 

# Photostimulated Crystal Lattice Change Induced by the Photochemical Ring-Opening Reaction of Diarylethene Molecules

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Single crystals of the closed-ring isomer of the diarylethene derivative 1,2-bis(2-methyl-6-styryl-1-benzothiophen-3-yl)perfluorocyclopentene underwent a ring-opening reaction with high conversion while keeping their crystalline shape and transparency. Polar plots of the absorption anisotropy revealed that the closed-ring isomer in the crystal maintained an ordered alignment even at high conversion, and the transparency of the single crystal remained intact during photoreaction. X-ray crystal structural analysis showed that the length of the *b* axis of the unit cell increases as the photoreaction proceeds. The photostimulated crystal-lattice change is attributed to the rotational movement of the thiophene rings of the molecule during the photochemical ring-opening reaction.

Crystalline-state reactions are useful for preparing constrained molecules or synthesizing desired products with high regio- or stereoselectivity.[1] Confinement of the molecules in the crystal lattice with a specific orientation is the main cause of the selectivity. In addition to the reaction selectivity, the dynamics of the reactions in the crystalline-state has attracted increasing interest. X-ray crystallography has revealed that molecules can move in the crystal lattice even in the solid-state reactions.[2] A striking example is the photochemical reversible surface-morphological change induced by the photochromic reactions.[3]

Photochromic compounds interconvert between two distinct structures upon stimulation with light.[4] Recently, some diarylethenes have been found to exhibit photochromic reactivity even in the single-crystalline phase.[5] Thermal stability and fatigue-resistant characteristics make diarylethenes promising candidates for optoelectronic devices.[6] For tuning the physical property of the crystal, the conversion during the photochromic reaction should be high. Although the photochromic reaction of diarylethenes takes place in a single-crystal to single-crystal fashion, there are two obstacles in terms of high conversion. One is quenching by the photoproduct, and the other is loss of crystallinity. The quenching effect means that the photogenerated colored closed-ring isomers have lower energy than the initial open-ring isomers, and the energy transfer from the open- to the closed-ring isomers limits conversion. The inner-filter effect by the colored isomers also suppresses the photocyclization reaction. For example, 1,2-bis(2,5-dimethyl-3-thienyl)perfluorocyclopentene undergoes photocyclization in the single-crystalline phase; however the conversion is 8% or less.[7] The closed-ring isomers generated by the cyclization reaction absorb in the visible region, but the open-ring isomers generated by the ring-opening reaction do not. This means that the photochemical ring-opening reaction can occur with high conversion. By irradiating at the absorption edge, a homogeneous reaction takes place. But in most cases, the photochemical reaction in the single-crystalline phase causes a loss of crystallinity.[5] In the ring-opening reaction of 1,2-bis(2,5-dimethyl-3-thienyl)perfluorocyclopentene, crystallographic analysis has been carried out only up to a conversion of 9%.[8] The crystallinity decreased significantly as the reaction proceeds. When the crystal undergoes photochemical reaction up to a high yield, crystallographic parameter changes, such as crystal lattice changes, can be monitored throughout the reaction.

During the course of the study of single crystalline photochromism, we found that the closed-ring isomer of 1,2-bis(2-methyl-6-styryl-1-benzothiophen-3-yl)perfluorocyclopentene (**1b**) undergoes photochemical ring-opening reaction with high conversion while keeping the crystal shape (Scheme 1). Therefore, the crystallographic parameter change can be followed during the reaction. In this paper, the reaction was investigated using polarizing optical microscopy, single-crystal X-ray structural analysis, and powder X-ray diffraction. For reference, the behavior of the closed-ring isomer of 1,2-bis(2-methyl-1-benzothiophen-3-yl)perfluorocyclopentene (**2b**) was investigated under the same condition.

## Experimental

**Materials.** 1,2-Bis(2-methyl-6-styryl-1-benzothiophen-3-yl)-perfluorocyclopentene (**1a**)[9] and 1,2-bis(2-methyl-1-benzothiophen-3-yl)perfluorocyclopentene (**2a**)[10] were synthesized according to the literature. The identity and purity of the sample were confirmed by $^1$H NMR and HPLC. Isolation of the closed-ring isomer was carried out by HPLC (eluent: hexane:ethyl acetate = 99:1; column: Wako Chemical Wakosil-5SIL 250-20 mm). Block single crystals **1a**, **1b**, **2a**, and **2b** were prepared by recrystallization from hexane.

**Photochemical Reaction and Measurement of the Order**

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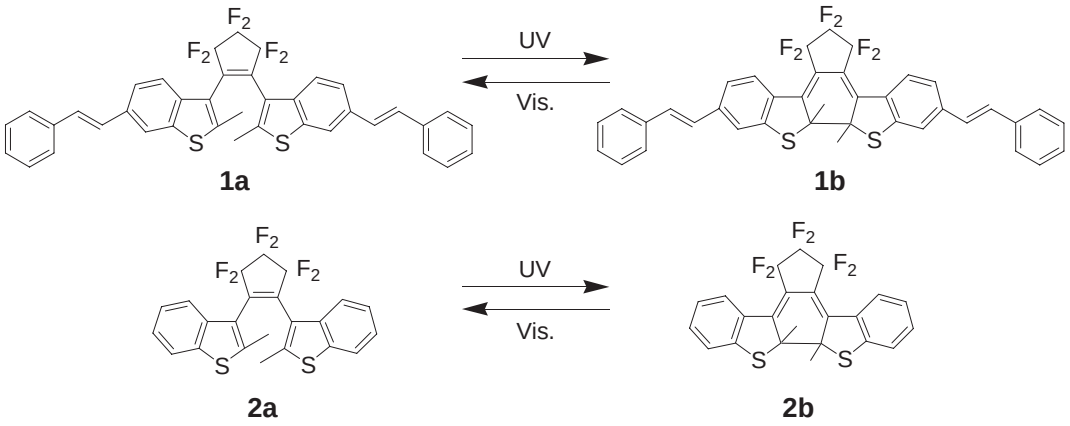


Scheme 1.

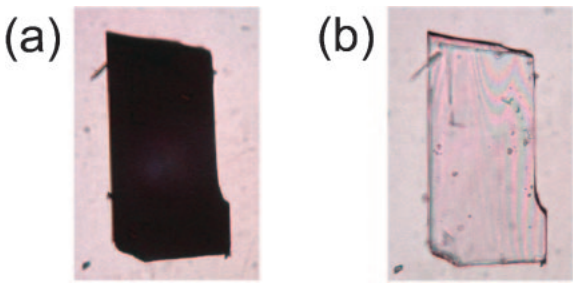


Fig. 1. Photographs of **1b** crystal (a) before irradiation with visible light and (b) after irradiation with visible light.

**Parameter.** A good quality single crystal was placed on a polarizing optical microscope (Leica DMLP), and the intensity of the absorption band in the visible region was measured with a Hamamatsu PMA-11 upon rotating the crystal. A xenon lamp (75 W) and a halogen lamp (100 W) with a band-pass filter of appropriate wavelength were used as the light sources for ultraviolet and visible light irradiation, respectively. The polarizer and analyzer were set parallel to each other. For the ring-opening reaction from **1b** to **1a**, the absorption anisotropy was measured at 575 nm. In the early stages, polarized absorption spectra were saturated, so $A_{\parallel}$ and $A_{\perp}$ were measured at an absorption edge longer than 575 nm. For the ring-opening reaction from **2b** to **2a**, the absorption anisotropy was measured at 530 nm. In the early stages of photoreaction, a wavelength longer than 530 nm was used for the measurement of $A_{\parallel}$ and $A_{\perp}$. The irradiation of visible or UV light to the single crystal has been carried out on a crystal face, which appears in Fig. 1.

**Single-Crystal X-ray Structural Analysis.** A good quality crystal (ca. $0.1 \times 0.1 \times 0.03\,mm^3$) was selected for the X-ray diffraction study. The data collection was performed on a Bruker SMART 1000 CCD-based diffractometer (60 kV, 30 mA) with Mo K$\alpha$ radiation. The crystal was cooled at 123 K using a cryostat (RIGAKU GN2). The data were collected by covering a hemisphere of the reciprocal space and combining four sets of runs. Each frame covered 0.3° in $\omega$, and the exposure time was 50 s. Crystal decay was monitored by repeating the 50 initial frames at the end of data collection and analyzing the duplicate reflections. Data reduction was performed using SAINT software,[11] which corrects for Lorentz and polarization effects, and decay. The cell constants were calculated by using global refinement. The structure was solved by direct methods using SHELXS-86 and refined by full least-squares on $F^2$ using SHELXL-97.[12] The positions of the hydrogen atoms were calculated geometrically and refined using a riding model. Crystallographic analysis was repeated at different stages of photochromic reaction. The conversion of the photochemical ring-opening reaction was estimated by the ratio of the sulfurous occupancy between the disordered open- and closed-ring isomer. Crystallographic data of **1b** and photoirradiated **1b** have been deposited at the Cambridge Crystallographic Data Centre (CCDC), 12, Union Road, Cambridge, CB2 1EZ, UK. Copies of the data can be obtained by quoting the publication citation and deposition number CCDC-610623 (**1b**) and CCDC-610624 (photoirradiated **1b**) via http://www.ccdc.cam.ac.uk/conts/retrieving.html (Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

**Powder X-ray Diffraction.** Powder X-ray diffraction pattern was measured on a Shimadzu XRD XD-D1 instrument. Powdered sample was irradiated with visible light of the same wavelength as used in the single-crystal measurement. The measurement was repeated at different stages of photochemical ring-opening reaction. The conversion of the photochromic reaction was estimated by HPLC analysis (eluent: hexane:ethyl acetate = 95:5; column: Wako Chemical Wakosil-5SIL 250-10 mm).

## Results and Discussion

**Photochromism of Compound 1.** Compound **1a** undergoes a photochromic reaction in solution, as previously reported.[9] The absorption maximum of the closed-ring isomer in hexane is observed at 550 nm. In a single-crystalline phase, **1a** did not show any photochromic reactivity. Crystals of compound **1a** were too small for single-crystal X-ray crystallography.

On the other hand, purple crystals of **1b** turned colorless upon irradiation with visible light. The polarized absorption spectra of the crystal showed an absorption maximum at 575 nm. The absorption maximum remained at the same position even upon rotating the crystal. When the sample was irradiated with visible light ($\lambda = 700$ nm), the absorption band at 575 nm decreased and finally became completely bleached, with keeping the transparency (Fig. 1). Absorption spectral changes in the **1b** crystal are shown in Fig. 2.

Completely bleached colorless crystal **1a′** became purple upon irradiation with UV light in contrast to that the open-ring crystal of **1a** did not show any coloration as mentioned before. The colored crystal will be referred to as **1b′**. From this result,

the molecular conformational structure of **1a′** is considered to be different from **1a**, which is supported by the result that the melting point of **1a′** (130 °C) is different from that of **1a** (178 °C).

The absorption band of **1b′** showed a red shift in comparison with that of **1b**. The absorption maximum of **1b** crystal was observed at 575 nm while the absorption maximum of **1b′** crystal was 585 nm. It is known that the closed-ring isomer photogenerated in the open-ring isomer crystal shows red-shift compared to the closed-ring isomer in solution or in the closed-ring isomer crystal.[13] This is attributed to the constrained conformation of the photogenerated closed-ring isomer. The red shift indicates that the structure of the closed-ring isomer generated in **1a′** crystal has a different conformation from the structure of the closed-ring isomer in **1b** crystal.

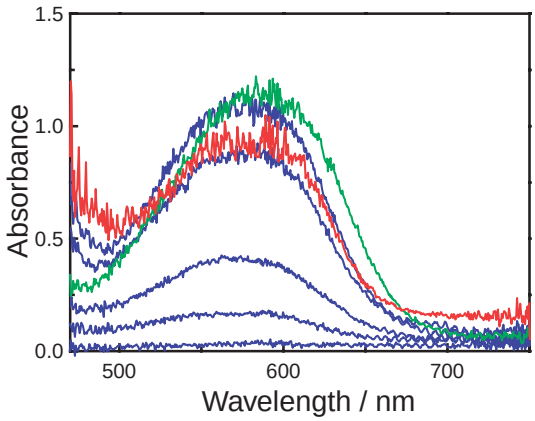


Fig. 2. Absorption spectral change of **1b** crystal upon irradiation. Red line shows the spectrum of an extremely thin **1b** crystal before irradiation with visible light. Blue lines show the spectra during irradiation with visible light. The spectra were measured after irradiation with visible light for a long time to see the absorption maximum clearly. Green line denotes the **1b′** crystal, which was obtained by the irradiation with UV light to the completely bleached **1a′** crystal. Blue lines and green line were obtained from the same crystal.

For **2b** crystal, the same photobleaching procedure was performed. During irradiation with visible light ($\lambda = 700$ nm), single crystal **2b** exhibited cracking during photochemical ring-opening reaction.

**Order Parameters.** Single crystals were placed on a polarizing microscope and the absorption anisotropy was followed during the photoreaction to determine the crystallinity of the crystal. The absorption maximum of **1b** crystal was 575 nm. Upon rotation, the absorption maxima did not change, but the intensity dramatically decreased. At a certain angle, the intensity of the color was strongest ($\theta = 0°$; $A_{\parallel}$). When the crystal is rotated by 90° ($A_{\perp}$), the intensity of the color became very weak. Absorption spectra at $\theta = 0$ and 90° are shown in Fig. 3a (black line), and the polar plot is shown in Fig. 3b. The polar plot of **1b** was taken using an extremely thin crystal. The order parameter $((A_{\parallel} - A_{\perp})/(A_{\parallel} + 2A_{\perp}))$ was 0.88. The absorption intensity depended on the direction of electronic transition moments of the molecules in the crystal, so that a high-order parameter indicates that the molecules are regularly oriented in the crystal. Polarized absorption spectra of single crystal **1b** after irradiation with visible light ($\lambda = 700$ nm) to 50% conversion was measured (Fig. 3a). The order parameter $((A_{\parallel} - A_{\perp})/(A_{\parallel} + 2A_{\perp}))$ was determined at different stages of photochemical ring-opening reaction (Fig. 3c and Fig. 4). Even at a high conversion stage, the absorption anisotropy remained higher than 0.6, although it slightly decreased as the photoreaction proceeded. The order parameter of crystal **1b′**, which was obtained by UV irradiation to the complete photobleached **1a′**, was as high as 0.65. The ordered alignment was maintained even at high conversion.

Single crystals **2b** were irradiated with visible light ($\lambda =$ 618 nm), and the order parameter change against conversion

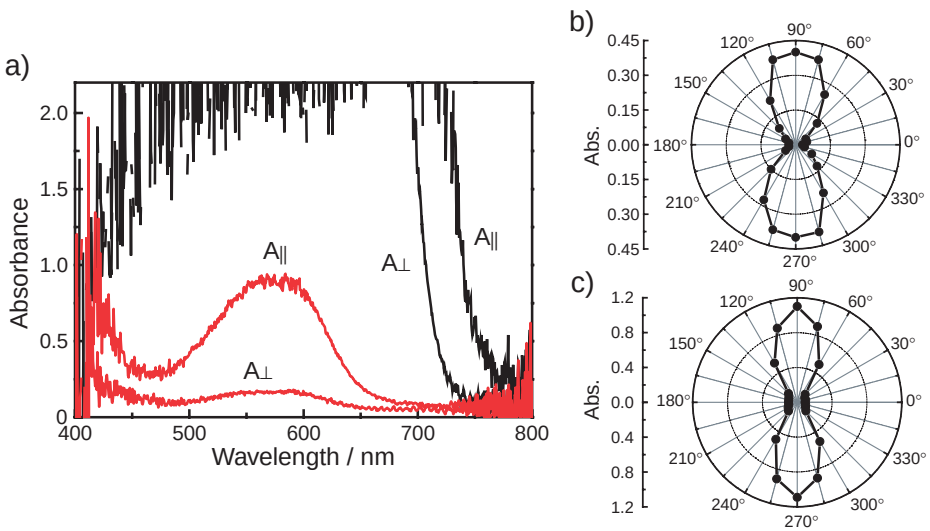


Fig. 3. (a) Polarized absorption spectra of the single crystal of **1b** before and after visible photoirradiation. Black lines are the spectra before irradiation. Red lines are the spectra of the photoirradiated sample (50% conversion). (b) Polar plot of the sample before irradiation, which was measured at 700 nm. (c) Polar plot of the photoirradiated sample (40% conversion), which was measured at 575 nm. An extremely thin crystal was chosen for the measurement of the polar plot of **1b**. Polar plots and absorption spectra were measured for different samples.

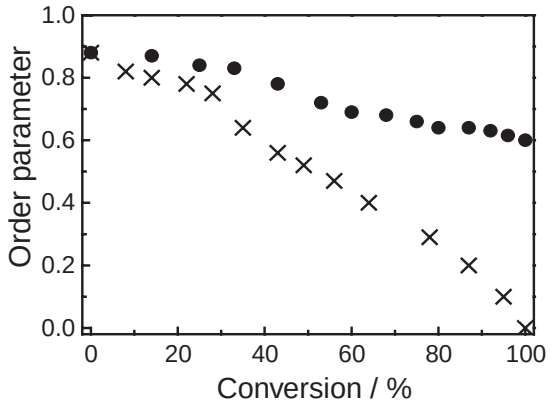


Fig. 4. The change in the order parameter along with the photochromism from the closed-ring isomer to the open-ring isomer: (●) **1b**; (×) **2b**.

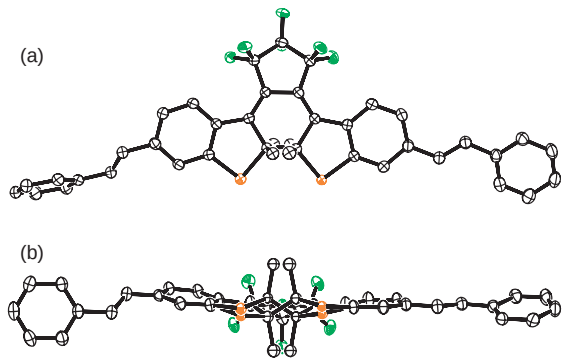


Fig. 5. ORTEP drawing of **1b** crystal. Hydrogen atoms are omitted for clarity. Cyclohexadiene moiety contains a disordered structure. (a) Side view. (b) Top view.

is shown in Fig. 4. Before visible irradiation, the order parameter was 0.87. The order parameter dramatically decreased upon photoirradiation and finally reached 0. It means that crystallinity is completely lost during the photochemical ring-opening process.

**X-ray Structural Analysis.** In order to obtain crystallographic information during photoirradiation, single-crystal X-ray structural analysis was performed. Figure 5 shows an ORTEP drawing of crystal **1b** before photoirradiation, and the crystallographic parameters are summarized in Table 1. Figure 6 shows the crystal packing of **1b**. The crystal lattice is monoclinic, and the space group is $C2/c$. One diarylethene molecule is included in the asymmetric unit, and eight molecules are included in the unit cell.

Single crystal **1b** was irradiated with 700 nm light and crystallographic analysis was performed at the different stages of the photochromic reaction. Structural analysis of the photoirradiated sample showed that the open-ring isomer **1a′**, photogenerated by visible light, is observed in the single crystal **1b** as a disordered structure. Figure 7 shows an ORTEP drawing of the photoirradiated sample (18% conversion), and the crystallographic parameters are summarized in Table 1. The distance between reactive carbon atoms of **1a′** is 2.631 Å, which is shorter than the distance of typical open-ring isomers, meaning that **1a′** is constrained.[5j]

Table 1. Crystallographic Data of **1b** Crystal

| | **1b** | Photoirradiated **1b** |
|---|---|---|
| Formula | $C_{39}H_{26}F_6S_2$ | $C_{39}H_{26}F_6S_2$ |
| fw | 672.75 | 672.75 |
| Temperature | 123 | 123 |
| Crystal system | monoclinic | monoclinic |
| Space group | $C2/c$ | $C2/c$ |
| $a$/Å | 24.338(5) | 24.386(13) |
| $b$/Å | 17.451(4) | 17.568(10) |
| $c$/Å | 17.011(4) | 17.000(9) |
| $\beta$/° | 122.372(3) | 122.223(7) |
| $V$/Å$^3$ | 6102(2) | 6162(6) |
| $Z$ | 8 | 8 |
| Data/Restraints/Params | 6165/0/465 | 5811/0/483 |
| $R1$ ($I > 2\sigma$) | 0.0506 | 0.1500 |
| $wR2$ (all data) | 0.1049 | 0.2890 |

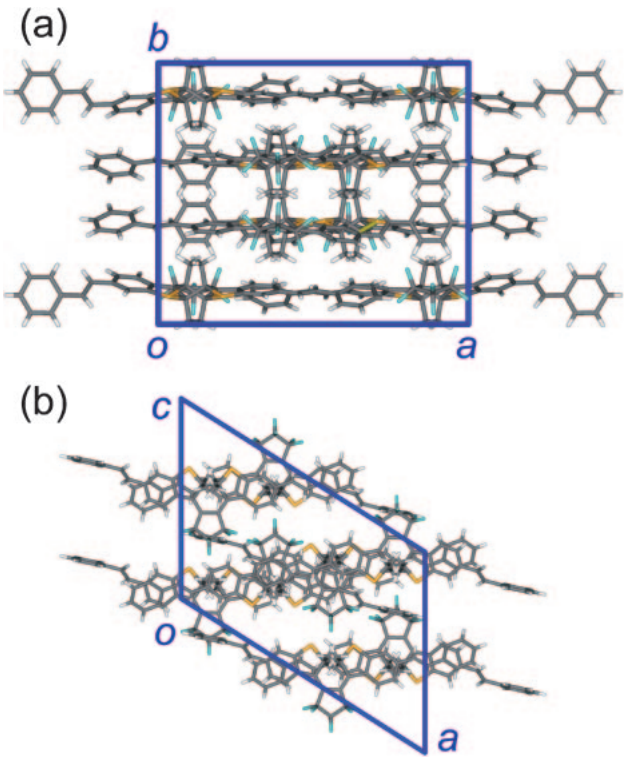


Fig. 6. Packing diagram of the closed-ring isomer crystal **1b**. (a) Viewed normal to the $c$ axis. (b) Viewed normal to the $b$ axis.

Fig. 7. ORTEP drawing of photoirradiated **1b**. Conversion from the open- to closed-ring isomer was 18%.

The crystal of the closed-ring isomer **1b** contained two enantiomeric closed-ring isomers (*R*,*R* and *S*,*S*) originating from asymmetric carbon atoms. The disordered structure in Fig. 5 shows that the two enantiomers are placed in the same crystallographic position randomly. Figure 7 shows that one of

the enantiomers in the disordered site preferentially underwent ring-opening reaction. This is attributed to the environmental difference between the two sites. Since the space group $C2/c$ contains centrosymmetry, each enantiomer has an enantiomorph. Chiral induction is not expected.

The conversion from the closed-ring isomer **1b** to the open-ring isomer **1a′** can be estimated by the occupancy of the sulfur atoms of **1b** and **1a′**. Up to a conversion of 20%, the crystal structure was solved without a problem. When the conversion was over 25%, the structure could not be solved though diffraction patterns were clearly observed. This is attributed to that the photogenerated open-ring isomer **1a′** affects the packing in the crystal at high-conversion stages. The cell parameters slightly changed at 20% conversion. The changes in the length of the $a$ axis, $b$ axis, and $c$ axis were $-0.5\%$, $+2.0\%$, and $-1.0\%$, respectively. The change in $\beta$ angle was $-0.5\%$, and the change in the cell volume $V$ was $+2.0\%$.

**Powder X-ray Diffraction.** Because the diffraction pattern can be observed even when the conversion exceeds 25%, the crystal structure changes were followed using powder X-ray diffraction. Figure 8 shows the diffraction peaks at different stages of the photoreaction. The peaks of (110) and (002) remained at the same position, but the position of the peak of $(42-3)$ changed to a smaller angle. The peak position change indicates that the crystal cell change is mainly in the $b$ axis.

By using the position of five peaks, (110), (002), (400), $(11-1)$, and $(42-3)$, the cell parameters were calculated.[14] The results are shown in Fig. 9 along with the result of the single-crystal analysis. The unit cell parameters change as the reaction proceeds. The overall change in the unit cell parameter is less than 10%. This graph also shows that the change in the $b$ axis is the largest. As can be seen in Fig. 6, the $b$ axis is located perpendicular to the molecular plane of the closed-ring isomers. When the ring-opening reaction takes place, the molecular structure expands along the $b$ axis. This is the reason

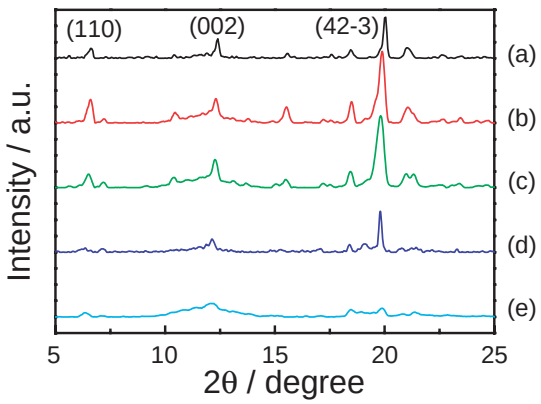


Fig. 8. The change in diffraction pattern during ring-opening reaction of **1b**: (a) the closed-ring isomer; (b) after irradiation with visible light up to conversion of 18%; (c) 28%; (d) 68%; (e) 90%.

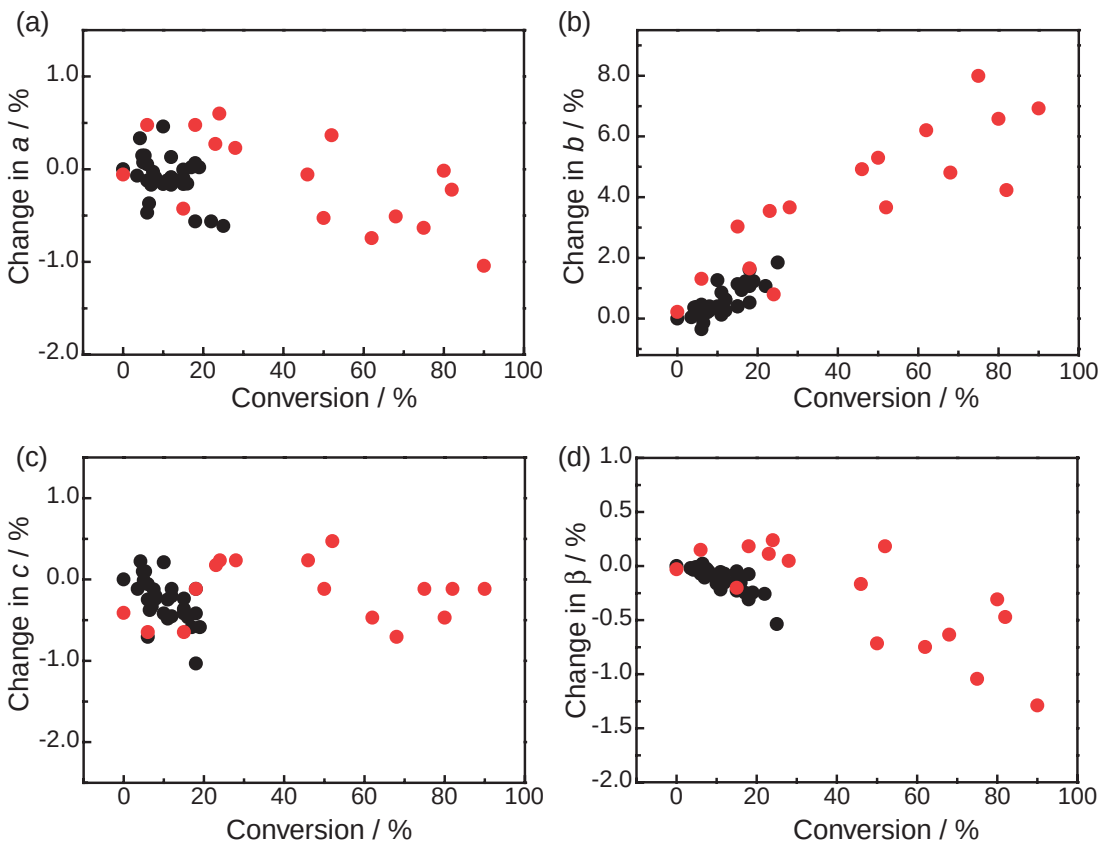


Fig. 9. Change in the cell parameters of the crystal **1b** during the photochromic reaction. a) Change in $a$; b) change in $b$; c) change in $c$; d) change in $\beta$. Black circle denotes the parameter obtained from single-crystal X-ray diffraction, and the red circle denotes the parameters obtained from powder X-ray diffraction.

why the change in the *b* axis is the largest, and the changes in *a* and *c* axes are small. Figure 6 shows the direction of the *a* and *c* axes.

The change in the cell parameters is a result of the accumulation of the molecular structure changes. The accumulated change is the most distinctive in the direction of the *b* axis, which is the direction that the sulfur and carbon atoms around the reactive center move. The molecular movement induces the change in the whole crystal.

## Conclusion

Crystalline-state photochromism of the closed-ring isomer of diarylethene **1a** was examined using polarizing optical microscopy, single-crystal X-ray structural analysis, and powder X-ray diffraction. Polarizing optical microscopy observation showed that absorption anisotropy remains even in the bleached crystal. X-ray crystallography showed that the *b* axis of the unit cell increases as much as 10% as the photoreaction proceeds. This photostimulated change is attributed to the rotational movement of the thiophene rings during the ring-opening reaction.

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