

# Single-crystalline photochromism of diarylethene dimers bridged by a spiro structure

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**ABSTRACT:** New types of diarylethene dimers bridged by a spiro structure were synthesized. One of their dimers formed three kinds of polymorphic forms by recrystallization from different solvents: hexane (**1a- $\alpha$** ), acetone (**1a- $\beta$** ), and acetonitrile (**1a- $\gamma$** ). In crystals of **1a- $\alpha$**  and **1a- $\beta$**  the molecules are packed in solvent-free crystal structures, whereas crystal **1a- $\gamma$**  includes acetonitrile molecules in the crystal. The difference of significant photochromic reactivities in their polymorphic crystals was observed for photocoloration reactions. Crystals **1a- $\beta$**  and **1a- $\gamma$**  showed photochromism in the single-crystal phase, but **1a- $\alpha$**  did not do so. Their photochromic reactivity was found to depend on the distance between the reactive carbon atoms by X-ray crystallographic analysis. When the distance is less than 4.2 Å in the antiparallel conformation, the molecule can undergo photochromism in the crystal. On the other hand, crystals of bromo-substituted diarylethene dimer (**2a**) cannot be suitable for X-ray crystallographic analysis when it was recrystallized from hexane, acetone, and acetonitrile. However, it formed single crystal by recrystallization from *p*-xylene, which showed photochromism in the crystalline phase. The edge-to-face aromatic interaction between *p*-xylene molecules assisted the crystal growth of the diarylethene dimer. Upon irradiation with ultraviolet light, two kinds of the enantiomers, (*M,SS*)- and (*P,RR*)-**2b**, are produced. Partial photobleaching reactions of either of the two enantiomers by irradiation with linearly polarized visible light were confirmed by polarized absorption spectroscopy. Copyright © 2007 John Wiley & Sons, Ltd.

**KEYWORDS:** photochromism; crystal; diarylethene; dimer; enantiomer

## INTRODUCTION

Photochromism is referred to as a photochemical reversible transformation of a chemical species between two isomers having different absorption spectra.<sup>1,2</sup> Although many types of photochromic compounds have been reported so far, crystals that show photochromic reactions in the crystal are very rare.<sup>3</sup> Typical examples of photochromic crystals are paracyclophanes,<sup>4</sup> triaryl-limidazole dimer,<sup>5,6</sup> diphenylmaleronitrile,<sup>7</sup> aziridines,<sup>8</sup> 2-(2,4-dinitrobenzyl)pyridine,<sup>9–12</sup> *N*-salicylideneanilines,<sup>13–15</sup> and triazenes.<sup>16</sup> In the most cases of photochromic crystals, the photogenerated isomers are thermally unstable and return to the initial isomers even in the dark. Some of diarylethene derivatives undergo thermally

stable and fatigue-resistant photochromic reactions even in the single-crystalline phase.<sup>17–33</sup> The photochromic diarylethene crystals have the following characteristic properties and functions: (1) The photogenerated colored crystals exhibit dichroism under polarized light;<sup>18,19</sup> (2) The conformations in the crystals strongly affect photocyclization and photocycloreversion quantum yields;<sup>24–26</sup> (3) Single-crystalline photochromism induces reversible nano-scale surface morphological changes;<sup>22</sup> and (4) Photochromic diarylethene crystals have potential applications to high-density three-dimensional optical memory media,<sup>23,34</sup> optical switches,<sup>35</sup> and color displays.<sup>27,28,32</sup>

Diarylethenes have two stable conformations with the two thiophene rings in mirror symmetry (parallel conformation) and in C<sub>2</sub> symmetry (antiparallel conformation).<sup>17</sup> They are in equilibrium each other in solution. The photocyclization reaction can proceed only from the antiparallel conformation. In crystals, their conformations are fixed. In most cases, they are oriented in the antiparallel or parallel conformation. Diarylethenes fixed in the parallel conformation in crystal cannot exhibit

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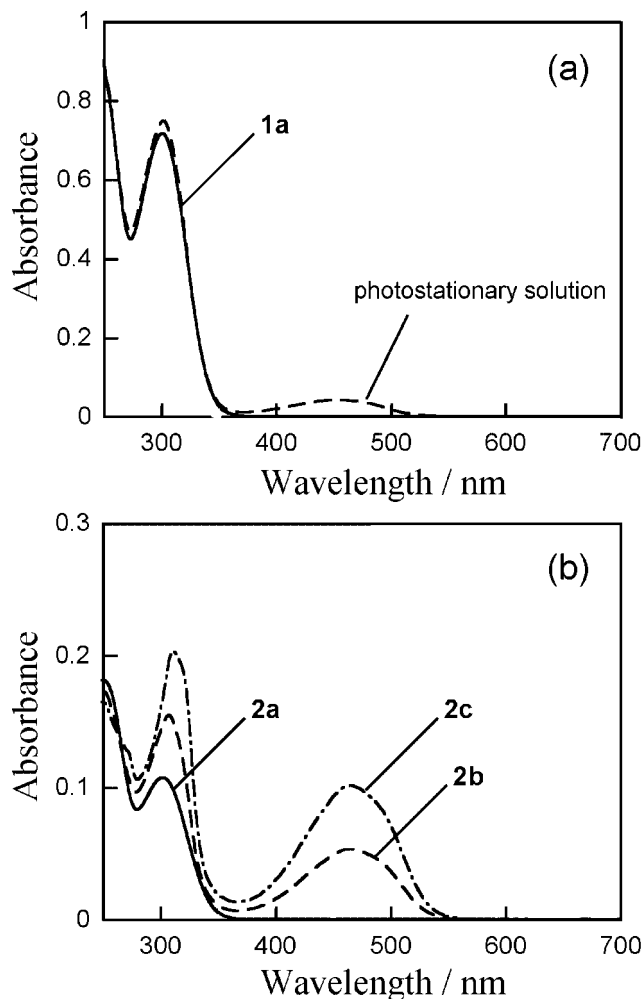
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any photochromism. Even in the antiparallel conformation diarylethenes cannot undergo photochromism in crystal if the distance between the reacting carbons of the diarylethene is longer than 4.2 Å.<sup>25</sup> Molecules which are packed in the antiparallel conformation with the distance shorter than 4.2 Å can undergo photochromism. Some of diarylethene dimers in which two diarylethenes are combined with ethene parts are reported.<sup>36,37</sup> However, no research in the crystalline phase has been reported yet. Here, we report on single-crystalline photochromism of novel diarylethene dimers (**1a** and **2a**, as shown in Scheme 1). We found that **1a** formed three kinds of polymorphic forms recrystallized from different solvents. Their polymorphic forms showed different photochromic reactivity. Furthermore, the dimer molecules in crystal **2a** including *p*-xylene molecules were noticed that they were packed in particular molecular structures.

## RESULTS AND DISCUSSION

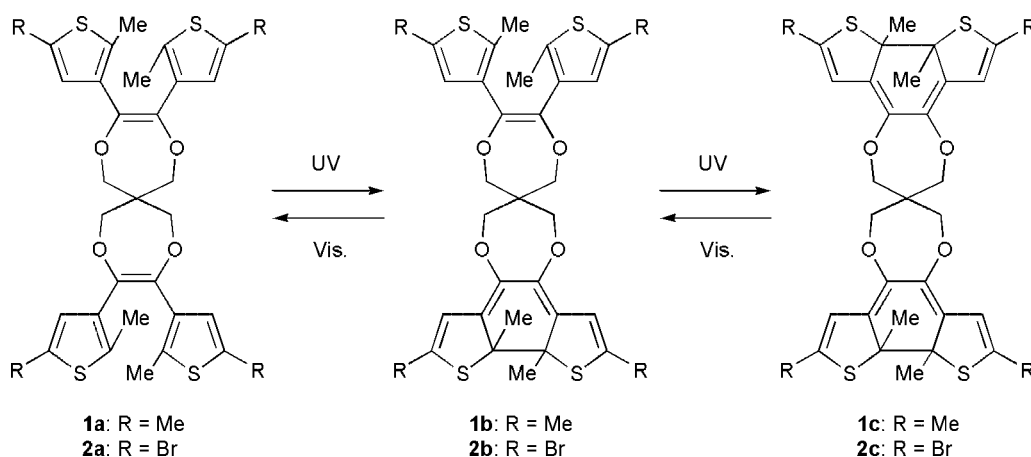
### Photochromism in solution

Diarylethene dimers **1a** and **2a** undergo photochromic reactions in hexane. Figure 1a shows absorption spectra of **1a** and the photostationary solution upon irradiation with 313-nm light. The hexane solution of **1a** was colorless and the color changed to yellow upon irradiation with 313-nm light. The colored solution has absorption maximum at 452 nm and returned to the initial colorless solution by irradiation with visible light. The low absorption intensity at 452 nm in the photostationary state indicates that the photocycloreversion quantum yield is larger than the photocyclization quantum yield. Dimer **2a** also showed similar spectral changes. Figure 1b shows absorption spectra of **2a**, **2b**, and **2c** in hexane, which were isolated by HPLC. Photochromic reaction of **2a** in hexane proceeded to **2b** in 16% conversion and **2c** in 0.6% conversion upon irradiation with 313-nm light. The low conversion is ascribed to the



**Figure 1.** Absorption spectra of (a) **1a** ( $4.3 \times 10^{-5}$  M) and the photostationary solution under irradiation with 313-nm light and (b) **2a**, **2b**, and **2c** ( $6.5 \times 10^{-6}$  M) in hexane

fact that the photocycloreversion quantum yield is larger than the photocyclization quantum yield. **2b** and **2c** have a same absorption maximum at 465 nm. Absorption coefficient of **2c** ( $\epsilon_{465} = 15700 \text{ M}^{-1} \text{ cm}^{-1}$ ) is twice as



**Scheme 1.** Photochromic reactions of diarylethene dimers, **1a** and **2a**

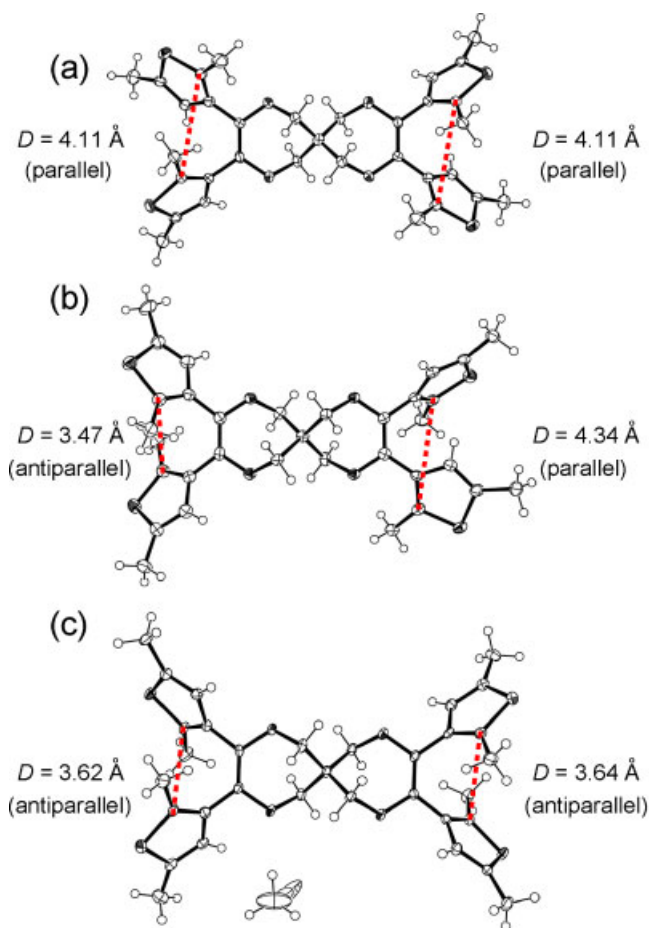
large as that of **2b** ( $\epsilon_{465} = 8300 \text{ M}^{-1} \text{ cm}^{-1}$ ) at 465 nm. There is no intramolecular interaction between two diarylethene chromophores in the dimer molecule. This indicates that two diarylethene chromophores independently undergo the photocyclization reaction.

### Polymorphism and single-crystalline photochromism of **1a**

Dimer **1a** was recrystallized from hexane, acetone, and acetonitrile solutions. Each crystal has different crystal shapes, which are named as **1a- $\alpha$** , **1a- $\beta$** , and **1a- $\gamma$** , respectively. X-ray crystallographic analysis of the crystals was carried out to confirm the polymorphic forms, and the resulting crystallographic data are shown in Table 1.

The crystal of **1a- $\alpha$**  belongs to monoclinic  $C2$ ,  $Z=2$ . The density was  $1.300 \text{ g cm}^{-3}$ . The ORTEP drawing of **1a- $\alpha$**  is shown in Fig. 2a. Half of the molecules were crystallographically independent. Therefore, two diarylethene units are in the same conformation. They are oriented in the parallel conformation, which indicates a non-reactive conformation for the photochromic reaction.

The crystal of **1a- $\beta$**  had a crystal system of monoclinic, a space group of  $C2/c$ , and  $Z=8$ . The density was  $1.335 \text{ g cm}^{-3}$ . The molecules are packed denser than those in **1a- $\alpha$** . Figure 2b shows the ORTEP drawing of **1a- $\beta$** . Two diarylethene units have different conformations. One of them is in an antiparallel conformation with a distance between the reactive carbons ( $D$ ) of  $3.47 \text{ \AA}$ . This has a possibility to undergo photochromic reaction in the crystalline phase.<sup>25</sup> On the other hand, the other diarylethene unit has a parallel conformation, which cannot undergo any photochromic reaction in the crystalline phase. Therefore, only half of the diarylethene



**Figure 2.** ORTEP drawings of (a) **1a- $\alpha$** , (b) **1a- $\beta$** , and (c) **1a- $\gamma$**  showing 50% probability displacement ellipsoids. The broken lines showed the distance between the reacting carbons ( $D$ ). This figure is available in colour online at [www.interscience.wiley.com/journal/poc](http://www.interscience.wiley.com/journal/poc)

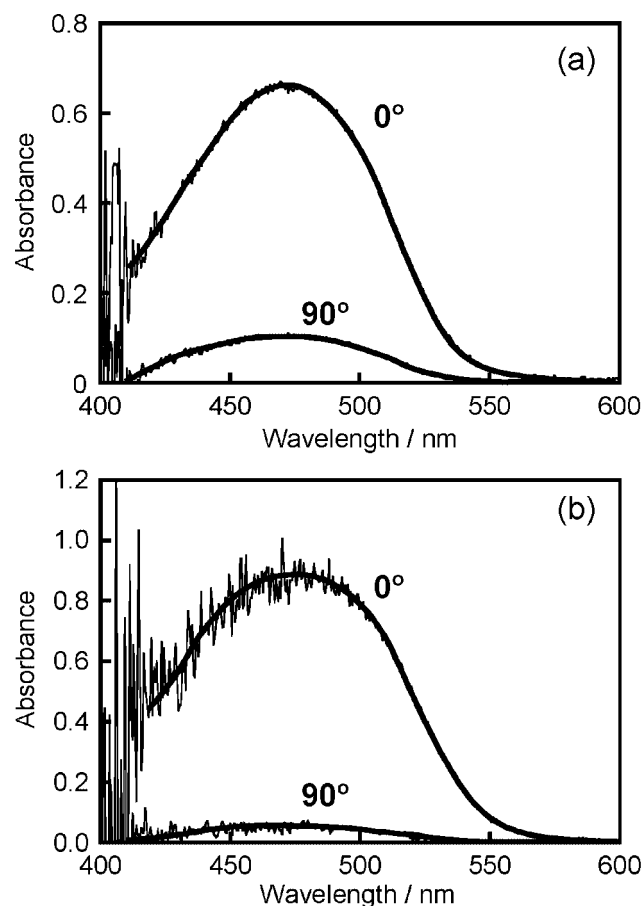
**Table 1.** X-ray crystallographic data of **1a- $\alpha$** , **1a- $\beta$** , **1a- $\gamma$** , and **2a**

|                               | <b>1a-<math>\alpha</math></b>                    | <b>1a-<math>\beta</math></b>                     | <b>1a-<math>\gamma</math></b>                                                       | <b>2a</b>                                                                                  |
|-------------------------------|--------------------------------------------------|--------------------------------------------------|-------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------|
| Recrystallization solvent     | Hexane                                           | Acetone                                          | Acetonitrile                                                                        | <i>p</i> -Xylene                                                                           |
| Formula                       | $\text{C}_{33}\text{H}_{36}\text{O}_4\text{S}_4$ | $\text{C}_{33}\text{H}_{36}\text{O}_4\text{S}_4$ | $\text{C}_{33}\text{H}_{36}\text{O}_4\text{S}_4 \cdot \text{C}_2\text{H}_3\text{N}$ | $\text{C}_{29}\text{H}_{24}\text{Br}_4\text{O}_4\text{S}_4 \cdot 2\text{C}_8\text{H}_{10}$ |
| $T$ (K)                       | 118 (2)                                          | 123 (2)                                          | 123 (2)                                                                             | 148 (2)                                                                                    |
| $M$                           | 624.90                                           | 624.90                                           | 665.95                                                                              | 1096.68                                                                                    |
| Crystal system                | Monoclinic                                       | Monoclinic                                       | Monoclinic                                                                          | Orthorhombic                                                                               |
| Space group                   | $C2$                                             | $C2/c$                                           | $P2_1/c$                                                                            | $Pna2_1$                                                                                   |
| $a$ (Å)                       | 17.700 (6)                                       | 39.982 (12)                                      | 9.720 (2)                                                                           | 9.035 (4)                                                                                  |
| $b$ (Å)                       | 6.024 (2)                                        | 10.129 (3)                                       | 11.047 (3)                                                                          | 16.712 (8)                                                                                 |
| $c$ (Å)                       | 15.376 (5)                                       | 15.373 (5)                                       | 32.017 (7)                                                                          | 30.395 (15)                                                                                |
| $\alpha$ (°)                  | 90                                               | 90                                               | 90                                                                                  | 90                                                                                         |
| $\beta$ (°)                   | 103.232 (5)                                      | 92.684 (5)                                       | 94.271 (4)                                                                          | 90                                                                                         |
| $\gamma$ (°)                  | 90                                               | 90                                               | 90                                                                                  | 90                                                                                         |
| Volume (Å <sup>3</sup> )      | 1595.9 (9)                                       | 6219 (3)                                         | 3428.3 (14)                                                                         | 4589 (4)                                                                                   |
| $Z$                           | 2                                                | 8                                                | 4                                                                                   | 4                                                                                          |
| Density (g cm <sup>-3</sup> ) | 1.300                                            | 1.335                                            | 1.290                                                                               | 1.587                                                                                      |
| $R1$ ( $I > 2\sigma(I)$ )     | 0.0577                                           | 0.0698                                           | 0.0548                                                                              | 0.0347                                                                                     |
| $wR2$ (all data)              | 0.2329                                           | 0.2220                                           | 0.1804                                                                              | 0.0725                                                                                     |
| Absolute structure parameter  | 0.09 (18)                                        | —                                                | —                                                                                   | 0.013 (6)                                                                                  |

units can participate in the photochromic reaction in the crystal.

The crystal of **1a-γ** had a crystal system of monoclinic, space group of  $P2_1/c$ , and  $Z=4$ . The density was  $1.290\text{ g cm}^{-3}$ . Figure 2c shows the ORTEP drawing of **1a-γ** in which an acetonitrile molecule is included. The two diarylethene units are in both antiparallel conformations. The distances between the reactive carbons are 3.62 and 3.64 Å, which are short enough to undergo photochromic reactions.<sup>25</sup> Crystals **1a-α**, **1a-β**, and **1a-γ** were found to be polymorphic forms by X-ray crystallographic analysis.

Single-crystalline photochromism of **1a-α**, **1a-β**, and **1a-γ** was examined using polarizing microscope upon irradiation with UV light. Crystal **1a-α** did not exhibit any color change upon irradiation with 366-nm light. This is ascribed to the parallel conformations for both diarylethene units. Crystals **1a-β** and **1a-γ** exhibited color change to orange upon irradiation with 366-nm light. The polarized absorption spectra of the colored crystals were measured using a polarizing microscopy under parallel polarizer and analyzer. Figure 3 shows polarized absorption spectra of the colored crystals. The absorption intensity dramatically changed when the sample stage was rotated as much as 90°. This indicates that the



**Figure 3.** Absorption spectra of the colored crystals of (a) **1a-β** and (b) **1a-γ** under polarized light. 0° denotes the direction of maximum absorption intensity

**Table 2.** Photochromic reactivity of the diarylethene dimers

| Crystal               | Distance (L) <sup>a</sup> /Å | Photochromism <sup>b</sup> | $\lambda_{\text{max}}$ <sup>c</sup> /nm |
|-----------------------|------------------------------|----------------------------|-----------------------------------------|
| <b>1a-α</b>           | 4.11, 4.11                   | No                         | —                                       |
| <b>1a-β</b>           | 3.47, 4.34                   | Yes                        | 470                                     |
| <b>1a-γ</b>           | 3.62, 3.64                   | Yes                        | 480                                     |
| <b>2a<sup>d</sup></b> | 3.53, 3.68                   | Yes                        | 480                                     |

<sup>a</sup> Distance between the reacting carbon atoms.

<sup>b</sup> Photochromism in crystal.

<sup>c</sup> Absorption maxima of the photogenerated colored crystal.

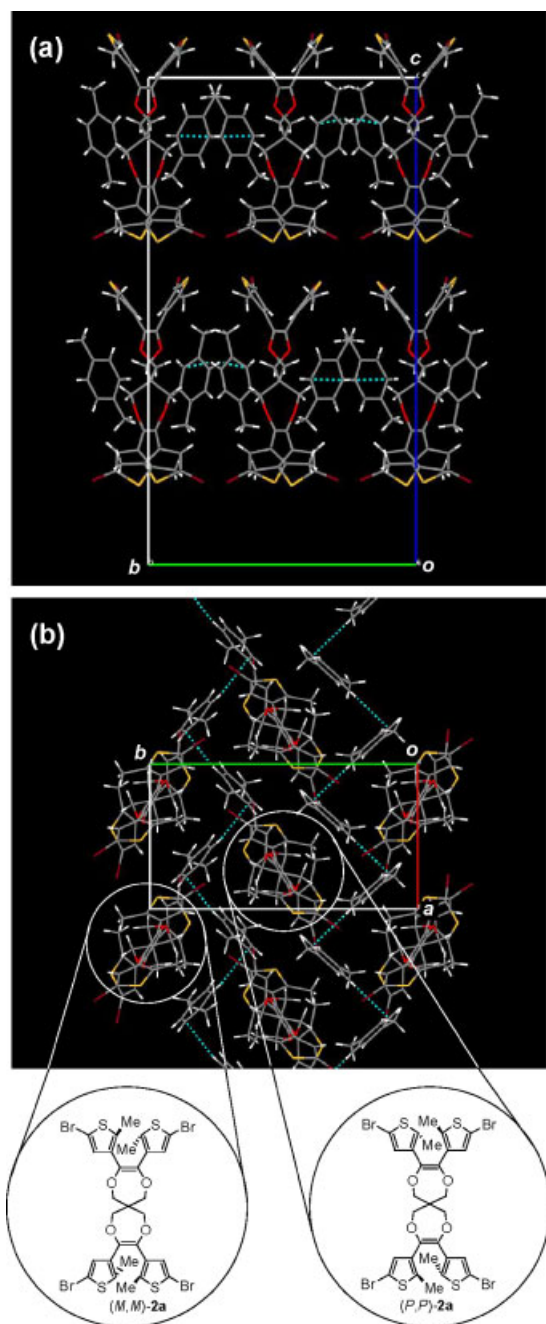
<sup>d</sup> Recrystallized from *p*-xylene.

molecules are regularly oriented in the crystal. If the cyclization reaction proceeded in an amorphous phase, the color intensity change should not be observed by rotating the sample stage of the microscope. The absorption anisotropy was observed for both **1a-β** and **1a-γ**. The dichroism under polarized light clearly indicates that the photochromic reaction took place in the crystal lattice.

Table 2 shows absorption maxima of the photogenerated colored crystals. The closed-ring isomer in crystal **1a-β** has an absorption maximum at 470 nm. On the other hand, the closed-ring isomer in crystal **1a-γ** has an absorption maximum at 480 nm. The shift of the absorption maximum between the two colored crystals is ascribed to the difference of the strained structure of the closed-ring forms arising from the different conformations of the open-ring forms.<sup>26,38</sup>

### Crystal growth assisted by *p*-xylene and single-crystalline photochromism of the crystal

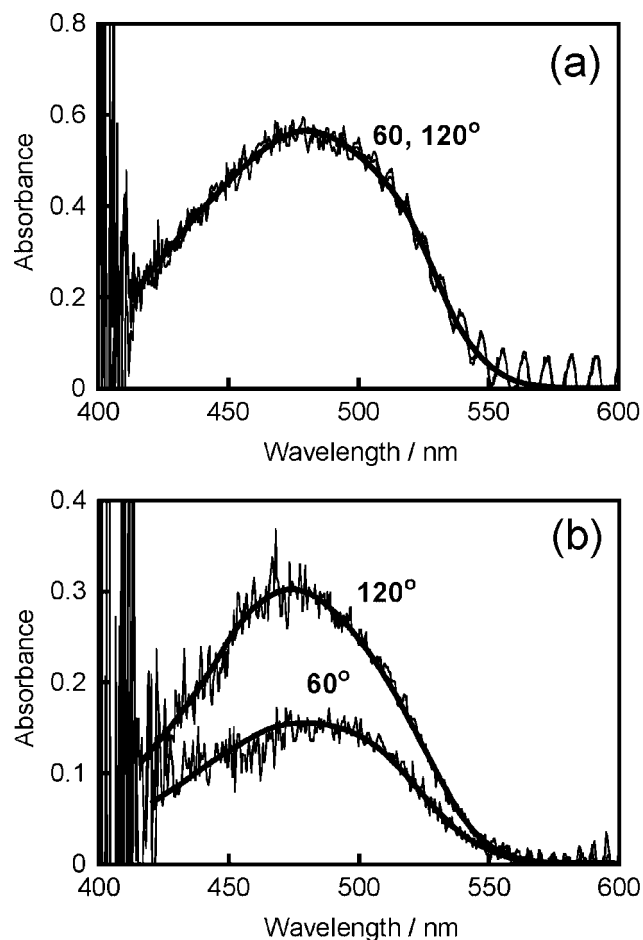
Dimer **2a** was recrystallized from hexane, acetone, and acetonitrile solutions. However, well-developed single crystal for X-ray analysis was not obtained. When **2a** was recrystallized from *p*-xylene, well-developed single crystals were obtained. X-ray crystallographic analysis of the crystal indicates that the crystal includes *p*-xylene molecules, as shown in Fig. 4. Dimer **2a** formed co-crystals with *p*-xylene (1:2). The edge-to-face aromatic interaction between *p*-xylene molecules led to form a one-dimensional chain. The contact lengths of C...H in the interaction were 2.79 and 2.88 Å. The chain is arranged parallel to the *a*-axis. The molecules of **2a** are packed into the *p*-xylene chain to chain. The presence of *p*-xylene assisted the crystal growth of **2a**. The distances between the reacting carbon atoms in the diarylethene parts were 3.53 and 3.68 Å. It indicates that **2a** can undergo photochromism in the crystal. Two diarylethene parts in the dimer have the same helical structures. In other words, the molecules are fixed into either (*M,M*)-**2a** or (*P,P*)-**2a**, which are oriented perpendicular each other. (*M,P*)-**2a** was not present in the crystal. When crystal **2a** was irradiated with 366-nm light, the color of the crystal changed from colorless to yellow. The colored forms are



**Figure 4.** Molecular packing diagram of crystal **2a** viewed along (a) *a*-axis and (b) *c*-axis. *a* and *b* correspond to diagram viewed normal to (100) and (001) faces, respectively. This figure is available in colour online at [www.interscience.wiley.com/journal/poc](http://www.interscience.wiley.com/journal/poc)

due to the production of (*M,SS*)-**2b** and (*SS,SS*)-**2c** from (*M,M*)-**2a** or (*P,RR*)-**2b** and (*RR,RR*)-**2c** from (*P,P*)-**2a**. Figure 5a shows absorption spectra of the colored crystal. The absorption maximum of the closed-ring form in crystal **2a** was observed at 480 nm.

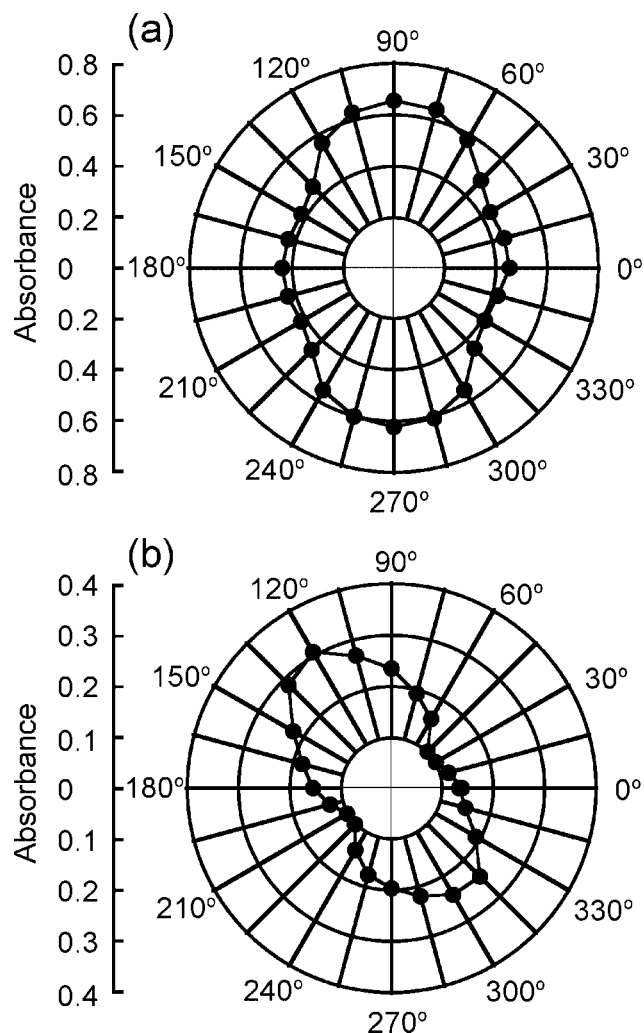
The molecular packing of the diarylethene dimer viewed normal to the (001) face as shown in Fig. 4b indicates that the long axes of the diarylethene chromophores in the dimer are aligned at an angle of *ca.* 60° to each other. This suggests that linearly polarized



**Figure 5.** Polarized absorption spectra of the colored crystal of **2a** on the (001) face (a) before and (b) after the partial bleaching reaction upon irradiation with polarized visible light at the angle of 30°. 0° denotes the direction along with *a*-axis

light can selectively isomerize the closed-ring forms to the open-ring forms. A colorless dimer crystal was irradiated with non-polarized 366-nm light to give a yellow-colored crystal. When the crystal was irradiated with linearly polarized light ( $\lambda > 450$  nm) in the direction of 30°, the colored forms along the polarized light were preferentially bleached and the molecules oriented perpendicularly to the irradiated polarized light remained. The polarized absorption spectra and the polar plots after partial bleaching are shown in Figs 5b and 6b. The polar plots show the partial bleaching reactions took place under the polarized light in the crystal. The order parameter  $((A_{\parallel} - A_{\perp}) / (A_{\parallel} + 2A_{\perp}))$  was determined to be 0.37 after partial bleaching. The partial photobleaching reactions are expected to produce selectively either of the two enantiomers (*M,SS*)- or (*P,RR*)-**2b** at the low conversion by irradiation with polarized light, as shown in Scheme 2.

In conclusion, we synthesized novel two kinds of diarylethene dimers bridged by a spiro structure. The diarylethene dimers underwent photochromism in solution and even in the single-crystalline phase. One



**Figure 6.** Polar plots of absorbance at 480 nm in Fig. 5 (a) before and (b) after the partial bleaching reaction upon irradiation with polarized visible light at the angle of 30°. 0° denotes the direction along with *a*-axis

of their dimers formed polymorphic forms. The photochromic reactivity in the polymorphic crystals depended on the conformation of the diarylethene units. Either of the two enantiomers ((*M,SS*)- or (*P,RR*)-**2b**) was produced by partial bleaching reactions of the colored crystal including both enantiomers by irradiation with linearly polarized visible light. Although the formation of diastereomers and enantiomers of diarylethene closed-ring isomers in the crystal has been so far reported,<sup>39–43</sup> our present work can selectively produce either of the two enantiomers by partial bleaching reactions using linearly polarized visible light.

## EXPERIMENTAL

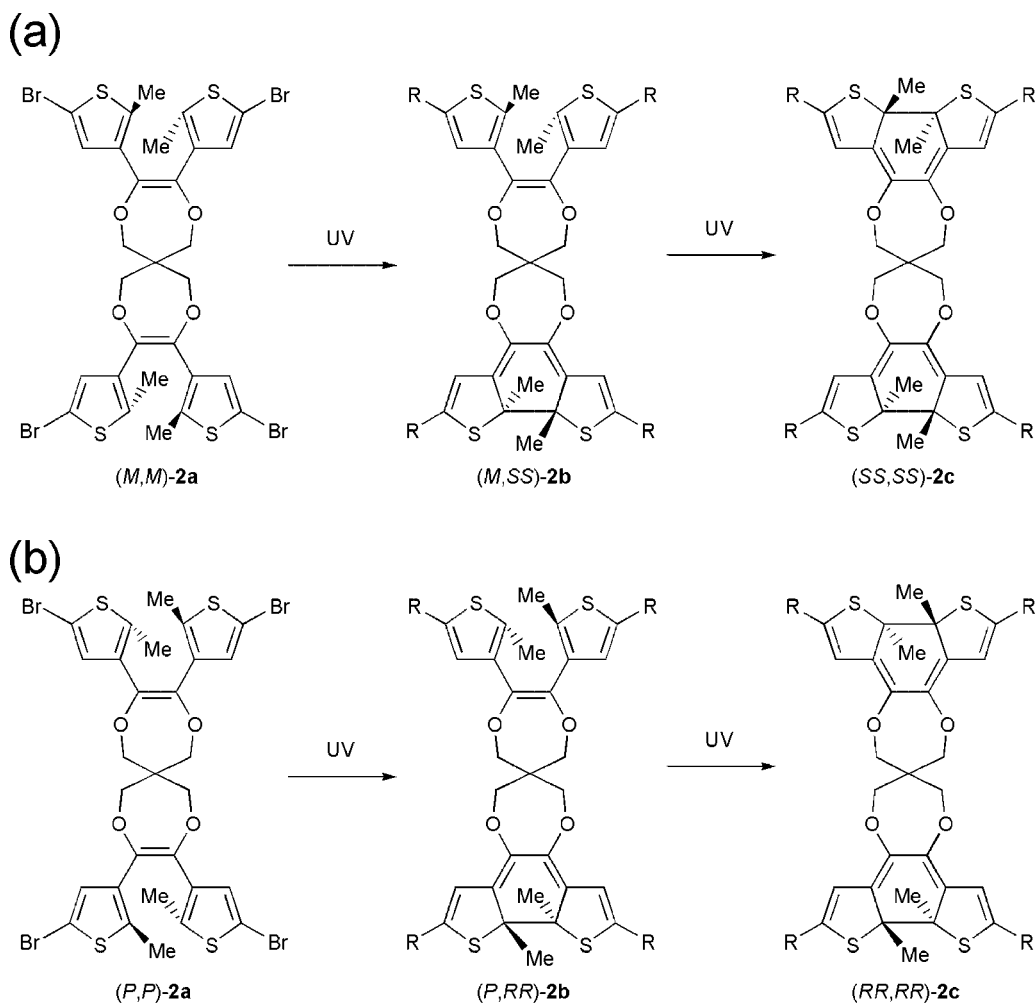
### General

<sup>1</sup>H NMR spectra were recorded on a Varian Gemini 200 spectrometer (200 MHz). Tetramethylsilane was used as an internal standard. Mass spectra were taken with a

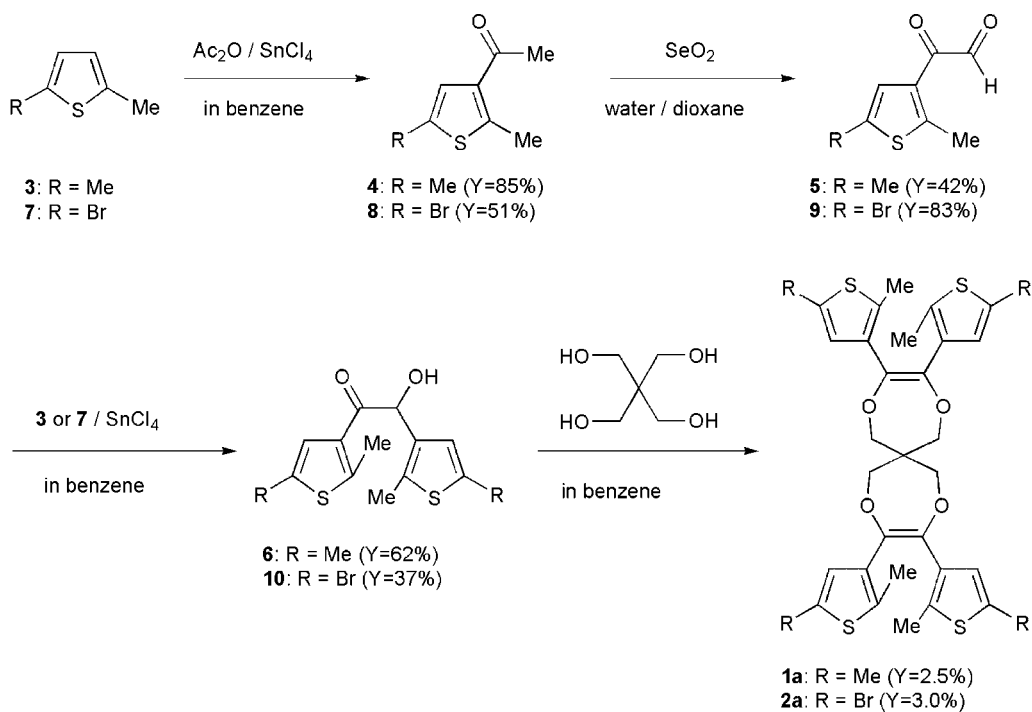
Shimadzu GCMSQP5050A mass spectrometer. Absorption spectra in a solution were measured with a Hitachi U-3410 absorption spectrophotometer. Absorption spectra in a single-crystalline phase were measured using a Leica DMLP polarizing microscope connected with a Hamamatsu PMA-11 detector. The polarizer and analyzer were set parallel to each other. Photoirradiation was carried out using a USHIO 500-W high-pressure mercury lamp or a xenon lamp attached to the microscope. Monochromatic light was obtained by passing the light through a monochromator (Ritsu MV-10N) or a band pass filter. X-ray crystallographic analysis was carried out using a Bruker SMART CCD X-ray diffractometer.

Diarylethene dimers (**1a** and **2a**) were synthesized according to the routes shown in Scheme 3. 3-Acetyl-2,5-dimethylthiophene (**4**) was prepared by a reaction of 2,5-dimethylthiophene (15 g; 0.13 mol) with acetic anhydride (14 ml; 0.15 mol) in the presence of Tin(IV) chloride (21 ml; 0.18 mol) in benzene (130 ml) for 2 h at room temperature in 85% yield.<sup>36,44</sup> (2,5-Dimethyl-3-thienyl)oxoacetaldehyde (**5**) was prepared by a reaction of selenium dioxide (5.0 g; 45 mmol) in dioxane (30 ml) and water (1.4 ml) with **4** (5.0 g; 32 mmol) for 5 h at 105°C in 42% yield.<sup>36,44</sup> 1,2-Bis(2,5-dimethyl-3-thienyl)-2-hydroxyethanone (**6**) was prepared by a reaction of 2,5-dimethylthiophene (3.2 g; 29 mmol) with **5** (4.0 g; 24 mmol) in the presence of Tin(IV) chloride (6.0 ml; 51 mmol) in benzene for 12 h at room temperature in 62% yield.<sup>36,44</sup> Dimer **1a** was synthesized by reaction of **6** (1.0 g; 3.6 mmol) with pentaerythritol (160 mg; 1.2 mmol) in the presence of *p*-toluenesulfonic acid (20 mg) in benzene refluxing using Dean–Stark condenser for 22 h. The product was carefully purified by column chromatography (hexane/ethyl acetate = 9/1) and separative high performance liquid chromatography, and was obtained in 2.5% yield. <sup>1</sup>H-NMR (200 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.96 (s, 12H, CH<sub>3</sub>), 2.31 (s, 12H, CH<sub>3</sub>), 4.22 (s, 8H, CH<sub>2</sub>O), 6.39 (s, 4H, Ar); *m/z* = 624 (M<sup>+</sup>); Anal. Calc. for C<sub>33</sub>H<sub>36</sub>O<sub>4</sub>S<sub>4</sub>: C, 63.43; H, 5.81. Found: C, 63.40; H, 5.85%.

3-Acetyl-2-bromo-5-methylthiophene (**8**) was prepared by a reaction of 2-bromo-5-methylthiophene (2.0 g; 11 mmol) with acetic anhydride (1 ml; 11 mmol) in the presence of Tin(IV) chloride (1.8 ml; 15 mmol) in benzene (12 ml) for 3 h at room temperature in 51% yield. (200 MHz, CDCl<sub>3</sub>)  $\delta$  = 2.46 (s, 3H, CH<sub>3</sub>), 2.66 (s, 3H, CH<sub>3</sub>), 7.29 (s, 1H, Ar); MS *m/z* = 218 (M<sup>+</sup>). (5-Bromo-2-methyl-3-thienyl)oxoacetaldehyde (**9**) was prepared by a reaction of selenium dioxide (1.3 g; 12 mmol) in dioxane (10 ml) and water (0.3 ml) with **8** (1.0 g; 4.6 mmol) for 5 h at 105°C in 83% yield. <sup>1</sup>H-NMR (200 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.75 (s, 3H, CH<sub>3</sub>), 7.81 (s, 1H, Ar), 9.47 (s, 1H, CHO); MS *m/z* = 232 (M<sup>+</sup>). 1,2-Bis(5-bromo-2-methyl-3-thienyl)-2-hydroxyethanone (**10**) was prepared by a reaction of 2-bromo-5-methylthiophene (0.73 g; 4.1 mmol) with **9** (0.6 g; 2.6 mmol) in the presence of Tin(IV) chloride (0.48 ml;



**Scheme 2.** Photochromic reaction scheme of *M*-helical **2a** ((*M,M*)-**2a**) and *P*-helical **2a** ((*P,P*)-**2a**), and their photogenerated isomers



**Scheme 3.** Synthetic routes of **1a** and **2a**

4.1 mmol) in benzene for 12 h at room temperature in 37% yield.  $^1\text{H-NMR}$  (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 2.52 (s, 3H,  $\text{CH}_3$ ), 2.73 (s, 3H,  $\text{CH}_3$ ), 4.34 (d,  $J$  = 5.7 Hz, 1H,  $\text{CH-OH}$ ), 5.51 (d,  $J$  = 5.7 Hz, 1H,  $\text{CH-OH}$ ), 6.61 (s, 1H, Ar), 6.94 (s, 1H, Ar). Dimer **2a** was synthesized by reaction of **10** (0.39 g; 0.95 mmol) with pentaerythritol (40 mg; 0.29 mmol) in the presence of *p*-toluenesulfonic acid (10 mg) in benzene refluxing using Dean-Stark condenser for 26 h. The product was carefully purified by column chromatography (hexane/ethyl acetate = 9/1) and separative high performance liquid chromatography, and was obtained in 3.0% yield.  $^1\text{H-NMR}$  (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 2.00 (s, 12H,  $\text{CH}_3$ ), 4.21 (s, 8H,  $\text{CH}_2\text{O}$ ), 6.70 (s, 4H, Ar); MS  $m/z$  = 880 ( $\text{M}^+$ ); Anal. Calc. for  $\text{C}_{33}\text{H}_{36}\text{O}_4\text{S}_4$ : C, 39.38; H, 2.74. Found: C, 39.48; H, 2.72%. Dimers **2b** and **2c** were isolated by passing a photostationary solution containing **2a**, **2b**, and **2c** through a HPLC (Hitachi L-6250 HPLC system, silica gel column, hexane/ethyl acetate (97:3) as the eluent). **2b**:  $^1\text{H-NMR}$  (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 1.99 (s, 6H,  $\text{CH}_3$ ), 2.12 (s, 6H,  $\text{CH}_3$ ), 3.80–4.30 (m, 8H,  $\text{CH}_2\text{O}$ ), 6.21 (s, 2H, Ar), 6.70 (s, 2H, Ar). **2c**:  $^1\text{H-NMR}$  (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 2.11 (s, 12H,  $\text{CH}_3$ ), 3.95 (s, 4H,  $\text{CH}_2\text{O}$ ), 4.01 (s, 4H,  $\text{CH}_2\text{O}$ ), 6.22 (s, 4H, Ar).

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