2400II CHNS/O). ATR-IR spectra were recorded on a JASCO FT/IR-4200 spectrometer with ATR PRO410-S. Separative HPLC was performed on a HPLC system (HITA-CHI, LaChrom ELITE, L-2400 for detector, L-2130 for pump, D-2500 for chromate-integrator) with a packed column (Nacalai Tesque, COSMOSIL 55L-II,  $20 \times 250$  mm). Absorption spectra were studied with a spectrophotometer (JASCO V-670). Fluorescence spectra were studied with a spectrofluorometer (JASCO FP-6500). Fluorescence quantum yields were evaluated by using an absolute PL quantum yield measurement system with an integration sphere (Hamamatsu, C9920-02) for solutions and a spectrofluorometer (JASCO FP-6300ST-Y ILF-533) for films. Crystal structures were determined by using an X-ray crystal analyzer (Rigaku VariMAX-RAPID). DSC structural measurements were carried out using a differential scanning calorimeter (Seiko, EXSTAR6000 DSC6200) with a liquid nitrogen cooling system. The heating rate was 5 °C min<sup>-1</sup>. An

optical microscope (Olympus, BX51) was used for visible observation of the amorphous films. Photoirradiation was carried out with an ultra high-pressure Hg lamp (Ushio, BA-H501, 1 kW) and a Xe short-arc lamp (Ushio, BA-X500, 500 W) as the exciting light sources. Light with appropriate wavelength was obtained through optical filters and/or a monochromator (Shimadzu, SPG-120S, 120 mm, f = 3.5). Quantum vields of ring-cyclization reactions ( $\Phi_{oc}$ ) in solution were determined by using 1,2-bis(2-methylbenzo[b]thiophene-3-yl)perhexafluorocyclopentene (in hexane) as a reference whose  $\Phi_{oc}$  is 0.35 under UV light irradiation ( $\lambda = 313$  nm) in hexane.<sup>18</sup> Quantum yields of ring-cycloreversion reactions ( $\Phi_{co}$ ) were determined by 1,2-bis(thiophen-2-yl)perhexafluorocyclopentene using (in 3-methylpentane) as a reference compound, whose  $\Phi_{co}$  has been reported to be 0.37 at 432 nm in 3-methylpentane.<sup>19</sup>

#### Syntheses

Precursors P1 and P2 were prepared according to the procedures described in the previous literature.<sup>20,21</sup> Precursors P3 and P4 were purchased from TCI. Precursors P1, P2 and P3 were treated with 70% 3-chloroperbenzoic acid (*m*-CPBA, TCI, containing 30 wt% water) to afford compounds 1a, 2a and 3a, respectively, as has been reported for compound 4a.<sup>16a</sup>

4,5-Bis(2,4-dimethyl-5-phenylthiophene-S,S-dioxide-3-yl)-2phenylthiazole (1a). 4,5-Bis(2,4-dimethyl-5-phenylthiophen-3yl)-2-phenylthiazole (P1)<sup>20</sup> (0.50 g, 0.94 mmol) and m-CPBA (2.3 g, 9.4 mmol) were dissolved in CH<sub>2</sub>Cl<sub>2</sub> (100 mL). In the dark room, the mixture was stirred at room temperature for 24 h, and then washed with aqueous solution of NaHSO<sub>4</sub> followed by the extraction with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was dried with MgSO<sub>4</sub>, filtered, and concentrated. The residue was purified by silica gel column chromatography (hexane/ethyl acetate 3:1) and recrystallized with toluene to afford 1a (0.19 g, yield 33%) as a colorless solid. T<sub>d</sub> > 140 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>/ TMS):  $\delta$  (ppm) = 7.99–8.02 (2H, d), 7.60–7.67 (4H, m), 7.47–7.55 (9H, m), 2.19–2.22 (6H, d), 1.98–2.04 (6H, d); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>/TMS):  $\delta$  (ppm) = 137.11, 136.34, 132.15, 131.56, 130.00, 129.76, 129.38, 129.24, 129.21, 129.14, 127.13, 126.76, 126.70, 126.45, 14.52, 9.10, 8.76; ATR-IR: peak wavenumber (cm<sup>-1</sup>) = 1292 ( $\nu_{as}$  SO<sub>2</sub>), 1135 ( $\nu_{s}$  SO<sub>2</sub>); FAB HRMS [M + H]<sup>+</sup> (m/z), calcd for C<sub>33</sub>H<sub>28</sub>NO<sub>4</sub>S<sub>3</sub><sup>+</sup>: 598.11, found: 598.11; elemental analysis (%) calcd for C33H27NO4S3: C 66.31, H 4.55, N 2.34; found: C 66.06, H 4.32, N 2.36.

**4,5-Bis(2-methylbenzo[***b***]thiophene-***S***,***S***-dioxide-3-yl)-2-phenylthiazole (2a). This compound was prepared by the same procedure as had been used for <b>1a**. From 4,5-bis(2-methylbenzo[*b*] thiophen-3-yl)-2-phenylthiazole (**P2**)<sup>21</sup> (0.10 g, 0.22 mmol) and *m*-CPBA (0.33 g, 1.3 mmol), **2a** (0.087 g, yield 79%) was obtained as a colorless solid.  $T_d > 160 \text{ °C}$ . <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>/ TMS):  $\delta$  (ppm) = 8.04–8.07 (2H, d), 7.77–7.83 (2H, t), 7.49–7.57 (8H, m), 7.37 (1H, s), 1.97–2.05 (6H, d); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>/TMS):  $\delta$  (ppm) = 170.78, 146.22, 139.88, 135.85, 135.65, 133.77, 133.63, 132.15, 131.72, 131.68, 130.24, 129.68, 129.42, 127.89, 126.84, 125.66, 123.98, 122.58, 122.13, 121.67, 8.59, 8.50; ATR-IR: peak wavenumber (cm<sup>-1</sup>) = 1298–1163 ( $\nu_{as}$  SO<sub>2</sub>), 1111 ( $\nu_s$  SO<sub>2</sub>); FAB HRMS (*m*/*z*) [M + H]<sup>+</sup> calcd for C<sub>27</sub>H<sub>20</sub>NO<sub>4</sub>S<sub>3</sub><sup>+</sup>: 518.05, found: 518.05; elemental analysis (%) calcd for  $C_{27}H_{19}NO_4S_3$ : C 62.65, H 3.70, N 2.71; found: C 62.35, H 3.71, N 2.66.

**1,2-Bis(2,4-dimethyl-5-phenylthiophene-***S*,*S*-dioxide-3-yl)-**3,3,4,4,5,5-hexafluorocyclopentene (3a).** This compound was prepared by the same procedure as had been used for **1a**. From 1,2-bis(2,4-dimethyl-5-phenylthiophen-3-yl)-3,3,4,4,5,5hexafluorocyclopentene (**P3**, 0.10 g, 0.18 mmol) and *m*-CPBA (0.45 g, 1.8 mmol), **3a** (0.069 g, yield 62%) was obtained as a colorless solid.  $T_d > 100$  °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>/ TMS):  $\delta$  (ppm) = 7.53–7.56 (4H, m), 7.46–7.49 (6H, m), 2.17– 2.26 (6H, d), 1.92–1.99 (6H, d); <sup>13</sup>C NMR (75 MHz CDCl<sub>3</sub>/ TMS):  $\delta$  (ppm) = 143.55, 142.32, 137.06, 136.66, 130.37, 129.11, 129.10, 126.09, 125.97, 124.62, 124.53, 14.30, 13.61, 9.96, 9.90, 9.57. ATR-IR peak wavenumber (cm<sup>-1</sup>) = 1305–1271 (*v*<sub>as</sub> SO<sub>2</sub>), 1136–1112 (*v*<sub>s</sub> SO<sub>2</sub>); FAB HRMS (*m*/*z*) [M + H]<sup>+</sup> calcd for C<sub>29</sub>H<sub>23</sub>F<sub>6</sub>O<sub>4</sub>S<sub>2</sub><sup>+</sup>: 613.09, found: 613.09; elemental analysis (%) calcd for C<sub>29</sub>H<sub>22</sub>F<sub>6</sub>O<sub>4</sub>S<sub>2</sub>: C 56.86, H 3.62; found: C 57.03, H 3.61.

## **Results and discussion**

Colorless solutions of the open-ring isomers 1a, 2a and 3a in 2-methyltetrahydrofuran (2-MeTHF) were observed to turn yellow or orange upon irradiation with UV light ( $\lambda = 313$  nm). As shown in Fig. 1, 1a, 2a and 3a showed no absorption band in the visible wavelength range, while new absorption bands were observed at 400–550 nm after irradiation with UV light. Characteristic isosbestic points at 298 nm, 279 nm and 355 nm were found for compounds 1, 2 and 3, respectively. These spectral properties are similar to those of compound 4 and supported the two-component photochromic reaction as illustrated in Scheme 1. The ring-closed form isomers 1b, 2b and 3b were prepared by UV light irradiation to the solutions of 1a, 2a and 3a, and were isolated from the colored solutions by HPLC (hexane/ethyl acetate). Chemical structures of the ring-closed isomers 1b, 2b



**Fig. 1** Absorption spectral changes of compounds, (a) **1**, (b) **2**, (c) **3** and (d) **4** in 2-MeTHF; open-forms (dashed lines), closed-forms (bold solid lines) and P.S.S. under irradiation with 313 nm (dotted lines).

and **3b** were confirmed by <sup>1</sup>H NMR spectroscopy as well as that of **4b** (in  $CDCl_3$ ).<sup>22</sup>

A single crystal of colored form 1b was obtained by recrystallization from a hexane/ethyl acetate solution. The crystal structure of 1b was studied by X-ray crystal structural analysis.<sup>23</sup> An ORTEP drawing of 1b in the crystal indicated a coplanar cyclohexadiene-based structure as shown in Fig. 2. The twisting angle between phenvl and thiazole rings is about 32° (S1-C1-C4-C9) and the S and N atoms of the central thiazole group are close to the hydrogen atoms in the central phenyl groups with shorter distance than 0.27 nm, which is shorter than the sum of van der Waals' radii of each atom. The weak CH/N and CH/S hydrogen bonding interactions seem to tether the central phenyl ring with the thiazole ring, making the molecule have a coplanar structure. Also these S and N atoms are regarded to interact with hydrogen atoms in the two methyl groups at the 4th position of dioxidized thiophenes with distance 0.271 nm for CH-S and 0.259 nm for CH-N, also shorter than the sum of van der Waals' radii of each atom. The methyl groups at the reaction center carbon atoms are out of the molecular plane and are close to the SO<sub>2</sub> units. Distances between the hydrogen and the oxygen are also shorter than the sum of van der Waals' radii of each atom. It suggests weak CH/OS hydrogen bonding interactions between these methyl groups and the oxygen atoms.

Optical and photochromic properties of compounds 1, 2 and 3 are summarized in Table 1 with those of compound 4. The absorption spectra of ring-closed forms 1b, 2b and 3b showed



**Fig. 2** ORTEP drawings of **1b** in crystal, showing 50% probability displacement ellipsoids; (a) the front view and (b) the edge view. Distances between the hydrogen of methyl groups at the reactive carbon centers and the oxygen of  $SO_2$  units are 0.239 nm (for H6/O3) and 0.231 nm (for H17/O2), which are shorter than the sum of van der Waals' radius of hydrogen and oxygen atoms (0.26 nm).

Table 1 Absorption and photochromic properties of compounds 1–4 in 2-MeTHF

	λ/nm (ε [10 <sup>4</sup> M <sup>-1</sup> cm <sup>-1</sup> ])	$a_{\rm pss}{}^a$	${\Phi_{ m oc}}^b$	${\Phi_{ m co}}^c$
1a	307 (2.28)	>0.99	0.23 (±0.01)	_
1b	324 (4.20) 490 (1.71)	—		$3 \times 10^{-4d}$ (±0.1 × 10 <sup>-4</sup> )
2a	301 (1.83)	$\sim 0.80$	$0.46 (\pm 0.01)$	_
2b	319 (2.80) 460 (2.03) 487 (1.96)	_	_	0.024 (±0.002)
3a	288 (0.687)	>0.99	0.31 (±0.01)	—
3b	423 (1.62)	—		$4 \times 10^{-5d} (\pm 0.3 \times 10^{-5})$
4a 4b	309 (0.424) 400 (2.14)	~0.80	$-0.22^{e}$	$\frac{-}{0.036}$ (±0.002) 0.061 <sup>e</sup>

 $^a$   $a_{\rm pss}$ : the cyclization conversion ratio at P.S.S. with the irradiation at 313 nm light.  $^b$  At 313 nm.  $^c$  At 432 nm.  $^d$  The samples were degassed.  $^e$  In ethyl acetate.<sup>16d</sup>

a significant blue-shifted absorption band from those of precursor molecules P1, P2 and P3 whose data are presented in the ESI<sup>†</sup> (Table S1). This tendency of blue shift has been reported for compound 4 and other oxidized diarylethenes, which were reproduced here with TD-DFT calculations for present molecules (see ESI<sup>†</sup>).<sup>16</sup> The photochemical conversion ratios from 1a to 1b and from 3a to 3b at the photostationary states (P.S.S.) under irradiation at  $\lambda = 313$  nm were estimated to be almost 100% by using HPLC, which are mainly due to their very low cycloreversion quantum yields.

 $\Phi_{\rm oc}$  of **1a**, **2a** and **3a** were 0.23, 0.46 and 0.31, respectively, which are rather smaller than those of the precursor molecules, 0.58, 0.6 and 0.46 for P1, P2 and P3, respectively. This tendency has already been suggested in the previous compound 4 which shows  $\Phi_{\rm oc} = 0.22$  and was less reactive than the precursor diarylethene P4 ( $\Phi_{oc} = 0.35$ ).<sup>16d</sup> Upon irradiation with visible light, compounds 2b and 4b were completely converted to 2a and 4a, respectively.  $\Phi_{co}$  of **2b** and **4b** were 0.024 and 0.036, respectively, which are markedly smaller than those of the precursor molecules **P2** ( $\Phi_{co} = 0.45$  (ref. 21)) and **P4** ( $\Phi_{co} = 0.35$  (ref. 18)).  $\Phi_{co}$ value of 4b in 2-MeTHF is similar to that in ethyl acetate solution  $(\Phi_{co} = 0.061)$ ,<sup>16d</sup> which indicates no marked solvent-effect on the photochemical cycloreversion reactivity. On the other hand, the solutions of compounds 1b and 3b hardly showed photochromic bleaching reaction even after irradiation with visible light for several hours. Markedly low  $\Phi_{co}$  values of 1b and 3b were roughly estimated to be  $3 \times 10^{-4}$  and  $4 \times 10^{-5}$ , respectively. For evaluating such low  $\Phi_{co}$  values, careful degassing of the sample solution was desired. The extremely low  $\Phi_{co}$  values make these compounds 1 and 3 effectively one-way photochromic compounds. The extremely low photobleaching reactivity of compound **1b** is typically compared with that of **2b** in Fig. 3.

Fluorescence spectra of compounds **1**, **2**, **3** and **4** in 2-MeTHF are shown in Fig. 4 under excitation with visible light of appropriate wavelength for selective excitation of the ring-closed form isomers. Continuous UV light irradiation resulted in the progress

of fluorescence bands in these solutions. The colored solution of 2b exhibited intense green emission with fluorescence band at 543 nm. This emission band decreased upon irradiation with visible light and again increased upon irradiation with UV light, which indicates the reversible fluorescence switching capability. The colored solutions of 1b and 3b showed orange and yellow emission, respectively, whose emission maxima are 577 nm and 556 nm, respectively. Excitation spectra monitored at the emission maxima exhibited typical excitation bands corresponding to the absorption spectra of the ring-closed form isomers. UV light irradiation of the colorless solutions of 1a and 3a resulted in progression of the fluorescence emission band with almost irreversible nature. Fig. 5 shows a typical example of stable fluorescence emission intensity of compound 1b under continuous irradiation with visible light ( $\lambda_{ex} = 432 \text{ nm}$ ), where faster decay of emission from 2b is also provided for comparison. Fluorescence quantum yields,  $\Phi_{em}$ , of ring-closed isomers were evaluated to be 0.35, 0.37 and 0.03 for 1b, 2b and 3b, respectively.  $\Phi_{\rm em}$  of 4b was roughly in agreement with the previously reported values in ethyl acetate. Since the precursor diarylethene P4b gives weak emission at 77 K but not at room temperature,<sup>10c</sup> the  $\Phi_{\rm em}$  of 4b indicates the marked enhancement of emission nature by oxidation of S to SO<sub>2</sub>. Oxidized terarylenes 1b and 2b indicated about 10 times larger fluorescence emission quantum yields than those of oxidized diarylethenes **3b** and **4b**. **2b** displayed a  $\Phi_{\rm em}$  of 0.45 in toluene, as summarized in Table S5<sup>†</sup>. Fluorescence decay was studied for evaluating the fluorescence decay time constant for these compounds, of which results are provided in Fig. S4<sup>†</sup> and summarized also in Table 2. All compounds showed welldefined single exponential decay and compounds 1b and 2b showed notably longer lifetime than those of 3b and 4b. The larger fluorescence quantum yields of 1b and 2b seem to originate from the smaller non-radiative decay rate constant,  $k_{nr}$ , in comparison with those of **3b** and **4b**. Although the origin of these tendencies is not clear at present, we believe that the emission efficiency might be predominantly controlled with the central part of the molecules in this class of ring-fused  $\pi$ -conjugated compounds. One may consider about suppressed vibrational decay in the excited states of compounds 1b and 2b than those of Diarylethenes oxidized diarylethenes. with the perfluorocyclopentene units may have the specific flexibility with the flip motion on the central perfluorocyclopentene ring, which is usually observed in the X-ray analyses of diarylethenes as the structural disordering.24 Such flexibility of the



**Fig. 3** Absorbance changes at  $\lambda_{max}$  of **1b** (square line) and **2b** (rhombus line) in 2-MeTHF by continuous irradiation with visible light ( $\lambda = 432$  nm; 500 W, through a monochromator).



**Fig. 4** Fluorescence spectral changes of compounds (a)  $\mathbf{1}$  (2.7 × 10<sup>-5</sup> M), (b)  $\mathbf{2}$  (2.7 × 10<sup>-5</sup> M), (c)  $\mathbf{3}$  (7.8 × 10<sup>-5</sup> M) and (d)  $\mathbf{4}$  (4.5 × 10<sup>-6</sup> M) in 2-MeTHF upon UV light irradiation (313 nm); open-forms (dashed lines), closed-forms (bold solid lines), and P.S.S. under irradiation at 313 nm (dotted lines). Excitation wavelengths were 490 nm, 460 nm, 423 nm and 400 nm, for 1, 2, 3 and 4, respectively.



**Fig. 5** Relative fluorescence intensity (*III*<sub>0</sub>) at 577 nm and 543 nm of **1b** (square line) and **2b** (rhombus line) in 2-MeTHF, respectively, as a function of irradiation time continuous irradiation with visible light ( $\lambda = 432$  nm; 0.33 mW cm<sup>-2</sup>).

Table 2 Fluorescence properties of compounds 1b-4b in 2-MeTHF

	λ <sub>ex</sub> /nm	$\lambda_{\rm em}/{\rm nm}$	$\Phi_{\rm em}{}^a$	$\tau_{\rm em}{}^b/{\rm ns}$	$k_{\rm r}/10^7 {\rm ~s^{-1}}$	$k_{\rm nr}/10^8 {\rm ~s^{-1}}$
1b	490	577	0.35	4.5	7.8	1.4
2b 3b	460 423	543 556	0.37 0.03	4.3 0.37	8.6 8.1	1.5 26
4b	400	478	0.03	0.07	4.3	140

<sup>*a*</sup> Fluorescent quantum yields at room temperature; the sample concentration of  $3.5 \times 10^{-6}$ ,  $8.6 \times 10^{-6}$ ,  $3.4 \times 10^{-6}$ , and  $2.1 \times 10^{-6}$  M for **1**, **2**, **3** and **4**, respectively. <sup>*b*</sup> Fluorescence decay profiles are presented in Fig. S4<sup>†</sup>.

perfluorocyclopentene units in **3b** and **4b** is possible to contribute to their  $k_{nr}$  values and suppressed  $\Phi_{em}$ . Compounds **1b** and **2b** have no such flexibility and even suppressed rotational motion between phenyl and thiazole rings in the bridging unit tethered with the CH/S and SH/N interactions might make the molecules suitable for fluorescence emission. Considerably weaker fluorescence was observed in solutions of their open form isomers. **1a**  and **2a** showed a very weak emission band at 452 nm ( $\Phi_{\rm em} < 0.001$ ) and 418 nm ( $\Phi_{\rm em} < 0.003$ ), respectively. However, the fluorescence emission of the open-ring form isomers was hard to characterise precisely because of photochemical conversion reaction during the fluorescence measurements. The fluorescence intensities of the oxidized terarylenes, **1a** and **2a**, were lower than those of the oxidized terarylenes, **3a** and **4a**, which exhibited a weak emission band at 358 nm ( $\Phi_{\rm em} = 0.036$ ) and 451 nm ( $\Phi_{\rm em} = 0.026$ ), respectively. Compounds **1** and **2** can thus act as fluorescence turn-ON molecules with quasi-irreversible and reversible nature, which are worth to be noted as candidates for future applications such as ultra-high resolution bio-imaging with a PALM system, photo-patterned light emitting devices and high density optical memory.

We here briefly discuss the conformation and intramolecular hydrogen bonding in these molecules on the basis of quantum chemical calculations. Fig. 6 shows the most stable structures of 1a and 1b optimized with DFT calculation at the B3LYP/6-31G (d) level. The calculation for 1b well reproduced the structure solved with the X-ray analysis presented in Fig. 2. For example, the twisting angle between phenyl and thiazole rings in the central part is ca. 8.7° in Fig. 6 and ca. 32° in Fig. 2. CH/OS distances of 1b in Fig. 2 were 0.231 nm and 0.239 nm, and those in Fig. 6 were 0.224 nm. The distance between the hydrogen and oxygen was shorter than the sum of van der Waals' radii of each atom (0.26 nm) and indicates hydrogen bonding interaction between the methyl groups and the SO<sub>2</sub> units of side aryl groups in the opposite side of the ring-closed form isomer. These CH/OS hydrogen bonds may make the molecule rather rigid, which might partly contribute to the improved emission nature of oxidized ring-closed forms. It should also be noted that the CH/OS distance was evaluated to be as long as 0.306 nm and 0.311 nm in the optimized structure of 1a (Fig. 6a) even though it is in the quasi- $C_2$  symmetric reactive conformation. That is, the CH/OS hydrogen bonding seems to be invalid in the ring-open form. These results suggest that the CH/OS hydrogen bonding should be broken upon the photo-cycloreversion reaction and excess heat is required for the photochemical reaction from 1b to 1a. As summarized in Table 3, a similar tendency of CH/OS distance was also observed in compounds 2, 3 and 4. For all these compounds, hence, the CH/OS hydrogen bonding can be a possible origin of their suppressed cycloreversion reactivity, although further theoretical and experimental studies are desired for clear understanding. No such specific intramolecular interaction can be seen in corresponding precursor diarylethenes and terarylenes.



**Fig. 6** Optimized molecular structures of **1a** (a) and **1b** (b) calculated by Gaussian 03 at the B3LYP/6-31G(d) level. CH/OS interactions are indicated by dotted lines.

Table 3 CH/OS distance evaluated by DFT calculation

Compound	CH/OS distance/n	m
1a	0.306	0.311
1b	0.224	0.224
2a	0.315	0.310
2b	0.222	0.222
3a	0.390	0.382
3b	0.226	0.225
4a	0.506	0.504
4b	0.223	0.224



Fig. 7 DSC curve of compound 1a.

The present compound 1 was observed to form a transparent uniform film after the removal of solvent from the solution similar to those of amorphous photochromic molecules.<sup>25</sup> We herein studied their thermal properties with DSC for evaluating the glass transition temperature,  $T_{\rm g}$ , which provides principal information about the stability of the amorphous phase. In the DSC profile of 1a presented in Fig. 7, a clear shift in the heat capacity was observed at 80-100 °C which is a characteristic feature of glass transition.  $T_{g}$  of **1a** was evaluated to be 85 °C, from the onset temperature of baseline shift. Below  $T_{\rm g}$ , the molecular motion and crystal growth seem to be frozen making the amorphous state stable. Since the  $T_g$  is markedly higher than the room temperature, compound 1a is expected to form a bulk amorphous film which is stable at room temperature. Purified 1b also formed a stable amorphous film with a  $T_{s}$  of 55 °C, of which DSC profile is presented in Fig. S5<sup>†</sup>. These results suggest that terarylene derivatives having three aryl groups as backbone are suitable for stable amorphous materials.21



**Fig. 8** (a) Absorption and (b) fluorescence spectral changes of the amorphous film of compound 1 upon UV irradiation ( $\lambda = 313$  nm); openforms (dashed lines), closed-forms (bold solid lines), and P.S.S. under irradiation at 313 nm (dotted lines).

**Table 4**Absorption and emission property of compound 1 amorphousfilm

	$\lambda_{\rm max}/{\rm nm}$	$\lambda_{ex}/nm$	$\lambda_{\rm em}/{\rm nm}$	$a_{\rm pss}{}^a$	$\Phi_{ m em}{}^b$
1a	307	n.d. <sup>c</sup>	n.d. <sup>c</sup>	0.74	
1b	331, 500	500	600	—	0.15

<sup>*a*</sup>  $a_{pss}$ : the cyclization conversion ratio at 313 nm light irradiation was estimated by comparing absorbance at P.S.S. with that of **1b**. <sup>*b*</sup> Fluorescent quantum yields of the amorphous state (r.t.). <sup>*c*</sup> Fluorescence was unobserved at room temperature.

Fig. 8 shows absorption and fluorescence spectral changes of a bulk amorphous film of compound 1, whose optical properties are summarized in Table 4. The films were prepared by the spincoating method. Chloroform solutions of original and colored forms of 1 (2.0 mg mL<sup>-1</sup>) were cast onto quartz substrates (20 mm  $\times$  20 mm, thickness = 1 mm). These substrates were spun at 200 rpm for 10 s, then 1600 rpm for 30 s. The absorption spectrum of the original state of the 1a film showed no absorption band in the visible range and also no diffusion tail of lightscattering, indicating high transparency of the film. The transparent film was stable at least for 3 month. The thicknesses of this film was estimated to be about 70 nm, from the peak absorbance at 307 nm by assuming that its extinction coefficient and volume density are similar to those in solution phase and in crystals, respectively.<sup>23</sup> The **1a** film turned to pale orange in color after UV light irradiation, which shows progression of an absorption band at 500 nm. A clear isosbestic point was observed at about 307 nm supporting the two-component photochromic reaction also in the amorphous state. This spectral change was effectively irreversible and no spectral change can be observed under visible light irradiation. The maximum conversion ratio from 1a to 1b was about 74%, which was evaluated by comparing absorbance at 500 nm with that of a film prepared from pure 1b after normalized at the isosbestic point. Since 1b showed almost no photobleaching reaction, this maximum conversion must be 100% if all molecules would be uniformly photoreactive. It thus suggests that about 26% of the molecules in the amorphous film are not reactive for the photocyclization reaction. Such distribution of reactivity in the amorphous film would be attributed to fixed molecular conformations with different photo-reactivities. Since the central hexatriene structure must be in the  $C_2$ symmetric conformation for the photocyclization reaction, some of the molecules in non- $C_2$  symmetric conformation might be responsible for the decreased P.S.S. conversion ratio. Intermolecular interaction such as excited state energy transfer and



**Fig. 9** Photographs of the (a) visible and (b) emission pattern formed on the amorphous film of 1 (image size:  $2.2 \text{ mm} \times 3.4 \text{ mm}$ ).

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electron transfer might also be possible origins of the suppressed reactivity.

The emission band at 600 nm under excitation at 500 nm continuously increased with the progressive conversion of **1a** to **1b** upon UV irradiation in the film (Fig. 8b). The emission intensity at P.S.S. was completely maintained even after continuous irradiation at 500 nm for 4 h. The colored film showed an emission quantum yield of about 15% as also summarized in Table 4.

Fig. 9 shows a typical example of optical patterns formed on the amorphous film of **1a** by irradiating with UV light ( $\lambda = 330$ – 385 nm) through a patterned photomask (Edmund Optics, quartz test-target 1951 USAF). The irradiated area turned pale orange in apparent color and emissive in orange. Compound **1** can afford a high contrast optical pattern on the amorphous film of about 70 nm and its emission intensity is stable for continuous excitation with visible light, which made it a candidate for future write-once optical recording medium.

## Conclusions

We reported here three novel photochromic compounds **1**, **2** and **3** with relatively high fluorescence efficiencies,  $\Phi_{\rm em} = 0.34$ , 0.36, and 0.036, respectively, in their colored isomers. The extremely low photo-cycloreversion reactivity ( $\Phi_{\rm co} < 10^{-4}$ ) was found in the compounds **1** and **3** having phenylthiophene-*S*,*S*-dioxide-3-yl groups, whose photoisomerization reactions are almost irreversible.

The oxidized terarylene **1** forms a stable amorphous state with relatively high glass transition temperature. Optical formation of high contrast fluorescent patterning on the bulk amorphous film was demonstrated, which has substantial stability for continuous excitation with visible light. Present results demonstrate a characteristic feature of oxidized terarylenes suitable for forming amorphous materials with clear fluorescence turn-on switching capability.

After submission of the present manuscript, similar compounds were independently reported by Prof. Irie and coworkers, which are based on oxidized diarylethenes having ethyl groups at the reaction center carbon atoms and also showing relatively large fluorescence quantum yield in the closed form.<sup>26</sup>

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- 22 <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>/TMS) chemical shifts for **1b**:  $\delta$  (ppm) = 7.99–8.01 (2H, d), 7.48–7.66 (13H, m), 2.68 (3H, s), 2.39 (3H, s), 1.92–1.93 (6H, d). For **2b**:  $\delta$  (ppm) = 8.93–8.95 (1H, d), 8.13–8.15 (2H, d), 7.93–8.00 (2H, qual), 7.78–7.84 (3H, m), 7.58–7.69 (5H, m), 1.912 (6H, d). For **3b**:  $\delta$  (ppm) = 7.61–7.65 (4H, m), 7.53–7.55 (6H, m), 2.35 (6H, s), 1.85 (6H, s).
- 23 Crystallographic data for 1b: C<sub>33</sub>H<sub>27</sub>NO<sub>4</sub>S<sub>3</sub>, M = 597.76, monoclinic, a = 8.0132(8) Å, b = 17.357(2) Å, c = 20.210(2) Å, α = 90.0000°,
- $β = 93.007(2)^\circ$ ,  $γ = 90.0000^\circ$ , V = 2807.0(5) Å<sup>3</sup>, T = 123.1 K, space group P21/c (#14), Z = 4, μ(MoKα) = 0.305 mm<sup>-1</sup>, 22.307 reflections measured, 5129 independent reflections ( $R_{int} = 0.068$ ). The final  $R_1$  values were 0.1002 ( $I > 2\sigma(I)$ ). The final wR( $F^2$ ) values were 0.2638 (all data). The goodness of fit on  $F^2$  was 1.072. CCDC 829809,  $D_{calc} = 1.414$  g cm<sup>-3</sup>. Crystallographic data for **3b**: C<sub>29</sub>H<sub>22</sub>F<sub>6</sub>O<sub>4</sub>S<sub>2</sub>, M = 612.60, monoclinic, a = 7.9909(3) Å, b =26.7793(10) Å, c = 13.2356(6) Å,  $α = 90.0000^\circ$ ,  $β = 110.4300(12)^\circ$ ,  $γ = 90.0000^\circ$ , V = 2654.17(18) Å<sup>3</sup>, T = 123.1 K, space group P21/c (#14), Z = 4, μ(MoKα) = 0.279 mm<sup>-1</sup>, 21 554 reflections measured, 4861 independent reflections ( $R_{int} = 0.053$ ). The final  $R_1$  values were 0.0386 ( $I > 2\sigma(I)$ ). The final wR( $F^2$ ) values were 0.0886 (all data). The goodness of fit on  $F^2$  was 1.052. CCDC 829811,  $D_{calc} = 1.533$  g cm<sup>-3</sup>.
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